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Review

Bulky P-stereogenic ligands. A success story in asymmetric catalysis

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A B S T R A C T

Since the development of BisP* ligand by Imamoto, P-stereogenic phosphines bearing a bulky *tert*-butyl group and a smaller alkyl group have demonstrated extraordinary proficiency in a wide range of asymmetric processes. Over time, this class of ligands has brought about the introduction of more rigid backbones, the three-hindered quadrant concept, and the substitution of the *tert*-butyl group by adamantyl. The *tert*-butyl methyl fragment has also been introduced in phosphino-oxazoline-type ligands, and chemists in the industrial sector have also contributed to the evolution of this class of ligands by reporting the first successful P-stereogenic Buchwald-type monophosphines for asymmetric coupling reactions. The present review covers the synthesis and applications of bulky P-stereogenic phosphines that have been developed since the advent of BisP* in the late 1990s, with a special emphasis on ligands that have been successfully applied in asymmetric catalysis.

1. Introduction

Given their ability to bind metals, phosphines are one of the most prominent types of spectator ligands used in homogeneous metal catalysis. By changing the nature of the substituents attached to phosphorus, we can tune both the electronic and steric properties of the ligand, thereby allowing us to ultimately regulate the reactivity and selectivity of the metal center in a particular catalytic process. In asymmetric catalysis, the ligand is responsible for creating a chiral environment around the metal center that will ultimately determine the selectivity of the reaction. To attain high selectivity, the ligand has to deliver an effective chiral environment capable of forcing an energy bias between diastereomeric transition states that result from the interaction with the substrate.

We can classify chiral phosphine ligands into two groups on the basis of the location of chirality. For most ligands, chirality is found in the backbone of the ligand. As the chiral information is initially distant from the reaction center, it needs to be transmitted to the alkyl or aryl groups attached to phosphorus since these groups are closer and will define the environment around the reaction center. The other option is to place the chirality on phosphorus itself and utilize a P-stereogenic phosphine. A common argument in support of the use of P-stereogenic ligands is that the 'chiral information' is closer to the metal center. However, this proximity alone is not enough for the effective transmission of chiral information to the substrate (Fig. 1). There are many examples of P-stereogenic phosphine ligands that provide poor selectivity. The important point here is not where the chiral information lies but whether it is able to create an effective chiral environment. While there is no systematic rule on how to create such an environment for a given process, in the last two decades, a family of ligands has proved consistently and extremely successful in catalysis. The leading roles in this 'success story' are for bulky P-stereogenic phosphines usually bearing a *tert*-butyl group and a smaller group such as a methyl or methylene.

While there are some reviews and personal accounts of P-stereogenic

Abbreviations: Ac, acetyl; ACN, acetonitrile; Ad, adamantyl; Alk, alkyl; Ar, aryl; Bn, benzyl; Boc, *tert*-butoxycarbonyl; BOM, benzyloxymethyl; BQ, 1,4-benzoquinone; Bpin, pinacolborane, 4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl; Bz, benzoyl; Cbz, benzyloxycarbonyl; Cod, cyclooctadiene; CPME, cyclopentyl methyl ether; Cy, cyclohexyl; Cyp, cyclopentyl; DABCO, 1,4-diazabicyclo[2.2.2]octane; DAST, diethylaminosulfur trifluoride; Dba, *E,E*-dibenzylidene acetone; DBTA, dibenzoyl tartaric acid; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DCE, 1,2-dichloroethane; DCM, dichloromethane; DFT, density-functional theory; DME, dimethoxyethane; DMF, *N,N*-dimethylformamide; Dppp, 1,3-bis(diphenylphosphino)propane; HMPA, hexamethylphosphoramide; iAm, isoamyl, 3-methylbutyl; iBu, isobutyl; iPr, isopropyl; LDA, lithium diisopropylamide; Ms, mesyl, methanesulfonyl; Mes, mesityl, 2,4,6-trimethylphenyl; $NaBAr_F$, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; Naph, naphthyl; *n*-Bu, *n*-butyl; *n*-Hex, *n*-hexyl; NMM, *N*-methylmorpholine; *o*-An, *ortho*-anisyl, 2-methoxyphenyl; Piv, pivaloyl, trimethylacetyl; PMP, *para*-methoxyphenyl; Py, pyridine; *s*-Bu, *sec*-butyl; SIP, secondary iminophosphorane; SPO, secondary phosphine oxide; SPB, secondary phosphine borane; TBAF, tetrabutylammonium fluoride; TBME, *tert*-butyl methyl ether; *t*-Bu, *tert*-butyl; Tf, triflate trifluoromethanesulfonate; TFA, trifluoroacetic acid; THF, tetrahydrofurane; THQs, tetrahydroquinolines; TMEDA, *N,N,N′,N′*-tetramethylethylenediamine; TMS, trimethylsilyl; TPB, tertiary phosphine borane; TPO, tertiary phosphine oxide; Tripp, 2,4,6-triisopropylphenyl; Ts, tosyl, *p*-toluenesulfonyl.

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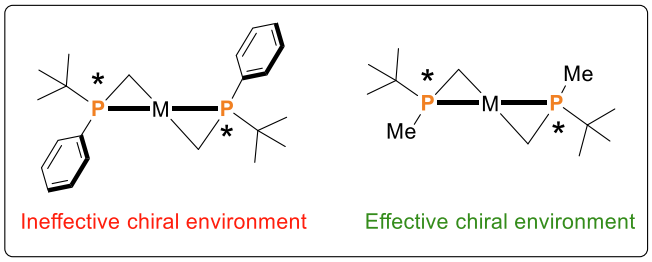


Fig. 1. Moving chiral information to phosphorus atoms is not enough to ensure good results. Certain combinations of substituents on P-stereogenic ligands do not provide an effective chiral environment around the metal center.

phosphines and their synthesis, [1] none of these give an overall view of the ligands with bulky phosphines developed in the last two decades. The present review aims to cover the synthesis and applications of bulky P-stereogenic phosphines that have emerged since the advent of BisP* ligand developed by Imamoto in the late 1990s and that have also been successfully applied to asymmetric catalysis. What is understood as "bulky" phosphine? We consider a bulky phosphine to be one that bears at least a *tert*-butyl or an adamantyl group directly attached to phosphorus. Also, phosphines bearing phenyl groups with *ortho*-substituted alkoxy and aryl groups are taken into account.

The present review includes a brief historical overview of the first generation of P-stereogenic phosphines like PAMP and DIPAMP and rapidly jumps to the second generation of modern bulky electron-rich phosphines. The content is organized around the method used to synthesize the P-stereogenic phosphine ligand or intermediate. The review seeks to highlight the most prominent and key contributions to the field. We believe the content of this review will be of interest to chemists, in both academia and industry, working on stereoselective chemical transformations and catalysis.

2. The early days: The first generation of P-stereogenic ligands

In 1911, Meisenheimer and Lichtenstadt isolated the first enantioenriched phosphorus compound by the resolution of ethylmethylphenylphosphine oxide (Fig. 2). [2] Their work proved that, like C-stereogenic molecules, P-stereogenic compounds can also be separated into configurationally stable enantiomers. Despite this initial breakthrough, it was another 50 years until Horner isolated the first enantioenriched trivalent phosphines with a free electron pair. This was achieved by reduction of phosphine oxides or alkaline hydrolysis of phosphonium salts. [3] In both cases, the precursors were previously enantioenriched by resolution. Unlike amines, chiral trivalent phosphines were stereochemically stable at room temperature.

Not long after, Wilkinson and co-workers were the first to use an achiral phosphine as ligand in a metal-catalyzed hydrogenation. [4] They observed that $RhCl(PPh_3)_3$–later named Wilkinson's catalyst–was a very active catalyst for the hydrogenation of alkenes and acetylenes in mild conditions. This finding marked an important breakthrough in the field of homogeneous catalysis. Following this work, the teams led by Knowles and Horner simultaneously replaced the achiral triphenylphosphine in Wilkinson's catalyst for enantioenriched (*R*)- and (*S*)-

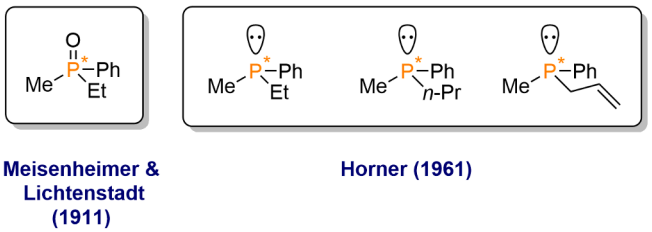
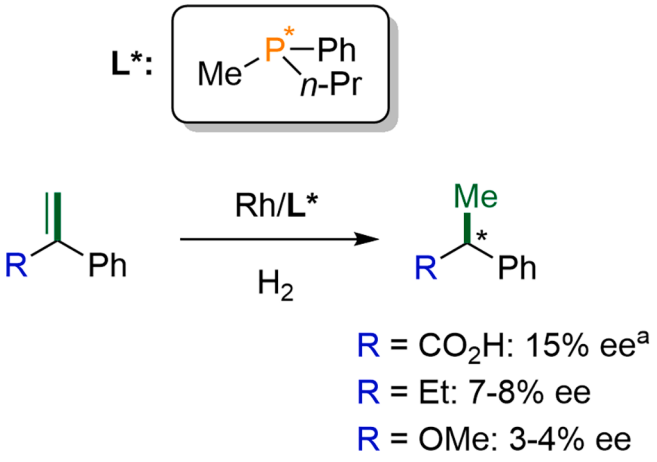


Fig. 2. First reported enantioenriched tetravalent and trivalent phosphines.

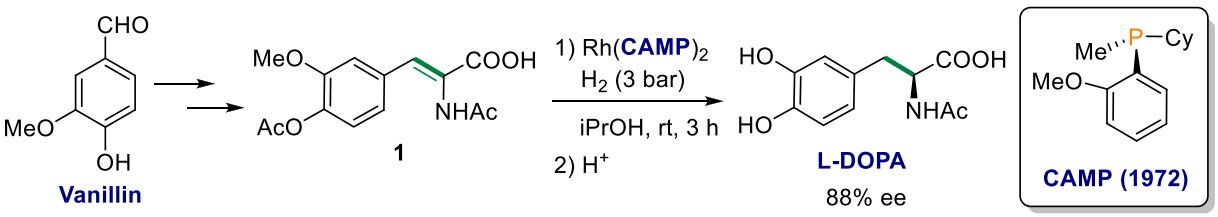
methylphenyl-*n*-propylphosphine. [5,6] The use of the resulting complex in the asymmetric hydrogenation of olefins showed a certain degree of enantioinduction (Scheme 1). Although enantioselectivity was very low, this experiment proved the feasibility of catalytic asymmetric hydrogenation with P-stereogenic ligands. Heterogeneous catalytic enantioselective hydrogenation had been reported earlier, [7] but this was the first time that such a process was described in homogeneous media.

At that time, L-3,4-dihydroxyphenylalanine (L-DOPA) emerged as an efficient drug for the treatment of Parkinson's disease. The growing demand for this pharmaceutical led Knowles and co-workers to apply the newly discovered enantioselective catalytic hydrogenation for its preparation. The Rh-catalyzed asymmetric hydrogenation of L-DOPA precursor **1** was tested with various P-stereogenic ligands, CAMP providing 88% ee (Scheme 2). [8] This result was so outstanding at that time that Monsanto scaled up this process for industrial production, giving rise to the first industrial catalytic enantioselective transformation. [9].

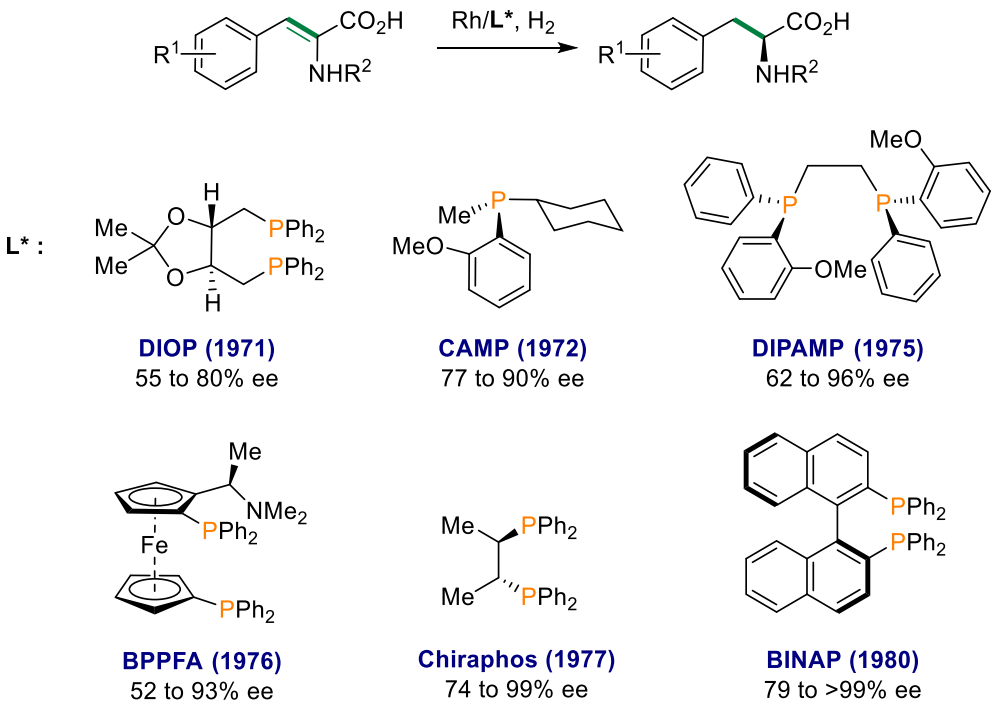
In parallel, Dang and Kagan reported the first C_2-symmetric diphosphine ligand, named DIOP, which was non-P-stereogenic but had chirality in the carbon backbone (Scheme 3). [10] This ligand was tested in the Rh-catalyzed asymmetric hydrogenation of several α-dehydroamino acids, yielding ee's up to 80%. [11] These results proved that chirality at the phosphorus atom was not essential to induce high enantioselectivity in an asymmetric hydrogenation and that this could also be achieved with ligands bearing stereocenters in the carbon structure. In contrast to CAMP monophosphine, Dang and Kagan stated that the stereoselectivity obtained with DIOP could probably be attributed to the conformational rigidity conferred by the diphosphine chelation to rhodium. Following on with this concept, Knowles prepared the P-stereogenic diphosphine DIPAMP, which excelled in the Rh-catalyzed asymmetric hydrogenation of diverse α-dehydroamino acids, reaching ee's up to 96% (Scheme 3). [12] This achievement also led DIPAMP to replace CAMP as the ligand of choice for the industrial production of L-DOPA. [13] Despite the success of DIPAMP, the methods to prepare P-stereogenic ligands at that time were scarce and challenging. Thus, most research groups followed the lead of Dang and Kagan and opted for the development of non-P-stereogenic chiral ligands, such as BPPFA, Chiraphos, and BINAP (Scheme 3). [14] The latter two proved that ligands with backbone chirality could even surpass P-stereogenic DIPAMP in the Rh-catalyzed asymmetric hydrogenation of certain β-aryl-α-dehydroamino acids, which are precursors of relevant amino acids such as phenylalanine and tyrosine. Later, the discovery of the Ru-BINAP catalytic system expanded the scope of reducible substrates beyond α-dehydroamino acids to other olefins and ketones. [15] The successful results with non-P-stereogenic ligands, along with the difficulty of



Scheme 1. First homogeneous catalytic asymmetric hydrogenation, reported simultaneously by Knowles and Horner. [a] The phosphine used was not enantiomerically pure (69% ee).



Scheme 2. Synthetic methodology for the preparation of L-DOPA with CAMP ligand.



Scheme 3. P-stereogenic and non-P-stereogenic phosphines and their results in the Rh-catalyzed asymmetric hydrogenation of (*Z*)-β-aryl-α-dehydroamino acids.

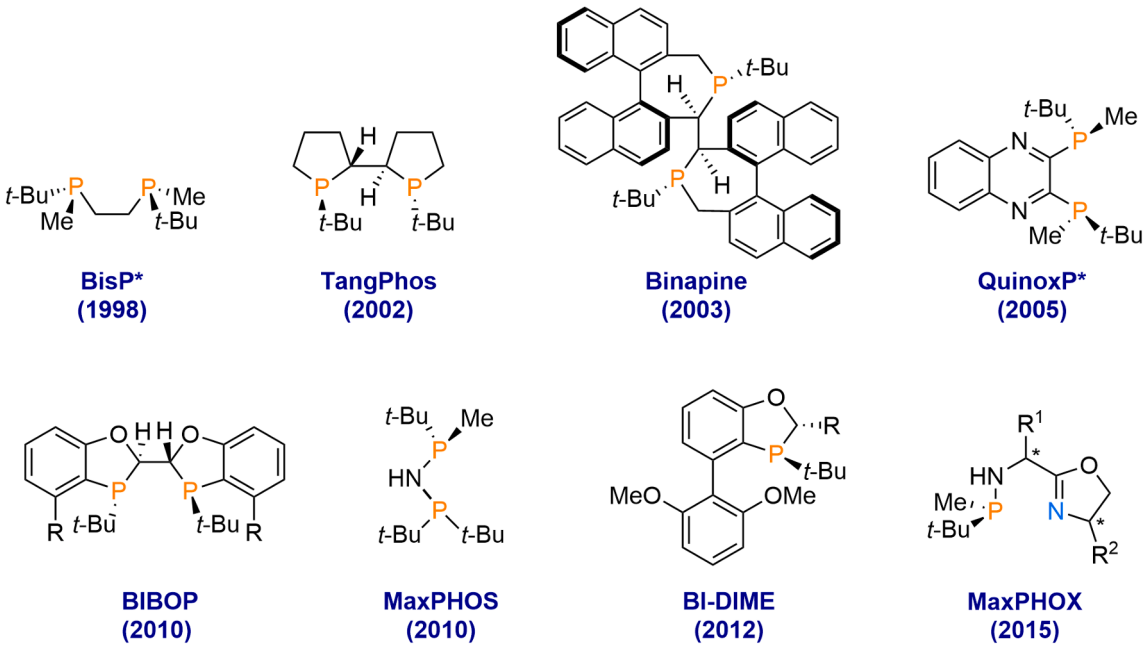


Fig. 3. Representative examples of the second generation of P-stereogenic ligands in asymmetric catalysis.

preparing enantioenriched P-stereogenic compounds in their early days, diminished interest in these for many years.

3. Bulky and electron-rich: The second generation of P-stereogenic ligands

While in the 1980's P-stereogenic ligands were somewhat overlooked in favor of ligands with backbone chirality, the methods for their preparation kept improving slowly. In 1985, Imamoto introduced borane as a versatile and robust protecting group in P-stereogenic chemistry. [16] This group offered milder deprotection conditions than phosphine oxides. The use of phosphine boranes enabled the development of important synthetic strategies throughout the 1990s, such as those reported by Jugé and Evans. [17] However, perhaps the milestone that set the starting point for the second generation of P-stereogenic ligands was the development of BisP* ligand by Imamoto in the late 1990s (Fig. 3). BisP* has the key features that characterize this second generation of P-stereogenic ligands. In this regard, these ligands are: a) bulky, often containing the *tert*-butyl methyl pair attached to phosphorus; b) electron-rich alkyl phosphines. The presence of large ball-shaped group (*tert*-butyl) and small group (methyl or methylene) near the metal center provides a large steric bias that is extremely beneficial in terms of selectivity. Also, the good σ-donor properties of these ligands make the catalysts very active in hydrogenation and other processes. Further evolution of the ligand design introduced an aromatic flat backbone as in QuinoxP* and BenzP*. This simple change afforded two key attributes for the success of these ligands, namely stability towards oxidation of the free ligand, which allowed widespread use among chemists, and a more rigid metal-chelate complex, which further improved selectivity.

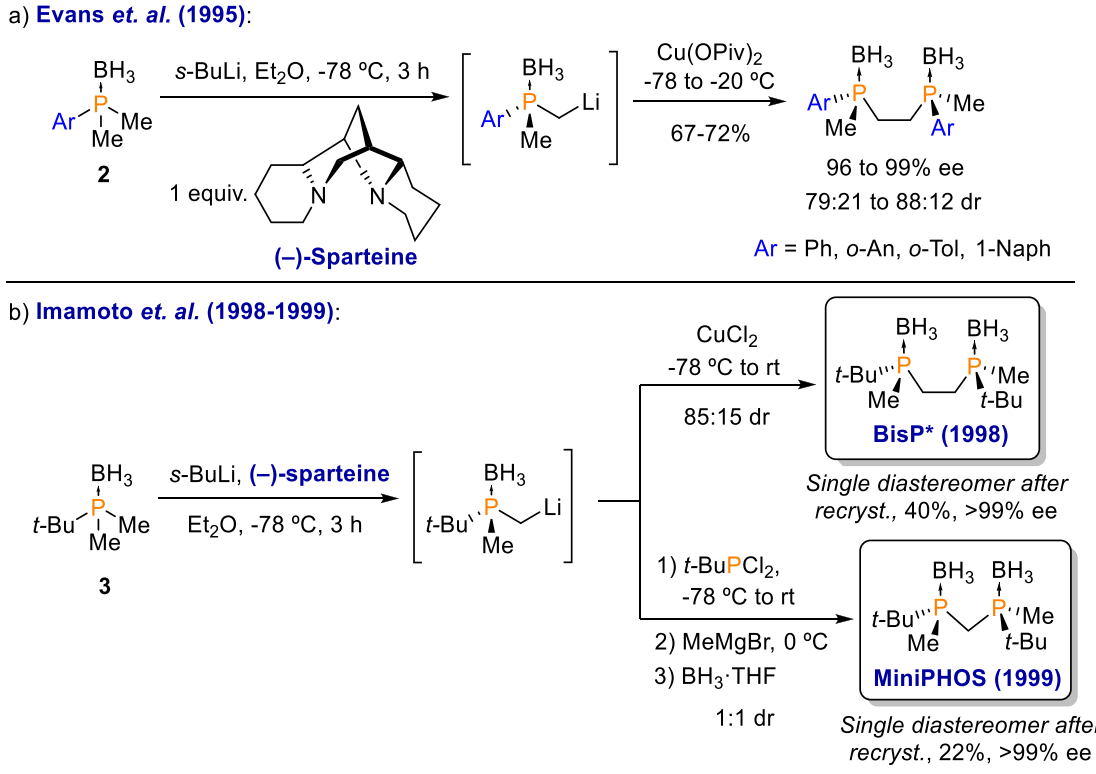
The same features that are beneficial in catalysis become a drawback when attempting to synthesize P-stereogenic electron-rich bulky phosphines in enantiomerically pure form. For instance, the reactions on the phosphorus center are hampered by the steric hindrance of the bulky *tert*-butyl group. This type of phosphines is highly prone to oxidation in air, thus making the protection of phosphorus as an oxide or borane complex mandatory during the synthesis. However, due to the σ-donor properties of these phosphines, harsh deprotection conditions are usually needed, thereby potentially jeopardizing the chemical and stereochemical integrity of the ligand. Thus, the synthesis of bulky P-stereogenic ligands is highly challenging. Established methods that work well in the synthesis of aryl-containing P-stereogenic compounds fail when a *tert*-butyl group is attached to phosphorus. In this context, dedicated methods have been developed for the preparation of such classes of compounds.

4. Methods used to synthesize bulky P-stereogenic phosphines

In the next sections, we describe the synthesis and applications of the most useful bulky P-stereogenic synthons and ligands in catalysis. We classified the ligands on the basis of the methodology used to synthesize the phosphine ligand. While a completely historical description is not feasible, to pay tribute to the seminal work of Imamoto, we grouped the ligands into the following sections: 1) Stereoselective deprotonation of enantiotopic alkyl groups; 2) Stereoselective synthesis using chiral auxiliaries; 3) Use of carbon or metal–carbon chiral templates; 4) Resolution of racemic mixtures; and 5) Asymmetric catalytic synthesis.

4.1. Stereoselective deprotonation of enantiotopic alkyl groups

In 1995, Evans and co-workers described the desymmetrization of aryl(dimethyl)phosphine-boranes through an enantioselective deprotonation with a stoichiometric amount of (–)-sparteine and *sec*-butyllithium (Scheme 4a). [17] The chiral diamine and *s*-BuLi formed a chiral complex that preferentially deprotonated one of the two enantiotopic methyl groups of **2**. The homocoupling of the lithium species generated allowed the preparation of distinct C_2-symmetric dialkylaryl diphosphines with an ethylene bridge, in very high enantioselectivity. After that, Imamoto applied this strategy to *tert*-butyl(dimethyl)phosphine-borane **3** to prepare BisP*, a trialkyl diphosphine bearing *tert*-butyl and methyl groups at the phosphorus atom (Scheme 4b). [18] After



Scheme 4. a) Enantioselective deprotonation with (–)-sparteine developed by Evans *et. al.* b) Use of the sparteine method for the preparation of BisP* and MiniPHOS.

recrystallization, the ligand was obtained as a single diastereomer, in 40% yield and > 99% ee. Imamoto also prepared the methylene-bridged analog MiniPHOS by consecutive addition of *t*-BuPCl$_2$, MeMgBr, and borane to the alkyllithium intermediate. [19] In this case, the reaction was non-diastereoselective but the *meso* diastereomer was again effectively removed by recrystallization. MiniPHOS has a smaller bite angle than BisP*. As a result of this small bite angle, unlike most diphosphines, two units of MiniPHOS are attached to rhodium upon coordination. The enantioselective deprotonation with (–)-sparteine provided access to only the *S* enantiomers of such ligands. Later, O'Brien and co-workers developed a surrogate of (+)-sparteine that allowed the preparation of the *R* enantiomers. [20] Moreover, O'Brien's team proved that (+)-sparteine and its corresponding surrogate could be used in substoichiometric amounts (0.1 to 0.5 equivalents).

BisP* and MiniPHOS ligands proved to be highly effective in the Rh-catalyzed asymmetric hydrogenation of terminal, trisubstituted, and tetrasubstituted functionalized olefins (Fig. 4). [18,19,21] Among the different BisP* and MiniPHOS ligands that were prepared bearing a small methyl group and a larger substituent, the ones with a bulky *tert*-butyl group (or also 1-adamantyl in the case of BisP*) were superior in catalysis to other ligands with substituents such as 1,1-diethylpropyl, cyclopentyl, cyclohexyl, isopropyl or phenyl. Imamoto and co-workers rationalized that the large steric bias between the *tert*-butyl and methyl substituents generate a clearly defined asymmetric environment around the phosphorus atom. [22].

A few years later, Imamoto's group developed a considerable number of non-symmetric BisP* analogs. [23] Ligands bearing an 1-adamantyl methyl phosphine pair at one phosphorus atom and distinct groups at the other phosphorus atom gave high enantioselectivity in the Rh-catalyzed hydrogenation of olefins, but provided inferior results to those achieved with BisP* (Fig. 5a). In 2004, Hoge and co-workers also developed a non-symmetric analog of MiniPHOS with an achiral P(*t*-Bu)$_2$ moiety at one phosphorus atom, named Trichickenfootphos (TCFP). [24] The rhodium complex of TCFP proved highly efficient in the Rh-catalyzed asymmetric hydrogenation of many different functionalized olefins (Fig. 5b). [25] The TCFP ligand was more active than MiniPHOS, and it introduced the concept of the "three-hindered quadrant" ligand (Fig. 6). This event demonstrated that this type of C_1-symmetric ligands could outperform C_2 ligands. More recently, Imamoto *et. al.* developed the di(1-adamantyl)phosphine analog of TCFP, named BulkyP*, which also showed high potential in Rh-catalyzed asymmetric hydrogenation. [26] BulkyP* is more crystalline than TCFP and shows air stability in the solid state.

In 2002, X. Zhang and co-workers also took advantage of the stereoselective deprotonation with (–)-sparteine to prepare the TangPhos ligand (Scheme 5a). [27] Initially, *t*-BuPCl$_2$ was reacted with 1,4-bis (bromomagnesio)butane to form phospholane **4**, after protection with sulfur powder. The deprotonation with *n*-BuLi and (–)-sparteine was highly stereoselective for one of the enantiotopic methylene groups, and upon addition of CuCl$_2$, TangPhos sulfide was formed with high diastereoselectivity. Recrystallization gave the optically pure protected ligand in 20% yield. Desulfuration with Si_2Cl_6 in benzene at high temperature delivered air-sensitive TangPhos in 88% yield. Over the years, TangPhos has been used in the Rh-catalyzed asymmetric hydrogenation of many functionalized olefins, as well as in other asymmetric transformations catalyzed by first-row transition metals (Scheme 5b). [28].

A few years after the development of TangPhos, X. Zhang *et. al.* reported a similar ligand named DuanPhos, bearing a more rigid backbone. [29] The preparation of this ligand involves the resolution of racemic DuanPhos P-oxide (*vide infra*). In the last fifteen years, DuanPhos has shown enormous potential in the Rh-catalyzed asymmetric hydrogenation of a vast range of olefins (Fig. 7). [30] In contrast to TangPhos, DuanPhos is air-stable. It is among the ligands most used in the field of Rh-catalyzed asymmetric hydrogenation, and it has also found applications in other asymmetric transformations.

Imamoto and co-workers also used the (–)-sparteine strategy to prepare *tert*-butylmethyl secondary phosphine-borane **5**, which is a key P-stereogenic intermediate (Scheme 6a). [31] After deprotonation of **3**, the oxidation of the formed anion yielded the hydroxymethyl phosphine in 92% ee. The addition of a benzoyl group followed by recrystallization increased the ee to >99%. [32] Finally, this intermediate was hydrolyzed under basic conditions and subjected to Ru-catalyzed oxidation-decarboxylation, yielding **5** in very high enantiopurity. To circumvent the sparteine shortage, the synthesis of **5** and the corresponding enantiomer has also been described via resolution of the racemate using borneol or (*S*)-α-methylbenzylisocyanate as resolving agents. [33] Upon deprotonation with *n*-BuLi, compound **5** is a nucleophilic P*-intermediate that has demonstrated to be very useful in the straightforward preparation of many P-stereogenic diphosphine ligands, including BisP* and MiniPHOS. [34] Phosphine **5** can be transformed in only one step to QuinoxP*, which has shown outstanding potential in the Rh-catalyzed asymmetric hydrogenation of many olefins, as well as in a vast number of other asymmetric C-C and C-heteroatom bond-forming reactions catalyzed by different metals (Scheme 6b). [32,35] These include the Co-catalyzed asymmetric hydrogenation of olefins, Ru-catalyzed reduction of ketones, different Cu-catalyzed borylation reactions, a wide range of Rh-, Pd-, Fe- and Ni-catalyzed C-C coupling transformations, and Ni- or Ag-catalyzed C-N and C-O bond formation reactions. QuinoxP* is arguably the most common and successful P-stereogenic ligand used in asymmetric catalysis.

Over the years, Imamoto and co-workers have developed several analogs of QuinoxP* (Scheme 7). [36] Three-hindered quadrant derivatives have shown improved performance in comparison to QuinoxP*, especially in Cu-catalyzed borylation reactions.

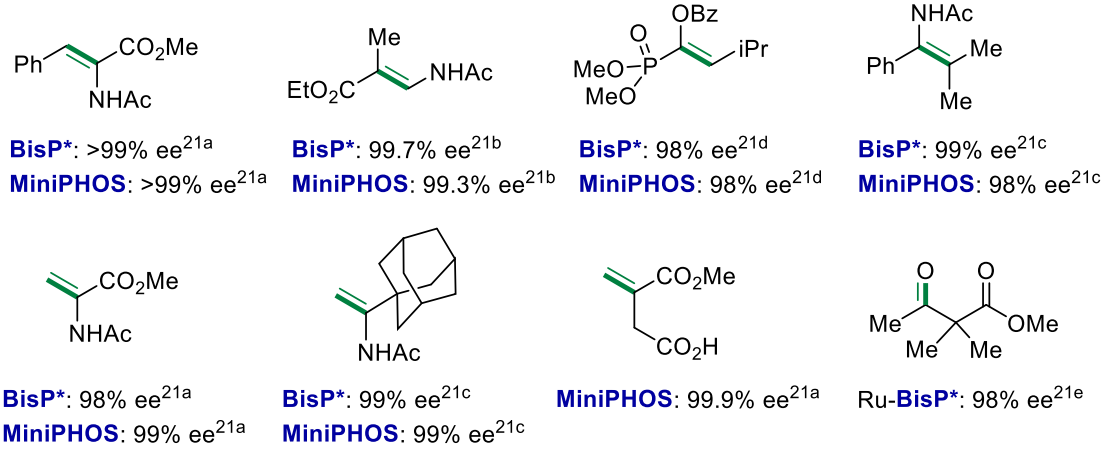


Fig. 4. Application of BisP* and MiniPHOS in the Rh-catalyzed hydrogenation of olefins. Hydrogenated double bonds are shown in green.

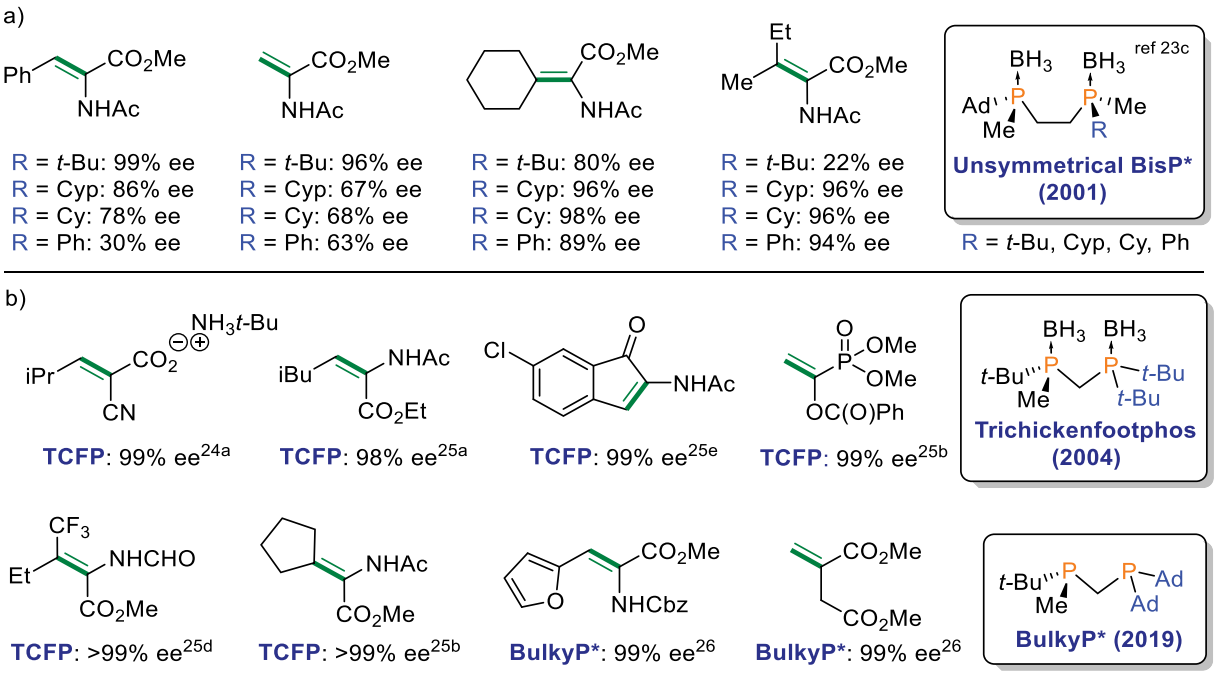


Fig. 5. Highlighted results in Rh-catalyzed asymmetric hydrogenation with a) unsymmetric analogs of BisP* and b) Trichickenfootphos and BulkyP* ligands. Cyp = cyclopentyl. Hydrogenated double bonds are shown in green.

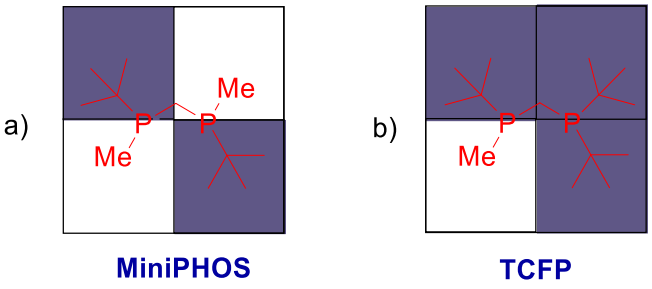


Fig. 6. a) Quadrant diagram for C_2-symmetric ligand like MiniPHOS. b) A three-hindered quadrant diagram for TCFP. Occupied quadrants are shown in purple.

In 2010, inspired by the structure of QuinoxP*, Imamoto's team prepared the BenzP* ligand (Scheme 8a). [37] In this case, the phosphine groups were sequentially introduced into the aryl ring; after deprotonation of **5**, the excess of *n*-BuLi reacted with 1,2-dibromobenzene to give a benzyne intermediate, which was attacked by lithiated **5** to give **6** with complete retention of configuration. After deprotection of the phosphine, the remaining bromide in **6** was lithiated and consecutively reacted with *t*-BuPCl$_2$ and MeMgBr, providing BenzP* as a single diastereomer in moderate yield. This ligand, like QuinoxP*, has demonstrated great potential in asymmetric catalysis, especially in Rh-catalyzed asymmetric hydrogenation and C-C and C-heteroatom couplings, bonded to different metals (Scheme 8b). [36,38].

More recently, the *o*-bromoaryl tertiary phosphine **6** has been used to prepare the P-stereogenic axially chiral BipheP* ligand (Scheme 9a). [39] The lithiation of the bromide followed by homocoupling assisted by Cu(OTf)$_2$ gave BipheP*-BH$_3$ as a single diastereomer, albeit in low yield. BipheP* has provided high enantioselectivity in Rh-catalyzed asymmetric hydrogenation and hydroacylation reactions (Scheme 9b). [40].

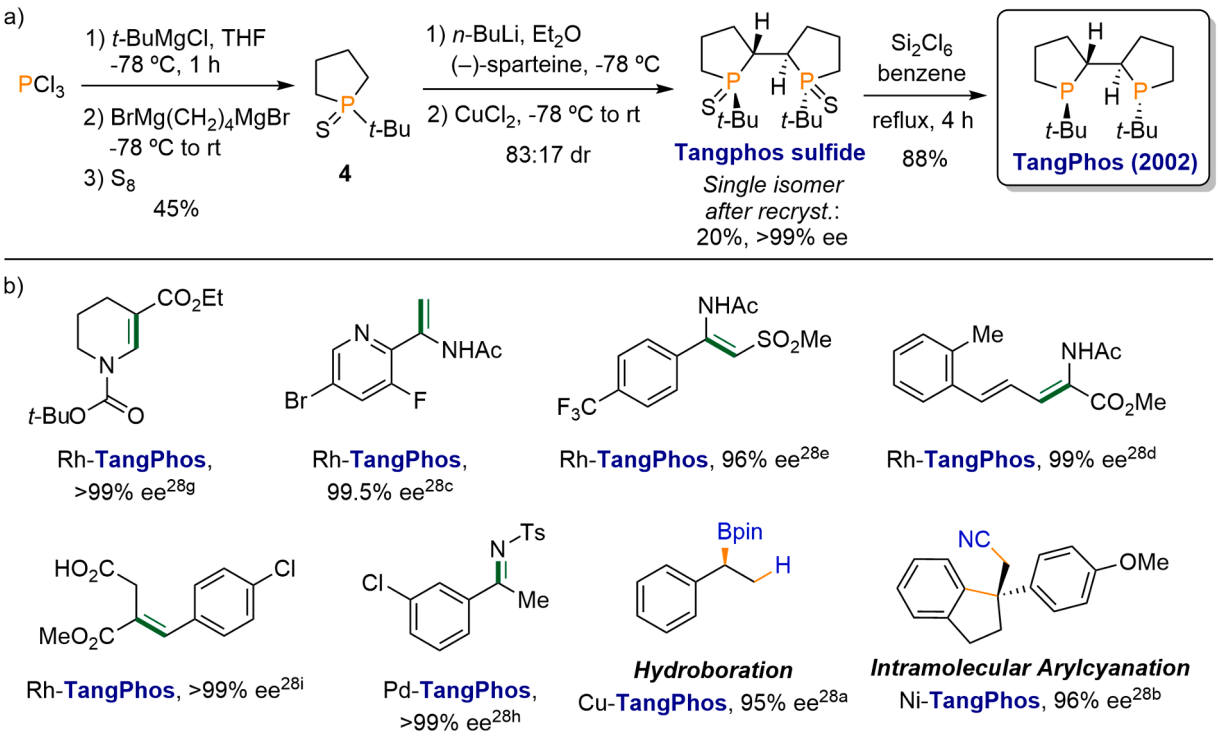
4.2. *Stereoselective synthesis using chiral auxiliaries*

To date, the use of chiral auxiliaries is still the method of choice for the synthesis of bulky P-stereogenic ligands. Here, the chiral auxiliary reacts with a phosphorus precursor to generate a diastereomerically enriched intermediate, in which auxiliary and phosphine are covalently bound. In the reaction between the two, the P-stereogenic center is either generated (prochiral precursor) or modified (chiral racemic precursor). In this regard, the chiral information of the auxiliary can influence the preferential formation of one of the two diastereomers. Unlike the classical resolution of racemates, this strategy gives high yields of the desired diastereomeric phosphine. The most used chiral auxiliaries are commercially available alcohols, amines, or amino alcohols. After separation of the two diastereomers, the auxiliar moiety is stereoselectively cleaved to yield the enantioenriched P-stereogenic compounds.

4.2.1. *Menthol as chiral auxiliary*

In 1967, Korpiun and Mislow were the first to use a chiral auxiliary to prepare P-stereogenic compounds. [41] Menthyl phosphinates **8** were prepared by reacting racemic chlorophosphine **7** with (–)-menthol, at ~300 g scale (Scheme 10a). However, the chiral auxiliary did not induce any stereoselectivity in the transformation, and a 1:1 diastereomeric mixture was obtained. Nevertheless, the two diastereomers could be separated by recrystallization in hexanes. Next, (S_P)-**8** was reacted with different alkyl and aryl Grignard reagents, yielding methylphenyl tertiary phosphines (Scheme 10b). This transformation was highly stereospecific with inversion of configuration at the phosphorus atom. It was observed that the reactivity and/or stereospecificity decreased as the steric hindrance of the groups at the phosphorus atom and on the Grignard reagent increased. In the following years, further work by Mislow and others allowed the preparation of a considerable number of P-stereogenic tertiary phosphines carrying a range of different aryl and alkyl groups. [42].

4.2.1.1. The DIPAMP ligand and derivatives. Knowles took advantage of the menthol methodology to prepare CAMP and DIPAMP ligands, the first trivalent phosphines to be used in asymmetric hydrogenation (Scheme 11). [5,8,12] After that, Imamoto and co-workers also employed (–)-menthol to prepare other tertiary phosphine boranes, which also gave access to DIPAMP. [16] Alternatively, tertiary



Scheme 5. a) Synthesis of the TangPhos ligand and b) highlighted results in Rh-catalyzed asymmetric hydrogenation and other reactions. Hydrogenated double bonds are shown in green and newly formed bonds in orange.

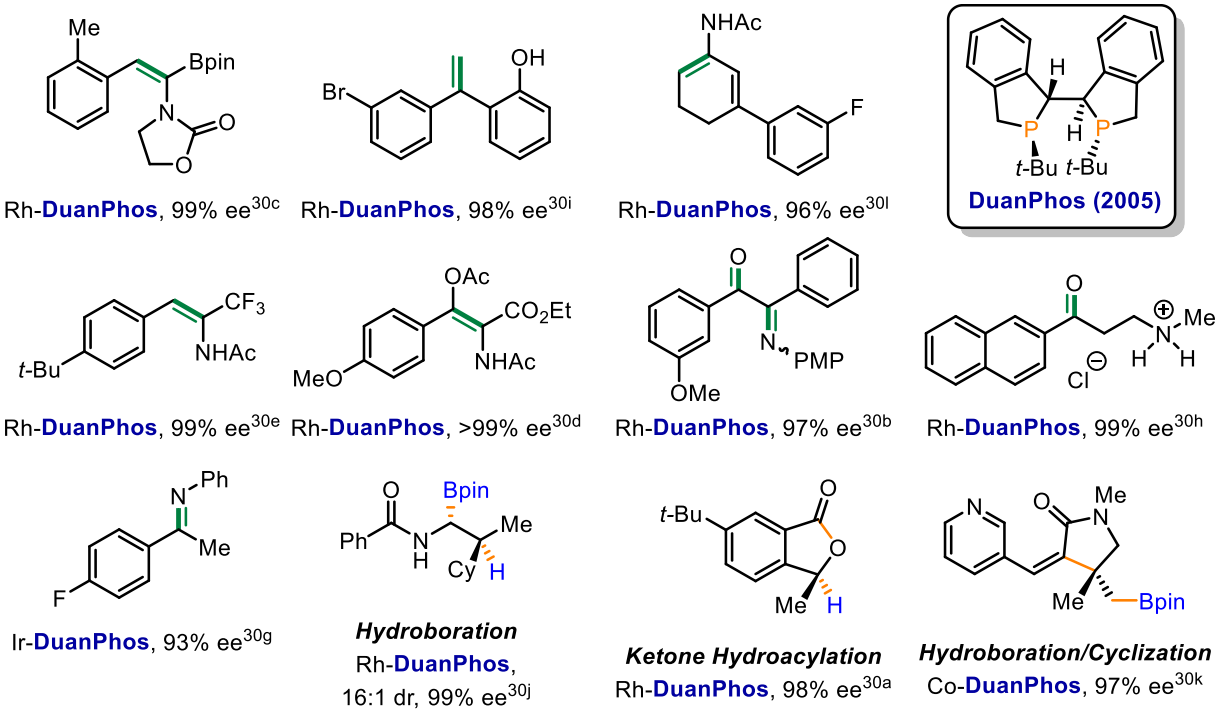
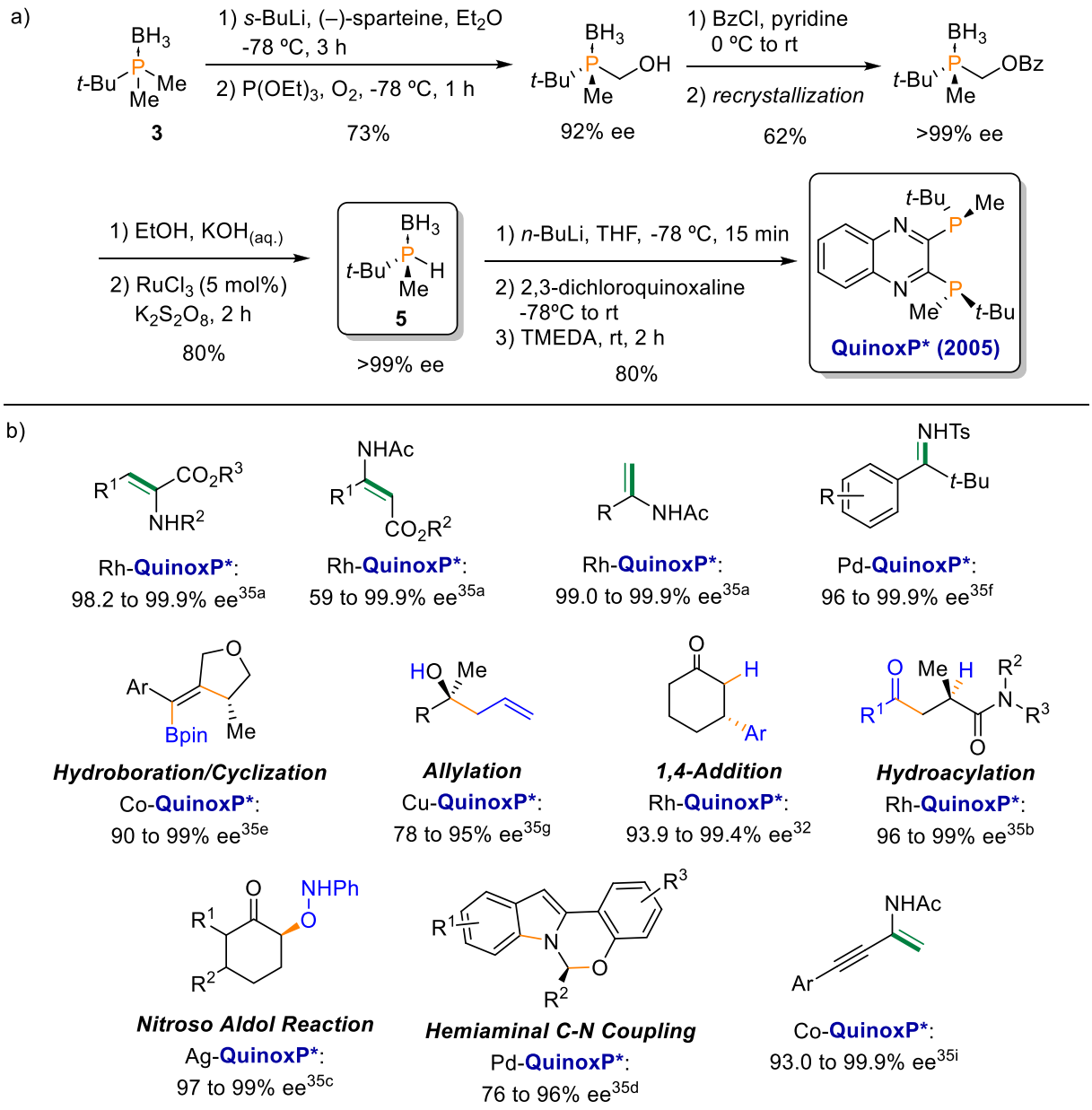


Fig. 7. Highlighted results of DuanPhos in asymmetric hydrogenation and other reactions. PMP = *p*-methoxyphenyl. Hydrogenated double bonds are shown in green and newly formed bonds in orange.

phosphine boranes and oxides were achieved by stereospecific reductive cleavage of the menthyl moiety in **8** with lithium naphthalenide or Li-NH_3, followed by addition of an electrophile. [43].

The Rh-DIPAMP catalytic system hydrogenated several trisubstituted and terminal olefins bearing different coordinating groups in very high enantioselectivities, in comparison to the values obtained with the few ligands available at that time (Fig. 8). [12,13] Also, as stated earlier, the exceptional results for the hydrogenation of **1**, a precursor of L-DOPA, allowed the use of DIPAMP in the industrial production of this drug. [9].

Thanks to the initial success of DIPAMP, several research labs studied the catalytic performance of other bis(diarylphosphine)ethane ligands with modified aryl groups. The results with ligands **9** and **11**–**14**

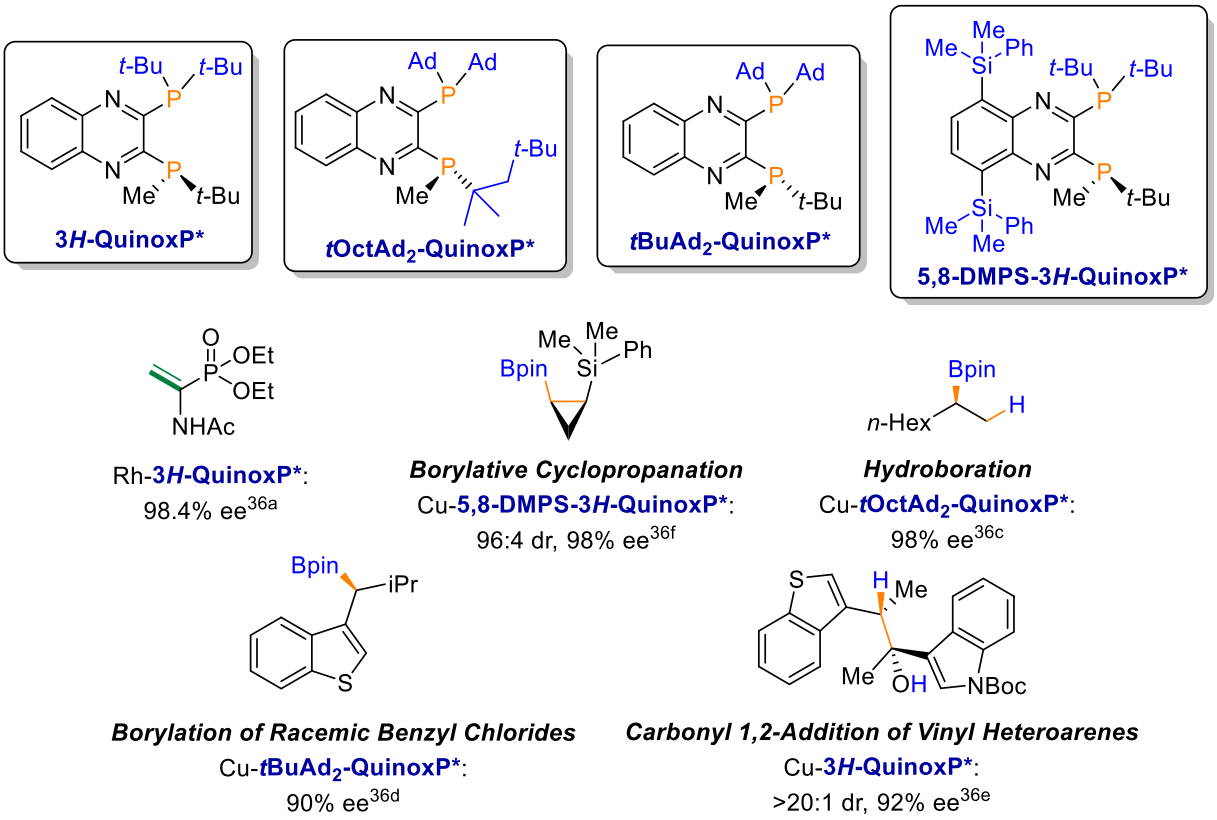


Scheme 6. a) Synthetic strategy for the preparation of **5** and ligand QuinoxP*. b) Selected results obtained in asymmetric catalysis with QuinoxP*. TMEDA = *N,N,N',N'*-tetramethylethylenediamine. Hydrogenated double bonds are shown in green and newly formed bonds in orange.

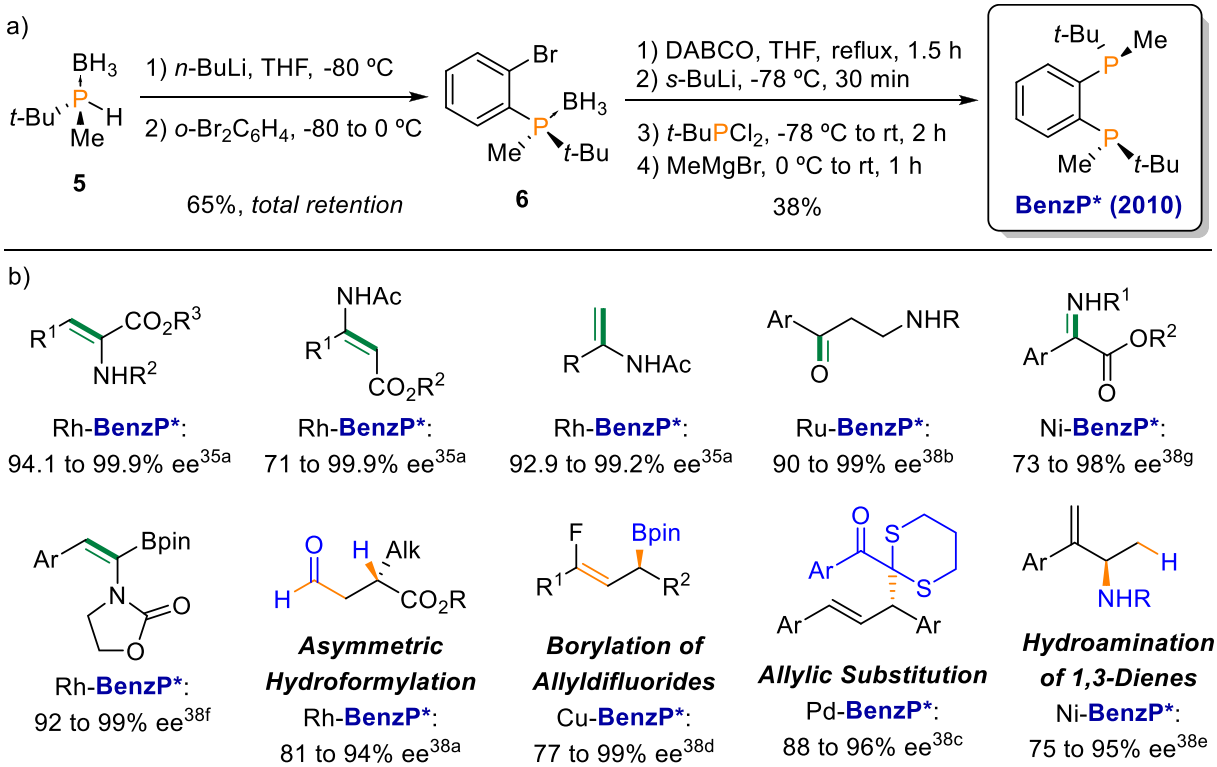
demonstrated that increasing the bulk of the *ortho* substituent or introducing extra groups in the anisyl ring improved performance in the asymmetric hydrogenation of certain substrates (Fig. 9). [44] Of note, ligands **9** and **10** reduced challenging tetrasubstituted olefins in good to high enantioselectivities.

Stephan, Mohar and co-workers have also reported a broad number of analogs of DIPAMP, named SMS-Phos, which bear bulkier substituents in the alkoxy group of the functionalized aryl ring. [45] The rhodium complexes of several of these ligands have demonstrated marked ability to hydrogenate a wide range of terminal, trisubstituted, and certain tetrasubstituted olefins, in high enantioselectivities (Fig. 10). These results showcase the importance of differentiating the two aryl groups in C_2-symmetric diphosphines to attain high enantioselectivity. In particular, the scope of this catalytic system in asymmetric hydrogenation has been extensively studied for ligands bearing iPr, *t*-Bu and Cy groups. [45,46] Recently, chemists at Boehringer Ingelheim (BI) reported a scalable, chromatography-free synthesis of *t*-Bu-SMS-Phos. [46] This ligand excels in the hydrogenation of trifluoromethyl vinyl acetate (99% ee) that yields after hydrolysis enantiomerically pure 1,1,1-trifluoro-2-propanol, a relevant pharmaceutical intermediate.

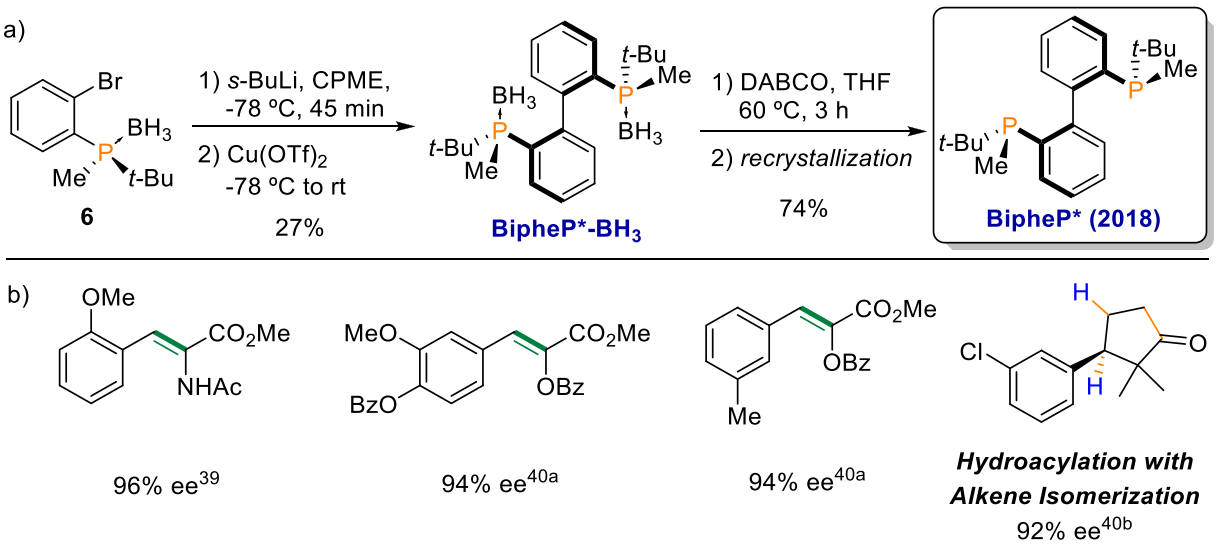
4.2.1.2. Menthyl H-phosphinates as building blocks. Inspired by the work of Mislow, [47] Buono and co-workers described the preparation of menthyl *H*-arylphosphinates **15** and their reaction with different organometallic reagents to prepare secondary phosphine oxides (SPOs) **16** in high ee (Scheme 12). [48] They also demonstrated that these SPOs could be transformed to phosphinous acid-boranes **17** in three simple steps. Using a methodology devised by Pietrusiewicz and co-workers, [49] these intermediates were activated and reduced to secondary phosphine boranes **18** (SPBs), with global retention of configuration from **16**. The secondary phosphine boranes were deprotonated and functionalized with diverse electrophiles to yield bulky tertiary phosphine boranes (TPBs), with little loss of enantiopurity in most cases. In addition to their utility as versatile building blocks, SPOs have demonstrated potential as ligands in several metal-catalyzed asymmetric transformations. [50].



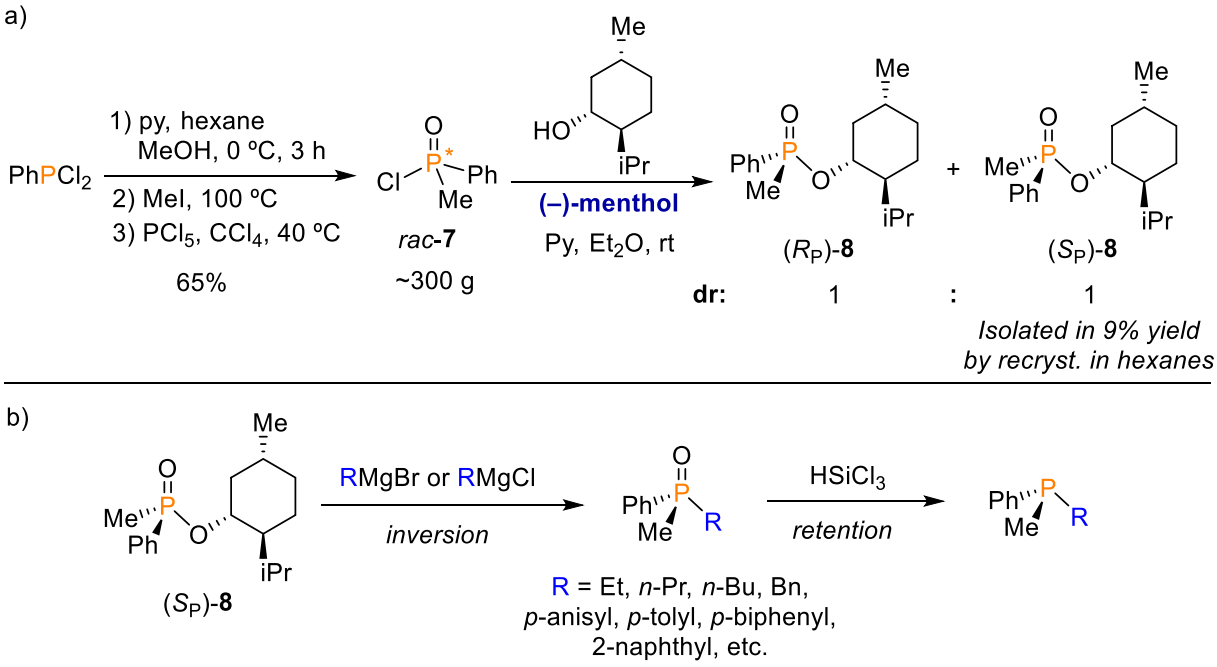
Scheme 7. Structure of C_1-symmetric QuinoxP* analogs and application in asymmetric catalysis. Hydrogenated double bonds are shown in green and newly formed bonds in orange.



Scheme 8. a) Synthesis of the BenzP* ligand, b) highlighted applications in asymmetric catalysis. DABCO = 1,4-diazabicyclo[2.2.2]octane. Hydrogenated double bonds are shown in green and newly formed bonds in orange.



Scheme 9. Synthesis of BipheP* and its application in Rh-catalyzed asymmetric catalysis. CPME = Cyclopentyl methyl ether. Hydrogenated double bonds are shown in green and newly formed bonds in orange.

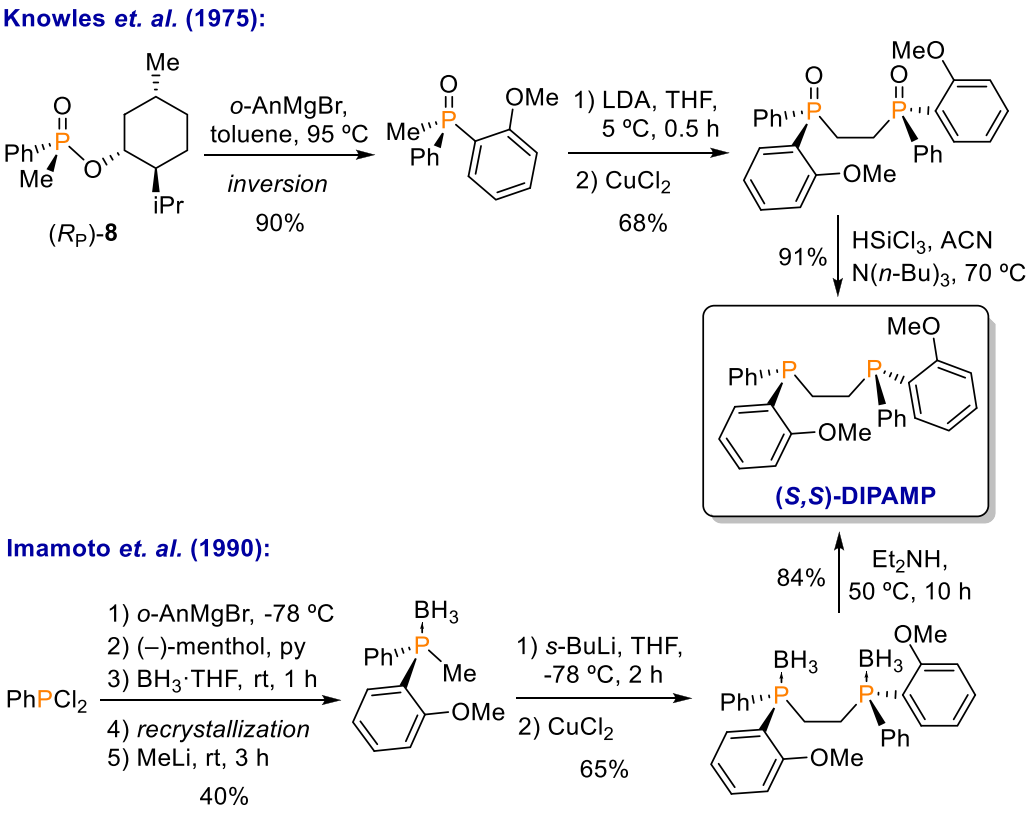


Scheme 10. a) Synthesis of diastereomeric menthyl phosphinates **8** by Korpiun and Mislow. b) Enantioselective S_N2@P for the preparation of P-stereogenic tertiary phosphines.

Later, Buono's group resolved the related adamantyl *H*-phenylphosphinate by chiral HPLC (see Fig. 17) and used it to access *tert*-butyl phenyl SPO **18a** in very high yield and ee, without need of recrystallization. [51] *H*-Phosphinate **18a** has also been used to prepare hydroxyalkyl tertiary phosphine boranes, which are masked secondary phosphine boranes that can be activated *in situ* to prepare TPBs, mostly with high ee's. [35,52].

Similarly, in 2008, L. B. Han and co-workers also used the S_N2@P of menthyl *H*-phenylphosphinate with organometallic reagents to prepare a wide range of secondary phosphine oxides, mostly with high enantioselectivity. [53] In some instances, the phosphide intermediate was trapped with alkyl halides instead of a proton source to generate tertiary phosphine oxides (TPOs). More recently, other groups have expanded the number of described TPOs with the *tert*-butyl phenyl pair at phosphorus by functionalizing enantioenriched **18a** via several strategies; Chrzanowski and co-workers have described the Pd-catalyzed arylation of **18a** with aryl halides, with high ee's. [54] Che's team has reported the light-induced coupling of **18a** with pyridinyl halides in basic media, with very high stereospecificity. [55].

Recent years have witnessed considerable development of the preparation and chemistry of menthyl phosphinates. [56] One of the main advantages of menthol over other chiral auxiliaries is that it is inexpensive. However, in most synthetic strategies, menthol does not provide any diastereoselectivity. [57] This has led to the predominant choice of other more efficient methods to tackle the synthesis of P-stereogenic synthons and ligands.



Scheme 11. Preparation of the DIPAMP ligand by the teams led by Knowles and Imamoto.

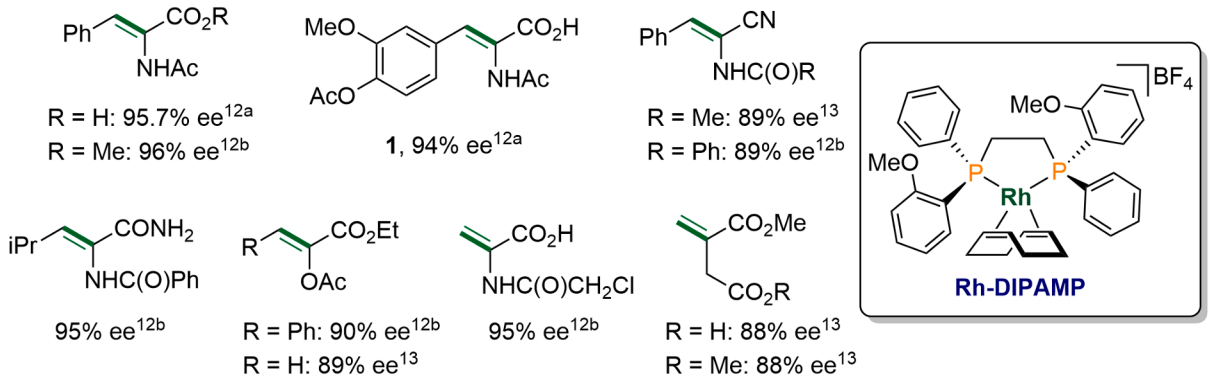


Fig. 8. Selected results of DIPAMP in the Rh-catalyzed asymmetric hydrogenation of olefins. Hydrogenated double bonds are shown in green.

4.2.2. Amines as chiral auxiliaries

In 2003, Kolodiazhnyi and co-workers reported that the reaction between racemic chlorophosphines and a chiral amine, (*S*)-1-phenylethan-1-amine, proceeded with considerable diastereoselectivity. [58] Later, Riera and Verdaguer took advantage of this strategy and prepared several aminophosphines by reacting *tert*-butylphenyl and *tert*-butylmethyl chlorophosphines with different chiral amines, achieving moderate to good diastereomeric ratios (Scheme 13). [59] After recrystallization, **19a** was transformed to primary aminophosphine **20** by reductive cleavage at the benzylic position with Li/NH_3. More recently, other groups have also used chiral 1,1-disubstituted methylamines to prepare P-stereogenic intermediates and ligands. [60].

Riera and Verdaguer's lab used aminophosphine **20** for the preparation of the MaxPHOS ligand, an analog of TCFP (Scheme 14a). [59] After reaction with *t*-Bu_2PCl and deprotection with HBF_4, the salt of the ligand was obtained in high yield. The ^{1}H NMR spectra of **21** and MaxPHOS·HBF_4 suggest that the tautomeric equilibrium is completely displaced towards the P-H form in both compounds. Also, the X-ray structure of MaxPHOS·HBF_4 showed that the positive charge is evenly distributed between the two phosphorus atoms. [61] The Rh-MaxPHOS complex showed excellent results in the asymmetric hydrogenation of a wide range of terminal and trisubstituted enamides (Scheme 14b). This catalyst has also been used in the intramolecular Pauson-Khand reaction of enynes. [62].

Intermediate **20** was also used in the preparation of secondary iminophosphorane (SIP) ligands (Scheme 15). [63] Upon addition of a rhodium source, SIPs coordinated as bidentate P,O ligands. The Rh-SIP catalyst with a 2,4,6-triisopropylphenyl (Tripp) substituent proved effective in the Rh-catalyzed [2+2+2] intramolecular cycloaddition of terminal enediynes, achieving good to high enantioselectivities.

In 2011, Jones reported that the reaction between chiral oxazolidinone **22** and racemic chloromethylphenylphosphine oxide took place with excellent diastereoselectivity (Scheme 16). [64] Moreover, the cleavage of the P-N bond with Grignard reagents was highly

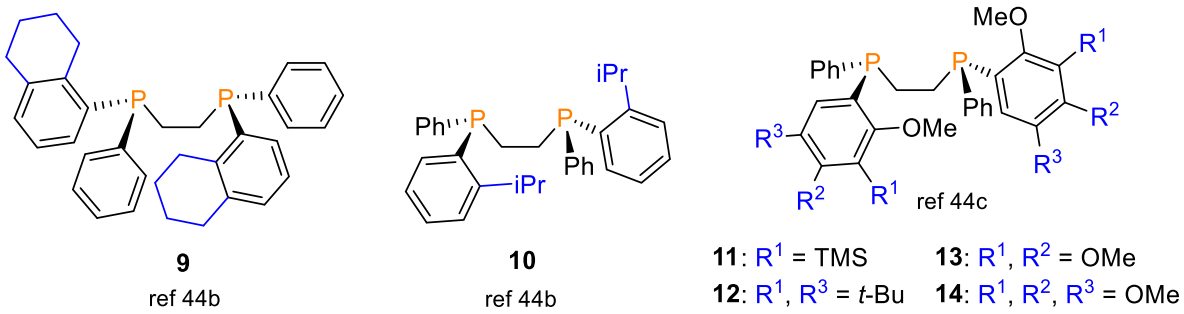


Fig. 9. DIPAMP analogs and prominent results in Rh-catalyzed asymmetric hydrogenation. Hydrogenated double bonds are shown in green.

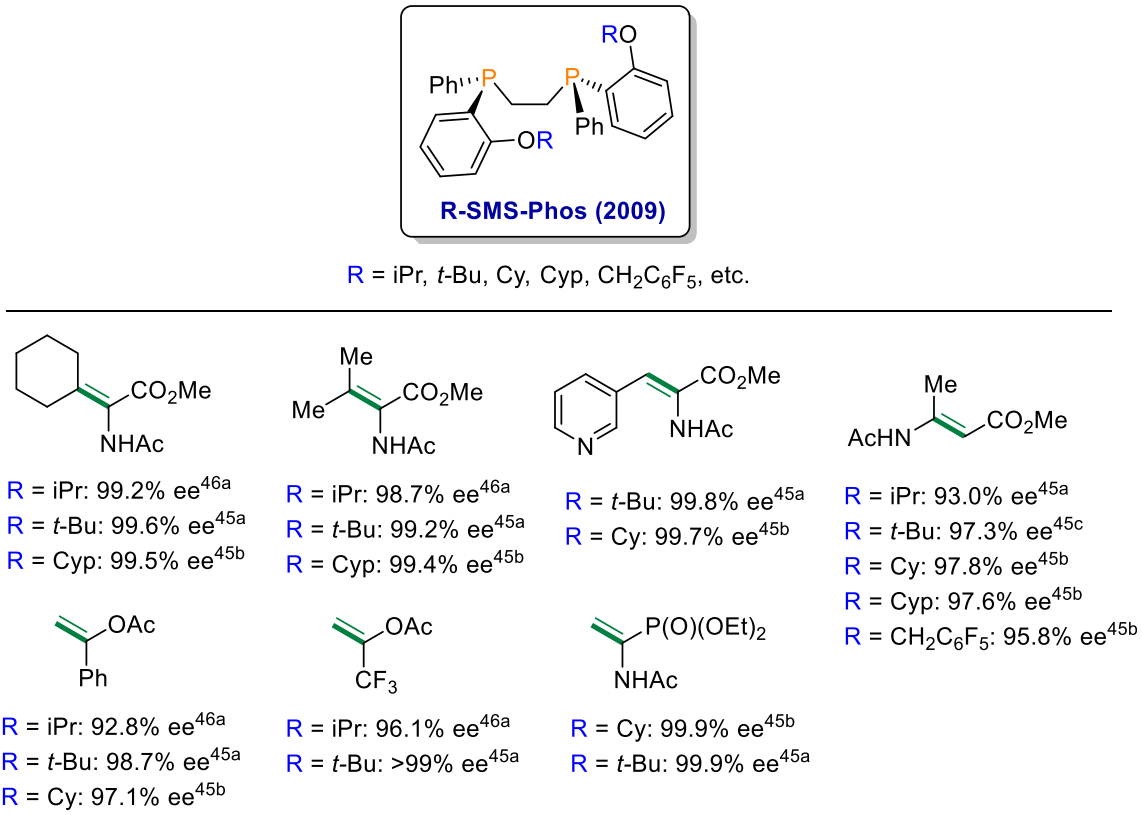
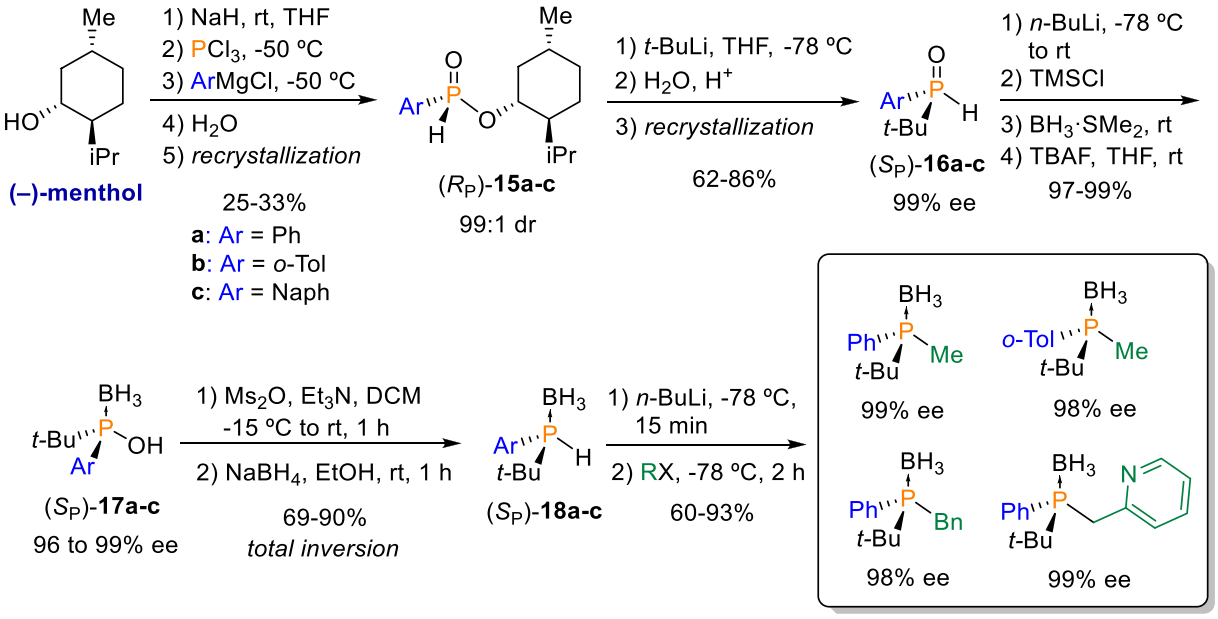


Fig. 10. Highlighted results of SMS-Phos ligands in Rh-catalyzed asymmetric hydrogenation.

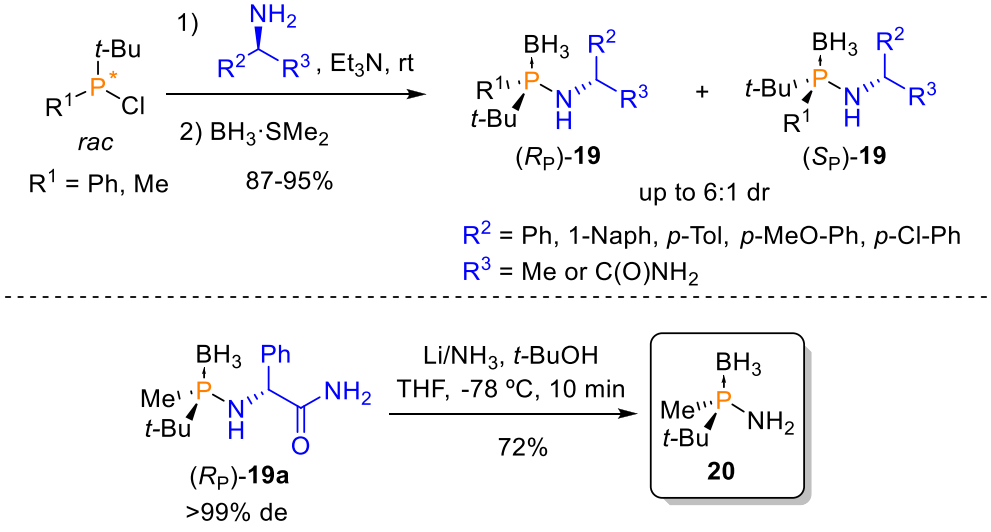
stereospecific, allowing the synthesis of several tertiary methylphenylphosphine oxides in very high ee's.

4.2.3. *Bifunctional chiral auxiliaries*

4.2.3.1. Ephedrine as chiral auxiliary. In 1990, Jugé and co-workers reported a strategy for the preparation of tertiary phosphine boranes involving the amino alcohol (–)-ephedrine as chiral auxiliary. [17] The method started with a highly diastereoselective condensation between prochiral bisamido phosphine **23** and (–)-ephedrine, yielding oxazaphospholidine **24** in >95:5 dr (Scheme 17). After recrystallization, **24** was isolated as a single diastereomer in 80% yield. The oxazaphospholidine was then opened by cleavage of the weaker P-O bond with organolithium reagents at low temperature, achieving diastereoselectivities higher than 92:8 and retention of configuration at the phosphorus atom. This stereochemical outcome was rationalized by a kinetically controlled front-side attack of the nucleophile, followed by reorganization in the pentacoordinated phosphorus intermediate. [65] Next, the stereospecific methanolysis of the P-N bond provided the



Scheme 12. Preparation of secondary and tertiary phosphines via menthyl *H*-phosphinates by Buono and co-workers. TBAF = tetrabutylammonium fluoride.



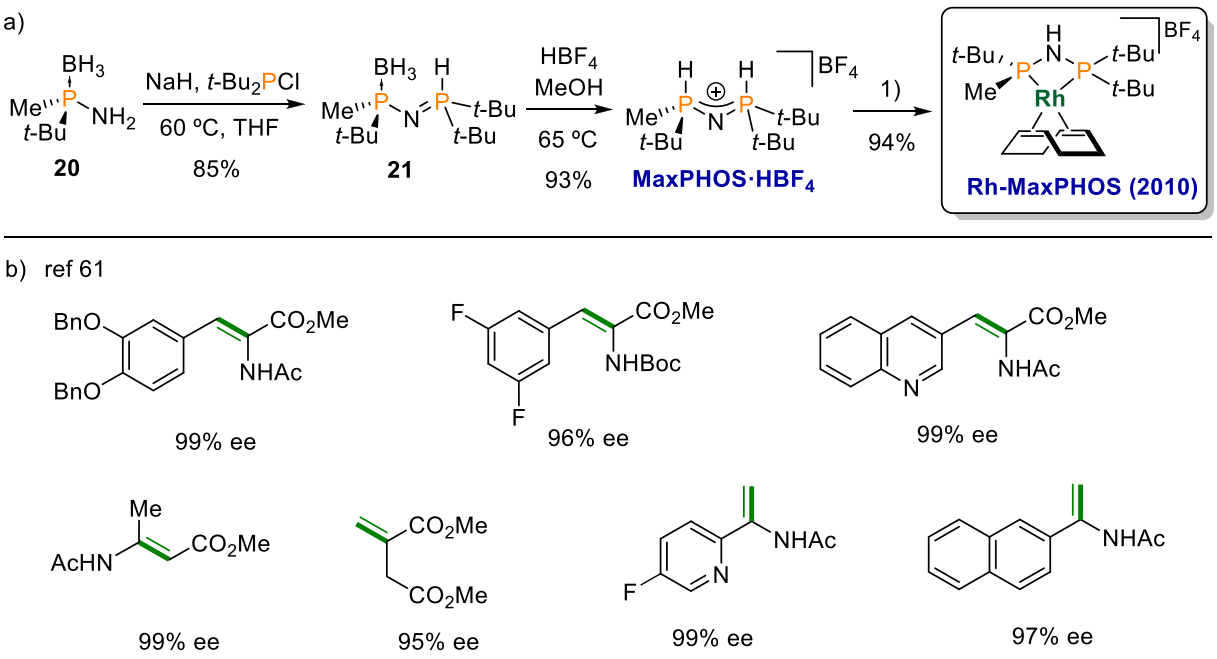
Scheme 13. Preparation of chiral aminophosphines with 1,1-disubstituted methylamines and transformation of **19a** to synthon **20**.

phosphinite boranes, which were substituted again with organolithiums to yield the tertiary phosphines. Each of these last two steps occurred with inversion of configuration at the phosphorus atom. The hydrolysis of the aminophosphine intermediate **25** was also carried out with HCl, yielding relatively stable chlorophosphine boranes. [66].

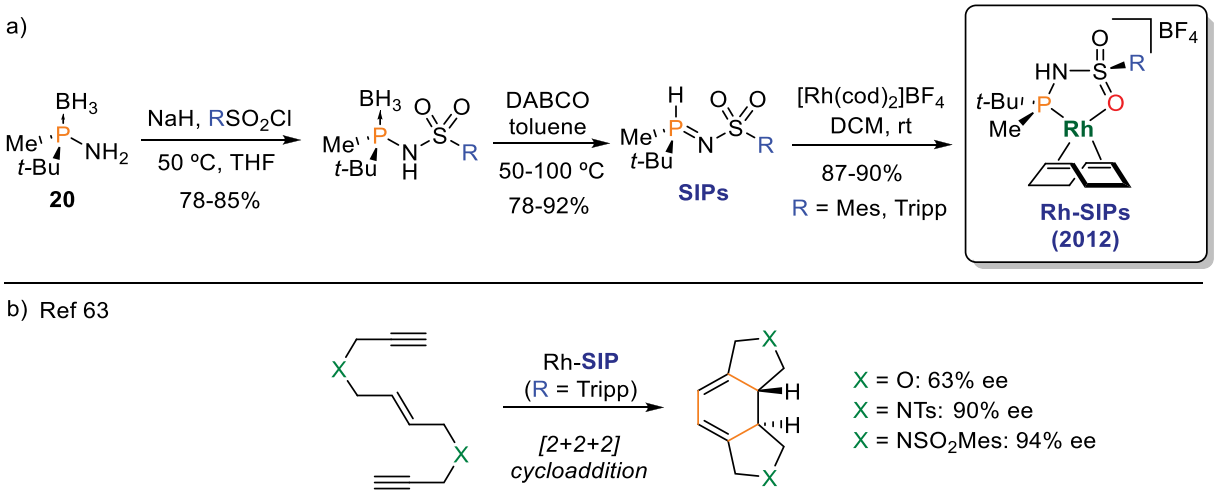
Over the years, Jugé and others have used this methodology to prepare many different tertiary phosphine boranes and numerous P-stereogenic ligands (Fig. 11). [44a,46a,67] In fact, this approach is one of the most commonly used strategies for the synthesis of P-stereogenic compounds.

However, the ephedrine method is not efficient when bulky substituents are present either in the organolithium reagent or at the phosphorus atom. Mezzetti and co-workers reported null or very low reactivity in the reaction between **24** and organolithiums with *tert*-butyl, 9-anthryl or mesityl groups. [44a] Jugé also observed that the acidolysis of the P-N bond in **25** did not occur when the phosphine carried a *tert*-butyl moiety. [66] Also, Laing's group observed a considerable degree of racemization in the reaction of phenyllithium with a phosphinite bearing an adamantyl group when harsh conditions were used to force the reaction. [67b] Because of their potential in asymmetric hydrogenation and other transformations P-stereogenic phosphines bearing bulky groups (especially *tert*-butyl) are very coveted for chemists, and therefore, some research groups have developed alternative diastereoselective syntheses that overcome the drawbacks presented by this method.

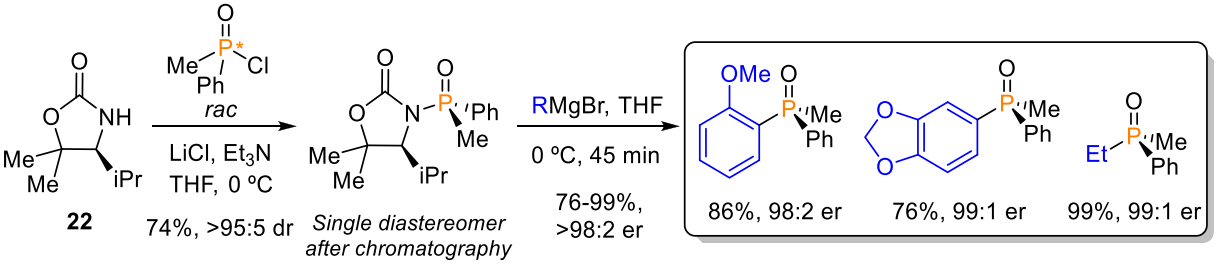
4.2.3.2. cis-1-Amino-2-indanol as chiral auxiliary. In 2011, Riera, Verdaguer and co-workers developed an improved synthetic route for the preparation of the *tert*-butylmethyl aminophosphine **20** (Scheme 18). [68] Reaction between *tert*-butylchloro(diethylamino)phosphine and *cis*-1-amino-2-indanol yielded oxazaphospholidine **26** with 18:1 dr. After recrystallization, **26** was isolated as a single diastereomer. Ring opening with MeMgBr at high temperature then took place with high yield and complete diastereoselectivity. This transformation was also very efficient with other bulky Grignard reagents. Opposite to that observed in the ephedrine method, the reaction occurred with inversion of configuration at the phosphorus atom. [65] The same team later



Scheme 14. a) Synthesis of the Rh-MaxPHOS catalyst. Reagents and conditions: 1) $[Rh(cod)_2]BF_4$, Na_2CO_3, MeOH, rt. b) Highlighted results in Rh-catalyzed asymmetric hydrogenation. Hydrogenated double bonds are shown in green.



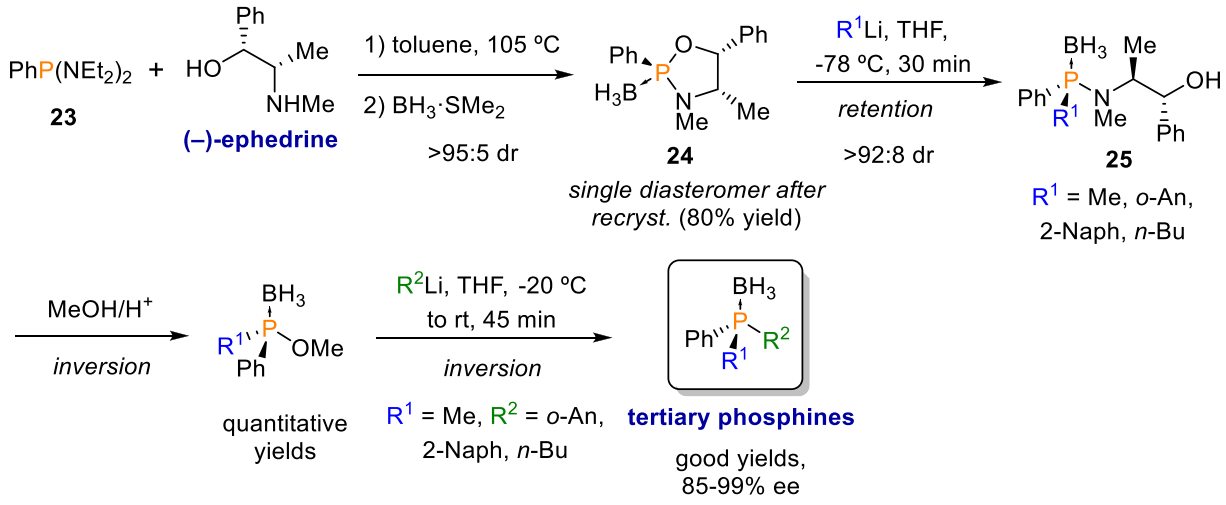
Scheme 15. a) Synthesis of Rh-SIP catalysts and b) application in [2+2+2] cycloadditions. Newly formed bonds are shown in orange.



Scheme 16. Use of oxazolidinones in the preparation of tertiary methylphenylphosphine oxides.

demonstrated that the absence of the *N*-methyl group was responsible for this difference in stereochemical outcome [69]. Finally, reductive cleavage at the benzylic position yielded aminophosphine **20**. Alternatively, acidolysis of intermediate **27** afforded *tert*-butylmethyl phosphinous acid **28,** with very high yield and with total inversion of configuration. [70] This synthon was kept as a dialkylammonium salt (**28b**) to increase its stability. [71].

As previously mentioned, Pietrusiewicz [49] and Buono [48c] showed that mesyl-activated aryl(*tert*-butyl)phosphinous acids **29a** undergo nucleophilic reduction with $NaBH_4$ to give the corresponding



Scheme 17. Initial results in the preparation of tertiary phosphines via (–)-ephedrine by Jugé *et. al.*

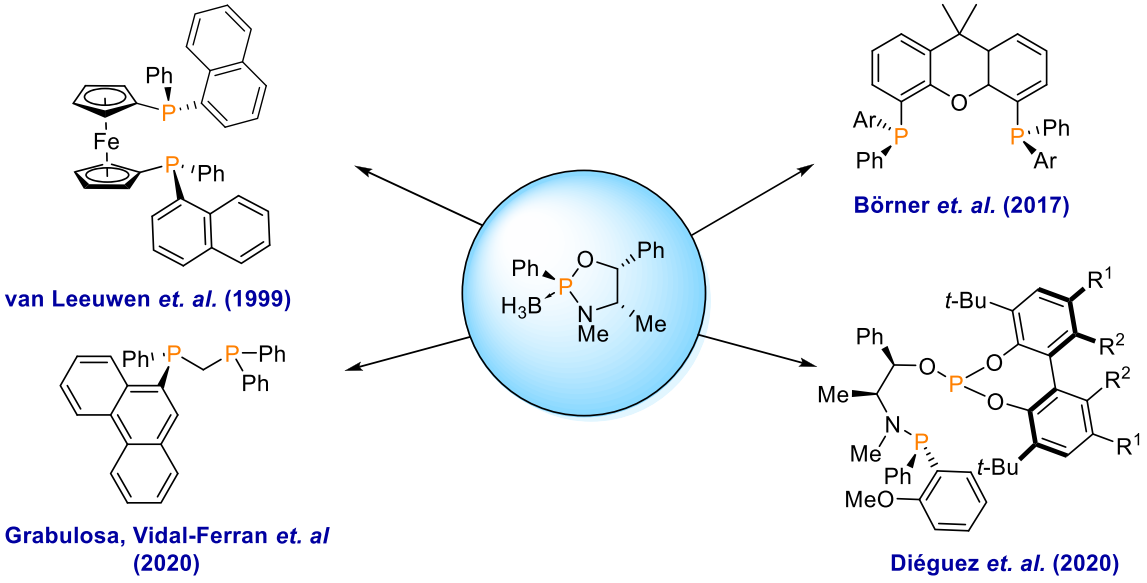


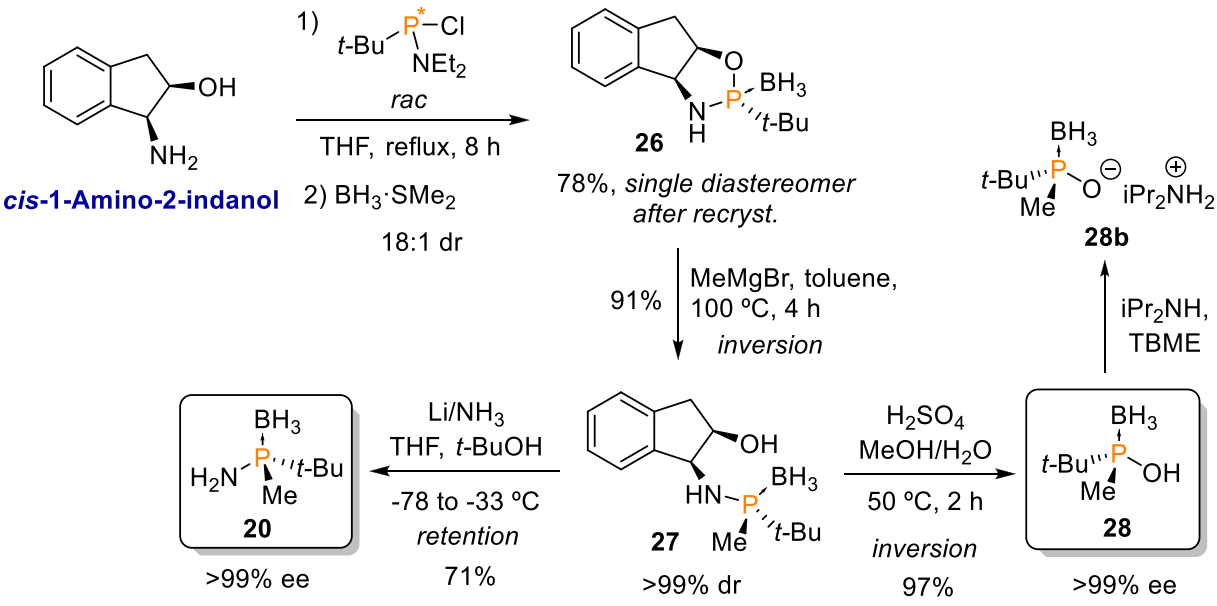
Fig. 11. Examples of P-stereogenic ligands prepared by the ephedrine method.

secondary phosphine borane **18** (Scheme 19). In the case of *tert*-butylmethyl phosphinous acid **28**, the reduction was accomplished in a one-pot reaction using tetrabutylammonium borohydride at –20 °C, with excellent results. [72] This approach represents an alternative route to Imamoto's secondary phosphine intermediate **5**.

Riera, Verdaguer and co-workers expanded this methodology using amines as nucleophiles (Scheme 20a). [70] In this regard, several primary amines and cyclic secondary ones were coupled to phosphinous acid **28**, providing P-stereogenic aminophosphines in high yield and very high enantiopurity. The reaction was not efficient with non-cyclic secondary amines, alcohols, or thiols. The phosphino-oxazoline MaxPHOX family of ligands was prepared using this methodology (Scheme 20b). [73] After an initial coupling between a readily available amino acid and an amino alcohol, the resulting amide was reacted with mesyl-activated phosphinous acid **29b**, obtaining **30** in moderate to high yields. The reaction was completely chemoselective for the primary amine, and a single diastereomer was observed by ^{1}H NMR. Finally, cyclization to form the oxazoline ring and coordination to iridium delivered the Ir-MaxPHOX catalyst. The fact that each of the three stereocenters of the catalyst comes from three independent chiral building blocks allowed the facile arrangement of a library of ligands, with different substituents in the oxazoline ring and distinct configurations at the oxazoline, backbone bridge, and phosphine moieties.

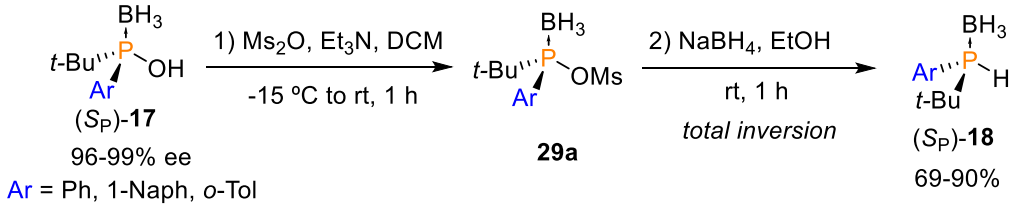
Of note, MaxPHOX catalysts with different configurations and substituents in the oxazoline ring proved extremely effective in the hydrogenation of several types of alkenes (Fig. 12). The hydrogenation of cyclic enamides with catalyst **A**, with the *tert*-butyl groups of the oxazoline and phosphine in a *cis* disposition, provided an outstanding 99% ee in up to 11 examples (Fig. 12a). Catalyst **A** outperformed the most efficient Ru and Rh catalysts, which are more typical for the hydrogenation of these coordinative substrates. [73] The reaction also gave excellent results when performed with greener solvents, such as methanol or ethyl acetate, instead of DCM. The MaxPHOX catalysts **B** and **C**, in this case with a *trans* disposition of the bulky groups on the oxazoline and phosphine moieties, also provided excellent results in the hydrogenation of terminal 2-aryl allyl phthalimides and challenging tetrasubstituted olefins, respectively (Fig. 12bc). [74,75] Ir-MaxPHOX catalysts have also found application in the asymmetric isomerization of allyl amines and allyl alcohols. [76].

The Ir-MaxPHOX catalyst was also used in the hydrogenation of *N*-aryl imines with selectivity up to 96% ee (Scheme 21). [77] Pfaltz and co-workers reported that, in the hydrogenation of imines with an Ir-P,N

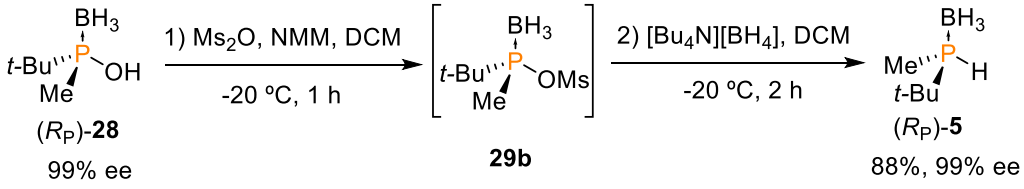


Scheme 18. Synthesis of synthons **20** and **28** using *cis*-1-amino-2-indanol as chiral auxiliary.

Buono *et. al.* (2011):



Riera, Verdaguer *et. al.* (2016):



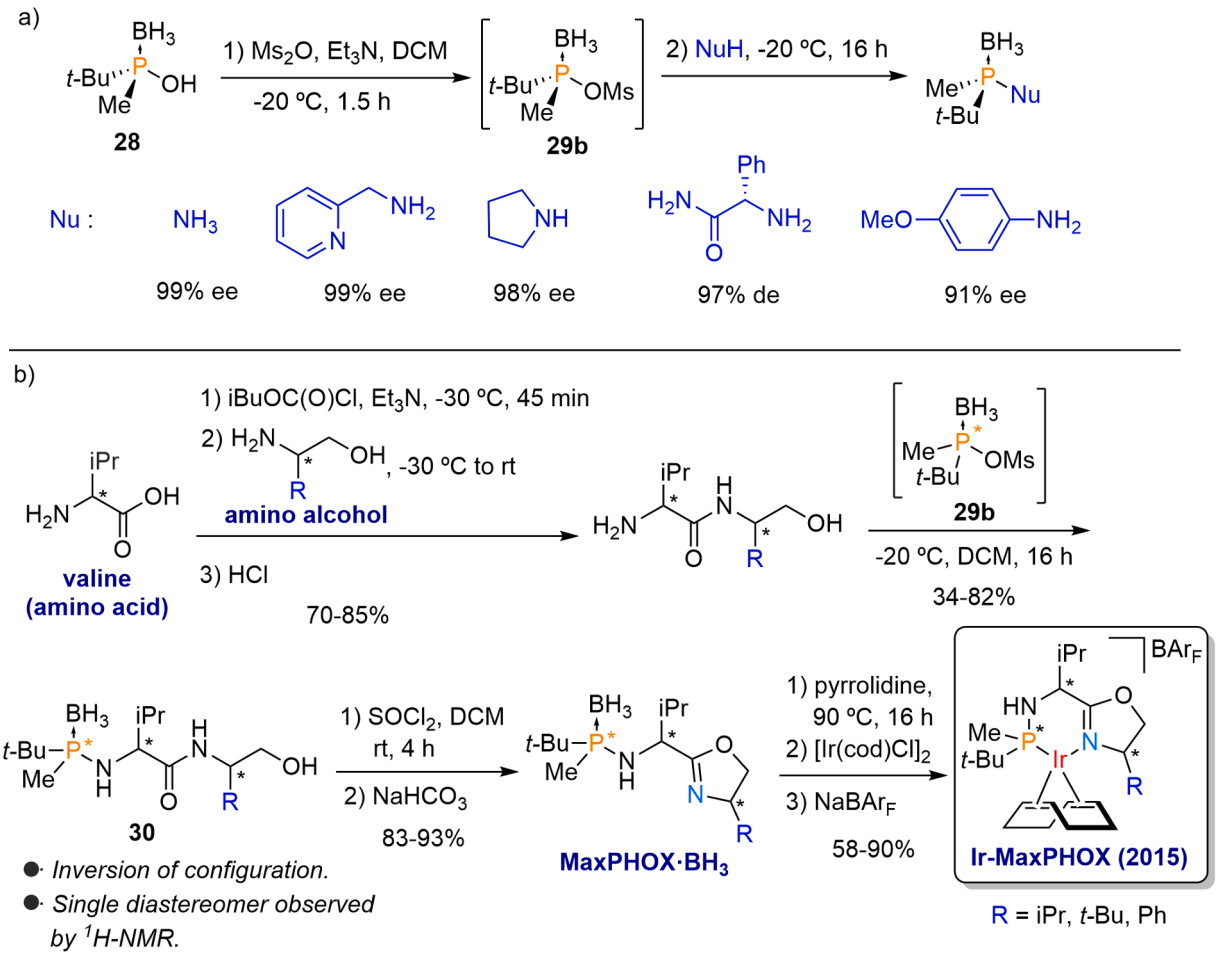
Scheme 19. Preparation of secondary phosphine boranes by reduction of phosphinous acids. NMM = *N*-methylmorpholine.

complex, the actual catalyst is an iridacycle formed by cyclometallation of the imine substrate. [78] Following this lead, Riera, Verdaguer and co-workers isolated the neutral imine-cyclometallated complex **32** and demonstrated that, upon abstraction of the chloride with $NaBAr_F$, the resulting complex catalyzed the hydrogenation of **31**. This finding confirmed that the cyclometallated iridacycle was also the real catalyst in the Ir-MaxPHOX system. Further development of this system allowed the isolation of cationic complex **33**, where the vacant coordination site is occupied by a molecule of THF (Fig. 13). Most notably, this cyclometallated catalyst is active in the hydrogenation of *N*-methyl imines, which are challenging substrates. [79] This complex also proved very active and highly enantioselective for other *N*-alkyl imines at 3 bar of H_2 pressure. In some instances, to further increase selectivity, the temperature was lowered to 0 or −10 °C. This was the first report of highly enantioselective direct hydrogenation of *N*-methyl imines.

Activated phosphinous acid **29b** has recently been used to build another family of P-stereogenic phosphine-oxazoline ligands based on threonine (Scheme 22a). [80] Catalyst **34** containing a 3,5-di-*tert*-butylphenyl group in the oxazoline ring provided the best results in the hydrogenation of *N*-Boc-2,3-diarylallyl amines, with selectivity up to 99% ee (Scheme 22b). Cyclization of the reduced substrates allowed for an enantioselective synthesis of chiral 3-aryl tetrahydroquinolines (THQs).

Phosphinous acid salt **28b** was also transformed into the corresponding benzyloxymethyl (BOM)-phosphinite **35**, resulting in an efficient electrophilic P-stereogenic transfer reagent for the synthesis of bulky tertiary phosphines (Scheme 23). [81] The methodology relies on a one-pot deprotection/substitution on the trivalent phosphinite—a process that takes place with very high stereospecificity. The potential of this strategy was demonstrated with the synthesis of a wide range of tertiary phosphines with excellent ee. The methodology was applied to the synthesis of a *super* bulky analog of BisP* **36**, which showed promising results in Rh-catalyzed asymmetric hydrogenation.

4.2.3.3. 2-(N-Tosyl-1-aminoethyl)-4-chlorophenol as chiral auxiliary. In 2013, researchers at Boehringer Ingelheim (BI) developed a



Scheme 20. a) S_N2@P of **29b** with different amines. b) Optimized synthesis of MaxPHOX catalysts.

diastereoselective synthesis of compound **43**, which is a key intermediate in the preparation of numerous P-stereogenic ligands developed in-house. The chemists at that company used tosylamide phenol **37** as chiral auxiliary (Scheme 24a). [82] Condensation between dichlorophosphine **38** and the chiral auxiliary occurred with a very high diastereomeric ratio (>99.5:0.5 dr). Reaction of the cyclic oxazaphosphinine oxide **39** with *tert*-butyllithium at −40 °C occurred at the weaker P-N bond with inversion of configuration and provided phosphinate **40** as a single diastereomer after recrystallization, in 94% yield. Subsequent cleavage of the P-O bond with methyllithium gave tertiary phosphine oxide **41** in ~97% ee. This sequence was also used to prepare a significant number of other bulky tertiary phosphine oxides in very high ee's (Scheme 24b). Finally, from **41**, it was possible to access the P-stereogenic synthon by formation of the iodo compound **42**, followed by a consecutive demethylation-cyclization process to yield **43**.

Related precursor **44** had initially been prepared by racemic resolution with (+)-menthyl chloroformate and used for the synthesis of POP and BIBOP ligands (Scheme 25a). [83] These P-stereogenic diphosphines showed very high enantioselectivity in the Rh-catalyzed asymmetric hydrogenation of α- and β-(acylamino)acrylic acids. The MeO-BIBOP ligand in particular was highly efficient in the asymmetric hydrogenation of other alkenes and ketones, catalyzed by rhodium and ruthenium respectively (Scheme 25b). [84] MeO-BIBOP and derivatives have also found success in a range of asymmetric C-C coupling reactions catalyzed by rhodium, copper or palladium. [85] The products delivered by catalysis with BIBOP ligands were used in the total synthesis of natural products and other biologically active compounds.

Shortly after the development of BIBOP, Tang and co-workers designed the WingPhos ligand, an analog with a deep and rigid chiral pocket (Fig. 14). [86] This ligand is effective in the asymmetric hydrogenation of trisubstituted cyclic and acyclic enamides. Recently, WingPhos has also given excellent results in a range of Rh-catalyzed additions to ketones and imines, [87] as well as in several Pd-catalyzed cross-coupling transformations. [88].

More recently, researchers at BI also managed to develop an efficient hydrolysis of *tert*-butyl-oxazaphosphinine **45** to generate *H*-phosphinate **46**, with very high diastereoselectivity (Scheme 26a). [89] By nucleophilic substitution at the phosphorus atom with Grignard reagents, this building block allowed the preparation of several secondary phosphine oxides with a *tert*-butyl and aromatic or heteroaromatic groups, in enantioselectivities ranging from low to excellent. Alternatively, the phosphide oxide generated after the first S_N2@P was trapped with pyridyl halides to produce heteroaromatic tertiary phosphine oxides. They also developed the reductive cleavage of phosphinate intermediates of type **47** with NH_2Li and ammonia at low temperature for the preparation of phosphinamides in very high enantioselectivities (Scheme 26b). [90] The functionalization of these synthons with an additional phosphine oxide moiety delivered effective organocatalysts for the enantioselective hydrosilylation of α,β-unsaturated ketones (ee up to 95%).

The research group at BI has also explored *N*-sulfonyl amino alcohols derived from norephedrine (**48**) and *cis*-1-amino-2-indanol (**50**) to prepare other aryl(*tert*-butyl) secondary phosphine oxides, with high enantioselectivities (Scheme 27). [91] In this case, the *H*-arylphosphinates **49** and **51** were formed in the first place, and the *tert*-butyl group was then introduced by S_N2@P with *t*-BuLi at low temperature. Perhaps the major drawback of this methodology is the large excess of *tert*-butyllithium needed to cleave the chiral auxiliary. Several SPOs

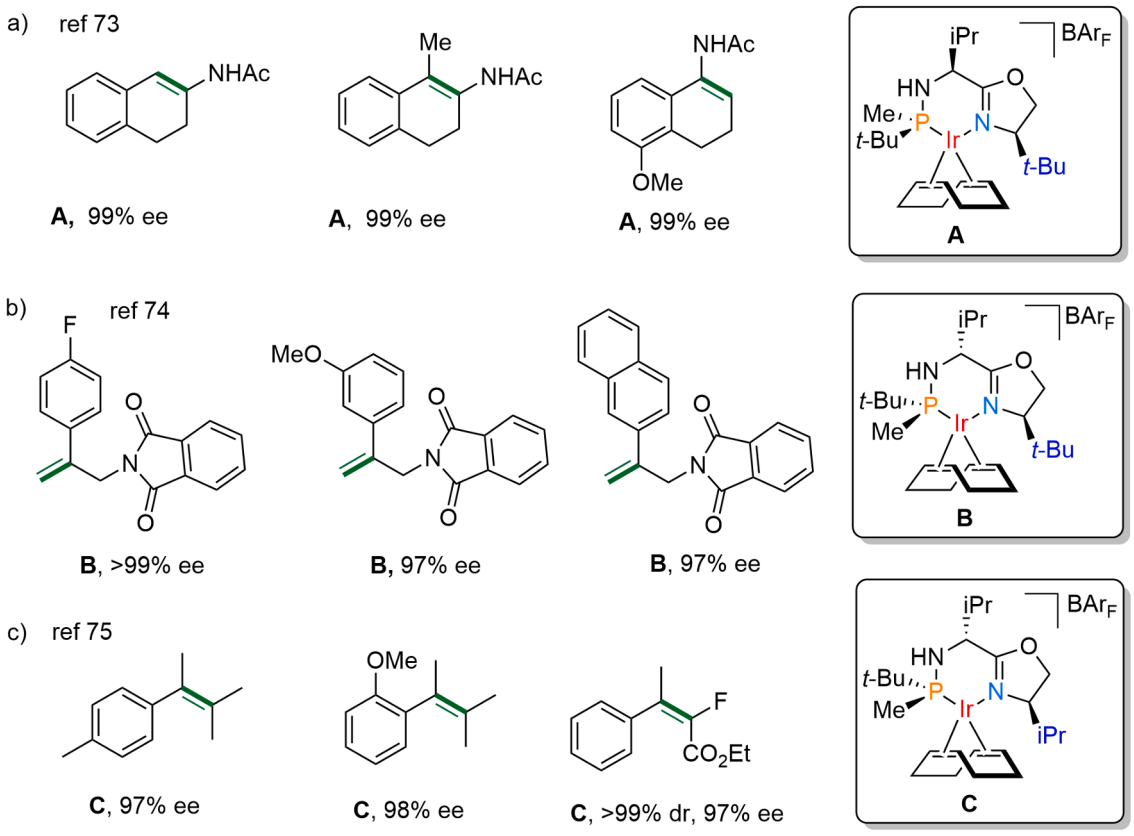
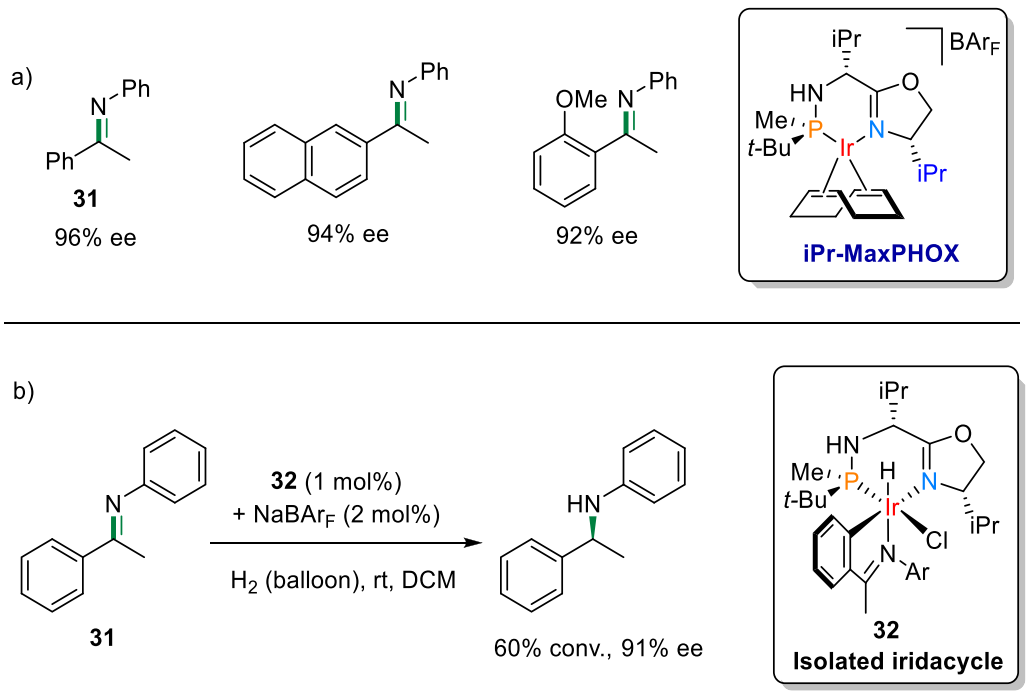


Fig. 12. Highlighted results of Ir-MaxPHOX in the hydrogenation of: a) cyclic enamides, b) 2-aryl allyl phthalimides, and c) tetrasubstituted olefins. Hydrogenated double bonds are shown in green.



Scheme 21. a) Selected results of Ir-MaxPHOX in the hydrogenation of *N*-aryl imines. b) Isolated iridacycle and results in the hydrogenation of **31**. Hydrogenated double bonds are shown in green.

prepared in this manner were coupled to 2-bromo-pyridine via palladium catalysis to generate *tert*-butylpyridyl tertiary phosphine oxides. Other research groups have shown that amino alcohols with backbones other than ephedrine or 1-amino-2-indanol can also be useful for the stereoselective preparation of tertiary phosphines and P-stereogenic ligands. [92].

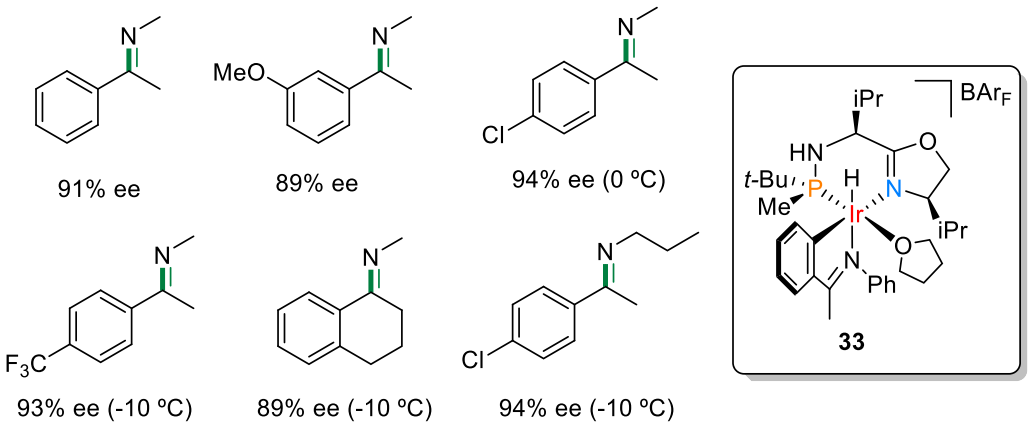
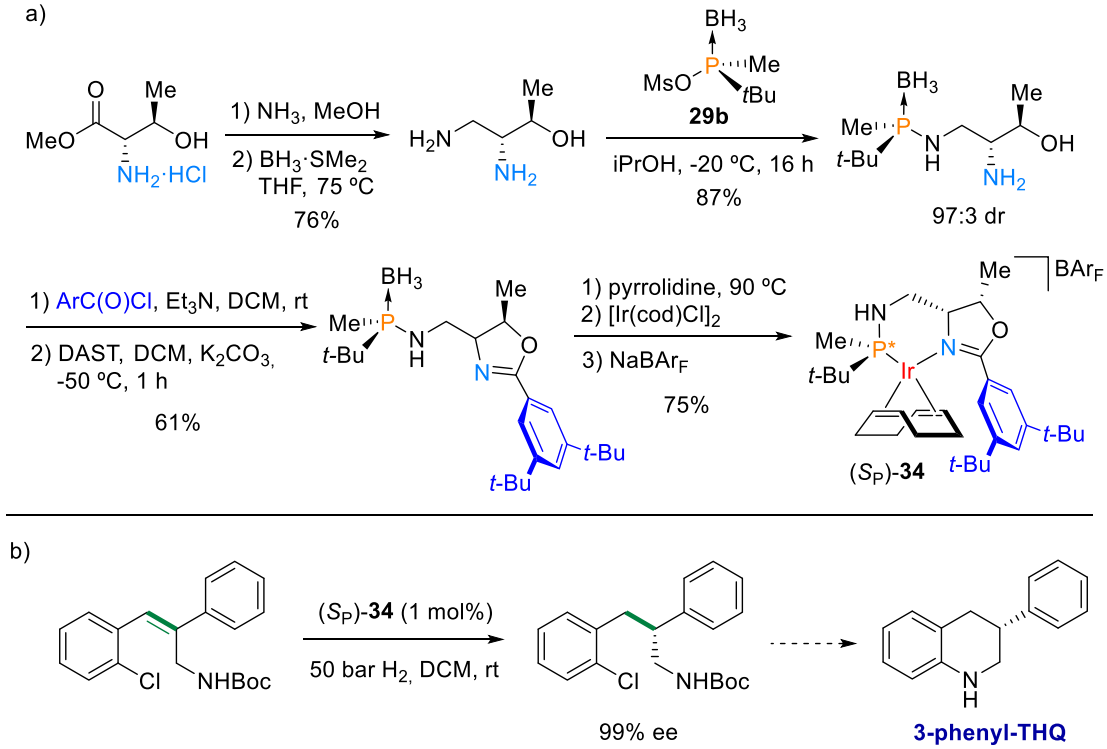


Fig. 13. Isolated iridacycle and results in the hydrogenation of *N*-methyl imines. Hydrogenated double bonds are shown in green.

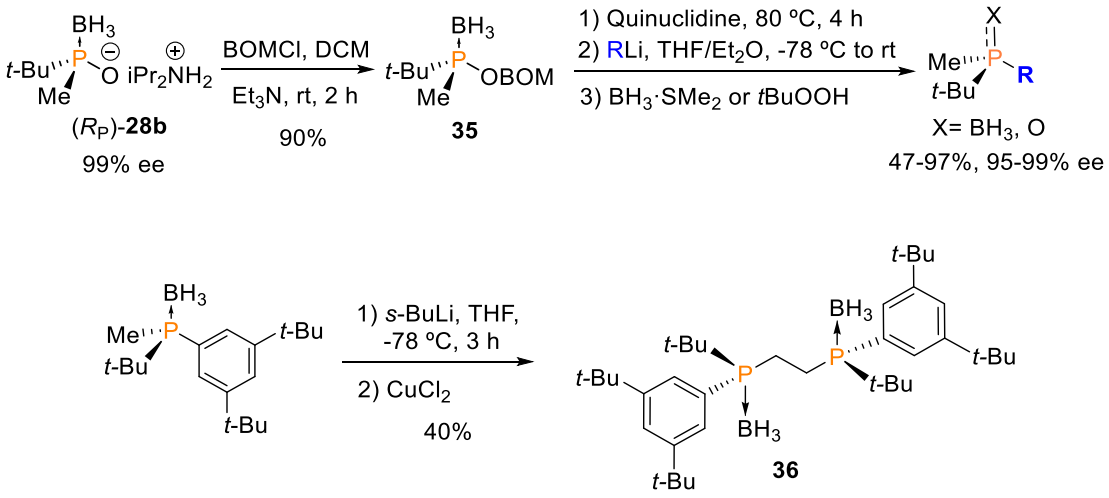


Scheme 22. Threonine-based P-stereogenic catalyst **34** and its application in the asymmetric synthesis of 3-aryl-tetrahydroquinolines. DAST = diethylaminosulfur trifluoride.

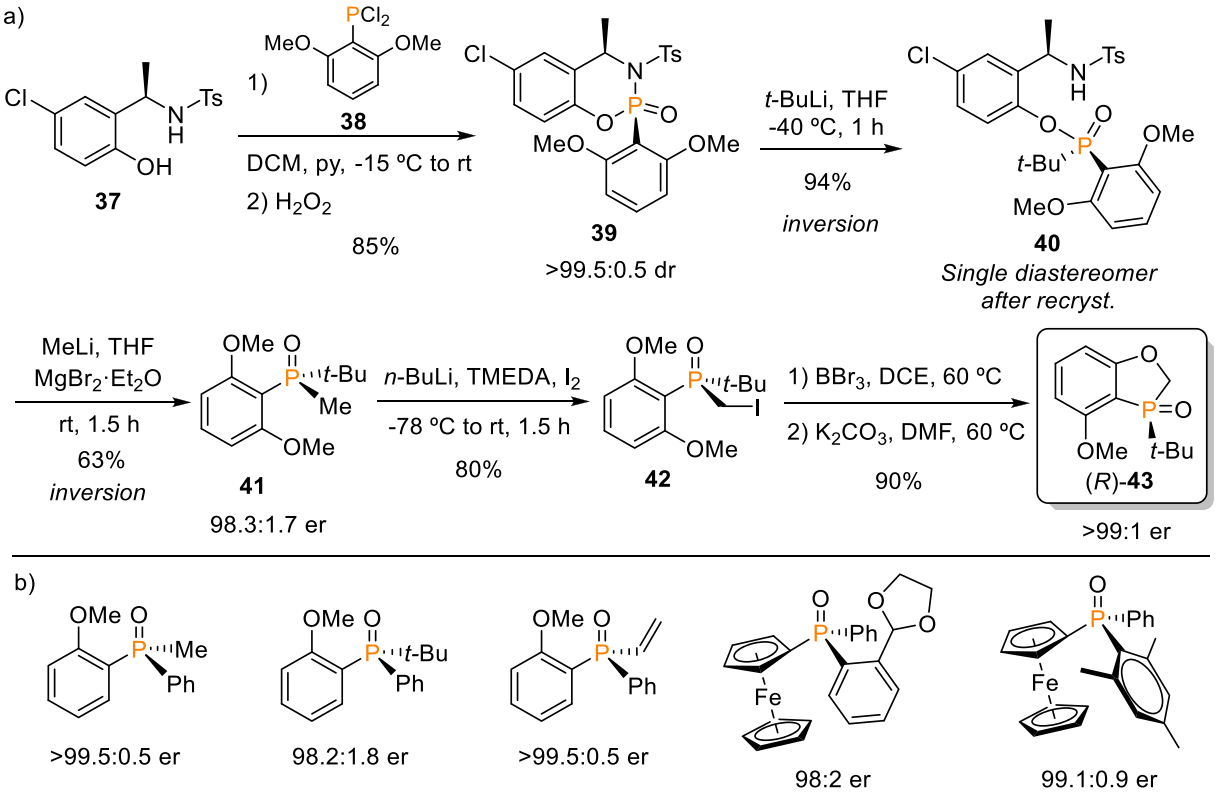
In 2010, researchers at BI used racemic dihydrobenzooxaphosphole **44** to develop the BI-DIME and AntPhos monophosphine ligands, which excelled in several non-asymmetric Pd-catalyzed Suzuki-Miyaura cross couplings. [93] Inspired by these results, they prepared the single enantiomer version of such ligands and observed that they could induce high enantioselectivity in asymmetric Suzuki-Miyaura cross-couplings to prepare axially chiral tri-*ortho*-substituted biaryls (Scheme 28). [85d,94] Over recent years, these ligands and their derivatives have found application in many other asymmetric cross-coupling transformations catalyzed mostly by palladium but also by nickel, rhodium and copper. [95].

The key intermediate **44** was also functionalized with a pyridine moiety in the oxaphosphole core to prepare the BoQPhos P,N ligand (Fig. 15). [96] BoQPhos has demonstrated to be privileged for the Ir-catalyzed asymmetric hydrogenation of pyridinium salts, a process that is useful for the synthesis of piperidine derivatives. [97] Also, more recently, the coupling of two dihydrobenzooxaphosphole units by the phenyl moiety resulted in the *O*-BABIPHOS ligands, which proved useful in the Rh-catalyzed asymmetric hydrogenation of enamides and the Pd-catalyzed asymmetric hydrogenation of ketones. [98] The azaphosphole derivative *N*-BABIPHOS has shown good results in various Cu-catalyzed transformations, such as asymmetric amination reactions and the asymmetric hydrogenation of 2-substituted tetralones via dynamic kinetic resolution. [99].

4.2.3.4. Limonene oxide as chiral auxiliary. Recently, Baran and coworkers developed a synthetic strategy to prepare tertiary phosphine oxides using limonene oxide as chiral auxiliary, with good to excellent ee's (Scheme 29). [100] The formation of intermediate **52** occurred swiftly with excellent diastereo- and enantioselectivity. The methodology involves two consecutive $S_N2@P$ with Grignard reagents that occur with retention of configuration, followed by cleavage of limonene by methylation at the sulfur atom. After that, the methoxy leaving group is



Scheme 23. BOM-phosphinite as an electrophilic P-stereogenic transfer reagent for the synthesis of bulky phosphines.

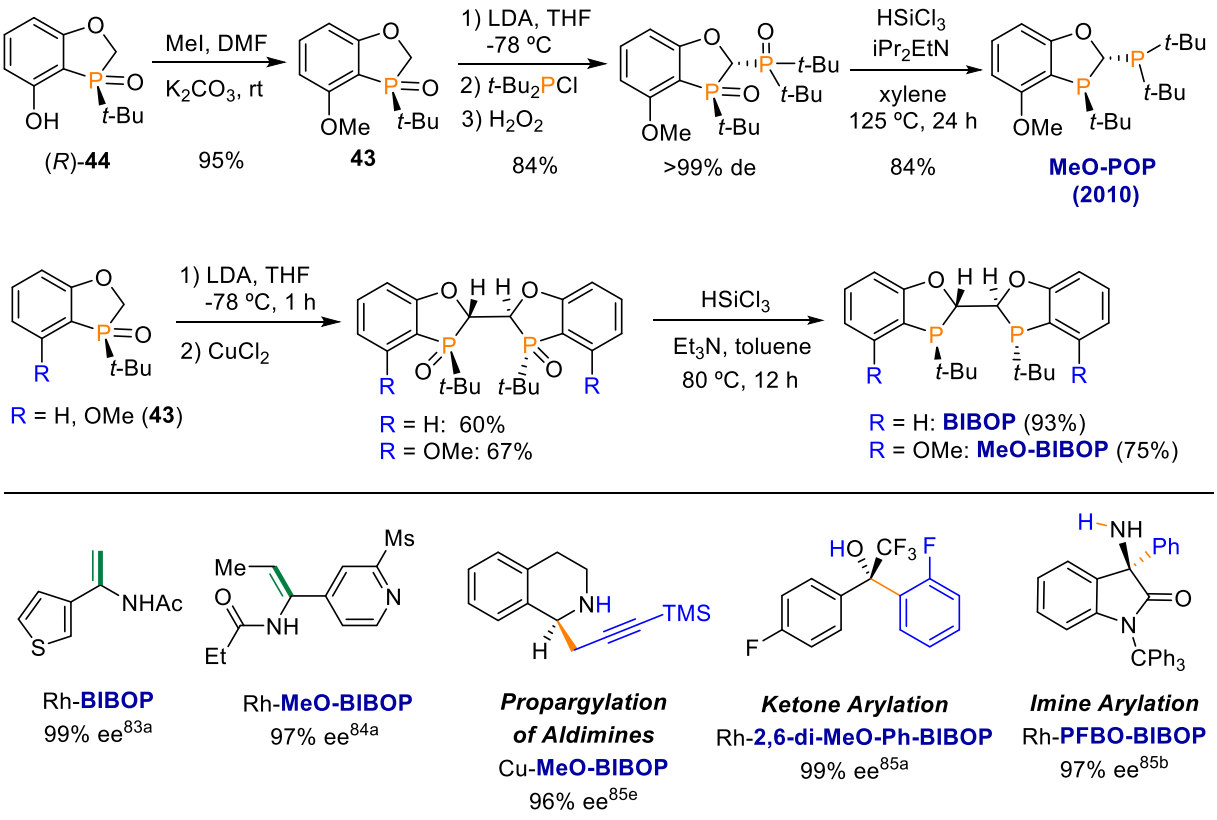


Scheme 24. a) Diastereoselective synthesis of P-stereogenic synthon **43**. b) Other bulky TPOs prepared using this strategy.

introduced by treatment with NaOMe, and a final substitution at P with organometallic reagents yields the tertiary phosphine oxide, with net retention over two steps. The distinct stereochemical outcome of the different nucleophilic substitutions allows tuning of the absolute configuration of the product by changing the order of addition of the organometallic reagents. However, the final reaction with bulky organometallic reagents is somewhat less stereoselective, thus highlighting the difficulty to attain stereospecific processes for this class of compounds. Baran and co-workers also applied this auxiliary system in the preparation of P-stereogenic methylphosphonate oligonucleotides of biological interest.

4.3. Carbon or metal–carbon chiral templates

Several research groups have tackled the preparation of P-stereogenic ligands by carrying out stereoselective reactions with axially chiral biaryls or ferrocenes with planar chirality. In these strategies, the chiral inductor is not cleaved after the stereoselective reaction and is part of the final ligand. In 2003, X. Zhang and co-workers prepared the Binapine ligand by taking advantage of the axially chiral (*S*)-2,2′-dimethylbinaphthyl template (Scheme 30a). [101] Deprotonation of **53** with *t*-BuLi at −78 °C followed by homocoupling mediated by $CuCl_2$ afforded a single diastereomer of Binapine sulfide in 25% yield, along with the recovery of 50% of the starting material. Over the last twenty years, Binapine has demonstrated a great ability in Ni- and Rh-catalyzed asymmetric hydrogenation reactions, among a considerable number of



Scheme 25. a) Synthesis of MeO-POP and BIBOP ligands. b) Highlighted applications of BIBOP ligands. Hydrogenated double bonds are shown in green and newly formed bonds in orange.

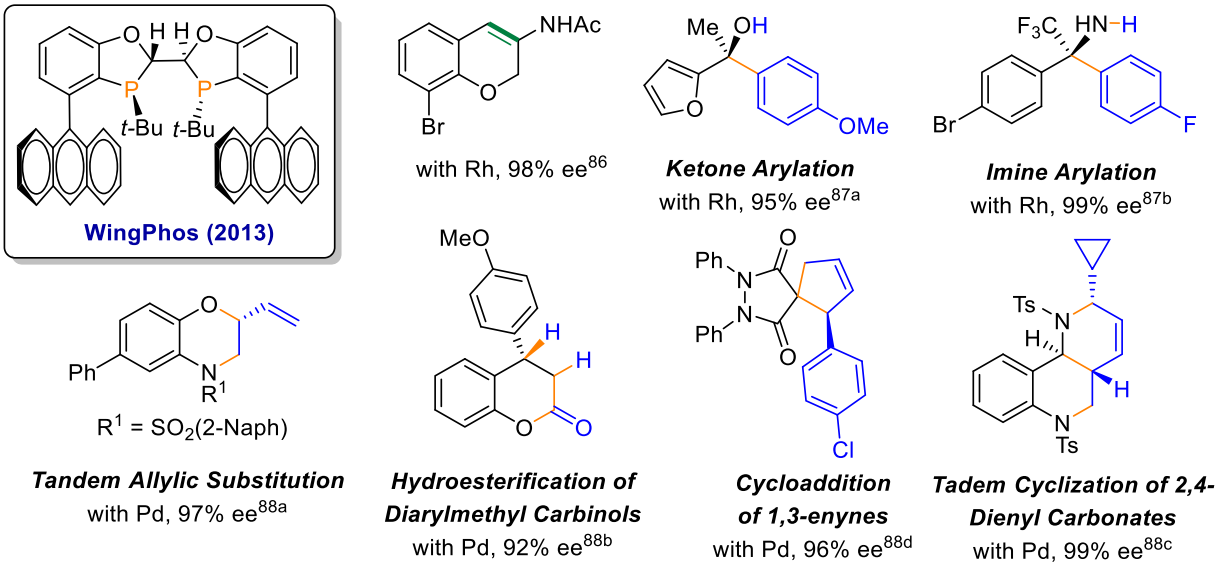
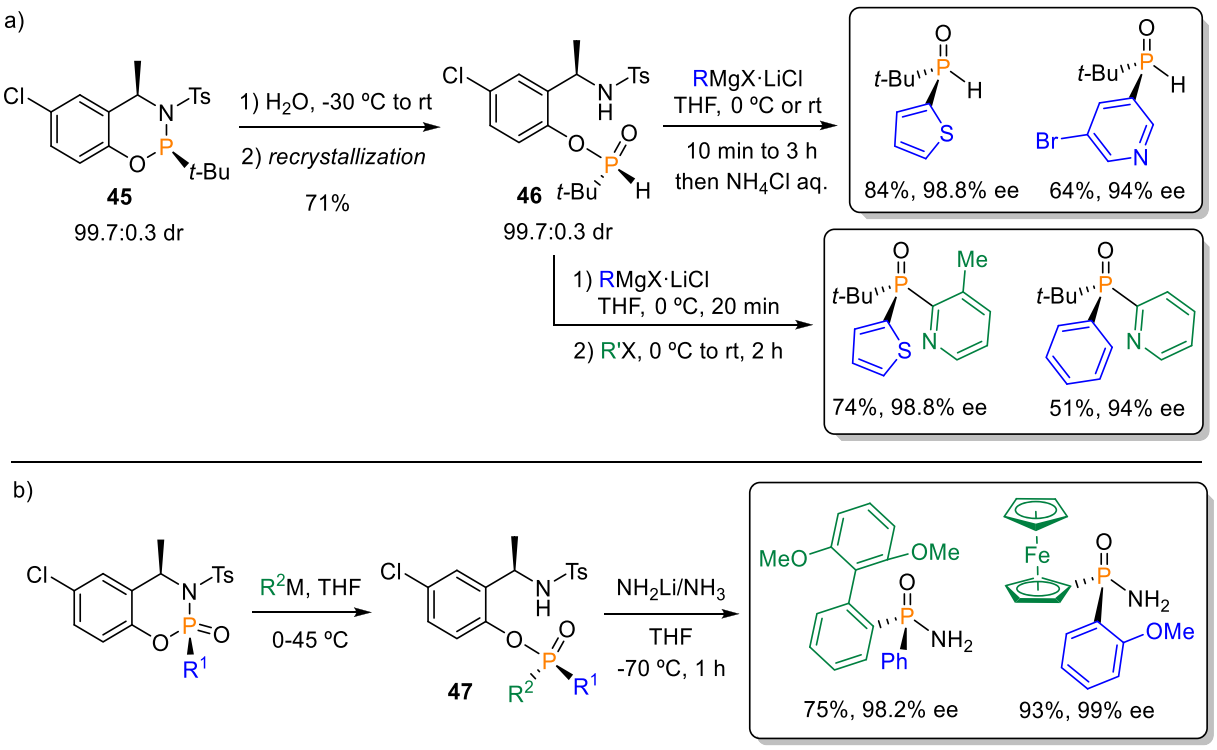


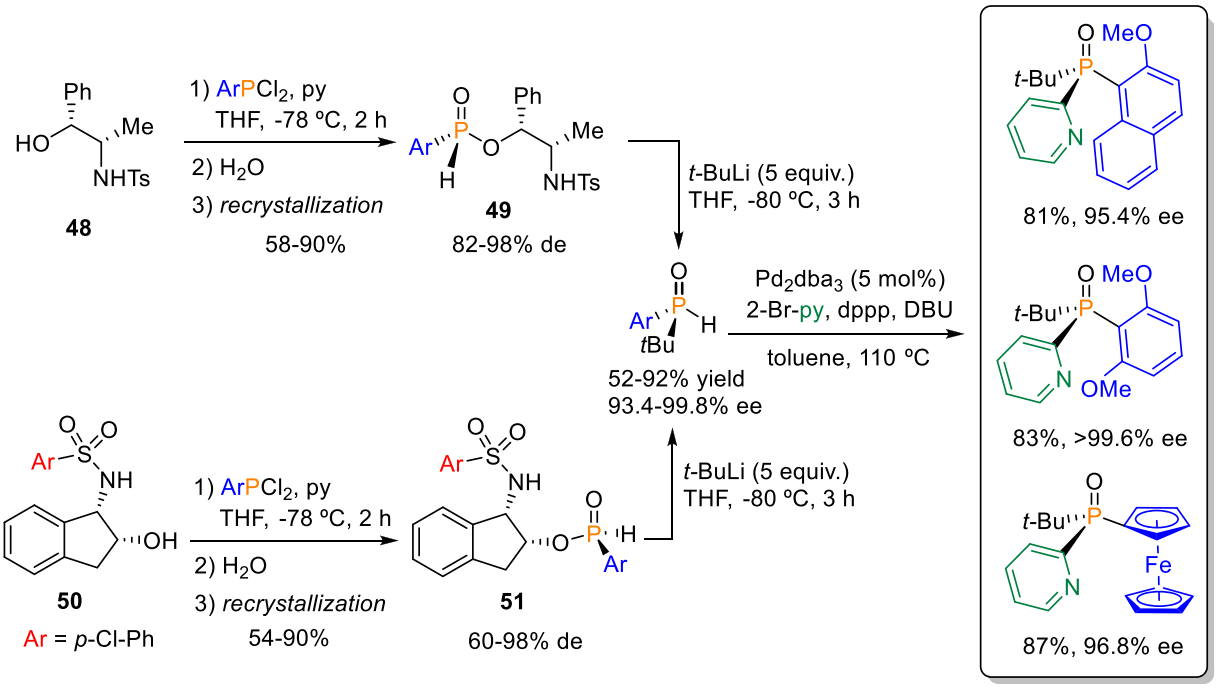
Fig. 14. Structure of WingPhos and highlighted applications in asymmetric catalysis. Hydrogenated double bonds are shown in green and newly formed bonds in orange.

other transformations (Scheme 30b). [102] By functionalization of the methylene position in **53** with 2-(bromomethyl)pyridine, Mazet and co-workers reported related phosphine-pyridine bidentate ligands useful for Pd-catalyzed C-C couplings. [103].

Since 2006, W. Chen and co-workers have developed several P-stereogenic ferrocene-based ligands using chiral Ugi's amine (Fig. 16a). [104] To prepare these ligands, the α-position to the alkylamine moiety of Ugi's amine is deprotonated with *t*-BuLi, followed by stepwise addition of a chlorophosphine and Grignard reagents to generate the P-stereogenic center. In the case of ChenPhos, the synthesis is not highly diastereoselective, but it was observed that the ligand can be enriched in the more stable diastereomer by thermal epimerization because of the attainable energy barrier of pyramidal inversion of certain trivalent phosphines. [105] P-stereogenic BoPhoz and ChenPhos have been successful in the Rh-catalyzed asymmetric hydrogenation of several challenging olefins (Fig. 16b). [106].



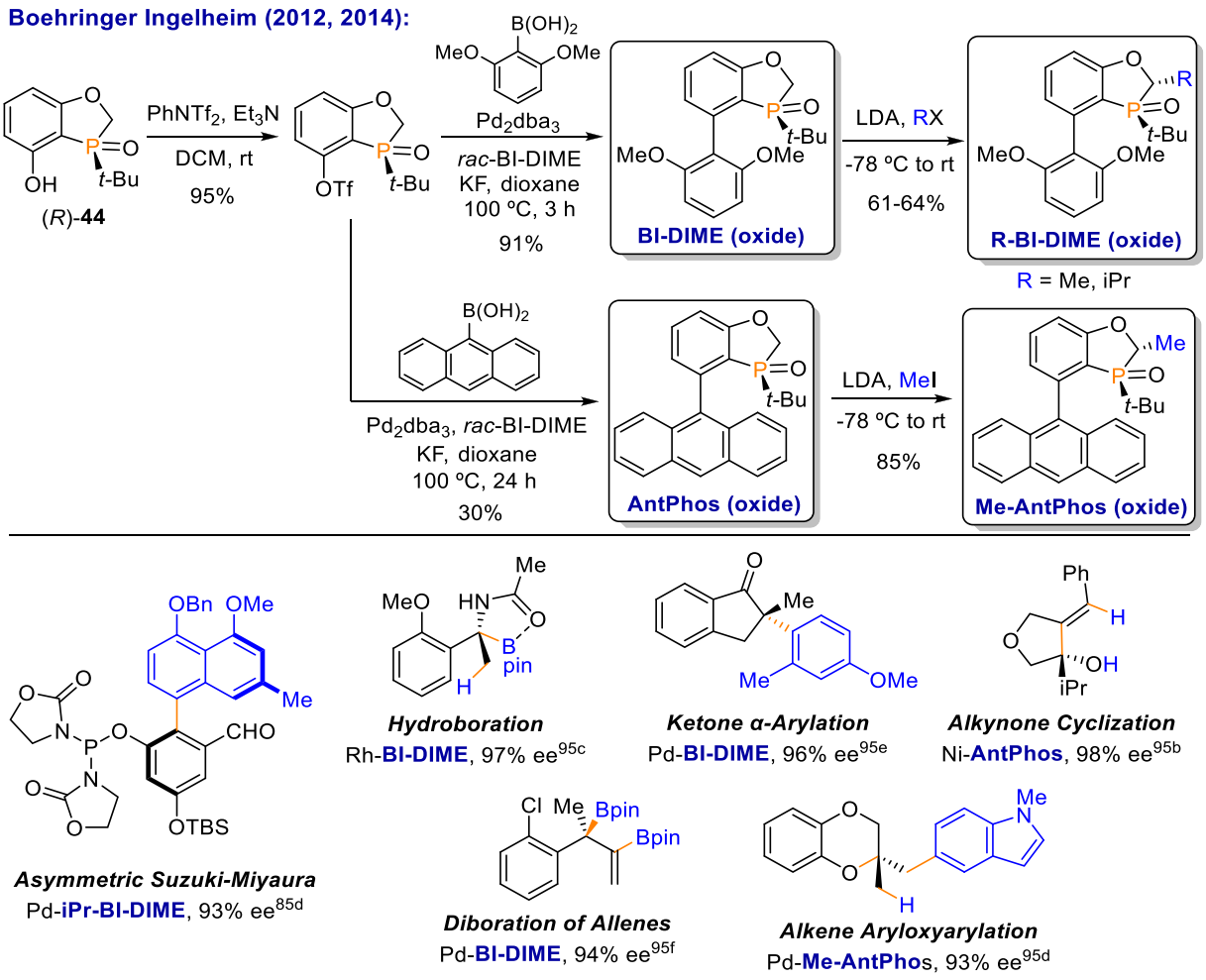
Scheme 26. Use of *H*-phosphinates for: a) the preparation of SPOs and TPOs with heteroaromatic groups; and b) the synthesis of P-stereogenic amino-phosphine oxides.



Scheme 27. Equivalent strategies for the preparation of aryl(*tert*-butyl) SPOs and derivatization to pyridine-containing TPOs.

In 2010, Pfaltz and co-workers prepared JoSPOphos, a ferrocene-based diphosphine ligand bearing one P-stereogenic secondary phosphine oxide (Scheme 31a). [107] The stereochemistry of the major diastereomer formed in the first reaction of the synthesis depends on the nature of the chlorophosphine. Upon coordination of phosphorus to rhodium, the SPO moiety is transformed to phosphinous acid. JoSPOphos was the first highly efficient P-chiral SPO ligand in Rh-catalyzed asymmetric hydrogenation (Scheme 31b). In the last decade, JoSPOphos ligands with distinct combinations of *t*-Bu and Ph substituents in each phosphine have also found application in other asymmetric transformations catalyzed by rhodium or nickel. [108].

More recently, X. Zhang and co-workers developed Wudaphos, a ferrocenyl P-stereogenic diphosphine in which both phosphorus atoms are connected to a phenyl backbone (Scheme 32a). [109] Alternatively,



Scheme 28. Synthesis and highlighted applications of BI-DIME and AntPhos ligands. Newly formed bonds are shown in orange.

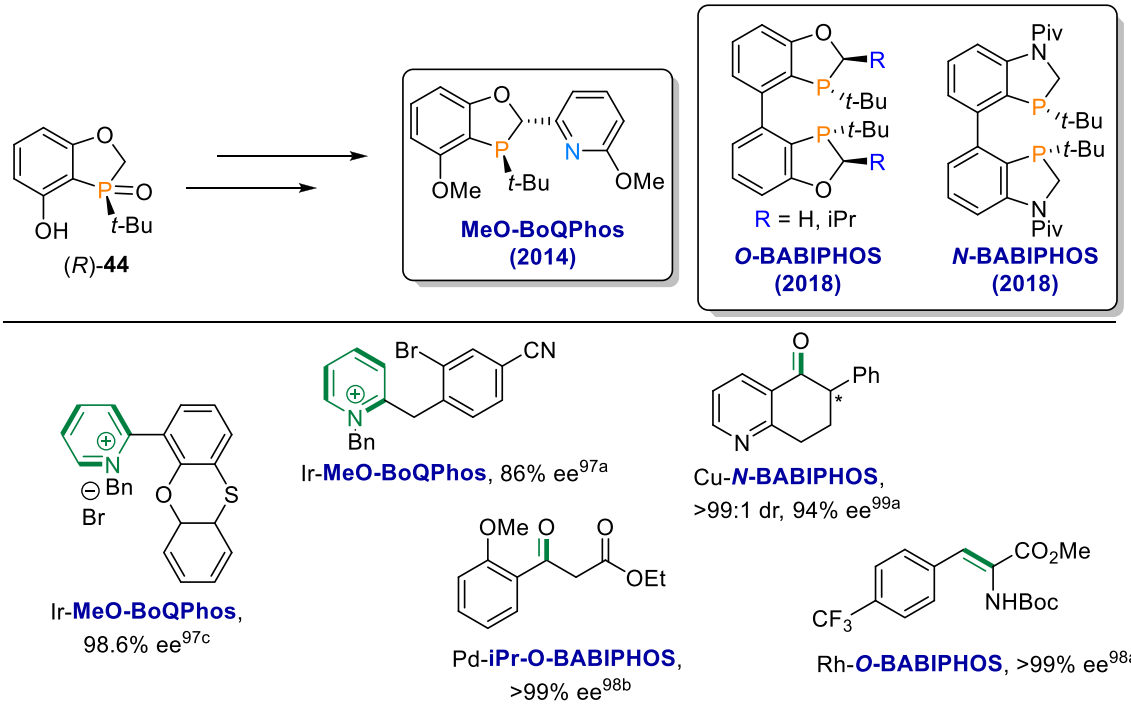
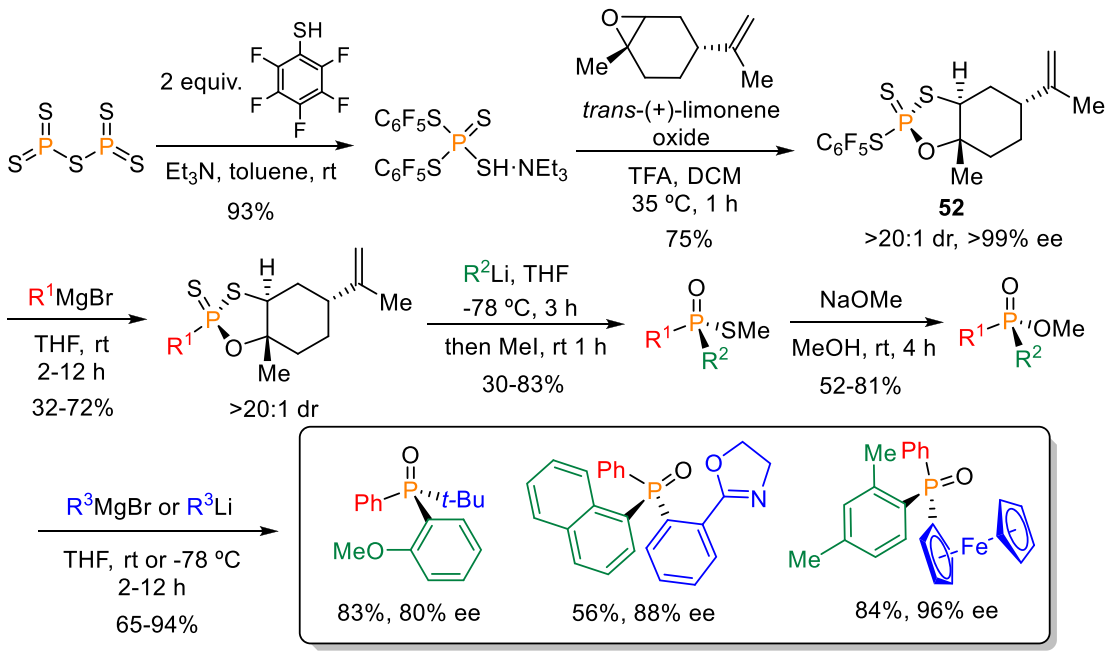
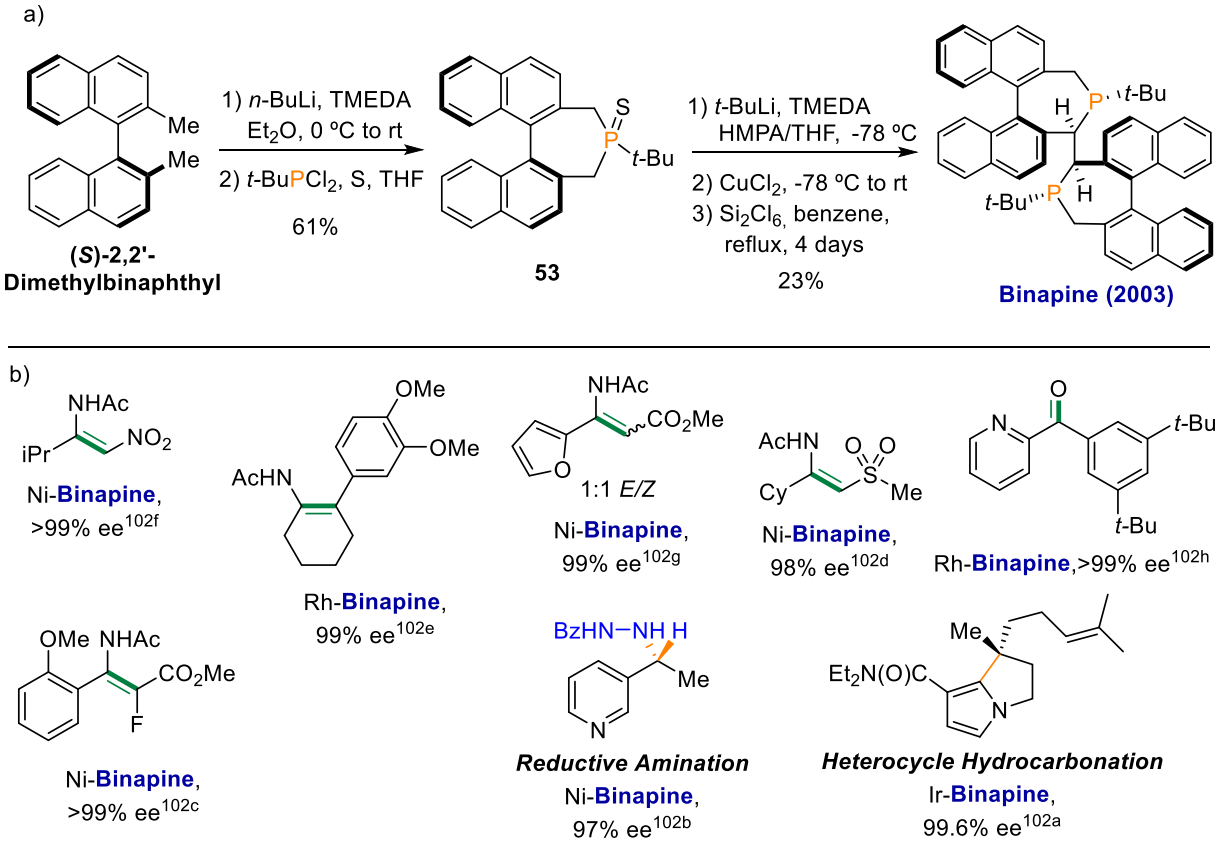


Fig. 15. Other ligands derived from synthon **44** and their application in asymmetric catalysis. Hydrogenated double bonds are shown in green.



Scheme 29. Methodology developed by Baran and co-workers to prepare tertiary phosphine oxides.



Scheme 30. a) Synthesis of the Binapine ligand. b) Highlighted application in asymmetric catalysis. Hydrogenated double bonds are shown in green and newly formed bonds in orange. HMPA = hexamethylphosphoramide.

the *t*-Bu-Wudaphos analog bears a methylene backbone bound to a P(*t*-Bu)$_2$ moiety, thereby mimicking the structure of the Trichickenfootphos ligand. [110] The consecutive addition of Grignard reagents to chlorophosphine intermediates bearing Ugi's amine delivered the ligands as single diastereomers, without the need for recrystallization. Simultaneously, the X. Zhang group also reported SPO-Wudaphos analogs by hydrolysis of the diarylchlorophosphine intermediate at low temperature. [109b,111] Wudaphos, *t*-Bu-Wudaphos and SPO-Wudaphos ligands have shown very good results in the Rh-catalyzed asymmetric hydrogenation of terminal olefins bearing carboxylic

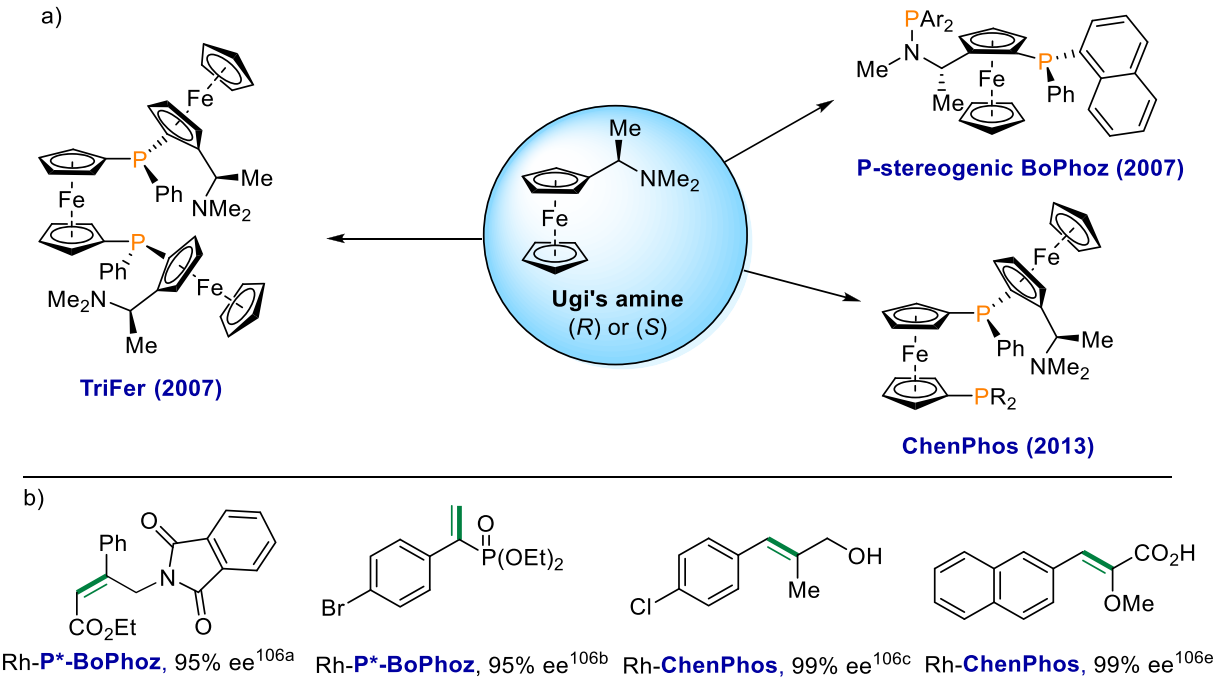
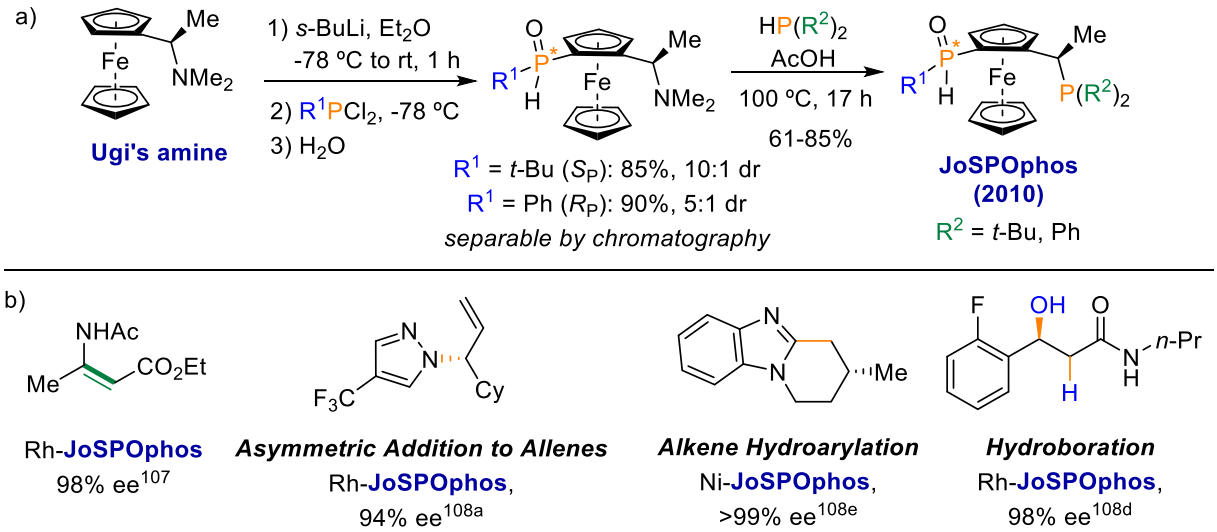


Fig. 16. Synthesis of different Fc-based ligands and application in Rh-catalyzed hydrogenation. Hydrogenated double bonds are shown in green.

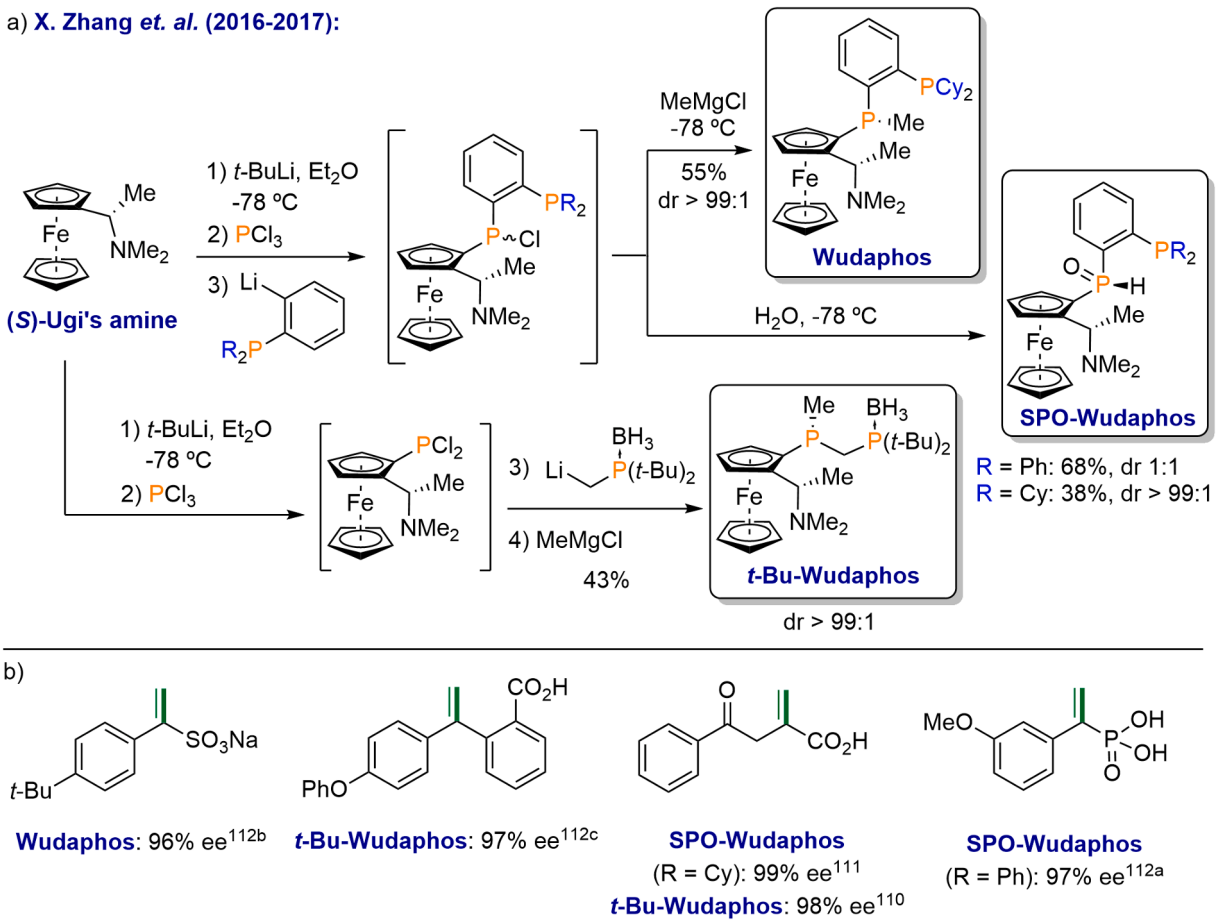


Scheme 31. Synthesis of JoSPOphos and highlighted applications in asymmetric catalysis. Hydrogenated double bonds are shown in green and newly formed bonds in orange.

acids, phosphonic acids, or sulfonates (Scheme 32b). [112] The non-covalent ion pair interaction between the dimethylamine group of Ugi's amine and the protic groups of these olefins strongly enhances the interplay between the catalyst and substrate and it is crucial to achieve high activity and enantioselectivity in the process. In the case of SPO-Wudaphos, the phosphoryl moiety can also interact with a protic substrate via H-bonding.

4.4. *Resolution of racemic mixtures*

In this strategy, the synthesis of the desired P-stereogenic compound is initially carried out in a racemic form and then the two enantiomers of the racemic mixture are separated by different means. The enantiomers are most commonly separated either by chiral HPLC or using a chiral resolving agent and crystallization of one of the resulting diastereomeric pairs. Distinct types of bonding can occur between the resolving agent and the racemic substrate: covalent resolving agents, salt-forming Brønsted acids or bases, or co-crystal-forming reagents. The synthesis of enantioenriched P-stereogenic phosphines by resolution of racemic mixtures entails the inherent drawback of obtaining–at most–only 50% of the enantiomer of interest. The chromatographic separation of racemic mixtures has some advantages, such as the straightforward preparation of chiral ligands for screening and the access to both enantiomers with the same procedure. Although nowadays it is possible to perform chiral chromatographic separations at industrial scale, these techniques are usually expensive. The use of resolving agents is strongly substrate dependent, it might be time consuming and the efficient isolation of a single diastereomer in very high purity might take several purification cycles. However, some ligands are still prepared at large scale by resolution of their racemates. We will review some key



Scheme 32. Synthesis of Wudaphos-type ligands and application in asymmetric catalysis. Hydrogenated double bonds are shown in green.

examples of these methodologies in the present section as well as a successful example of crystallization-induced dynamic resolution.

4.4.1. Direct resolution by chiral HPLC

The direct separation of the enantiomers by preparative or semi-preparative chiral HPLC is a very expensive technique that requires special apparatus and columns, as well as large volumes of high-quality solvents. Despite its elevated cost, this strategy might be the most rapid when small amounts of pure compounds are required. The separation of racemates by chiral HPLC has been reported for several P-stereogenic compounds (Fig. 17). In 2004, Hoge described the direct resolution of the Trichickenfootphos ligand via HPLC on a chiral stationary phase. [24] Imamoto and co-workers also reported the separation of racemic 1-*tert*-butylbenzophosphetane oxide using simulated moving bed chromatography. [113] More recently, Buono and co-workers described the preparation and resolution of *H*-adamantylphosphinates by chiral HPLC. [51] The separation was carried out at the gram scale and the optically pure phosphinates were transformed stereoselectively into secondary phosphine oxides and BH_3-protected monophosphines.

4.4.2. Resolution by crystallization with a resolving agent

The most widely used strategy to resolve racemic mixtures is by using a chiral resolving agent to form diastereomeric pairs that can be more easily separated either by chromatographic methods or, more conveniently at large scale, by crystallization. For instance, the formation of chiral diastereomeric cyclometallated palladium complexes allows the separation of enantioenriched P-stereogenic phosphines. [1a,1b] However, today this technique is scarcely used because it involves stoichiometric amounts of an expensive metal. Alternatively, covalently bonded chiral auxiliaries have been successfully used to resolve P-stereogenic intermediates at large scale. Chemists at BI used menthyl chloroformate for the resolution of key intermediate **44**

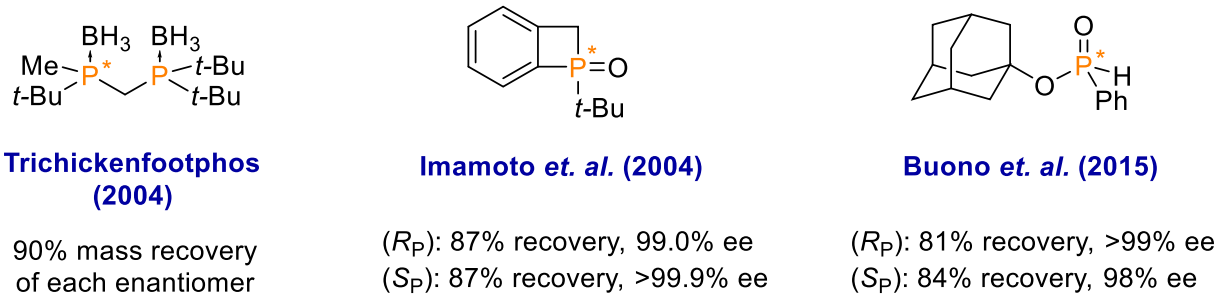
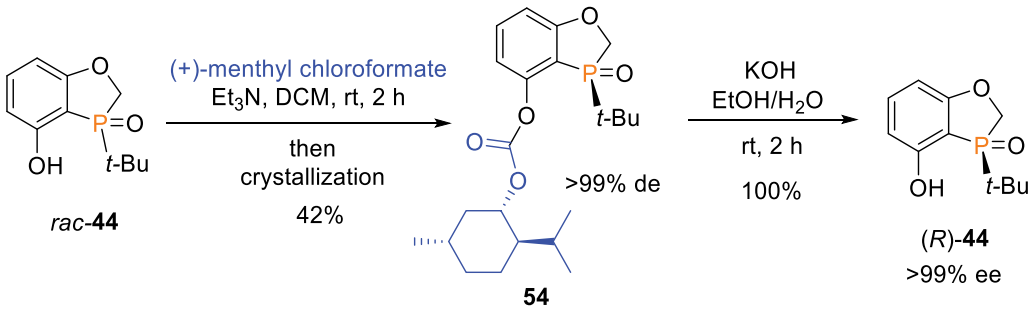


Fig. 17. Examples of P-stereogenic ligands and intermediates resolved by chiral HPLC.



Scheme 33. Application of a covalently bonded resolving agent at Boehringer Ingelheim.

(Scheme 33). [83a] Diastereomerically pure **54** was isolated after a single crystallization, and posterior basic hydrolysis afforded enantiomerically pure compound (*R*)-**44** at a kilogram scale. In a similar fashion, Imamoto also reported the resolution of the key *tert*-butylmethyl secondary phosphine-borane **5** using bornyl chloroformate as resolving agent. [33].

P-stereogenic compounds with an acidic or basic functionality can be resolved by diastereomeric Brønsted salt formation. The perfect example of this class of compounds are phosphinous acid-borane complexes. In 2007, Pietrusiewicz described the resolution of *tert*-butylphenylphosphinous acid-borane by means of a combination of ephedrine and cinchonine bases (Scheme 34). [49] Initial crystallization of **17a** with ephedrine afforded a diastereomerically pure salt from which pure (*S*)-**17a** was isolated in 31% overall yield. The opposite enantiomer was also isolated by crystallization of the mother liquors with cinchonine.

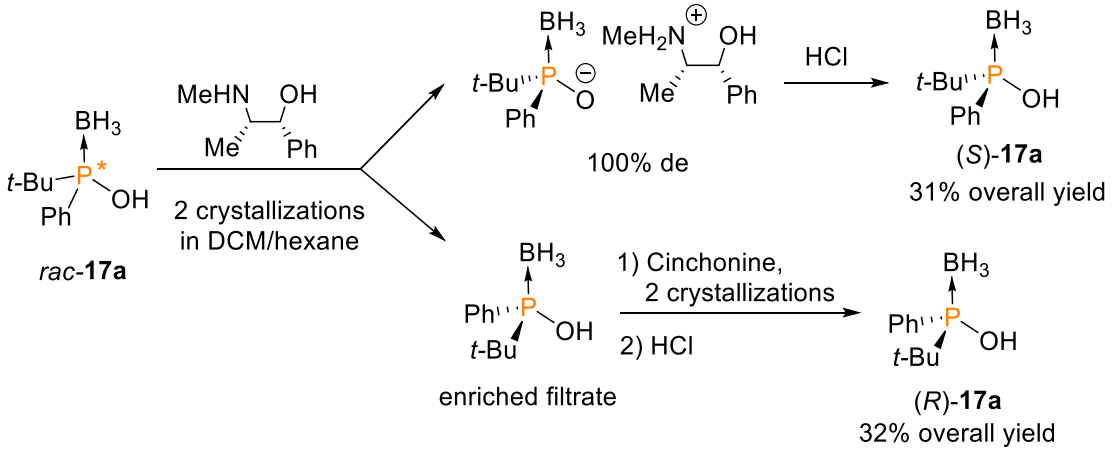
For racemic substrates with no acidic or basic functions but with suitable H-bond acceptor groups, resolution with a H-bond donor resolving agent is a good alternative. The most successful resolutions have been achieved by combining chiral carboxylic acids or alcohols derived from natural sources with P-stereogenic tertiary phosphine oxides or secondary phosphine oxides. Here the electron-rich oxygen atom of the P-oxide moiety acts as an efficient H-bond acceptor. For example, in 2005, X. Zhang and co-workers reported the efficient resolution of racemic DuanPhos oxide **56** with inexpensive dibenzoyl L-tartaric acid (L-DBTA), in >99% ee after only one resolution cycle (Scheme 35). [29] Also, when the remainder of **56** was treated with D-DBTA, the opposite enantiomer of DuanPhos was obtained with the identical ee. The use of TADDOL resolving agents has also been described for the resolution of TPOs and SPOs. [114] Very recently, the large-scale preparation of the P-stereogenic dihydrobenzoazaphosphole core using (1*S*,2*S*)-diaminocyclohexane has also been reported by chemists at BI. [115].

4.4.3. *Crystallization-induced dynamic resolution*

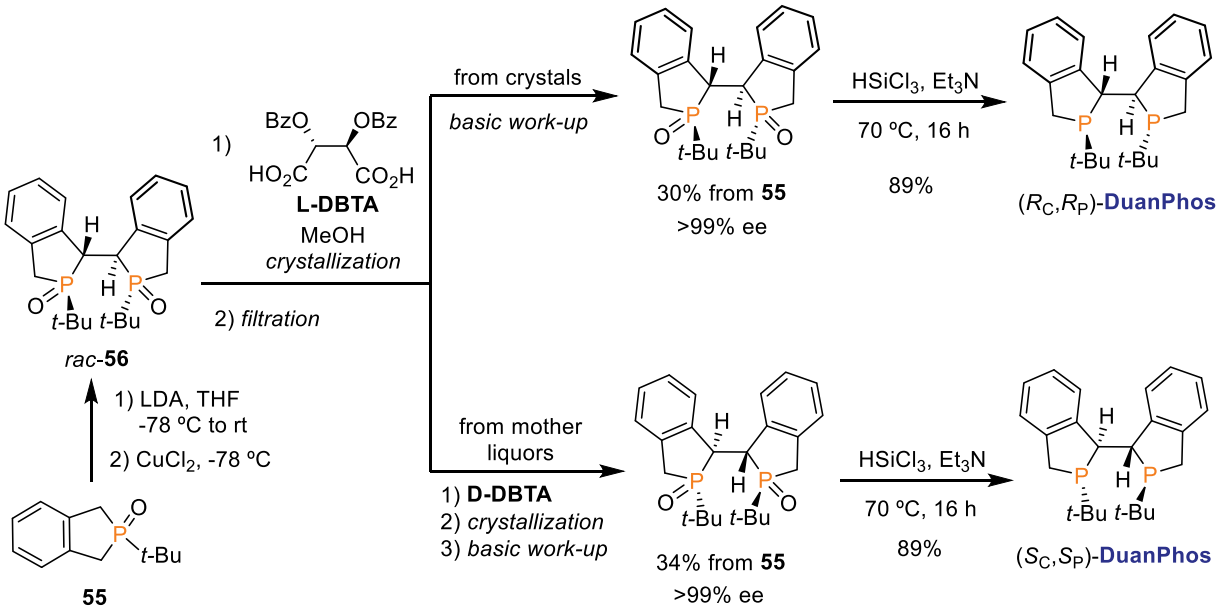
In a classical resolution process conducted in 2009 by Pietrusiewicz, Minnard and co-workers, (*R,R*)-dibenzoyl tartaric acid (DBTA) emerged as an efficient resolving agent for *tert*-butylphenylphosphine oxide **16**. [116] A few years later, the same group reported that **16** underwent crystallization-induced dynamic resolution mediated by iodine (Scheme 36). [117] This technique overcomes the 50% yield limitation for one of the two enantiomers and allows complete conversion to the enantiomer of choice. As in the classical resolution, the solubility difference between the two diastereomeric complexes induces the crystallization of single diastereomeric pair. Meanwhile, the opposite enantiomer in solution undergoes racemization catalyzed by iodine. This methodology allows the isolation of the (*R,R*)-DBTA:(*R*)-**16** complex in 92% yield and 96% ee. After a single crystallization in toluene/diisopropyl ether, the SPO was obtained as a single enantiomer. DFT calculations revealed that racemization occurs through a radical chain process in which equilibration between radical intermediates (*R*)-**57**/(*S*)-**57** has a barrier of only 11.59 kcal/mol.

4.5. *Asymmetric catalytic synthesis*

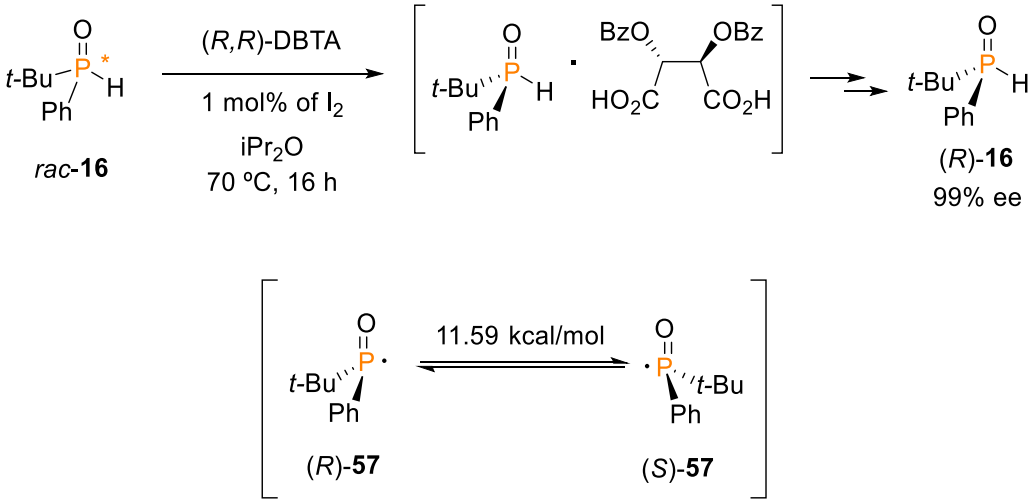
As we have seen in the previous sections, the synthesis of bulky P-stereogenic phosphines employed in catalysis is achieved mostly by using chiral auxiliaries, chiral bases, or by resolution of racemic mixtures. The presence of P(V) stereocenters in several recently developed drugs and bioactive compounds has further stimulated interest in the catalytic synthesis of P-stereogenic compounds. [118] An asymmetric catalytic approach to the preparation of these valuable compounds would circumvent the use of stoichiometric amounts of chiral resolving agents or auxiliaries. Since the pioneering work of Glueck and coworkers two decades ago, [119] the catalytic asymmetric synthesis of P-stereogenic phosphines has progressively gained interest. [120] In the last decade, several catalytic and highly enantioselective methodologies



Scheme 34. Resolution of *tert*-butylphenylphosphinous acid-borane through diastereomeric salt formation.



Scheme 35. Chiral resolution to obtain the two enantiomers of the DuanPhos ligand.



Scheme 36. Radical iodine-mediated dynamic resolution of *tert*-butylphenylphosphine oxide.

to prepare P-stereogenic compounds have been reported. [121] Nevertheless, these methods are often not suitable for the preparation of bulky *tert*-butyl-containing P-stereogenic compounds, and the compounds obtained are rarely applied in asymmetric catalysis. Most catalytic strategies focus on desymmetrization reactions [122] and kinetic or dynamic kinetic resolution of racemic secondary phosphines. [123] These methodologies, initially approached by palladium catalysis, have now been extended to other metals such as copper, iridium, nickel and cobalt. In this section, we will disclose some of the recent advances in the field that best suit the purpose of this review.

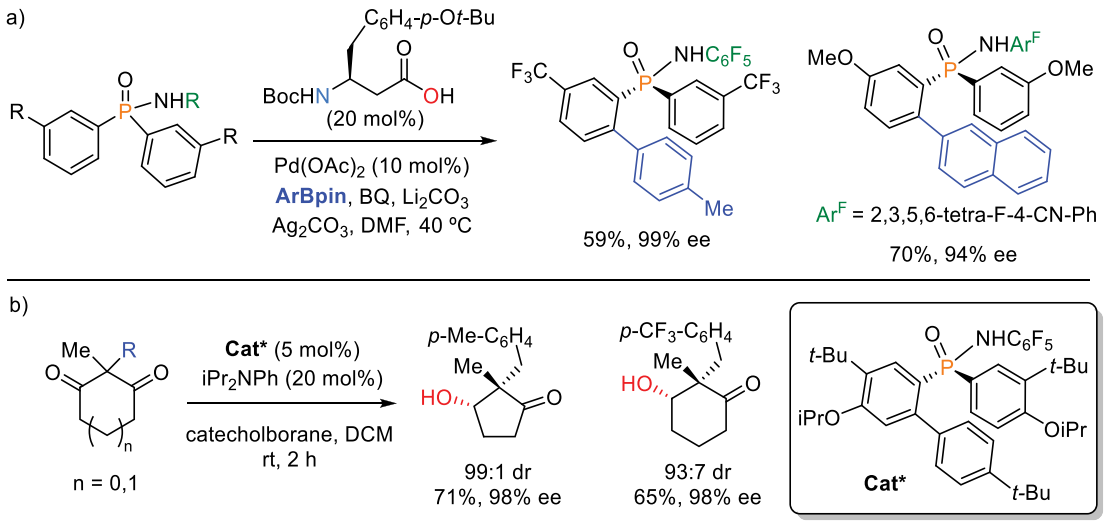
In 2015, F.-S. Han and co-workers developed the enantioselective Pd-catalyzed C-H arylation of prochiral diarylphosphinamides with arylboronic esters, obtaining the corresponding P-stereogenic phosphinamides in high enantioselectivities (Scheme 37a). [124] More recently, these P-stereogenic compounds have proven to be highly effective organocatalysts in the desymmetric enantioselective reduction of achiral cyclic 1,3-diketones with catecholborane (Scheme 37b). [125].

Very recently, Shi and co-workers have prepared similar phosphinamides by Co-catalyzed C-H functionalization of diarylphosphinamides with alcohols and amines, in outstanding enantioselectivities (Scheme 38). [126] Notably, upon addition of acetylene reagents instead of alcohols or amines, the reaction delivered the intramolecular cyclization of the aryl and phosphinamide moieties. [127].

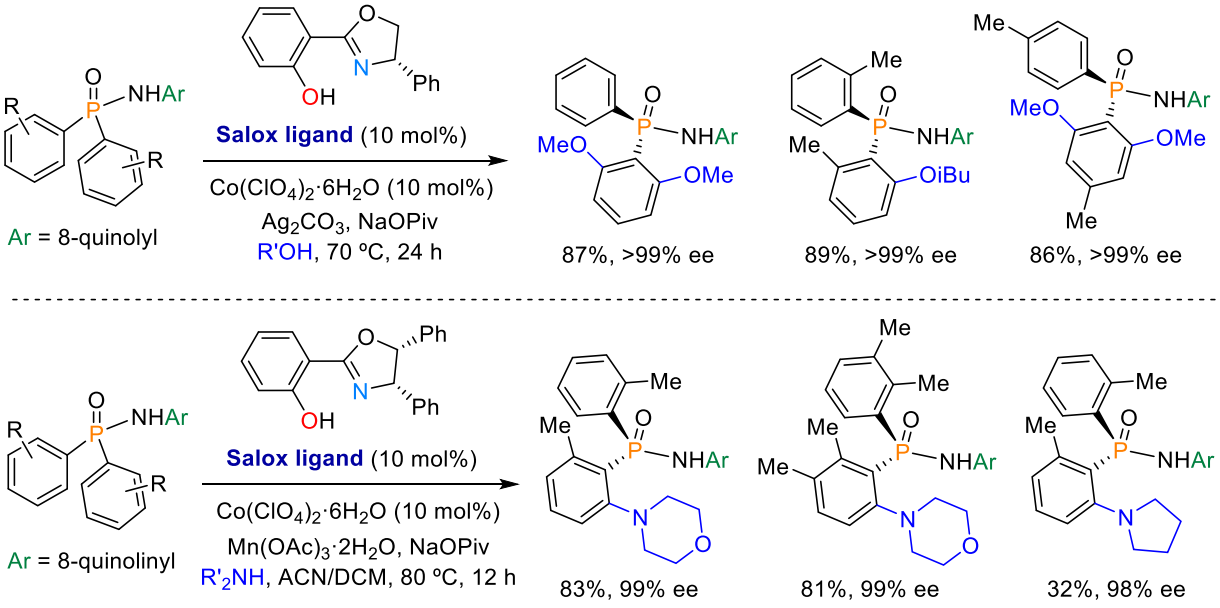
In 2019, inspired by the work of Gaunt and co-workers, [128] the J. Zhang team reported the Pd-catalyzed kinetic resolution of racemic secondary phosphine oxides by cross coupling with aryl bromides, yielding tertiary phosphine oxides in high enantioselectivity (Scheme 39). [129] The authors showed that the P-oxides derived from this strategy could be derivatized into DIPAMP-type ligands. The methodology was also extended to the synthesis of alkenyl(alkyl)(aryl)phosphine oxides. [130].

More recently, in 2021, Yin and co-workers developed the dynamic kinetic resolution of racemic and P-free secondary diarylphosphines by Cu-catalyzed asymmetric alkylation, producing tertiary phosphine sulfides in high to excellent enantioselectivities. [131] When a bifunctional alkyl halide was added, the reaction delivered the bridged diphosphines in good diastereomeric ratios and very high enantioselectivities (Scheme 40).

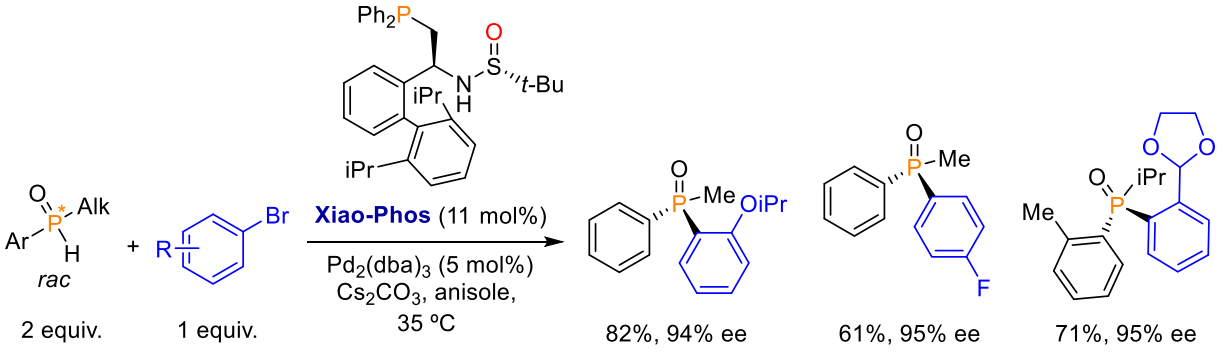
In 2022, Duan *et. al.* reported the Ir-catalyzed asymmetric oxidative double C-H coupling of diaryl(*tert*-butyl)phosphines and diarylalkynes



Scheme 37. Synthesis of P-stereogenic diarylphosphinamides and their use in asymmetric organocatalysis. BQ = 1,4-benzoquinone.



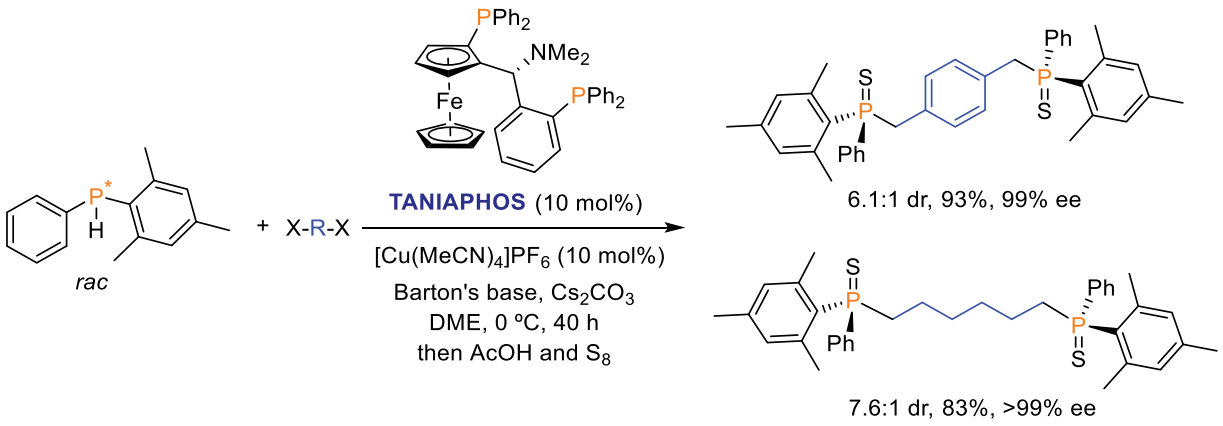
Scheme 38. Co/Salox-catalyzed C-H functionalization of diarylphosphinamides.



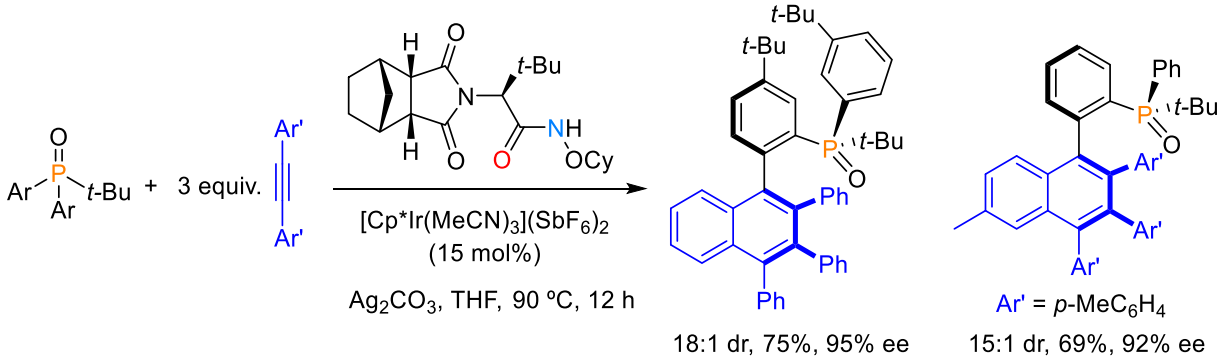
Scheme 39. Pd-catalyzed C-P coupling for the synthesis of P-stereogenic tertiary phosphine oxides.

for the synthesis of P- and axially chiral biaryl monophosphine oxides (Scheme 41). [132].

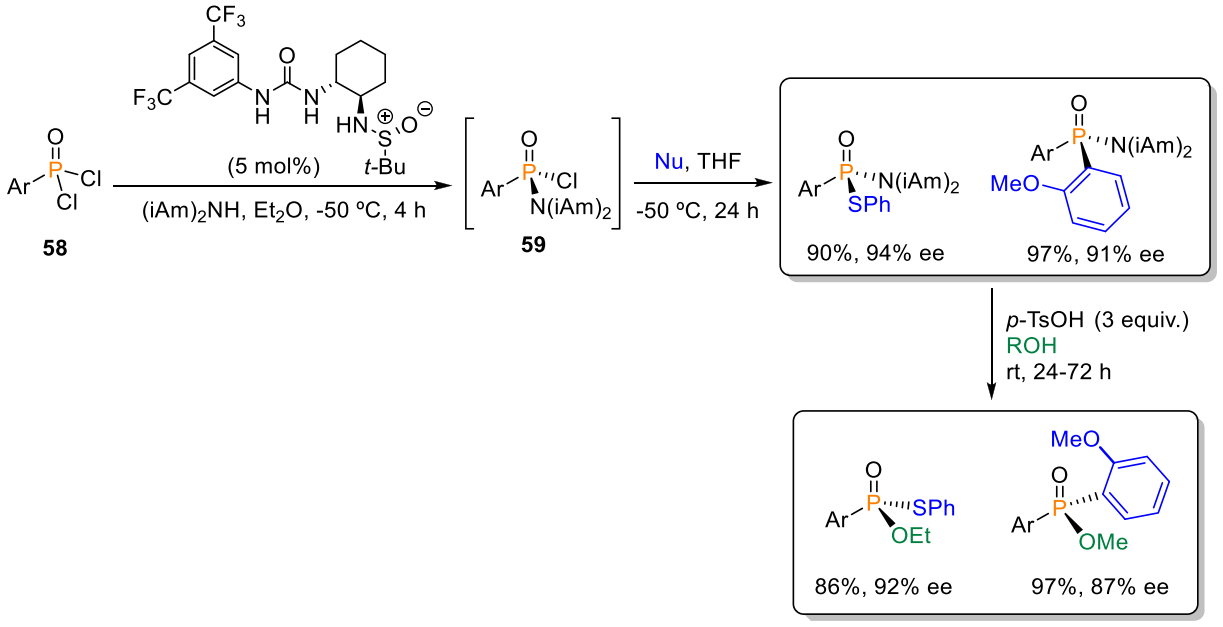
Very recently, Jacobsen and co-workers have reported the enantioselective organocatalyzed amination of phosphonic dichloride **58** with diisoamylamine (Scheme 42). [133] This process provided the versatile P-stereogenic key intermediate **59**. The displacement of the



Scheme 40. Cu-catalyzed C-P coupling for the synthesis of bridged P-stereogenic tertiary phosphine sulfides.



Scheme 41. Ir-catalyzed asymmetric oxidative C-H coupling to prepare P- and axially chiral biaryl monophosphines.



Scheme 42. Organocatalytic synthesis of P(V) derivatives. iAm = isoamyl, 3-methylbutyl.

chloro group in **59** with phenoxides, thiolates or Grignard reagents at low temperature produced a diversity of diisoamylamido derivatives. The products of the chloride-displacement reactions were further elaborated to afford alkoxy-substituted P(V) compounds via an acid-mediated stereoinvertive displacement of the diisoamylamino group. This strategy was applied in the preparation of certain biologically active P-stereogenic compounds bearing core structures of this kind.

5. Conclusions and outlook

Since the development of BisP* ligand by Imamoto in 1998, bulky P-stereogenic phosphines bearing a *tert*-butyl group and a smaller alkyl

group have demonstrated extraordinary proficiency in an array of asymmetric processes. Initial efforts focused on rigidifying the ligand backbone, which provided ligands like TangPhos or QuinoxP*. Soon after, the C_1-symmetric TCFP ligand introduced the concept of three-hindered quadrant ligands and that these types of ligands could be more easily synthesized and more efficient than their C_2-symmetric counterparts. Following this lead, Imamoto has developed several three-hindered quadrant analogs of QuinoxP* in which the *tert*-butyl groups are replaced by adamantyl, providing improved results in borylation reactions. The *tert*-butyl methyl phosphine moiety has also been introduced successfully in phosphino-oxazoline type ligands like MaxPHOX thanks to the development of appropriate electrophilic intermediates.

Since 2013, chemists at BI have developed their own family of P-stereogenic bulky phosphines, thereby demonstrating the financial and industrial importance of this class of compounds. Starting from a common P-stereogenic benzooxaphosphole intermediate, they reported the preparation of highly efficient diphosphine ligands like BIBOP and WingPhos. Most remarkably, they developed the first successful P-stereogenic Buchwald-type monophosphines for asymmetric palladium coupling reactions.

Although a considerable number of other highly enantioselective catalytic methods have been developed for the synthesis of P-stereogenic compounds over the last few years, the preparation of bulky P-stereogenic phosphines that are useful in catalysis relies heavily on the use of chiral auxiliaries or resolution techniques. The emergence of these strategies provides the opportunity for asymmetric catalysis to establish as a more efficient and greener approach for the preparation of P-stereogenic synthons and ligands. Further developments in the field include the discovery of other valuable P*-moieties that go beyond the *tert*-butyl methyl pair and could provide further structural diversity around the metal center, or the development and commercialization of air-stable P*-synthons that could be easily incorporated into ligand structures. These and other advances will continue to push the field forwards and provide even more efficient catalytic systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgments

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