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Highly Enantioselective Synthesis of Chiral Succinimides via Rh/Bisphosphine-Thiourea-Catalyzed Asymmetric Hydrogenation

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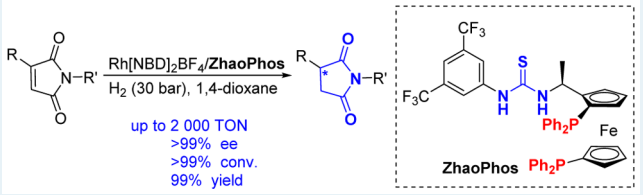
Supporting Information

ABSTRACT: We have successfully developed a highly enantioselective hydrogenation of various 3-aryl and 3-methyl maleinimides to access enantiomerically pure 3-substituted succinimides catalyzed by Rh/bisphosphine-thiourea (ZhaoPhos). This efficient catalytic system furnished the desired 3-substituted succinimide products with high yields and enantioselectivities (up to 99% yield, full conversions, almost all 3-aryl succinimide products up to 99% ee, and 3-methyl succinimide with 83% ee). Our catalytic system has a strong substrate tolerance and generality. Whether the N-substituted group of maleinimides is H or other protecting groups, the maleinimides were hydrogenated well (up to >99% ee, 99% yield). Moreover, the hydrogenation succinimide products can be readily utilized for the construction of biologically active molecules, such as chiral amides and pyrrolidines.



KEYWORDS: *asymmetric hydrogenation, bisphosphine-thiourea, enantioselectivity, ligand, 3-substituted succinimides*

Chiral succinimides and their derivatives are valuable structural motifs in many pharmaceuticals and biologically active molecules,[1] such as materumaimide, andrimid, brivaracetam, α-2-adrenoceptor antagonist, and HSD-1 inhibitor (Figure 1).[2] Owing to the great importance of chiral succinimides and their derivatives, much effort has been devoted to developing efficient methodologies to prepare these compounds in the past decades. However, there are few excellent synthetic methodologies to construct chiral succinimide derivatives through catalytic asymmetric reactions.[3,4] Asymmetric Rh-catalyzed 1,4-conjugate addition of nucleophiles to N-substituted maleinimides was regarded as one of the most common methods to produce chiral succinimide derivatives.[4] Several chiral ligands were applied to promote this conjugate addition with good results, but the enantioselectivity was largely dependent on the N-substituent groups of the maleinimide substrates.[5]

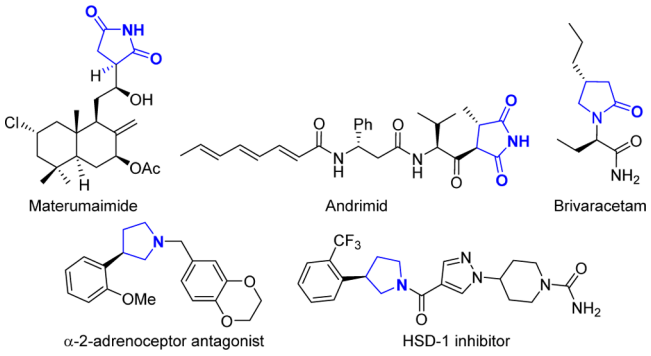


Figure 1. Selected examples of pharmaceuticals and biologically active molecules featuring chiral succinimides and derivatives motif.

It is well-known that transition-metal-catalyzed enantioselective hydrogenation of functionalized olefins was emerged as a powerful and environmentally friendly approach for the preparation of chiral compounds.[6] In 2012, Zhang and coworkers developed Ir/^{i}Pr-BiphPHOX-catalyzed asymmetric hydrogenation of α-alkylidene succinimides, which directly synthesized chiral 3-alkyl succinimides with good to excellent enantioselectivities.[7] However, it is still necessary to develop highly efficient enantioselective hydrogenation to construct chiral 3-alkyl and 3-aryl succinimides and their derivatives. Herein, we successfully report the asymmetric hydrogenation of 3-substituted maleinimides for the synthesis of various chiral succinimides catalyzed by rhodium/bisphosphine-thiourea (ZhaoPhos) with full conversions and excellent ee value (almost all products up to 99% ee). Based on our persistent effort in the field of asymmetric hydrogenation, the success of this transformation relies on the recent development of chiral bifunctional ligands and catalysts. We have developed a series of novel chiral bifunctional bisphosphine-thiourea ligands based

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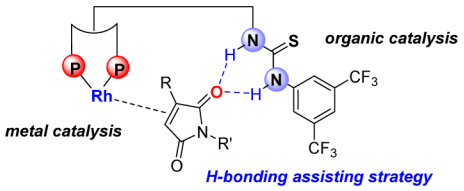
on the synergistic activation strategy via cooperating transition metal-catalysis and organo-catalysis.[8−11] Thiourea motif can activate the carbonyl group through hydrogen-bonding interaction, and the successful asymmetric hydrogenation of 3-substituted maleinimides is a strong showcase of our new catalytic system (Scheme 1).

Scheme 1. Activation Strategy for the Asymmetric Hydrogenation of Maleinimides



Our initial study was carried out by evaluating several phosphine ligands for the hydrogenation of 3-phenyl maleinimide (**1a**)[12] as the model substrate at 60 °C with the catalyst generated in situ by mixing $Rh(NBD)_2BF_4$ and ligands (S/C = 100) (see Figure 2). As shown in Table 1, except

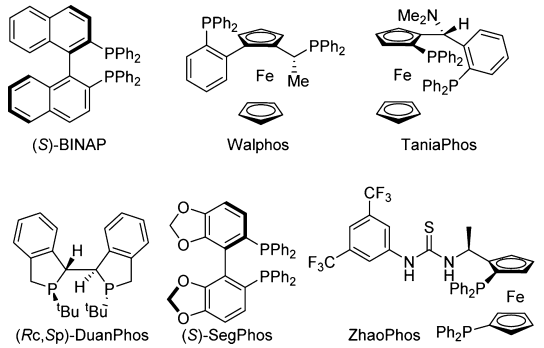
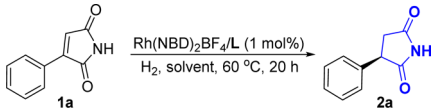


Figure 2. Several phosphine ligands for hydrogenation of 3-phenyl maleinimide (**1a**).

ZhaoPhos, other chiral phosphine ligands, such as (*S*)-BINAP, Walphos, TaniaPhos, (*Rc*,*Sp*)-DuanPhos, (*S*)-SegPhos showed poor results (entries 1−5 vs entry 6). The ZhaoPhos with a thiourea motif developed by our group recently can provide full conversion and excellent enantioselectivity (>99% conversion, 95% ee, entry 6). The solvents played an important role in this catalytic reaction. Poor results were observed in MeOH, CF_3CH_2OH and CH_3CN (64% → 99% conversions, 3%−79% ee, entries 8, 12, 13). To our delight, the transformation proceeded smoothly in toluene, THF, *i*-PrOH, $CHCl_3$, and 1,4-dioxane with full conversions and excellent enantioselectivities (93% → 99% ee, entries 7, 9−11, 14). 1,4-Dioxane was identified as the best choice in terms of both reactivity and selectivity (>99% conversion, > 99% ee, entry 14). When we reduced the reaction temperature from 60 to 25 °C (entry 15), the pressure of hydrogenation from 60 to 30 bar (entry 16), the reaction time from 20 to 12 h (entry 17), we still can obtain >99% conversion and >99% ee.

Encouraged by these promising results, another chiral bisphosphine-thiourea (Figure 3) **L1** was applied in this transformation in the optimized reaction conditions and provided lower enantioselectivity (95% ee, Table 2, entry 2 vs entry 1). It was shown that ZhaoPhos bearing two electron-withdrawing CF_3 groups on the phenyl ring emerged as the most effective bisphosphine-thiourea ligand. Poor conversion and enantioselectivity was observed when one of the N−H in the thiourea group of ZhaoPhos was protected by a methyl group (**L2**) (24% conversion, 64% ee, Table 2, entry 3). In addition, the ligand **L3** without thiourea group provided no conversion (Table 2, entry 4). These results displayed that the thiourea motif efficiently activated the carbonyl group through hydrogen-bonding interaction and worked as an excellent directing role.

Table 1. Optimization of Reaction Conditions for Rh-Catalyzed Asymmetric Hydrogenation of 3-Phenyl Maleinimide (1a)[a]



entry	ligand	solvent	H_2 (bar)	conv. (%)[b]	ee (%)[c]
1	(*S*)-BINAP	CH_2Cl_2	60	NR	NA
2	Walphos	CH_2Cl_2	60	>99	−21
3	TaniaPhos	CH_2Cl_2	60	>99	−27
4	(*Rc*,*Sp*)-DuanPhos	CH_2Cl_2	60	32	−13
5	(*S*)-SegPhos	CH_2Cl_2	60	28	15
6	ZhaoPhos	CH_2Cl_2	60	>99	95
7	ZhaoPhos	toluene	60	>99	98
8	ZhaoPhos	MeOH	60	>99	57
9	ZhaoPhos	THF	60	>99	98
10	ZhaoPhos	*i*-PrOH	60	>99	93
11	ZhaoPhos	$CHCl_3$	60	>99	94
12	ZhaoPhos	CF_3CH_2OH	60	89	3
13	ZhaoPhos	CH_3CN	60	64	79
14	ZhaoPhos	1,4-dioxane	60	>99	>99
15[d]	ZhaoPhos	1,4-dioxane	60	>99	>99
16[d,e]	ZhaoPhos	1,4-dioxane	30	>99	>99
17[d,e,f]	ZhaoPhos	1,4-dioxane	30	>99	>99

[a]Unless otherwise noted, all reactions were carried out with a $[Rh(NBD)_2BF_4]$/ligand/**1a** (0.1 mmol) ratio of 1:1.1:100 in 1.0 mL of solvent under hydrogen (60 bar) for 20 h. [b]Determined by ^1H NMR. [c]Determined by HPLC analysis using a chiral stationary phase. The configuration of **2a** was determined as (*R*) by comparing the optical rotation data with the reported by the literature.[4e] [d]Reaction temperature is 25 °C. [e]The pressure of H_2 is 30 bar. [f]The reaction time is 12 h. NR = No Reaction, NA = Not Available.

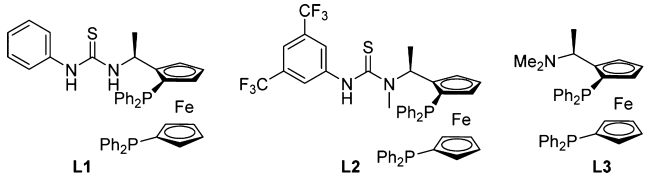


Figure 3. Other bisphosphine ligands for hydrogenation of 3-phenyl maleinimide (**1a**).

Subsequently, the scope and generality of this hydrogenation of various 3-substituted maleinimides was explored under the optimized experimental conditions. The results were summarized in Table 3. A series of 3-substituted maleinimides bearing electron-neutral (**1a**), electron-rich (**1b**−**1d**), or electron-deficient (**1e**−**1i**) groups on phenyl ring proceeded smoothly to afford the corresponding succinimides products (**2a**−**2i**) in high yields (96−99% yield) and excellent enantioselectivities (98 → 99% ee) at 25 °C within 12 h. It appears that the

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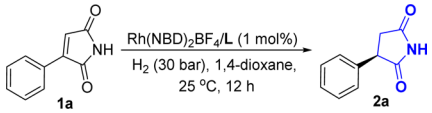
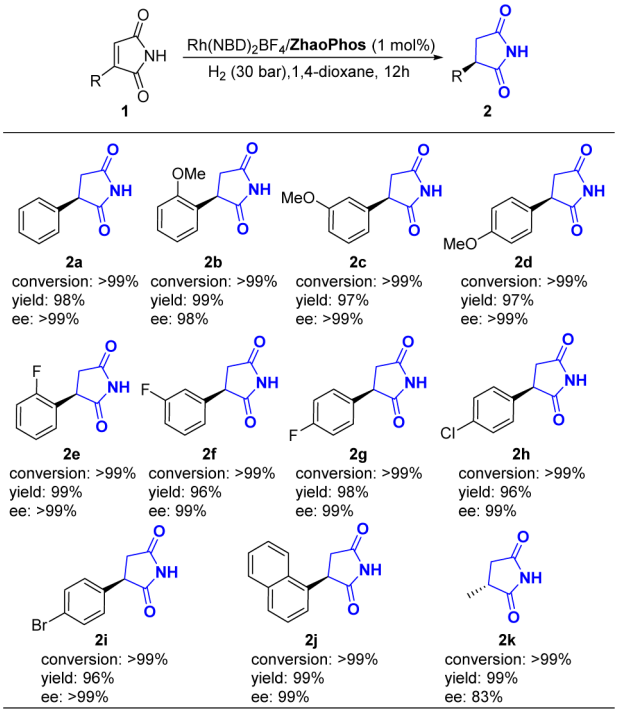
Table 2. Screening a Series of Bisphosphine-Thiourea Ligands[a]



entry	ligand	conv. (%)[b]	ee (%)[c]
1	ZhaoPhos	>99	>99
2	**L1**	>99	95
3	**L2**	24	64
4	**L3**	NR	NA

[a]Unless otherwise noted, all reactions were carried out with a [Rh(NBD)$_2$BF$_4$]/ligand/**1a** (0.1 mmol) ratio of 1:1.1:100 in 1.0 mL of 1,4-dioxane at room temperature under hydrogen (30 bar) for 12 h. [b]Determined by ^{1}H NMR. [c]Determined by HPLC analysis using a chiral stationary phase. The configuration of **2a** was determined as (*R*) by comparing the optical rotation data with the reported by the literature.[4e] NR = No Reaction, NA = Not Available.

Table 3. Scope Study of Rh-Catalyzed Asymmetric Hydrogenation of Maleinimides[a]

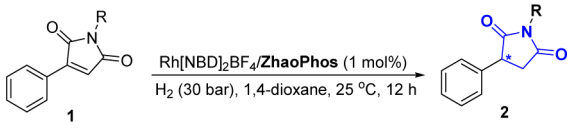


[a]Unless otherwise noted, all reactions were carried out with a [Rh(NBD)$_2$BF$_4$]/ZhaoPhos/**1** (0.1 mmol) ratio of 1:1.1:100 in 1.0 mL of 1,4-dioxane at room temperature under hydrogen (30 bar) for 12 h. The conversion was determined by ^{1}H NMR. The yield was isolated yield. The ee was determined by HPLC analysis using a chiral stationary phase. The configuration of **2** was determined as (*R*) by comparing the optical rotation data with that reported by previous studies.[4e,13]

position and the electronic property of the substituents on the phenyl ring have little effect on the reactivities and enantioselectivities. Noticeably, 99% ee was still achieved for 1-naphthyl (**1j**) substituted maleinimide. To our delight, the alkyl substrate (**1k**) also can obtain full conversion and good enantioselectivity (83% ee).[13]

Having succeeded in the highly enantioselective hydrogenation of various 3-substituted maleinimides, we turned our attention to investigate the transformation of other various N-substituted 3-phenyl malinimides. As shown in Table 4, the N-

Table 4. Scope Study for N-Substituted 3-Phenyl Maleinimides[a]



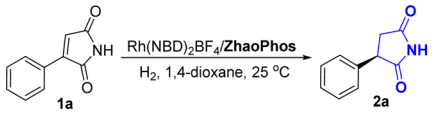
entry	R	1	2	conv. (%)[b]	yield (%)[c]	ee (%)[d]
1	H	**1a**	**2a**	>99	98	>99 (*R*)
2	Me	**1aa**	**2aa**	>99	98	98 (*R*)
3	Bn	**1ab**	**2ab**	>99	98	98 (*R*)
4	Ph	**1ac**	**2ac**	>99	99	97 (*S*)
5	Cy	**1ad**	**2ad**	>99	96	99 (*R*)

[a]Unless otherwise noted, all reactions were carried out with a [Rh(NBD)$_2$BF$_4$]/ZhaoPhos/**1** (0.1 mmol) ratio of 1:1.1:100 in 1.0 mL of 1,4-dioxane at room temperature under hydrogen (30 bar) for 12 h. [b]Determined by ^{1}H NMR. [c]The yield is isolated yield. [d]Determined by HPLC analysis using a chiral stationary phase. The configuration of **2** was determined by comparing the optical rotation data with the reported by the literature.[4e]

protecting group has little impact on the reaction yield and enantioselectivity of the substrates (Table 4, entries 1−5), resulting in the desired products with high yields (96−99%) and excellent enantioselectivities (97−99% ee). To our delight, when the steric bulk group of the N-substituents increased, there is little effect on the reaction yield and enantioselectivity of the substrates. Thus, the asymmetric hydrogenation of the 3-substituted succinimides provided an easy and efficient method for synthesis of a series of chiral compounds with potentially high biological activity.[14]

Our Rh-ZhaoPhos catalytic system is efficient in the asymmetric hydrogenation of 3-phenyl maleinimide (**1a**). When the catalyst loading was reduced to 0.5 mol % (S/C = 200), the 3-phenyl maleinimide (**1a**) was hydrogenated well in >99% ee with >99% conversion under mild reaction conditions (Table 5, entry 1). When the catalyst loading was further reduced to 0.2 mol % (S/C = 500), the catalytic system also can achieve >99% ee and >99% conversion (Table 5, entry 2). It is worth mentioning that we still can obtain >99% ee and >99% conversion when S/C is 1000 (Table 5, entry 3). Moreover,

Table 5. TON Study of Rh-Catalyzed Asymmetric Hydrogenation of 3-Phenyl Maleinimide (1a)[a]



entry	S/C	H_2 (atm)	time (h)	conv. (%)[b]	yield (%)[c]	ee (%)[d]
1	200	30	12	>99	97	>99
2	500	30	12	>99	97	>99
3	1000	50	48	>99	96	>99
4[e]	2000	50	72	>99	95	98

[a]Unless otherwise noted, all reactions were carried out with a [Rh(NBD)$_2$BF$_4$]/ZhaoPhos = 1:1.1 in 1,4-dioxane. [b]Determined by ^{1}H NMR. [c]The yield is isolated yield. [d]Determined by HPLC analysis using a chiral stationary phase. [e]Reaction temperature is 30 °C.

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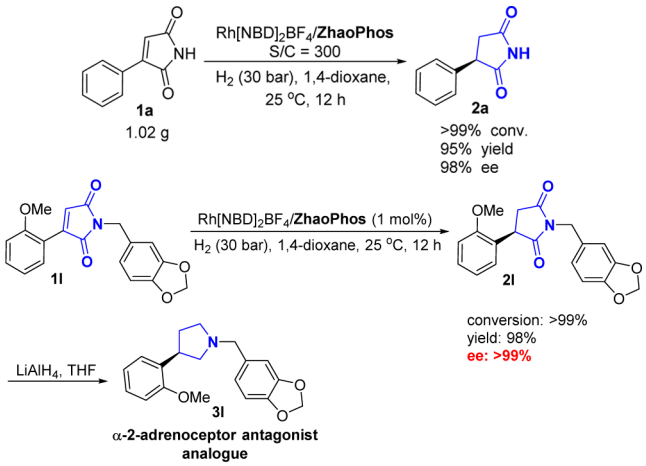
this hydrogenation was performed smoothly even when S/C is 2000 (98% ee, > 99% conversion, Table 5, entry 4).

In addition, the asymmetric hydrogenation of 3-phenyl maleinimide (**1a**) was performed well on gram scale, and the desired product (**2a**) was obtained with 95% yield and 98% ee (Scheme 2). As the synthetic utility of this catalytic

Scheme 2. Gram-Scale Experiment and Application of Hydrogenation Product to Construct Biologically Active Molecules



methodology, further derivatization and application can be carried out for the construction of biologically active molecules (Scheme 2). The substrate **1l** was easily hydrogenated to obtain chiral succinimide product **2l** (full conversion, 98% yield, > 99% ee). Additionally, **2l** can be efficiently converted to corresponding chiral pyrrolidine compound **3l** through reduction of the two carbonyl groups,[3g] which is the potent α-2-adrenoceptor antagonist analogue.[2j]

In summary, we have successfully developed a highly enantioselective hydrogenation of various 3-aryl and 3-methyl maleinimides with or without N-protecting group to access optically active 3-substituted succinimides catalyzed by Rh/bisphosphine-thiourea (ZhaoPhos) with full conversions and excellent enantioselectivities (almost all 3-aryl succinimide products up to 99% ee, and 3-methyl succinimide with 83% ee). In addition, the hydrogenation succinimide product **2l** can be efficiently converted to corresponding chiral pyrrolidine, which is the potent α-2-adrenoceptor antagonist analogue. Further studies on the extension of this novel catalytic system are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b01615.

Experimental procedures and compound characterization (PDF)

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Notes

The authors declare no competing financial interest.

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