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Efficient Asymmetric Synthesis of *P*-Chiral Phosphine Oxides via Properly Designed and Activated Benzoxazaphosphinine-2-oxide Agents

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Supporting Information

ABSTRACT: A general, efficient, and highly diastereoselective method for the synthesis of structurally and sterically diverse *P*-chiral phosphine oxides was developed. The method relies on sequential nucleophilic substitution on the versatile chiral phosphinyl transfer agent 1,3,2-benzoxazaphosphinine-2-oxide, which features enhanced and differentiated P−N and P−O bond reactivity toward nucleophiles. The reactivities of both bonds are fine-tuned to allow cleavage to occur even with sterically hindered nucleophiles under mild conditions.

For decades, chemists have been interested in the asymmetric synthesis of *P*-chiral phosphines because of their proven ability to impart excellent enantioselectivities in either transition-metal-catalyzed asymmetric processes[1] or as organocatalysts.[2] Although the prominent *P*-chiral ligand DIPAMP was prepared by Knowles and co-workers in the 1970s,[3] methods for the synthesis of optically active *P*-chiral phosphines have emerged slowly. Representative methods include the formation and separation of diastereomeric mixtures of menthyl phosphinates,[4] auxiliary-based transformations,[5,6] enantioselective deprotonation of phosphine−boranes and sulfides,[7] enzymatic resolution,[8] transition-metal-catalyzed asymmetric phosphine alkylations,[9] dynamic kinetic asymmetric oxidation of racemic phosphines,[10] and transformations of H-menthyl phosphinates.[11] Despite these elegant approaches, the currently available methods are often limited in terms of substrate scope and practicality, especially for the synthesis of sterically crowded *P*-chiral phosphines.

We have long been interested in developing an efficient and general method to prepare structurally, electronically, and sterically diverse *P*-chiral phosphine ligands to fine-tune the stereoselectivities of our many asymmetric processes. Recently, we developed a series of powerful bulky *P*-chiral phosphine ligands, such as MeO-BIBOP (**I**), MeO-BOP (**II**), and *P*-chiral biaryl ligands (**III**) (Figure 1), that have been effectively applied to a wide range of transformations, including Cu-catalyzed asymmetric propargylation,[12a] Rh-catalyzed asymmetric hydrogenation,[12b] and Pd-catalyzed asymmetric Suzuki−Miyaura coupling[12c] and Miyaura borylation reactions,[12d] with high stereoselectivities. Ligands **I**−**III** were all prepared from a key

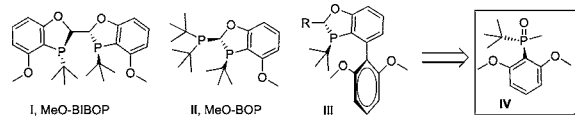
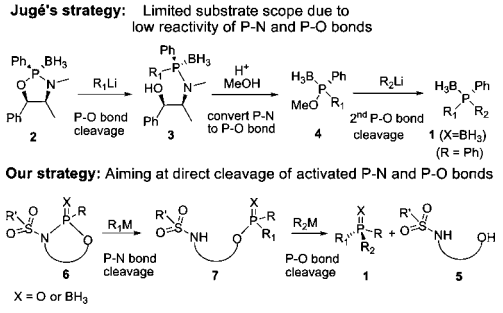


Figure 1. Bulky *P*-chiral phosphines with MeO functionality.

building block, the bulky *P*-chiral phosphine oxide **IV**. Unfortunately, attempts to synthesize **IV** in a stereoselective fashion using existing methods were unsuccessful, and we had to resort to a resolution-based route, which was a very tedious process. In searching for an efficient asymmetric route for the synthesis of **IV** and related structures, we designed and developed a new general method for the efficient and stereoselective synthesis of *P*-chiral phosphine oxides (**1**) with diverse structures and functionalities from the well-designed chiral phosphinyl transfer agent 1,3,2-benzoxazaphosphinine-2-oxide (Scheme 1).

Scheme 1. Strategy for the Synthesis of 1



Chiral amino alcohols have been employed as chiral auxiliaries for the asymmetric synthesis of *P*-chiral phosphines. Jugé and co-workers have elegantly demonstrated that the ephedrine-derived chiral template **2** can be opened by organolithium reagents stereospecifically to give **3**. Subsequent methanolysis can cleave the P−N bond to generate intermediate **4** containing a second P−O bond, which can then be displaced with another

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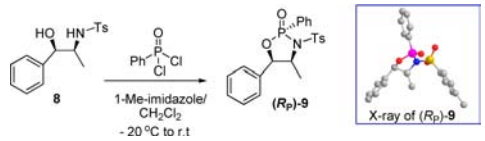
organolithium reagent to furnish *P*-chiral phosphine derivatives (Scheme 1).[6] The methanolysis to convert the P−N bond in **3** to the P−O bond in **4** is necessary because of the inertness of the P−N bond toward attack by carbon-based organometallic nucleophiles. Indeed, direct cleavage of the P−N bond in **3** with a carbon nucleophile has not been achieved to date. The generally low reactivity of the P−O and P−N bonds in these chiral templates has also restricted the substrate scope and rendered this method unsuitable for the synthesis of sterically hindered *P*-chiral building blocks such as **IV**. Bulky organolithium reagents either do not react with **2** or require more forcing conditions that can result in partial loss of stereospecificity during nucleophilic substitution at the P center.[13]

To overcome these limitations and develop a method with broad applicability, we designed a strategy in which the P−N bond is activated by an arylsulfonyl group on the N atom (Scheme 1). On the basis of our prior experience from the synthesis of chiral sulfinamides and sulfoxides, we anticipated that the P−N and P−O bonds in chiral template **6** would have differentiated bond strengths and therefore differentiated reactivity toward nucleophilic substitutions.[14] Thus, the sequential cleavage of the P−N bond and the P−O bond in **6** by two different organometallic reagents was expected to provide **1**.

Initially, compound **8** derived from *N*-*p*-tolylsulfonyl-(1*R*,2*S*)-norephedrine (Scheme 2) was examined to test this strategy.

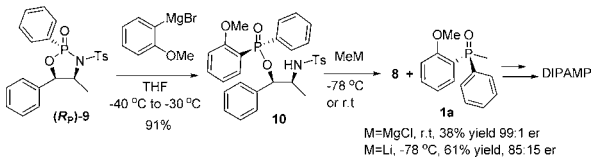
Scheme 2. Synthesis of Enantiomerically Pure (R_P)-9



Reaction conditions were surveyed for the synthesis of 1,3,2-oxazaphospholidine-2-oxide (R_P)-**9**. The selectivity depended on the nature of the base and solvent.[15] The use of 1-methylimidazole (1-MeIm) in dichloromethane (DCM) gave the highest dr (97:3). (R_P)-**9** is a crystalline solid, and its diastereomerically pure form was obtained by recrystallization. The absolute stereochemistry was unambiguously confirmed by single-crystal X-ray crystallography.[16] This methodology is amenable to large-scale synthesis, and >100 g of (R_P)-**9** was readily prepared in 75% yield with 99.5:0.5 dr.

Chiral template (R_P)-**9** was then examined for chemoselective P−N and P−O bond cleavage to synthesize **1a**, a key chiral starting material for DIPAMP (Scheme 3). Treatment of (R_P)-**9**

Scheme 3. Synthesis of 1a through (R_P)-9



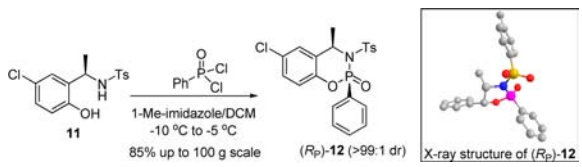
with 2-MeO-PhMgBr in tetrahydrofuran (THF) at −40 °C to −30 °C exclusively cleaved the sulfonyl-activated P−N bond with inversion of configuration at P,[16] affording phosphinate **10** as a diastereomerically pure crystalline product in 91% isolated yield. Notably, the introduction of the tosyl group enhanced the electrophilicity of the P−N bond in such a way that it was cleaved in preference to the P−O bond. This is in contrast to the relative bond strength of the P−O and P−N bonds in Jugé's chiral template **2**.

Cleavage of the P−O bond in **10** by treatment with MeMgCl was then studied. The reaction was sluggish even at ambient temperature with 6 equiv of MeMgCl, providing (*S*)-**1a**[10a] with inversion of configuration at P in only 38% yield, albeit with excellent stereoselectivity (99:1 er). Elevating the temperature failed to improve the yield of **1a**, and many impurities formed. Switching to the more active nucleophile MeLi (4 equiv) improved the yield to 61%, but the stereoselectivity suffered, as **1a** was obtained with 85:15 er. Additionally, the substrate scope was limited, as even slightly hindered lithium reagents such as EtLi or *i*PrLi provided the respective products in very poor yields (Scheme 3). These observations again underscored the challenges associated with the P−O bond cleavage and the need for further activation.

As reported previously,[17a] P−OR bond reactivity is affected by the basicity of the leaving group, which can be predicted by the pK_a of the resultant alcohol ROH: the reactivity of a P−OR bond increases as the pK_a of the resultant ROH decreases. We envisaged that a P−O bond derived from a phenol derivative (pK_a ≈ 10) would be much more reactive than that from an alkyl alcohol backbone (pK_a ≈ 15).[17b] Therefore, the new aminophenol-based auxiliary **11** was designed and readily prepared on a large scale from readily available (*R*)-2-(1-aminoethyl)-4-chlorophenol.[18]

Reaction conditions for the synthesis of (R_P)-**12** in enantiomerically pure form were first examined.[15] Studies showed that, analogous to **8**, high conversion and high diastereoselectivity were observed with 1-MeIm in DCM, yielding (R_P)-**12** with 98:2 dr. Diastereomerically pure (R_P)-**12** was obtained by crystallization, and its absolute configuration was confirmed by X-ray crystallographic analysis (Scheme 4).[16] The synthesis is simple and has been scaled to >100 g in 85% isolated yield.

Scheme 4. Synthesis of Enantiomerically Pure (R_P)-12



To demonstrate the potential of this new method, the synthesis of **1a** was first investigated. As anticipated, the reaction of 2-MeO-PhMgBr with (R_P)-**12** in THF at −20 °C selectively cleaved the P−N bond to yield **13a** in 91% yield with inversion of configuration at P, as confirmed by the single crystal X-ray structure (Scheme 5).[16] Notably, the reaction between 4 equiv of MeMgCl and **13a** occurred at −10 °C, cleaving the P−O bond in

Scheme 5. Ring Opening for the Synthesis of 13

13a, R_1M=2-MeO-PhMgBr, 91%
13b, R_1M=2-(1,3-dioxolanyl)PhMgBr, 75%
13c, R_1M=2-mesitylMgBr/LiCl (1 eq)/dioxane (1.1 eq), 58%
13d, R_1M=*t*-BuLi, 65%

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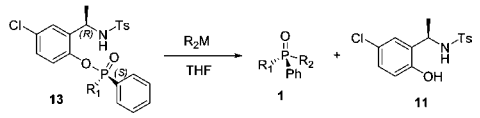
15 min to provide enantiomerically pure (*S*)-**1a**[10a] in 91% yield with inversion of configuration at P (Table 1, entry 1). This indicates that **13a** has a more reactive P−O bond than **10**.

Encouraged by the above results, we examined the synthesis of sterically hindered chiral phosphine oxides from **13a**. While slow reactions were observed when *i*PrMgBr and *t*BuMgCl were used, the P−O bond was cleaved at −70 °C with *i*PrLi and *t*BuLi to furnish **1b** and **1c**, respectively, in good yields with excellent enantiomeric purities (Table 1, entries 2 and 3). Moreover,

Table 1. Synthesis of *P*-Chiral Phosphine Oxides[a]



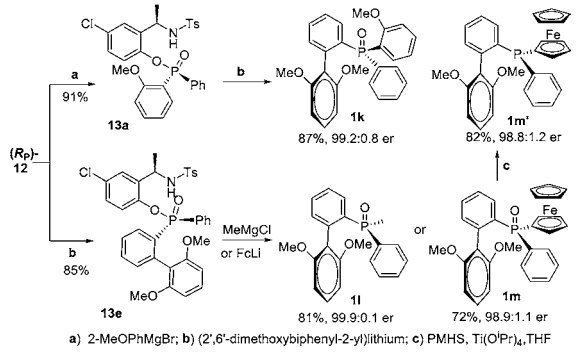
Entry	13	R_2M	Product	yield(%)	er[b]
1	**13a**	MeMgBr	**1a**	91	>99.5:0.5[d]
2	**13a**[c]		**1b**	63	>99.5:0.5[d]
3	**13a**		**1c**	84	98.2:1.8
4	**13a**		**1d**	82	99.6:0.4
5	**13a**		**1e**	70	>99.5:0.5
6	**13a**		**1f**	62	95:5
7	**13b**	MeMgCl	**1g**	73	99:1
8	**13b**		**1h**	82	98:2
9	**13c**	MeMgCl	**1i**	73	98.7:1.3
10	**13c**		**1j**	58	99.1:0.9

[a]See the SI for the reaction conditions. [b]Measured by chiral HPLC. [c]See the SI for the X-ray structure. [d]The other enantiomer was not observed.

compounds with other functionalities, such as a ferrocene (**1d**), an alkene (**1e**), or an alkyne (**1f**), were readily prepared in good yields and enantiomeric purities (entries 4−6). Notably, **13b** containing a latent aldehyde was a competent coupling partner, allowing the preparation of enantiomerically enriched **1g** and **1h**, which can be used as key precursors for ligand design (entries 7 and 8). Additionally, treatment of (R_P)-**12** with the hindered 2-mesitylmagnesium bromide under Turbo conditions successfully cleaved the P−N bond to yield **13c**, whereas no reaction was observed between 2-mesityllithium and Jugé's chiral template **2**.[1b] From **13c**, compounds **1i** and **1j** were synthesized in good yields and selectivities (entries 9 and 10). (R_P)-**12** was also active toward a hindered alkyl organometallic reagent, and the reaction with *t*BuLi afforded **13d** in good yield. Treatment of (R_P)-**12** with EtMgBr and *i*PrMgBr also furnished the desired products, but in low isolated yields. These results may be due to the acidity of the α-proton present in the products, and further optimization of the reaction conditions to exploit these nucleophiles is under investigation.

Chiral versions of Buchwald-type ligands can also be prepared effectively using this method (Scheme 6). Treatment of **13a** with

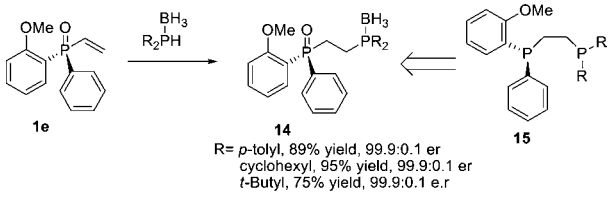
Scheme 6. Synthesis of Chiral Buchwald Ligands



(2′,6′-dimethoxybiphenyl-2-yl)lithium (DMOBP-Li) yielded enantiomerically pure **1k** in high yield. The reaction between DMOBP-Li and (R_P)-**12** provided intermediate **13e** in high yield, from which **1l** and **1m** were successfully prepared. Importantly, reduction of **1m** with polymethylhydrosiloxane (PMHS) in the presence of $Ti(OiPr)_4$ in THF afforded the free phosphine ligand **1m′** in excellent yield without erosion of the enantiopurity.

The structurally diverse chiral phosphine oxides **1** are key starting materials for the design of mono- or bidentate (**15**) *P*-chiral ligands. As a preliminary example, **1e** was reacted with dialkyl- or diarylphosphine−borane adducts, providing enantiomerically pure **14** in high yield (Scheme 7).

Scheme 7. Synthesis of Bidentate *P*-Chiral Ligands



Finally, the new method was applied to the asymmetric synthesis of the bulky *P*-chiral phosphine oxide **IV** (Scheme 8), which is a versatile intermediate that can be converted into many important *P*-chiral ligands, such as **I**−**III**.[12,19] Treatment of **11** with dichloro(2,6-dimethoxyphenyl)phosphine (**16**) followed by H_2O_2 oxidation afforded diastereomerically pure **17** in 85% isolated yield. Treatment of **17** with *t*BuLi at −40 °C gave **18** in excellent yield. Subsequent reaction of **18** with MeLi in the presence of 20 mol % $MgBr_2{\cdot}OEt_2$ afforded sterically hindered intermediate **IV** as a crystalline product in 63% yield with 98.3:1.7 er. According to the literature procedure,[19] conversion

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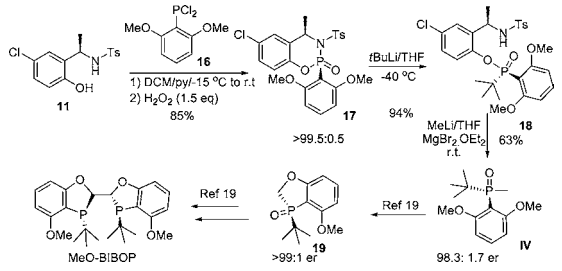
Scheme 8. Effective Synthesis of MeO-BIBOP



of **IV** to **19** was accomplished successfully without erosion of the chirality.

In summary, we have described a general, highly diastereoselective, and efficient synthesis of *P*-chiral phosphine oxides via sequential nucleophilic substitutions using 1,3,2-benzoxazaphosphinine-2-oxide (**12**). This cyclic intermediate contains enhanced and properly differentiated P−N and P−O bond reactivities, ensuring that the first nucleophile selectively cleaves the P−N bond while the second nucleophile cleaves the P−O bond with double inversion of configuration at the P center. This method overcomes the limitations of earlier methods in the synthesis of sterically hindered compounds and offers a practical, stereoselective, and high-yield route to *P*-chiral phosphine oxides that are key intermediates for accessing *P*-chiral phosphine ligands such as the powerful BIBOP family of ligands for asymmetric catalysis.[12] Further applications of this chemistry to the synthesis of new ligands and their use in asymmetric transformations are under investigation.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data and spectra, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(15) See the Supporting Information (SI) for results on the effect of bases and solvents on the selectivity.

(16) See the SI for information on single-crystal X-ray structures.

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