Asymmetric Catalysis

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Chiral Sulfinamide Bisphosphine Catalysts: Design, Synthesis, and Application in Highly Enantioselective Intermolecular Cross-Rauhut–Currier Reactions

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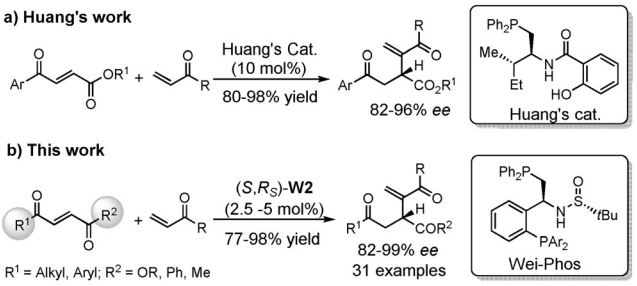
Abstract: *A novel type of highly efficient chiral sulfinamide bisphosphine catalysts (Wei-Phos) were developed. These could be easily prepared from commercially available starting materials. Wei-Phos has shown good performance in the very challenging intermolecular cross-Rauhut–Currier reactions of vinyl ketones and 3-acyl acrylates or 2-ene-1,4-diones, leading to the R-C products in high yields with up to 99 % ee under 2.5–5 mol% catalyst loading. The highly regio- and enantioselective cross-Rauhut–Currier reactions of 2-ene-1,4-diones and vinyl ketone have yet reported so far.*

Over the past decades, asymmetric nucleophilic catalysis with chiral phosphines has received particular attention for their distinct role in constructing densely functionalized organic building blocks.[1] In this context, chiral β-aminephosphines are one of the most attractive nucleophilic catalysts, and they have been utilized as nucleophilic catalysts in a broad spectrum of useful organic transformations. For instance, Miller and Cowen designed an elegant multifunctional β-aminophosphine derived from amino acid and employed it in highly efficient enantioselective allenoate–enone cycloadditions in 2007.[2] Later, Jacobsen and co-workers reported a series of bifunctional phosphine-containing thioureas catalysts and demonstrated their applications in enantioselective imine–allene annulations.[3] In 2010, Zhao and co-workers realized the first asymmetric [3+2] cycloaddition between allenoates and activated olefins using novel bifunctional *N*-acyl aminophosphine catalysts.[4] Recently, Lu et al. demonstrated that dipeptide- and L-threonine-derived phosphines were highly efficient nucleophilic catalysts for a wide range of asymmetric transformations.[5] Compared to the intensive attention given to the application of chiral β-aminephosphines in asymmetric catalysis, only a handful of methods have been reported so far for the synthesis of them, which often suffer from several drawbacks, such as long synthesis route (> 5 steps), harsh reaction conditions, and low diversity.[2,4,5] Thus, the design and synthesis of structurally novel β-aminophosphines from inexpensive commercially available chiral resources still remains a huge challenge and are highly desirable.

Recently, our group have developed a novel class of chiral sulfinamide phosphines catalysts[6] (Xiao-Phos) and chiral sulfinamide phosphine ligands[7] (Ming-Phos). These two new type of chiral phosphines could be easily and diversely achieved in good yields from inexpensive, commercially available aldehyde and chiral *tert*-butyl-sulfinamide[8] in 2–3 steps. Gratifyingly, Xiao-Phos have shown good performance in the enantioselective intramolecular Rauhut–Currier (R-C) reaction.[6,9] Inspired by this work and as part of our continual interest in asymmetric nucleophilic phosphine catalysis,[10] we wished to extend the application of Xiao-Phos compounds to much more challenging intermolecular cross-Rauhut–Currier reaction.[11] Very recently, Huang and co-workers have made a breakthrough to address this challenge and realized the first example of asymmetric intermolecular cross-R-C reaction of 3-aroyl acrylates and vinyl ketones (Scheme 1 a).[12] With respect to their facile synthesis in large scale, we attempted to apply our Xiao-Phos compounds to this challenging cross-R-C reaction. Unfortunately, the performance of Xiao-Phos compounds in the cross-R-C reaction of 3-benzoyl acrylate and methyl vinyl ketone was not satisfactory, delivering only moderate enantioselectivity (83 % *ee*; see the Supporting Information for details). Then, related but structurally novel sulfinamide bisphosphines (named as Wei-Phos) were then designed by merging the moieties of Xiao-Phos and Ming-Phos, which has sulfinamide moiety as the H-donor, and two diarylphosphine moieties, one as nucleophilic site and the other as tunable side chain (Scheme 2). Herein, we report the design, synthesis of this novel type of chiral sulfinamide bisphosphine catalyst and



Scheme 1. The enantioselective intermolecular cross-Rauhut–Currier reaction.

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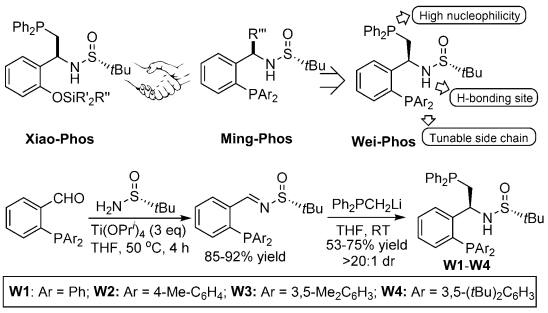


Scheme 2. Concise synthetic approach to Wei-Phos compounds.

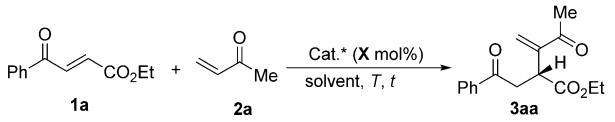
their application in the highly enantioselective intermolecular cross-R-C reaction of two active olefins (Scheme 1 b).

Our initial study was concentrated on the exploration for the concise synthetic route to Wei-Phos. Fortunately, we were pleased to find that this new type of bisphosphine catalyst could be easily prepared on a gram scale from commercially available starting materials through a two-step strategy. The chiral (R_S)-sulfinimines[13] could be obtained in good yields from the corresponding 2-diarylphosphino benzaldehyde[14] and *tert*-butylsulfinamide via Ti(O*i*Pr)$_4$ mediated condensation. The nucleophilc addition of Ph_2PCH_2Li,[15] generated in situ from Ph_2PCH_3 and *n*BuLi in the presence of TMEDA, to the sulfinimines furnished Wei-Phos compounds **W1**–**W4** in moderate yields with good diastereoselectivity (Scheme 2).

With Wei-Phos compounds **W1**–**W4** in hand, we then focused on the performance of Wei-Phos compounds in the reaction of 3-aroyl acrylate **1a** and methyl vinyl ketone **2a** (Table 1). To our delight, the desired R-C product **3aa** was achieved in 96% yield with 87% *ee* (Table 1, entry 5) by utilizing (S,R_S)-**W1** as catalyst. Further intensive screening of various solvents demonstrated that $CHCl_3$ was the best reaction medium in terms of reactivity and enantioselectivity (Table 1, entries 1–7). Gratifyingly, the *ee* value of **3aa** was improved to 93% without loss of efficiency when lowering the reaction temperature from 25 °C to −20 °C (Table 1, entries 8–10). However, much lower reaction temperature was not beneficial for the enantioselectivity and reactivity any more (Table 1, entries 11, 12). (S,R_S)-**W2** displayed better performance in enantioselectivity than (S,R_S)-**W1** and the corresponding **3aa** could be delivered in 96% yield with 94% *ee* (Table 1, entry 13). (S,R_S)-**W3** and (S,R_S)-**W4** with more bulkier aryl substituents on the side phosphine chain could not improve the efficiency and enantioselctivity (Table 1, entries 14, 15). It is noteworthy that lowering catalyst loading to 2.5 mol% did not bring negative effect on the yield and *ee* (Table 1, entries 16–18).

Having identified the optimized reaction conditions, we then investigated the generality of this enantioselective cross-R-C reaction with a variety of 3-acyl acrylates and vinyl ketones. Various electron-withdrawing groups, such as F, Cl, and Br, and electron-donating groups, such as CH_3, MeO, and Ph, on the phenyl rings of 3-aroyl acrylates **1b**–**1i** were well tolerated, and the desired R-C products were achieved in high yield with 90–96% *ee* (Table 2, entries 2–9). Of note, (S,R_S)-**W2** also displayed good performance in the reactions of

Table 1: Optimization of the reaction conditions and Wei-Phos compounds for 3-aroyl acrylates and methyl vinyl ketone.[a]



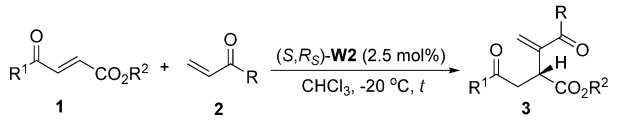
Entry	Cat.	X	Solvent	*T* [°C]	*t* [h]	Yield [%][b]	*ee* [%][c]
1	(S,R_S)-**W1**	10	THF	25	3	94	81
2	(S,R_S)-**W1**	10	Et_2O	25	3	90	83
3	(S,R_S)-**W1**	10	DCE	25	1	95	65
4	(S,R_S)-**W1**	10	CH_2Cl_2	25	3	93	81
5	(S,R_S)-**W1**	10	$CHCl_3$	25	1	96	87
6	(S,R_S)-**W1**	10	CH_3CN	25	4	92	71
7	(S,R_S)-**W1**	10	toluene	25	6	90	87
8	(S,R_S)-**W1**	10	$CHCl_3$	0	1	96	90
9	(S,R_S)-**W1**	10	$CHCl_3$	−10	1	96	91
10	(S,R_S)-**W1**	10	$CHCl_3$	−20	1.5	95	93
11	(S,R_S)-**W1**	10	$CHCl_3$	−25	4	90	93
12	(S,R_S)-**W1**	10	$CHCl_3$	−30	24	84	93
13	(S,R_S)-**W2**	10	$CHCl_3$	−20	1.5	96	94
14	(S,R_S)-**W3**	10	$CHCl_3$	−20	1.5	93	94
15	(S,R_S)-**W4**	10	$CHCl_3$	−20	1.5	95	93
16	(S,R_S)-**W2**	5	$CHCl_3$	−20	2	96	94
17	(S,R_S)-**W2**	2.5	$CHCl_3$	−20	8	96	94
18	(S,R_S)-**W2**	2	$CHCl_3$	−20	24	89	94

[a] Unless otherwise specified, all reactions were carried out with **1a** (0.2 mmol), **2a** (0.6 mmol) in solvent (2 mL); the absolute configuration of **3aa** were assigned by comparison with optical rotation in Huang's report.[12] [b] Yield of isolated products. [c] Determined by HPLC analysis using a chiral stationary phase.

naphthyl- and heteroaryl-containing substrates **1j**–**1m**, furnishing the corresponding products **3ja**–**3ma** in 91–97% yield with 91–95% *ee* (Table 2, entries 10–13). To our delight, (S,R_S)-**W2** was also effective for the challenging aliphatic substrates **1n** and **1o** to give the desired products in good yiled with high *ee*, albeit with a higher catalyst loading and longer reaction time (Table 2, entries 14, 15). Further results demonstrated that the reaction of 3-aroyl acrylates bearing bulky ester group result in the enantioselectivity dropping slightly to 90% *ee* (Table 2, entries 16–18). The scope of vinyl ketone component was then examined. We were pleased to find that ethyl vinyl ketone and propyl vinyl ketone are applicable to the present transformation, delivering the corresponding **3ab** and **3ac** in high yield with good to excellent *ee* (Table 2, entries 19, 20). Finally, with regard to aryl vinyl ketone, (S,R_S)-**W2** also performed effectively under slightly modified reaction conditions (Table 2, entry 21).

Encouraged by these results, we decided to pursue the application of Wei-Phos to the cross-R-C reaction of 2-ene-1,4-dione[16] and vinyl ketone, which has not been reported to date (Table 3). Gratifyingly, the reactions of (*E*)-1,4-diarylbut-2-ene-1,4-diones and methyl vinyl ketone works well under 2.5 mol% of (S,R_S)-**W2**, delivering the desired cross-R-C products **5aa**–**5ea** in good yield with 93–96% *ee* (Table 3, entries 1–5). Unfortunately, the change from (*E*)-1,4-diarylbut-2-ene-1,4-dione to (*E*)-hex-3-ene-2,5-dione leads to enantioselectivity decreasing to 73% *ee* (Table 3, entry 6). Gratifyingly, the *ee* value of **5fa** was improved to 82% when

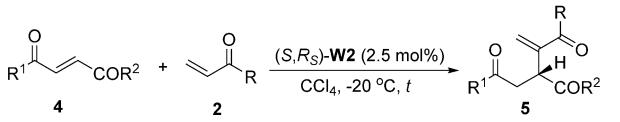
Table 2: Enantioselective RC reaction of 3-aroyl acrylates and vinyl ketone catalyzed by (S,R_S)-**W2**.[a]



Entry	R^1/R^2 (**1**)	R (**2**)	**3**	*t* [h]	Yield [%][b]	*ee* [%][c]
1	C_6H_5/Et (**1a**)	Me (**2a**)	**3aa**	8	96	94
2	4-FC_6H_4/Et (**1b**)	**2a**	**3ba**	5.5	89	93
3	4-ClC_6H_4/Et (**1c**)	**2a**	**3ca**	6	95	93
4	4-BrC_6H_4/Et (**1d**)	**2a**	**3da**	6	93	93
5	2-BrC_6H_4Et (**1e**)	**2a**	**3ea**	7	92	90
6	4-MeC_6H_4/Et (**1f**)	**2a**	**3fa**	8	93	95
7	4-$MeOC_6H_4$/Et (**1g**)	**2a**	**3ga**	16	91	95
8	3,4,5-$MeO_3C_6H_2$/Et (**1h**)	**2a**	**3ha**	20	93	96
9	4-PhC_6H_4/Et (**1i**)	**2a**	**3ia**	10	98	95
10	2-naphthyl/Et (**1j**)	**2a**	**3ja**	10	92	95
11	2-furyl/Et (**1k**)	**2a**	**3ka**	8	97	91
12	2-thienyl/Et (**1l**)	**2a**	**3la**	8	93	95
13[d]	benzothiophene/Et (**1m**)	**2a**	**3ma**	8	91	95
14[d]	*t*Bu/Et (**1n**)	**2a**	**3na**	24	77	96
15[e]	cyclohexyl/Et (**1o**)	**2a**	**3oa**	20	87	93
16	C_6H_5/Me (**1p**)	**2a**	**3pa**	9	90	96
17	C_6H_5/*i*Pr (**1q**)	**2a**	**3qa**	20	94	90
18[d]	C_6H_5/Bn(**1r**)	**2a**	**3ra**	6	96	95
19[d]	**1a**	Et (**2b**)	**3ab**	8	86	93
20[d]	**1a**	*n*Pr (**2c**)	**3ac**	20	94	95
21[f]	**1a**	4-MeC_6H_4 (**2d**)	**3ad**	8	81	90

[a] Unless otherwise specified, all reactions were carried out with **1** (0.2 mmol), **2** (0.6 mmol), (S,R_S)-**W2** (2.5 mol%) in $CHCl_3$ (2 mL) at −20 °C; [b] Yield of isolated products. [c] Determined by HPLC analysis using a chiral stationary phase. [d] (S,R_S)-**W2** (5 mol%) was used. [e] (S,R_S)-**W2** (10 mol%). [f] (S,R_S)-**W2** (10 mol%), 1,2-dimethoxyethane, 15 °C.

Table 3: Enantioselective RC reaction of 2-ene-1,4-diones and vinyl ketone catalyzed by (S,R_S)-**W2**.[a]



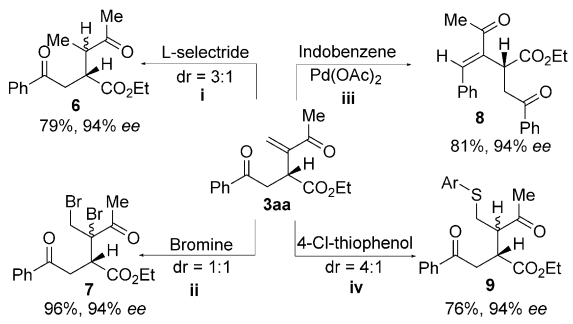
Entry	R^1/R^2 (**4**)	R (**2**)	**5**	*t* [h]	Yield [%][b]	*ee* [%][c]
1	C_6H_5/C_6H_5 (**4a**)	Me (**2a**)	**5aa**	12	96	95
2	4-FC_6H_4/4-FC_6H_4 (**4b**)	**2a**	**5ba**	10	93	93
3	4-ClC_6H_4/4-ClC_6H_4 (**4c**)	**2a**	**5ca**	10	92	95
4	4-BrC_6H_4/4-BrC_6H_4 (**4d**)	**2a**	**5da**	10	95	94
5	4-MeC_6H_4/4-MeC_6H_4(**4e**)	**2a**	**5ea**	12	90	96
6[d]	Me/Me (**4f**)	**2a**	**5fa**	12	92	73
7[e]	Me/Me (**4f**)	**2a**	**5fa**	12	90	82
8[f,g]	C_6H_5/Me (**4g**)	**2a**	**5ga**	10	92	89
9[f,g]	2-naphthyl/Me (**4h**)	**2a**	**5ha**	10	95	88
10[f]	**4a**	4-MeC_6H_4 (**2d**)	**5ad**	8	90	99
11[f]	**4a**	2-naphthyl (**2e**)	**5ae**	8	87	97

[a] Unless otherwise specified, all reactions were carried out with **4** (0.2 mmol), **2** (0.6 mmol), (S,R_S)-**W2** (2.5 mol%) in CCl_4 (2 mL) at −20 °C; [b] Yield of isolated product. [c] Determined by HPLC analysis using a chiral stationary phase. [d] (S,R_S)-**W2** (10 mol%). [e] (S,R_S)-**W1** (10 mol%). [f] (S,R_S)-**W2** (5 mol%). [g] The regioisomeric ratio was determined by ^{1}H NMR spectroscopy.

(S,R_S)-**W1** was employed (Table 3, entry 7). Of note, exciting regioselective and enantioselective cross-R-C reactions were realized when asymmetric 2-ene-1,4-dione **4g** and **4h** were employed, furnishing **5ga** (the ratio of regioisomers was 15:1) and **5ha** (the ratio of regioisomers was 18:1) in high yield with 88–89 % *ee* (Table 3, entries 8, 9). Gratifyingly, the aryl vinyl ketones such as **2d** and **2e** were also applicable to the present transformation to deliver the desired R-C products in good yield with up to 99 % *ee* (Table 3, entries 10, 11).

To demonstrate the synthetic utilities of the R-C products, several transformations of the representative product **3aa** were carried out (Scheme 3). The C=C double bond of **3aa** could undergo selective hydrogenation and bromination to deliver the corresponding products **6** and **7** in good yields without decreasing in the enantioselectivity albeit with low to moderate diastereoselectivity. Though the cross-R-C reaction of 3-aroyl acrylates with chaltone could not occur under the reaction conditions, the highly efficient and stereoselctive palladium-catalyzed Heck reaction of **3aa** and indobenzene offers an alternative access to these valuable optically active multiple carbonyl compound **8**. Additionally, compound **9** with a biologically and synthetically valuable thiophenol framwork[17] was able to be easily made by the nucleophilic addition reaction of thiophenol with **3aa** under mild conditions.

Though (S,R_S)-**W2** has shown excellent performance in the enantioselectivity intermolecular cross-R-C reaction of both 3-acyl acrylates and 2-ene-1,4-diones with vinyl ketones, the specific role of the two phosphine moities in Wei-Phos was not clear. To better understand of the catalytic process of (S,R_S)-**W2** in the cross-R-C reaction, a series of experiments monitored by ^{31}P NMR spectroscopy were carried out (Figure 1). The ^{31}P NMR spectrum showed there is no interaction between **1a** and the phosphine catalyst **W2** (Figure 1b) by comparison with the ^{31}P NMR spectrum of



Scheme 3. Further transformations of the representative product **3aa**.

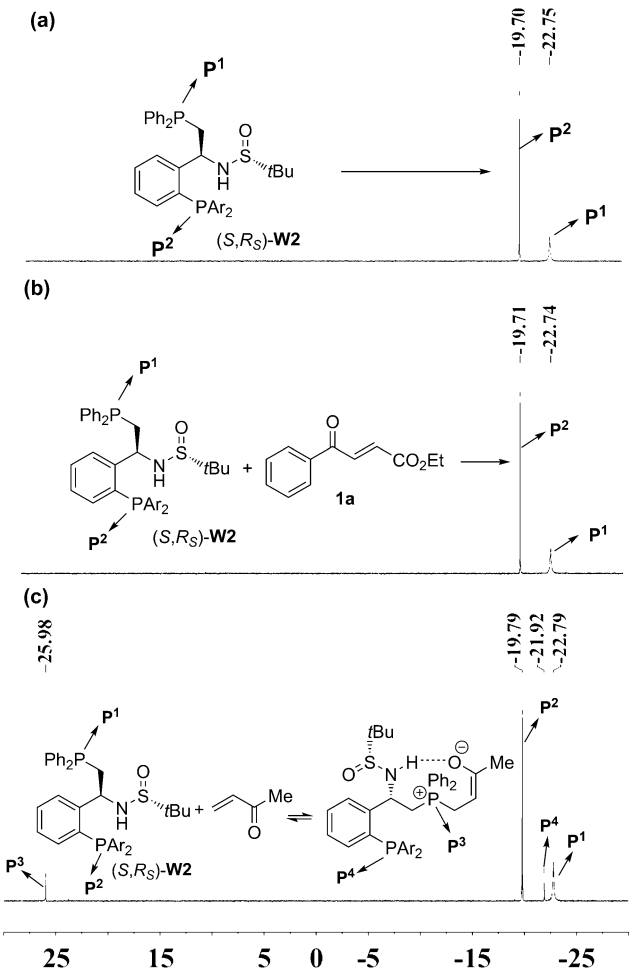


Figure 1. a) ^{31}P NMR spectrum (δ, ppm) of pure (S,R_S)-**W2**; b) ^{31}P NMR spectrum of (S,R_S)-**W2** containing 3-aroyl acrylates; c) ^{31}P NMR spectrum of (S,R_S)-**W2** containing methyl vinyl ketone.

pure (S,R_S)-**W2** (Figure 1 a). In contrast, there is an obvious interaction between **2a** and the phosphine catalyst **W2** (Figure 1 b) because two newly formed ^{31}P peaks (25.98, −21.92) were observed (Figure 1 c). Based on these ^{31}P NMR experiments and previous work,[12,18] some information related to the catalytic process of (S,R_S)-**W2** in the cross-R-C reaction could be obtained: the RC reaction was initiated by the nucleophilic addition of (S,R_S)-**W2** to the methyl vinyl ketone; only the more nucleophilic phosphine P^1 in (S,R_S)-**W2** displayed nucleophilic reactivity in the catalytic process; and the second diarylphosphine P^2 moiety may play a dual role: steric hindrance and as a Lewis base, which is able to strengthen the H-donor ability of the sulfinamide slightly (the ^{31}P NMR peak was shifted from −19.79 to −21.92).

In summary, we have described a concise and efficient strategy for the construction of a set of structurally novel chiral sulfinamide bisphosphine catalysts (Wei-Phos) from commercially available starting materials for the first time. The (S,R_S)-**W2** catalyst has shown excellent performance in the enantioselective intermolecular cross-R-C reactions of two different active olefins, leading to a series of optically active multicabonyl products in high yields with up to 99 % *ee* under relatively low catalyst loading (2.5–5 mol %). Moreover, to demonstrate the synthetic utilities of our method, several further transformations of the chiral multicabonyl product **3aa** were investigated. To gain insight into the catalytic process of (S,R_S)-**W2** in the cross-R-C reaction, a series of ^{31}P NMR experiments were also carried out. Further explorations of Wei-Phos compounds as organocatalyst or chiral bisphosphine ligand of transition metals in asymmetric catalysis are currently underway in our group and will be reported in due course.

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Keywords: alkenes · asymmetric catalysis · chiral sulfinamidephosphines · organocatalysis · Rauhut–Currier reaction

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