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Design, Synthesis, and Application of a Chiral Sulfinamide Phosphine Catalyst for the Enantioselective Intramolecular Rauhut–Currier Reaction**

*Xiao Su, Wei Zhou, Yangyan Li, and Junliang Zhang**

Abstract: *A novel class of chiral sulfinamide phosphine catalysts (Xiao-Phos) are reported, which can be easily prepared from inexpensive commercially available starting materials. The Xiao-Phos catalysts showed good performance in enantioselective intramolecular Rauhut–Currier reactions, generating α-methylene-γ-butyrolactones in high yields with up to 99% ee under mild conditions. Moreover, kinetic resolution and parallel kinetic resolution were also observed with the use of two different substituted racemic precursors.*

Over the past decade, asymmetric nucleophilic catalysis with chiral phosphines has emerged as a powerful approach to structurally diverse and synthetically valuable optically active organic building blocks.[1] Among the many types of chiral phosphines, chiral β-aminephosphines represent one of the most attractive and have been utilized as nucleophilic catalysts[2] or chiral ligands[3] in a broad spectrum of useful organic transformations. Compared to the intensive attention focused on the utility of chiral β-aminephosphines in organic synthesis, only a handful of methods have been reported so far for their synthesis. Among these, the approach from readily available natural or unnatural chiral amino acids is the most attractive.[4] Despite the fact that much progress has been made in the construction of chiral phosphine catalysts, the development/design of highly efficient new types of chiral phosphines, especially from inexpensive, commercially available chiral resources, remains a considerable challenge.

Recently, our group developed a new type of chiral sulfinamide phosphine (Ming-Phos ligands), which could be easily prepared in good yields from inexpensive commercially available chiral *tert*-butylsulfinamide in two steps. Gratifyingly, Ming-Phos ligands have shown good performance in asymmetric transition-metal catalysis and the sulfinamide plays a second role in stereoselectivity control.[5] With a series of chiral Ming-Phos ligands in hand and as a part of our program for developing chiral-phosphine-catalyzed enantioselctive transformations,[6] we wished to expand the applications of Ming-Phos variants from transition-metal catalysis to nucleophilic phosphine catalysis. In this context, recent elegant work by Sasai and co-workers[7] attracted our attention. They successfully accomplished a chiral-phosphine-catalyzed enantioselective intramolecular Rauhut–Currier (RC) reaction,[8] efficiently furnishing synthetically valuable α-methylene-γ-butyrolactones.[9] However, the performance of the Ming-Phos variants was disappointing; in most cases, the reaction did not give high conversions because of the low nucleophilic catalyst activity. We then envisaged that a new type of chiral sulfinamide phosphines, called Xiao-Phos, should have better nucleophilic activity than the Ming-Phos variants. With two stereocenters, an H-bonding site, and tunable side chains, the Xiao-Phos series may be applicable to asymmetric nucleophilic catalysis for organic transformations such as RC reactions (Figure 1). Herein, we report our efforts toward the stereodivergent synthesis of these new chiral phosphines and their application in enantioselective intramolecular RC reaction.

After many attempts, we were pleased to find that Xiao-Phos variants could be easily prepared from commercially available Ph_2PCH_3, *tert*-butylsulfinamide, and aldehyde (Scheme 1).[10] Treatment of Ph_2PCH_3 with BuLi in the presence of TMEDA at room temperature produced a solution of Ph_2PCH_2Li in THF according to the reported procedure,[11] which then undergoes nucleophilic addition to chiral (*R*s)-sulfinimines, thereby furnishing the corresponding phosphines **X1**–**X7** in good yield with moderate to high diastereoselectivity. Notably, **X8** was obtained from the corresponding *o*-hydroxyl-substituted sulfinimines. **X9**–**X12** were made through the silylation of **X8** under mild conditions. (see the Supporting Information). The absolute configura-

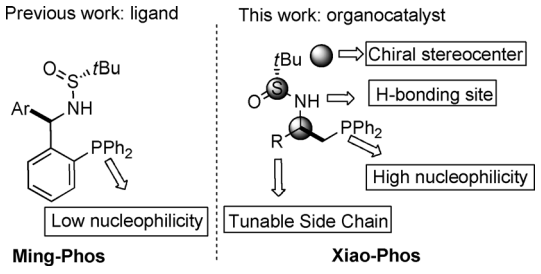

Figure 1. The design of novel chiral sufinamide phosphines.

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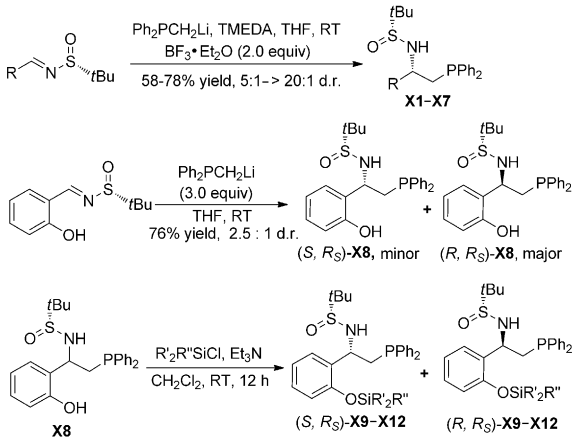
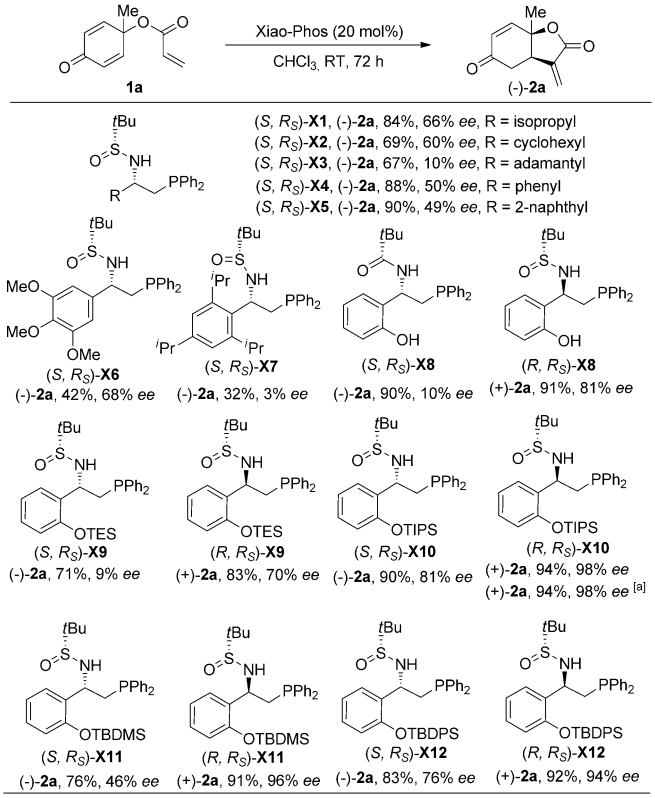


Scheme 1. Concise synthetic approach to Xiao-Phos variants. TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, THF = tetrahydrofuran.

tions of (*S*,R_S)-**X4** and (*R*,R_S)-**X8** were established by single-crystal X-ray diffraction.[12]

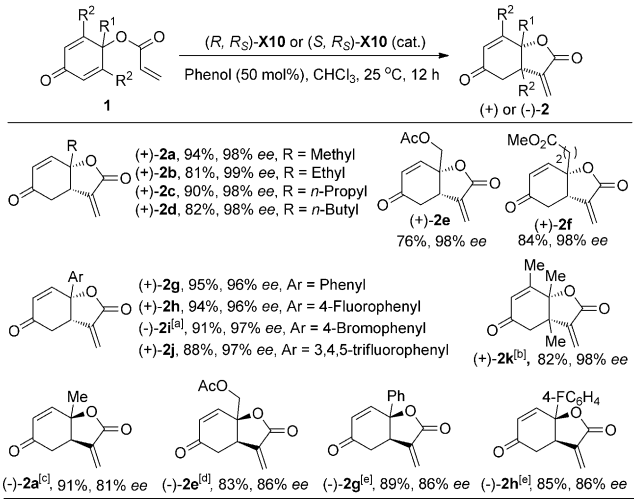
With the chiral phosphine catalysts in hand, we concentrated our investigation on their performance in the enantioselective intramolecular Rauhut–Currier reaction (Scheme 2). The desired product (−)-**2a** was obtained in good yield and with moderate enantioselectivity when Xiao-Phos catalysts derived from aliphatic sulfinimines, such as (*S*,R_S)-**X1** and (*S*,R_S)-**X2**, were employed. (*S*,R_S)-**X3**, which bears a bulky adamantanyl substituent, exhibited lower enantioselectivity. For higher reactivity and enantioselectivity, a survey of Xiao-Phos catalysts derived from aromatic sulfinimines was then conducted. Although the reaction proceeded with good yield, the *ee* values decreased slightly to 50% with the use of (*S*,R_S)-**X4** and (*S*,R_S)-**X5**. A positive effect on the enantioselectivity was observed when three methoxyl moieties were introduced to the phenyl ring, however, the yield was reduced slightly to 42%. The bulkier phosphine (*S*,R_S)-**X7**, which has three isopropyl groups in the phenyl ring, was clearly inferior in terms of reactivity and enantioselectivity when compared with (*S*,R_S)-**X4** and (*S*,R_S)-**X5**. Further improvements in reactivity and enantioselectivity were achieved when (*R*,R_S)-**X8** was employed, which led to the production of (+)-**2a** in 91% yield and 81% *ee*, whereas its diastereomer (*S*,R_S)-**X8** gave very low enantioselectivity. This remarkable difference between (*R*,R_S)-**X8** and (*S*,R_S)-**X8** revealed that the carbon stereocenter might also play a crucial role in realizing good enantioselectivity. Inspired by this interesting result, catalysts **X9**, **X10**, **X11**, and **X12**, which bear different silyl protecting groups, were next examined in the RC reaction. Unfortunately, phosphine catalysts containing the TES group, such as (*R*,R_S)-**X9** and (*S*,R_S)-**X9**, did not show any improvement in performance. To our delight, with the employment of (*R*,R_S)-**X10** as the catalyst, dramatic improvements in reactivity and enantioselectivity were achieved and the desired (+)-**2a** was produced in 94% yield and 98% *ee*. The absolute configuration of (+)-**2a** was established by single-crystal X-ray diffraction.[12] Ikegami[13] and co-workers showed that the addition of phenol facilitates the Baylis–Hillman reaction and significantly improves the reaction



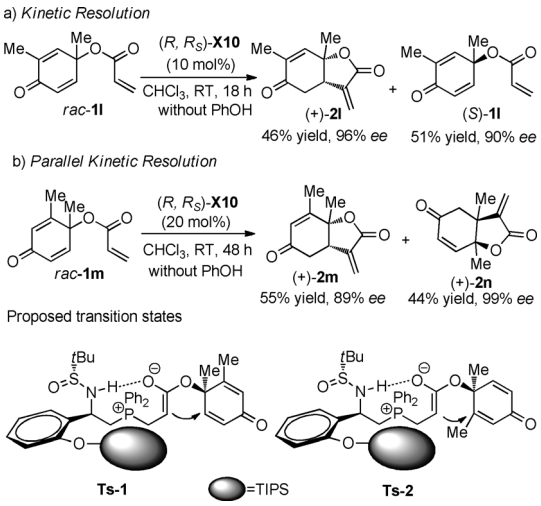
Scheme 2. Screening Xiao-Phos catalysts in the enantioselective intramolecular Rauhut–Currier reaction. [a] 50 mol% PhOH was added, 12 h. TES = triethylsilyl, TIPS = triisopropylsilyl, TBDMS = *tert*-butyldimethylsilyl, TBDPS = *tert*-butyldiphenylsilyl.

yield. In our case, with the addition of 50 mol% of phenol, the catalyst loading could be reduced to 10 mol% and the reaction could be completed within 12 h without loss of efficiency and enantiopselectivity. By contrast, the phenol has a slightly negative effect on the reactivity in the work of Sasai and co-workers.[7] The TBDMS- and TBDPS-derived Xiao-Phos catalysts (*R*,R_S)-**X11** and (*R*,R_S)-**X12** delivered high reactivity and enantioselectivity. Notably, (−)-**2a** could be obtained in 76–90% yield and 46–81% *ee* in the presence of (*S*,R_S)-**X10**, (*S*,R_S)-**X11**, and (*S*,R_S)-**X12**. No better results were obtained after the screening of various solvents and variation of reaction temperature (see Section S3 in the Supporting Information). Based on the results, the optimal reaction conditions were identified: 10 mol% (*R*,R_S)-**X10** as the catalyst, 50 mol% phenol as an additive and $CHCl_3$ as the reaction medium at 25 °C.

The substrate scope of this enantioselective intramolecular RC reaction was investigated under the optimized reaction conditions (Scheme 3). Variation of the alkyl substituent on the starting materials from methyl to *n*-butyl was tolerated and the corresponding cyclized products (+)-**2a–d** were obtained in good yield with 98–99% *ee*. Substrates **1e** and **1f**, which contain ester side chains, also worked well and the desired products (+)-**2e** and (+)-**2f** were isolated in 76–84% yield with 98% *ee*. To further investigate the substrate scope, a set of aryl-substituted substrates were synthesized and investigated under optimal reaction conditions. Phenyl-substituted **1g** underwent clean cyclization to produce (+)-**2g** in



Scheme 3. The scope of the **X10**-catalyzed enantioselective intramolecular Rauhut–Currier reaction. [a] 18 h. [b] (R,R_S)-**X10** (20 mol%), without phenol, 72 h. [c] (S,R_S)-**X10** (20 mol%), without phenol, 72 h. [d] (S,R_S)-**X10** (20 mol%), without phenol, 36 h. [e] (S,R_S)-**X10** (20 mol%), without phenol, 24 h.



Scheme 4. Kinetic resolution of *rac*-**1l**, parallel kinetic resolution of *rac*-**1m**, and proposed transition states.

95% yield with 96% *ee*. The enantioselective cyclization reactions of **1h–j**, which contain F, Br, or three F atoms on the phenyl ring, respectively, were all converted to the corresponding products in good yield with excellent enantioselectivity. Notably, substrate **1k**, which is derived from 3,4,5-trimethylphenol, offers an opportunity to evaluate the performance of (R,R_S)-**X10** in the construction of scaffolds with two contiguous quaternary carbon centers. Under slightly modified reaction conditions (20 mol% catalyst loading, longer reaction time, and without phenol), the valuable product (+)-**2k** was successfully obtained in 82% yield with 98% *ee*.

We next turned our investigation to the performance of (S,R_S)-**X10** in the intramolecular Rauhut–Currier reaction. To our delight, the enantiomer (−)-**2a** was obtained in 91% yield and 81% *ee* from the corresponding substrate **1a**. Additionally, the substrates **1e** and aryl-substituted **1g** and **1h** were also converted to the desired enantiomers (−)-**2e**, (−)-**2g**, and (−)-**2h** in good yield and with acceptable enantioselectivity. These results indicate that the performance of (S,R_S)-**X10** is much more sensitive to the structure of the substrate than its diastereomer (R,R_S)-**X10**.

Despite the dramatic progress that has been made in the field of enantioselective RC reactions during the past decades, kinetic resolution (KR)[14,15] and parallel kinetic resolution (PKR)[16] of racemic precursors through asymmetric RC process have been less studied. Given the fact that the reaction of **1k** with methyl groups on the dienone moiety is much slower than that of **1a**, we envisaged that the kinetic resolution of racemic precursors might be realized under the catalysis of Xiao-Phos. *Rac*-**1l** and *rac*-**1m** were then synthesized and subjected to the reaction with (R,R_S)-**X10** (Scheme 4). To our delight, a nice kinetic resolution process with a high s factor ($s = 95$)[17] was indeed observed in the reaction of *rac*-**1l**, furnishing the desired (+)-**2l** in 46% yield with 96% *ee* and the (S)-**1l** could be recovered in 51% yield with 90% *ee*. Notably, an exciting parallel kinetic resolution of *rac*-**1m** was realized and enantioenriched (+)-**2m** and (+)-**2n** could be obtained in satisfied yield and with high enantioselectivity. It is noteworthy that these two types of kinetic resolution were run without the addition of phenol. As far as we know, this is the first successful example of parallel kinetic resolution for the RC reactions. To account for the observed stereochemistry in the parallel kinetic resolution reactions, two possible transition states were proposed.[2a,b,7,8l,r,18] The zwitterion intermediate is formed through nucleophilic addition of (R,R_S)-**X10** to the acrylate chain of *rac*-**1m**, which is stabilized by the vital hydrogen-bonding interaction between sulfinamide and the enolate. The bulky TIPS group blocks the front site of the enolate. The steric repulsion between the TIPS group and the methyl group makes addition to the methyl-substituted olefin much slower than addition to the other olefin, thereby leading to parallel kinetic resolution.

In conclusion, we have developed a highly concise and efficient strategy for the construction of a new type of chiral sulfinamide phosphine catalyst from commercially available inexpensive starting materials. The Xiao-Phos catalyst (R,R_S)-**X10** has shown excellent performance in the enantioselective intramolecular RC reactions, leading to α-methylene-γ-butyrolactones in high yields and up to 99% *ee* under mild conditions. Moreover, kinetic resolution and parallel kinetic resolution were also realized with the use of two different substituted racemic precursors, both of which worked nicely with a very high s factor. As far as we know, this is the first successful example of a parallel kinetic resolution in the Rauhut-Currier reaction. Further applications of Xiao-Phos variants as organocatalysts or chiral ligands for transition metals in asymmetric reactions and as a precursor to other chiral phosphines[19] are currently underway in our laboratory and will be reported in due course.

Keywords: chiral phosphines · enantioselectivity · kinetic resolution · organocatalysis · Rauhut–Currier reaction

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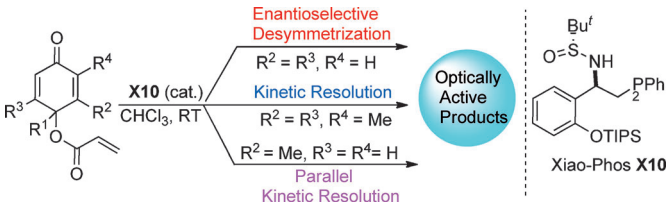
Design, Synthesis, and Application of a Chiral Sulfinamide Phosphine Catalyst for the Enantioselective Intramolecular Rauhut–Currier Reaction



Xiao-Phos: A new class of chiral sulfinamide phosphine catalyst was developed. These Xiao-Phos catalysts can be prepared from inexpensive commercially available starting materials and show good performance in the enantioselective intramolecular Rauhut–Currier reaction under mild conditions. Moreover, kinetic resolution was also observed with the use of two different substituted racemic precursors.