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# Diastereoselective Radical Oxidative C−H Aminations toward Chiral Atropoisomeric (*P, N*) Ligand Precursors

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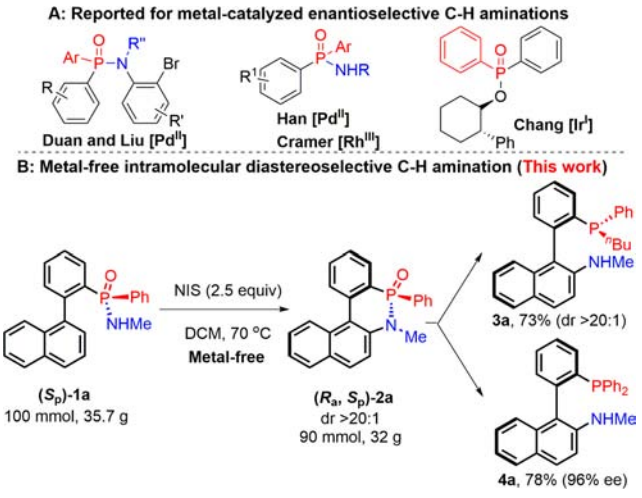
Supporting Information

**ABSTRACT:** A new class of chiral atropoisomeric (*P, N*) ligand precursors has been obtained with excellent diastereoselectivities and high yields through diastereoselective metal-free intramolecular radical oxidative C−H amination with chiral phosphamide as the auxiliary group. This method provides a concise and highly valuable pathway for the synthesis of enantiopure aminophosphine ligands in large-scale.


Chiral aminophosphine compounds with biaryl backbones as an important type of chelating bidentate ligand (MAP-type ligand) have been widely applied to many asymmetric reactions because of their high reactivities and selectivities.[1] Among them, the ligands possessing both axial chirality and a chirogenic phosphorus center display unique advantages in some asymmetric reactions in relation to the traditional axial chirality ligands.[2] Moreover, chiral aminophosphine ligands are also easier to modify and convert into a variety of other chiral ligands or organocatalysts.[3] At present, the preparation of enantiopure chiral aminophosphine ligands has relied generally on the direct phosphinylation of optically pure binaphthyl skeletons of (*R*)-2,2′-hydroxy-1,1′-binaphthyl (BINOL), (*R*)-2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN), and (*R*)-2-amino-2′-bromo-1,1′-binaphthyl (NBBIN).[4] However, not only are the functional group transformations required of this preparation tedious and comprised of many steps, the accompanying operations such as chiral resolution, lithiation, and esterification are also complicated, greatly increase preparation costs, and fail to meet the atom economy. Moreover, the inert scope of binaphthyl skeletons also qualifies as diversity-oriented. Nonbinaphthyl skeleton chiral biaryl ligands in particular lack an effective synthesis method. Recently, transition metal catalyzed asymmetric C−H amination has provided a general and powerful means of building C−N bonds.[5,6] Application of this strategy to the chiral aminophosphine synthesis has also achieved remarkable progress. Representative contributions can be found from the Duan,[7] Liu,[8] Han,[9] Chang,[10] and Cramer groups.[11] Because of enantiodetermining steps, different transition metal catalysts utilizing $Pd^{II}$, $Ir^{I}$, and $Rh^{III}$ have been used to activate C−H bonds, respectively (Scheme 1A). However, the enantioselectivities in many reactions are substrate-dependent, so exploring more efficient approaches for synthesizing a new structural chiral aminophosphine, especially approaches that could be satisfied by large-scale preparations, remains an important and challenging task. In the past year, by using the chiral phosphorous oxide as a directing group, we have succeeded in achieving Pd(II)-catalyzed asymmetric C−H activation and dynamic kinetic resolution.[12] We have questioned whether chiral phosphinamide and metal-free direct oxidative C−H amination[13] might be successfully combined to create a new pattern for the enantiopure synthesis of both axially chiral and P-stereogenic ligand precursors in large-scale through dynamic kinetic resolution or a desymmetrisation proccess. In general, metal-free direct C−H functionalization is often conducted by a radical process;[14] therefore, the absence of a chiral transition metal complex makes stereoselective control

**Scheme 1. Different Strategies for Asymmetric C−H Aminations**

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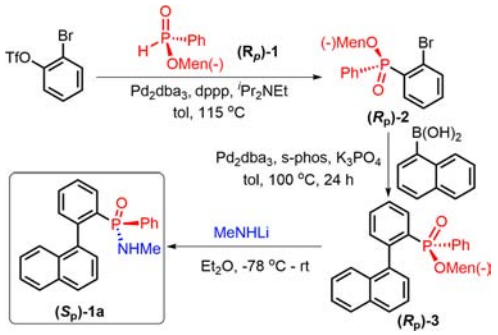
very difficult. If the key challenge of overcoming the conflict between enantioselectivity with metal-free C−H amination could be addressed, such a sequence would offer great advantages. With these design principles in mind, we first developed a new route with a Pd-catalyzed chiral phosphonate-induced cascade asymmetric cross-coupling reaction for synthesis of optically pure (*S*)-*N*-methyl-*P*-(2-(naphthalen-1-yl)-phenyl)-*P*-phenylphosph amide (**1a**)[15] as the substrate (Scheme 2) wherein we wished to achieve chiral atropoisomeric (*P, N*)

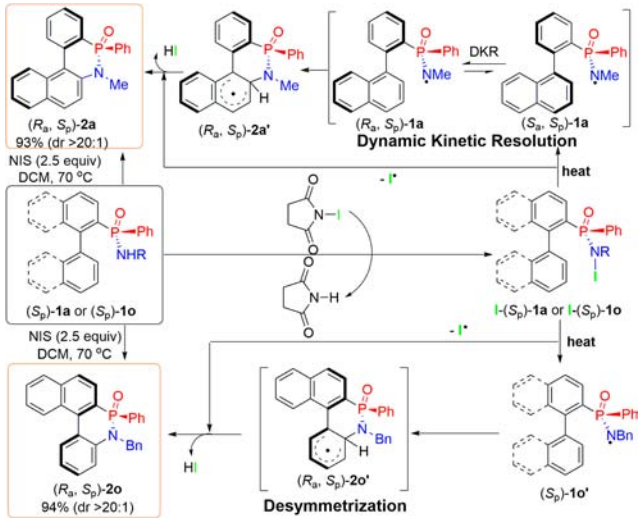
**Scheme 2. Route for Synthesis of ($S_p$)-1a**




ligand precursors through metal-free intramolecular C−H amination and cyclization. Under our endeavors, the first NIS-mediated diastereoselective radical oxidative C−H amination to synthesize a new class of chiral atropoisomeric (*P, N*) ligand precursors was developed under mild reaction conditions with high yields and excellent diastereomeric ratios (Scheme 1B). These phosphamide moieties could be easily transformed into the enantiopure aminophosphine ligands **3a** and **4a** in good yields with high ee values. In particular, our method can synthesize chiral phosphamides in large-scale in very good yields and with excellent dr values.

We initiated our experimental efforts by studying the metal-free diastereoselective C−H amination reaction of (*S*)-*N*-methyl-*P*-(2-(naphthalen-1-yl)phenyl)-*P*-phenyl phosphamide (**1a**) using a variety of different hypervalent iodine reagents, which promoted metal-free oxidative C−H amination reactions properly and displayed excellent activation and functional group tolerance. In general, hypervalent iodine(III) species possessing an iodine−nitrogen bond were efficient reagents in the oxidative C−H amination of nonprefunctionalized arenes and heteroarenes.[16] Through extensive screening of oxidants, solvents, and other parameters (for details, see the Supporting Information), we found that NIS (*N*-iodosuccinimide) facilitates the cyclization of **1a** through oxidative C−H amination to give the desired product **2a** in high yield and in an excellent diastereomeric ratio. To test the practicality of this protocol, a scaled-up reaction of **1a** (100 mmol, 35.7 g) was performed to give **2a** (90 mmol, 32 g) in 90% yield with no decrease in diastereoselectivity. We know that the metal-free direct C−H functionalization is often conducted in a radical process, so a radical pathway was presumed to be involved in our metal-free oxidative C−H amination reactions. The preliminary mechanistic studies supported this assumption. When equimolar amounts of TEMPO or BHT were added to the solution of **1a** and NIS in DCM, the reactions were remarkably suppressed (for details, see the Supporting Information). In order to further understand this transformation, mass spectrometry experiments of **1a** and **1m** have also been done by adding 2.0 equiv of TEMPO under the model reaction (Scheme 1). The peak of radical intermediates of **1a′** (*m/z* 513.1397) and **1m′** (*m/z* 539.1) were observed via ESI/MS detection in situ. Morover, more than 1 equiv of succinimide was obtained after the reaction was completed. These results indicate that this metal-free diastereoselective C−H amination was probably carried out by a radical process (Scheme 3). According to a

**Scheme 3. Proposed Mechanistic Pathway**




different substrate structure, the transformation went through a dynamic kinetic resolution[17] or desymmetrization course.[18] In terms of utility the former methodology would allow for substrates with relatively low rotational barriers to permit a dynamic process.

Having established the optimized reaction conditions, we next explored the substrate scope with various phosphamides (Scheme 4). Different *N*-protecting groups were examined and the results indicated that alkyl and benzyl were suitable for this reaction and products of **2b** and **2c** were obtained with good yields and excellent diastereomeric ratios. When Cl- and F-groups were introduced in the 4 position (**2d**−**2e**), the corresponding chiral atropoisomeric phosphamides were obtained with the best results. For these products (**2a**−**e**), it is well established that steric repulsion occurs between the naphthalene moiety and the *ortho R*-substituent when the *P*−*N* bond is opened, which is pivotal to retain a nonracemizing axially chiral biaryl. As the biaryls with three or four *ortho*-substituents at the axis were relatively stable,[19] we mainly examined substrates with at least one substituent at the 6 or 2′-position. A range of 2-phenyl-*P*-phenylphosphamides substituted with 2′-position of aryl groups bearing electron-donating, electron-withdrawing, and alkyl substituents furnished products (**2f**, **2h**, **2j**−**2k**) in good yields and high diastereomeric ratios (dr >20:1). In addition, polysubstituted 2-phenyl-*P*-phenylphosphamides provided the corresponding cyclization products (**2g** and **2i**) in moderate yields with excellent diastereoselectivities. The absolute configuration of the product **2i** was confirmed by single-crystal X-ray crystallography. Even if the substituent free 2-phenyl-*P*-phenylphosphamide was used in the reaction, the chiral atropoisomeric product (**2m**) was also afforded in good yield and dr value. These results demonstrate that these C−H aminations proceed by way of a dynamic kinetic resolution process. However, to the (*S*)-*N*-benzyl-*P*-phenyl-*P*-(1-phenylnaphthalen-2-yl)phosphamide (**2o**) and its derivatives, desymmetrisation is the key step in the reactions. Notably, when the



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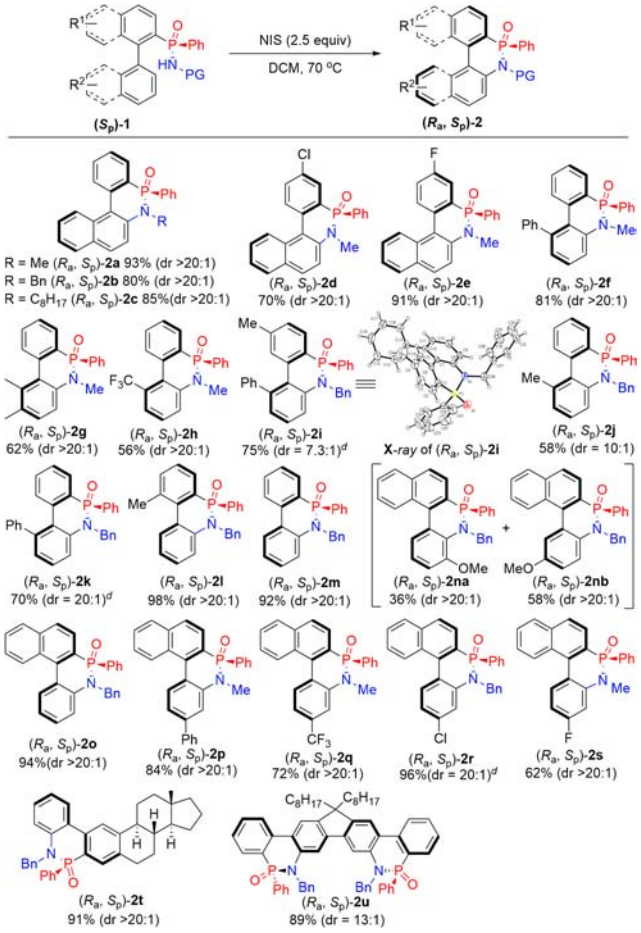
**Scheme 4. Substrate Scope for Diastereoselective Intramolecular C−H Aminations**[a,b,c]

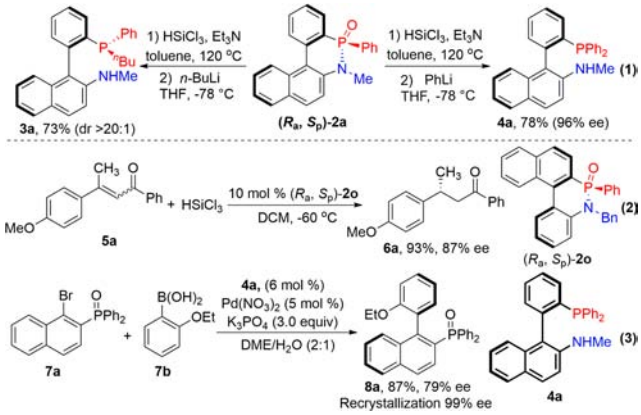



[a]Conditions: ($S_p$)-**1** (0.5 mmol) and NIS (1.25 mmol) in DCM (5 mL) at 70 °C under air. [b]Isolated yield. [c]The dr value was determined by $^{31}P$ and $^{1}H$ NMR. [d]The dr value was determined through chromatography separation on silica gel.

methoxy group is on the 3′-position of (*S*)-*N*-benzyl-*P*-phenyl-*P*-(1-phenylnaphthalen-2-yl) phosphamide (**1n**), a mixture of two regioisomers (**2na** and **2nb**) were obtained in high yield and diastereoselectivity, but these two regioisomers can be separated by flash chromatography on silica gel. Moreover, other (*S*)-*P*-phenyl-*P*-(1-phenylnaphthalen-2-yl)phosphamides also displayed good functional group tolerance and resulted in good yields accompanied by excellent diastereoselectivities (**2p**−**2s**). We also extended this method to modify estrone and afforded chiral atropoisomeric product **2t** in high yield and diastereoselectivity, a process which was coordinated with metal species to be used as drug and diagnostic reagents in cancer therapy extensively.[20] Finally, we further synthesized the atropoisomeric fluorene derivatives ($R_a$, $S_p$)-**2u**, which is a novel chiral metal ion probe and could be applied to biology or pharmaceuticals in the future.[21]

Our products of phosphamide moieties could be easier to reduce to trivalent phosphine compounds with $HSiCl_3$[22] and then cleave the P−N bond with different lithium reagents to obtain the enantiopure aminophosphine ligands (**3a**) possessing both axial chirality and a chirogenic phosphorus center in good yield and excellent diastereomeric ratio or the axially chiral ligand (**4a**) in good yield with high ee value (Scheme 5, eq 1). In order

**Scheme 5. Utility of ($R_a$, $S_p$)-2o and 4a in Asymmetric Catalysis**




to display the utility of our chemistry, we first used the product of chiral aminophosphine ($R_a$, $S_p$)-**2o** as an organocatalyst to prompt the asymmetric reduction of **5a** preliminarily and obtained **6a** in 93% yield with an 87% ee value (Scheme 5, eq 2). Furthermore, we also chose the modified compound of **4a** as the chiral ligand to the palladium-catalyzed asymmetric Suzuki−Miyaura cross-coupling to synthesize axial chirality biaryl compounds (**8a**) in 87% yield and 79% ee value,[23] which could be improved to 99% ee by simple recrystallization (Scheme 5, eq 3).

In summary, we have described a metal-free oxidative intramolecular C−H amination reaction furnishing axially chiral atropoisomeric phosphamides in high yields and excellent diastereoselectivities with mild reaction conditions. Through further transformation of these products, we have obtained a series of new P−N ligands.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03625.

Experimental details and characterization data for all new compounds are provided (PDF)

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### Notes

The authors declare no competing financial interest.

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