Organic LETTERS
Cite This: Org. Lett. XXXX, XXX, XXX−XXX
Letter
pubs.acs.org/OrgLett

Rh-Catalyzed Asymmetric Hydrogenation of β-Substituted-β-thio-α,β-unsaturated Esters: Expeditious Access to Chiral Organic Sulfides

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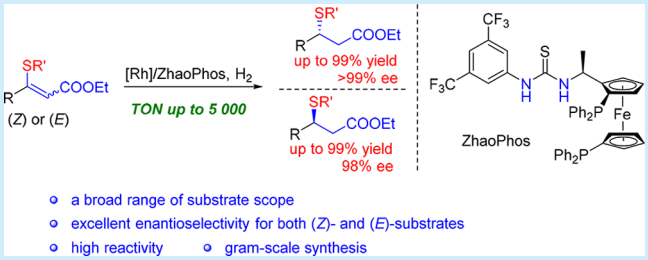
Supporting Information

ABSTRACT: Rh/bifunctional bisphosphine-thiourea ligand (ZhaoPhos)-catalyzed asymmetric hydorgenation of both (*Z*)- and (*E*)-isomers of β-substituted-β-thio-α,β-unsaturated esters was successfully developed. This new asymmetric catalytic methodology provided highly efficient access to two enantiomers of chiral organic sulfides ethyl β-substituted-β-thio-propanoates with excellent results (up to 99% yield and >99% ee for (*Z*)-substrates, up to 99% yield and 98% ee for (*E*)-substrates, TON up to 5000), which are important intermediates in organic synthesis.



Optically active chiral organic sulfides are widely distributed in natural products[1] and also have a broad range of applications in the fields of organic chemistry, biology, and pharmaceuticals, for example, working as chiral building blocks, chiral auxiliaries, chiral ligands, chiral organocatalysts, and bioactive molecules.[2] As shown in Figure 1, Montelukast is a

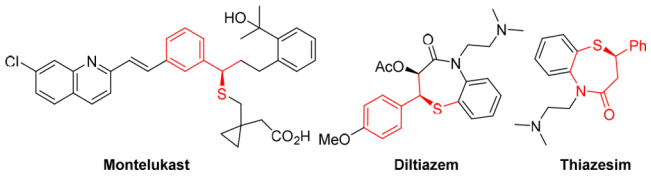


Figure 1. Examples of some chiral organic sulfides with bioactivity.

potent antagonist of cysteinyl leukotriene (cysLT) receptor used for the treatment of asthma,[2b,c] and Diltiazem is mainly used for the treatment of hypertension and angina pectoris,[2d−f] while Thiazesim displays antidepressant activity.[2g−k]

Owing to the remarkable importance of chiral organic sulfides, considerable attention has been focused on the development of efficient asymmetric catalytic methodologies to construct them in recent decades.[3−7] Among the existing methods, both metal- and organic-catalyst-promoted asymmetric sulfa-Michael addition (SMA) of thiol nucleophiles to a variety of activated electron-deficient alkenes,[4−7] such as α,β-unsaturated aldehydes/ketones,[4] α,β-unsaturated esters,[4c,5] α,β-unsaturated imides,[6] and nitroolefins,[7] have been a reliable and powerful route for the generation of carbon−sulfur bonds in organic synthesis. Despite great efforts toward achieving significant progress, most of these catalytic methodologies have always required a relatively high catalyst loading. Therefore, it is necessary to develop highly efficient catalytic synthetic methods to prepare chiral organic sulfides. Transition-metal-catalyzed asymmetric hydrogenation of prochiral unsaturated compounds has been regarded as a direct, simple manipulation and high atom economy method in asymmetric synthesis.[8] Based on the long-standing research in this field and the powerful performance of a bifunctional bisphosphine-thiourea ligand (ZhaoPhos) in asymmetric hydrogenation utilizing important interactions between the thiourea scaffold and the functional group of substrates,[9] we envisaged that the asymmetric hydrogenation of prochiral β-substituted-β-thio-α,β-unsaturated esters could proceed well with high reactivity and excellent stereoselective control contributed by the possible H-bonding interactions between the substrates and catalyst. Herein, our Rh/ZhaoPhos catalytic system exhibited powerful catalytic ability for the asymmetric hydrogenation of both (*Z*)- and (*E*)-isomers of β-substituted-β-thio-α,β-unsaturated esters, providing two enantiomers of chiral organic sulfide ethyl β-substituted-β-thio-propanoates with excellent results (Scheme 1, up to 99% yield, >99% ee for (*Z*)-substrates, up to 99% yield, 98% ee for (*E*)-substrates). Furthermore, our Rh/ZhaoPhos catalytic system displayed high catalytic activity (TON up to 5000), which was not affected by the possible deactivation of the sulfur atom from the substrates and hydrogenation products. In addition, our hydrogenation products are the key intermediates to construct biologically active molecules, and they also can be easily converted into other chiral sulfur containing compounds.

We began our initial study to investigate the solvent effect for the Rh-catalyzed asymmetric hydrogenation of model substrate

Received: July 24, 2018

DOI: 10.1021/acs.orglett.8b02339
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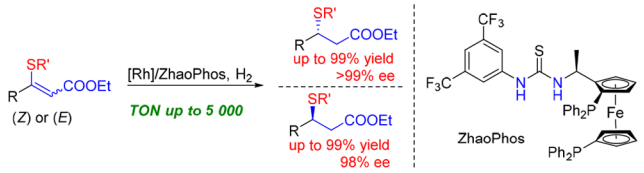
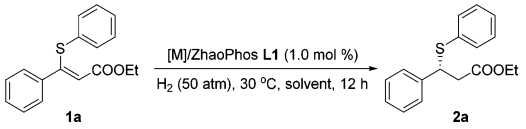
Scheme 1. Rh/ZhaoPhos-Catalyzed Asymmetric Hydrogenation for the Construction of Chiral Organic Sulfides



ethyl (*Z*)-3-phenyl-3-(phenylthio)acrylate (**1a**)[10] under 50 atm of H_2 at 30 °C with the catalyst generated *in situ* by mixing $Rh(NBD)_2BF_4$ with ZhaoPhos **L1**. As shown in Table 1,

Table 1. Screening Solvents and Metal Precursors for the Asymmetric Hydrogenation of Ethyl (*Z*)-3-Phenyl-3-(phenylthio)acrylate (1a)[a]



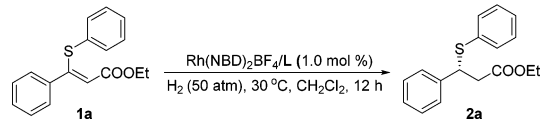
entry	metal precursor	solvent	conv (%)[b]	ee (%)[c]
1	$Rh(NBD)_2BF_4$	MeOH	28	>99
2	$Rh(NBD)_2BF_4$	THF	11	>99
3	$Rh(NBD)_2BF_4$	1,4-dioxane	46	>99
4	$Rh(NBD)_2BF_4$	toluene	77	>99
5	$Rh(NBD)_2BF_4$	TFE	92	>99
6	$Rh(NBD)_2BF_4$	DCE	93	>99
7	$Rh(NBD)_2BF_4$	CH_2Cl_2	>99	>99
8	$Rh(COD)_2BF_4$	CH_2Cl_2	98	>99
9	$[Ir(COD)Cl]_2$	CH_2Cl_2	NR	NA

[a]Unless otherwise noted, all reactions were carried out with a metal precursor/ZhaoPhos **L1**/**1a** (0.1 mmol) ratio of 1:1.1:100 in 1.0 mL of solvent under 50 atm of H_2 at 30 °C. The catalyst was precomplexed in CH_2Cl_2 (0.1 mL for each reaction vial). [b]Conversion was determined by ^1H NMR analysis. [c]Ee was determined by chiral HPLC analysis. The configuration of **2a** was determined by comparing the optical rotation data with those reported in the literature.[2j,4c,l] THF is tetrahydrofuran. TFE is trifluoroethanol. DCE is dichloroethane. NR = no reaction, NA = not available.

although excellent enantioselectivity can be obtained in various solvents, the solvents have great influence on the reactivity (11% – >99% conversions, > 99% ee, Table 1, entries 1–7). Full conversion and >99% ee can be obtained in CH_2Cl_2 (Table 1, entry 7). Other metal precursors, such as $Rh(COD)_2BF_4$ and $[Ir(COD)Cl]_2$, were also inspected in this transformation (Table 1, entries 8–9). Excellent results were afforded with $Rh(COD)_2BF_4$ working as the metal precursor (98% conversion, >99% ee, Table 1, entry 8). No product was detected with $[Ir(COD)Cl]_2$ as the metal precursor (Table 1, entry 9).

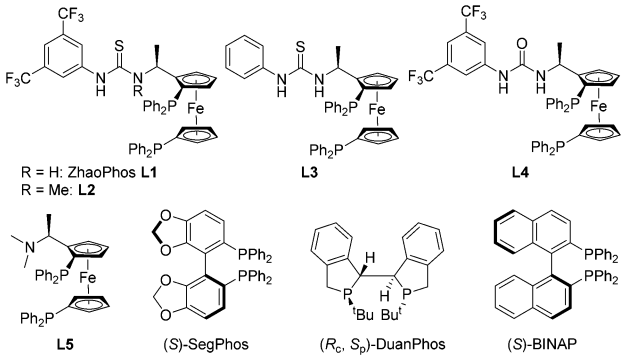
Subsequently, various chiral bisphosphine ligands were applied to this $Rh(NBD)_2BF_4$-catalyzed asymmetric hydrogenation of ethyl (*Z*)-3-phenyl-3-(phenylthio)acrylate (**1a**) in DCM. These results are summarized in Table 2. A series of bifunctional bisphosphine-(thio)urea ligands **L1**–**L4** provided poor to excellent reactivities and >99% ee (11% – >99% conversions, >99% ee, Table 2, entries 1–4). ZhaoPhos **L1** achieved the best results with full conversion and >99% ee (Table 2, entry 1). In addition, no reaction was obtained in the presence of ligand **L5** without a thiourea group (Table 2, entry 5). Other important chiral bisphosphine ligands, such as (*S*)-

Table 2. Screening Ligands for the Rh-Catalyzed Asymmetric Hydrogenation of Ethyl (*Z*)-3-Phenyl-3-(phenylthio)acrylate (1a)[a]



entry	ligand	conv (%)[b]	ee (%)[c]
1	ZhaoPhos **L1**	>99	>99
2	**L2**	78	>99
3	**L3**	50	>99
4	**L4**	11	>99
5	**L5**	NR	NA
6	(*S*)-SegPhos	NR	NA
7	(*Rc*,*Sp*)-DuanPhos	NR	NA
8	(*S*)-BINAP	NR	NA

[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 CH_2Cl_2 under 50 atm of H_2 at 30 °C. [b]Conversion was determined by ^1H NMR analysis. [c]Ee was determined by chiral HPLC analysis. NR = no reaction, NA = not available.



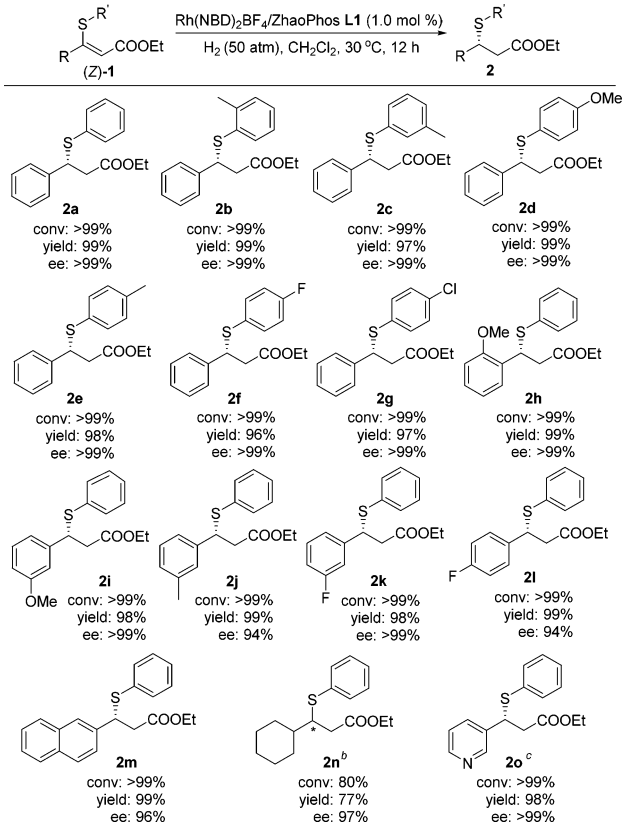
SegPhos, (*Rc*, *Sp*)-DuanPhos, and (*S*)-BINAP, did not work in this asymmetric transformation (Table 2, entries 6–8).

Having established the optimized reaction conditions, we started to inspect the substrate generality of this Rh-catalyzed asymmetric hydrogenation of ethyl (*Z*)-3-substituted-3-thio-acrylates. As shown in Scheme 2, a series of ethyl (*Z*)-3-substituted-3-thio-acrylates proceeded well to provide the desired hydrogenation products with excellent results (up to >99% conversion, 99% yield, >99% ee). We found that the electron-neutral (**1a**), electron-rich (**1b**–**1e**), or electron-deficient (**1f**–**1g**) substituents on the phenyl ring of the arylthio group can be hydrogenated smoothly to prepare hydrogenation products (**2a**–**2g**) with full conversions, 96%–99% yields, and >99% ee. In addition, the electric properties and positions of the substituents on the 3-aryl ring substituted group also exhibited little influence on the reactivity and enantioselectivity, affording hydrogenation products (**2h**–**2l**) with excellent results (>99% conversion, 98%–99% yields, 94% – >99% ee). The 2-naphthyl substituted substrate (**1m**) also worked well with 99% yield and 96% ee. The challenging alkyl substrate ethyl (*Z*)-3-cyclohexyl-3-(phenylthio)acrylate (**1n**) and heteroaromatic substrate ethyl (*Z*)-3-(phenylthio)-3-(pyridin-3-yl)acrylate (**1o**) also displayed good to excellent results (80% – >99% conversions, 77%–98% yields, 97% – >99% ee).

Having succeeded in the highly enantioselective hydrogenation of ethyl (*Z*)-3-substituted-3-thio-acrylates, we turned our attention to investigating the reactivity and enantioselectiv-

DOI: 10.1021/acs.orglett.8b02339
Org. Lett. XXXX, XXX, XXX–XXX

Scheme 2. Substrate Scope of Rh-Catalyzed Asymmetric Hydrogenation of Ethyl (*Z*)-3-Substituted-3-thio-acrylates[a]

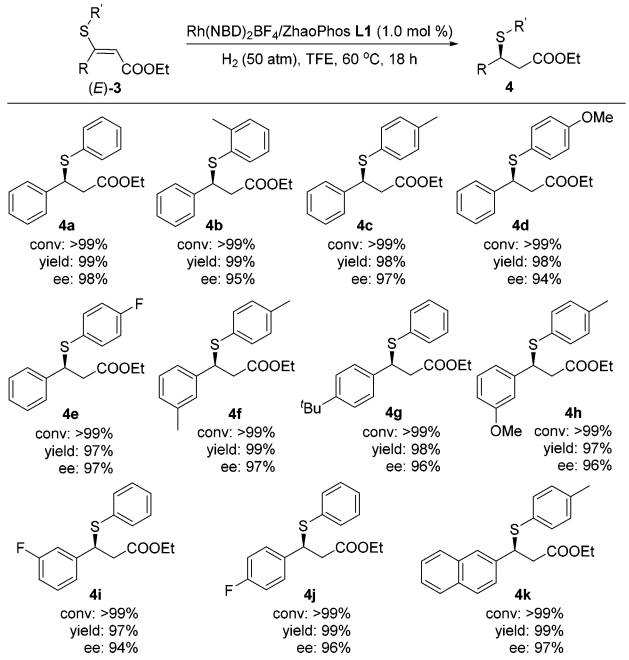


[a]Unless otherwise noted, all reactions were carried out with a $Rh(NBD)_2BF_4$/ZhaoPhos **L1**/**1** (0.1 mmol) ratio of 1:1.1:100 in 1.0 mL of CH_2Cl_2 under 50 atm of H_2 for 12 h at 30 °C. Conversion was determined by ^1H NMR analysis. Yield was isolated yield. Ee was determined by chiral HPLC analysis. [b]The reaction was carried out at 40 °C for 18 h. [c]The reaction was carried out at 60 °C for 48 h.

ity of (*E*)-3-substituted-3-thio-acrylates[10a] catalyzed by the Rh/ZhaoPhos system, which can provide the hydrogenation products with opposite configuration. The optimization of reaction conditions was summarized in Table S1 in the Supporting Information. As shown in Scheme 3, we found that the substituents either on the phenyl ring of the arylthio group or on the 3-aryl ring group have little effect on this asymmetric hydrogenation. The asymmetric hydrogenation of substrates (**3a**−**3j**) proceeded well, affording the desired products with full conversions, 97%−99% yields, and 94%−98% ee. In addition, the 2-naphthyl substituted substrate (**3k**) also worked well with excellent results (>99% conversion, 99% yield, and 97% ee).

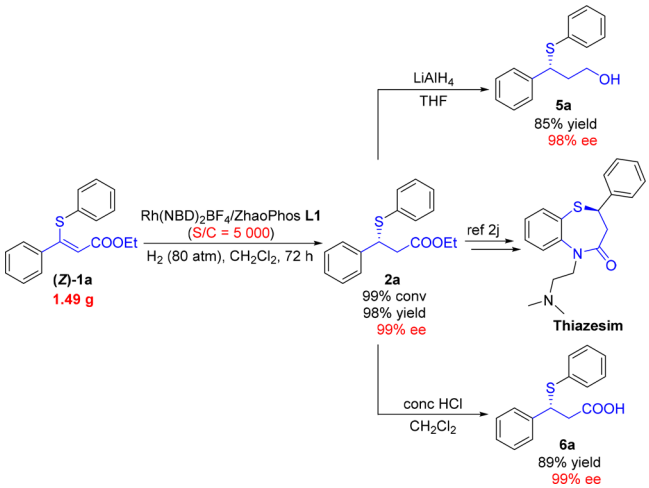
To our delight, the gram-scale asymmetric hydrogenation of ethyl (*Z*)-3-phenyl-3-(phenylthio)acrylate (**1a**) proceeded smoothly to obtain product (**2a**) with 98% yield and 99% ee, even only in the presence of 0.02 mol % catalyst (S/C = 5000), which displayed that our Rh/ZhaoPhos system showed high activity in this transformation (Scheme 4). Moreover, the hydrogenation product (**2a**) was an important synthetic intermediate for the construction of biologically active molecule Thiazesim.[2j] In addition, it was easily reduced by $LiAlH_4$ to generate (*R*)-3-phenyl-3-(phenylthio)propan-1-ol (**5a**) in 85% yield and nearly without loss of ee (98% ee).[11] The carboxylate group of compound **2a** was efficiently hydrolyzed to carboxylic

Scheme 3. Substrate Scope of Rh-Catalyzed Asymmetric Hydrogenation of Ethyl (*E*)-3-Substituted-3-thio-acrylates[a]



[a]Unless otherwise noted, all reactions were carried out with a $Rh(NBD)_2BF_4$/ZhaoPhos **L1**/**3** (0.1 mmol) ratio of 1:1.1:100 in 1.0 mL of TFE under 50 atm of H_2 for 18 h at 60 °C. Conversion was determined by ^1H NMR analysis. Yield was isolated yield. Ee was determined by chiral HPLC analysis.

Scheme 4. Gram-Scale Experiment with High TON and Transformations of Hydrogenation Product



acid (*R*)-3-phenyl-3-(phenylthio)propanoic acid (**6a**) in 89% yield and 99% ee.[2j,12]

In summary, we successfully developed a highly enantioselective Rh/ZhaoPhos-catalyzed asymmetric hydrogenation of both ethyl (*Z*)- and (*E*)-3-substituted-3-thio-acrylates, providing two enantiomers of chiral organic sulfides ethyl *β*-substituted-*β*-thio-propanoates with excellent results (up to 99% yield and >99% ee for (*Z*)-substrates, up to 99% yield and 98% ee for (*E*)-substrates, TON up to 5000). In addition, the hydrogenation products are important synthetic intermediates, which can be efficiently converted to other useful sulfur-containing compounds.

DOI: 10.1021/acs.orglett.8b02339
Org. Lett. XXXX, XXX, XXX−XXX

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02339.

Optimization reaction conditions; procedures; NMR and HPLC spectra (PDF)

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§G.L. and Z.H. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from the National Natural Science Foundation of China (Grant No. 21432007, 21502145), the Natural Science Foundation of Hubei Province (Grant No. 2016CFB449), the Wuhan Morning Light Plan of Youth Science and Technology (Grant No. 2017050304010307), Shenzhen Nobel Prize Scientists Laboratory Project (Grant No. C17213101), and the Fundamental Research Funds for Central Universities (Grant No. 2042018kf0202). The Program of Introducing Talents of Discipline to Universities of China (111 Project) is also appreciated.

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DOI: 10.1021/acs.orglett.8b02339
Org. Lett. XXXX, XXX, XXX−XXX