

Nickel-Catalyzed Highly Enantioselective Hydrogenation of β -Acetylamino Vinylsulfones: Access to Chiral β -Amido Sulfones

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S Supporting Information

ABSTRACT: The nickel/(*S*)-Binapine complex was found to be an efficient catalyst for asymmetric hydrogenation of β -acetylamino vinylsulfones to afford chiral β -Amido sulfones with excellent yields and enantioselectivities (up to 95% yields and >99% ee). This protocol has good compatibility with a series of substituted (*Z*)- β -acetylamino vinylsulfones or *Z/E* isomeric mixtures. A gram-scale reaction has also been achieved in the presence of a 0.2 mol % catalyst loading.



Owing to its perfect atom economy and high efficiency, transition-metal-catalyzed asymmetric hydrogenation has been considered one of the most powerful tools for the synthesis of chiral molecules.¹ In past decades, asymmetric hydrogenation has been intensively investigated and remarkable progress has been made in both academic research and industrial application.² However, traditional research on asymmetric hydrogenation is focused on noble transition metal catalysts based on Ru, Rh, Ir, or Pd,^{1,2} which unavoidably suffer from some inherent drawbacks of the precious metal catalyst, such as being expensive, toxic, and environmentally harmful. Therefore, first-row transition-metal-catalyzed asymmetric hydrogenation has drawn a great deal of attention due to its potential advantages in cost and sustainability.³ In this context, Hamada,⁴ Zhou,⁵ and Chirik⁶ reported their pioneering work in nickel-catalyzed asymmetric (transfer) hydrogenation, greatly promoting the development of nickel-catalyzed asymmetric hydrogenation. Although Ni-catalyzed asymmetric hydrogenation of alkenes,^{5a–c,6} ketones,^{4,7} enamides,^{5a} imines,^{5e} and hydrazones^{5d,e} have been achieved, Ni-catalyzed asymmetric hydrogenation is still in its infancy, and exploiting a new catalytic system which can work as well as (or even better than) the precious-metal-catalyzed system is highly desirable.

Chiral β -amino sulfones are privileged motifs occurring in many natural products and biologically active compounds (Figure 1).⁸ Thus, great efforts have been made for the synthesis of β -amino sulfones, and a variety of approaches have been developed. The typical methods include asymmetric aza-Michael additions to α,β -unsaturated sulfones⁹ and stereoselective additions of sulfonyl carbanions to chiral *N*-sulfinyl imines.¹⁰ In 2014, Zhang and co-worker reported Rh-catalyzed asymmetric hydrogenation of β -acylamino vinylsulfones with a

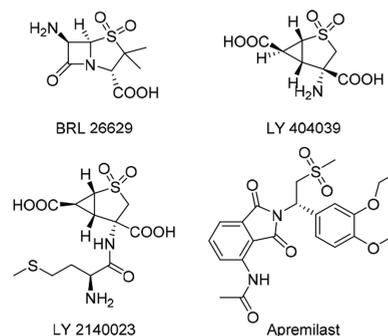


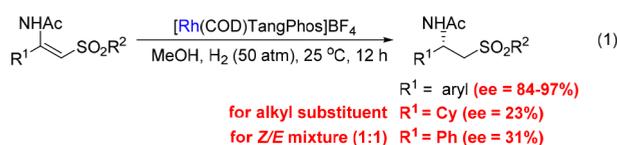
Figure 1. Examples of bioactive molecules containing β -amido sulfone scaffolds.

high yield and good to excellent ee.¹¹ However, the substrate scope of this reaction is limited to (*Z*)-aryl substituted β -amido sulfones, alkyl substituted β -amido sulfones, and a *Z/E* isomeric mixture of β -amido vinylsulfones which gave the target products with poor enantioselectivity (Scheme 1, eq 1). To develop a general method for asymmetric hydrogenation of β -acylamino vinylsulfones with a broad substrate scope including both a *Z/E* isomeric mixture and alkyl substituted β -acylamino vinylsulfones is still a problematic issue. Recently, our group achieved nickel-catalyzed asymmetric hydrogenation of β -acylamino nitroolefins¹² and β -acylaminoacrylates¹³ and found that a nickel catalytic system has good substrate compatibility. Inspired by these result, we envision that nickel-catalyzed asymmetric hydrogenation of β -acylamino vinylsulfones may be

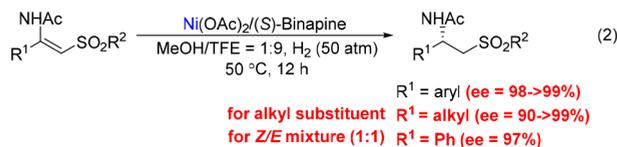
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Scheme 1. Asymmetric Hydrogenation of Sulfones

Previous work



This work

Table 1. Solvent Screening for the Ni-Catalyzed Asymmetric Hydrogenation of 1a^a

entry	solvent	conv (%)	yield (%) ^b	ee (%) ^c
1	MeOH	>99	trace	—
2	EtOH	>99	trace	—
3	<i>i</i> PrOH	trace	—	—
4	CF ₃ CH ₂ OH	>99	69	99
5	(CF ₃) ₂ CHOH	>99	67	99
6	toluene	trace	—	—
7	THF	trace	—	—
8	CH ₂ Cl ₂	trace	—	—
9	EtOAc	trace	—	—
10	CH ₃ CN	trace	—	—
11 ^d	CF ₃ CH ₂ OH	>99	88	99

^aUnless otherwise noted, all reactions were carried out with a Ni(OAc)₂/(*S*)-Binapine/substrate (0.05 mmol) ratio of 1:1.1:20 in 1 mL of solvent at 50 °C under H₂ (50 atm) for 12 h. The catalyst was prepared beforehand with a mixture of methanol and tetrahydrofuran (in a 1:1 volume ratio) at room temperature for 1 h in a nitrogen-filled glovebox. ^bYield was determined by ¹H NMR analysis, using 1,3,5-trimethoxybenzene as the internal standard. ^cDetermined by HPLC analysis using a chiral stationary phase. ^dThe solvent contains 10% methanol.

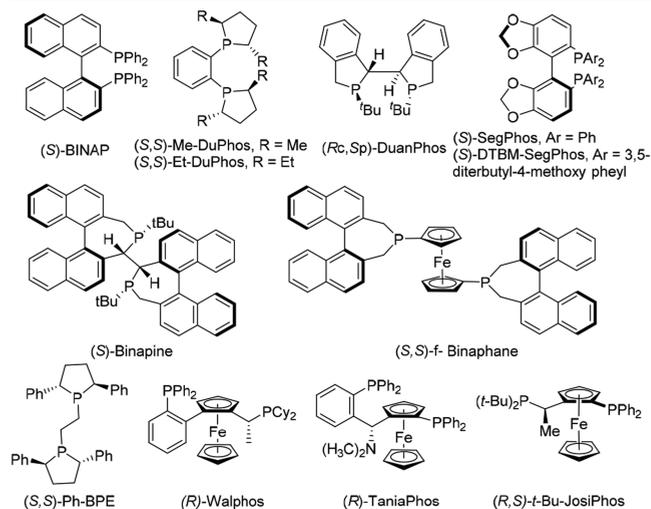
potentially efficient to access to chiral β -amino sulfones. Herein, we report the first nickel-catalyzed asymmetric hydrogenation of β -acetylamino vinylsulfones with high yields, excellent enantioselectivities, and good substrate tolerance (Scheme 1, eq 2).

We began the initial investigation with the asymmetric hydrogenation of β -acetylamino vinylsulfones **1a** to optimize the reaction conditions. A variety of solvents were examined when the reaction was carried out in the presence of 5 mol % Ni(OAc)₂ at 50 °C under 50 atm of H₂. As shown in Table 1, the exploration of various solvents indicated that CF₃CH₂OH is a good solvent for this reaction, generating target product **2a** with moderate yield and excellent enantioselectivity (Table 1, entry 4). A similar result can be achieved with hexafluoroisopropanol, giving chiral β -amido sulfone **2a** with a 67% yield and 99% ee (Table 1, entry 5). However, when *i*PrOH and nonprotic solvents toluene, THF, CH₂Cl₂, EtOAc, and CH₃CN were used, only trace conversions were detected (Table 1, entries 3, 6–10). Although MeOH and EtOH afforded full conversions, mixed

Table 2. Ligands Screening for the Ni-Catalyzed Asymmetric Hydrogenation of 1a^a

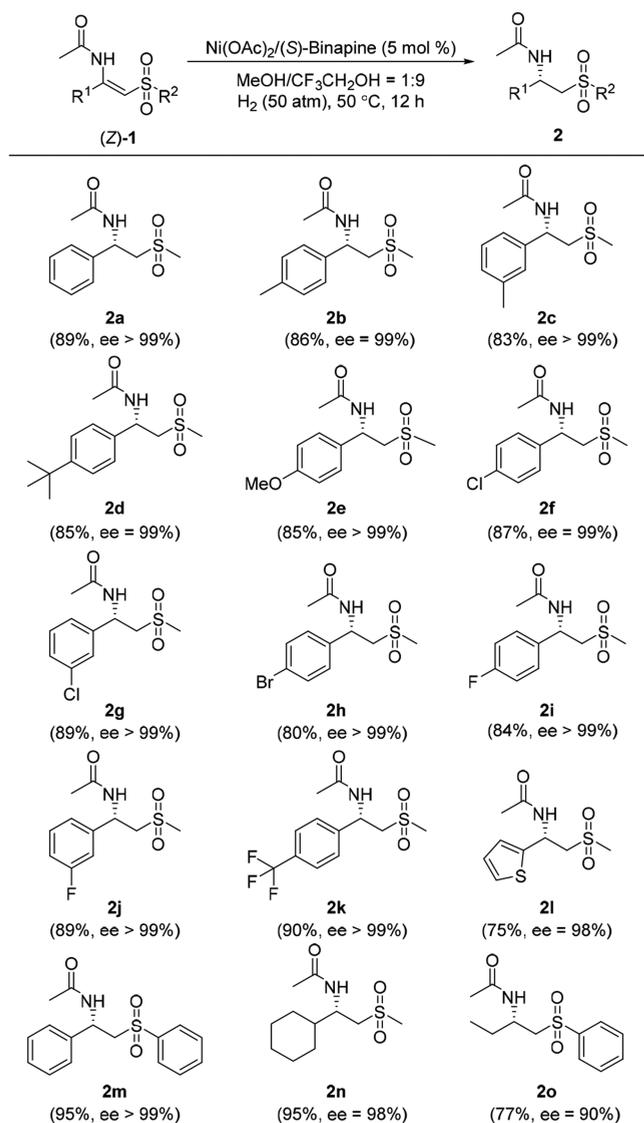
entry	ligand	conv (%)	yield ^b (%)	ee ^c (%)
1	(<i>S</i>)-BINAP	52	<5	—
2	(<i>S,S</i>)-Me-DuPhos	27	trace	—
3	(<i>S,S</i>)-Et-DuPhos	24	trace	—
4	(<i>R_C,S_P</i>)-DuanPhos	>99	10	—
5	(<i>S</i>)-SegPhos	63	trace	—
6	(<i>S</i>)-DTBM-SegPhos	48	<5	—
7	(<i>S</i>)-Binapine	>99	88	99
8	(<i>S,S</i>)- <i>f</i> -Binaphane	<5	—	—
9	(<i>S,S</i>)-Ph-BPE	33	trace	—
10	(<i>R</i>)-Walphos	<5	—	—
11	(<i>R</i>)-TaniaPhos	<5	—	—
12	(<i>R,S</i>)- <i>t</i> -Bu-JosiPhos	53	<5	—
13 ^d	(<i>S</i>)-Binapine	90	79	99
14 ^e	(<i>S</i>)-Binapine	81	72	99
15 ^f	(<i>S</i>)-Binapine	trace	—	—

^aUnless otherwise noted, all reactions were carried out with a Ni(OAc)₂/ligand/substrate (0.05 mmol) ratio of 1:1.1:20 in 1 mL of solvent at 50 °C under H₂ (50 atm) for 12 h. ^bYield was determined by ¹H NMR analysis, using 1,3,5-trimethoxybenzene as the internal standard. ^cDetermined by HPLC analysis using a chiral stationary phase. ^dHydrogen pressure was 20 atm. ^eReaction time was 8 h. ^fAt room temperature.

Figure 2. Structures of the phosphine ligands for hydrogenation of β -acetylamino acrylosulfones **1**.

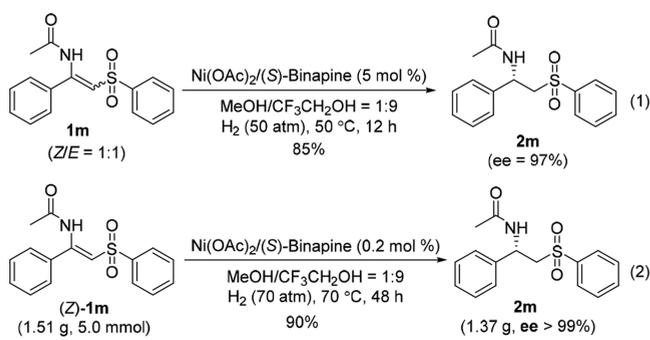
systems containing a *N*-(1-phenylethyl)acetamide byproduct were detected with no target product (Table 1, entries 1–2). According to the above results, we speculated that methanol and tetrahydrofuran may inhibit the formation of the target product. However, methanol is indispensable in the system because nickel acetate is hardly soluble in other solvents, and ligand has good solubility in tetrahydrofuran. Therefore, we adjusted the ratio of methanol, tetrahydrofuran, and trifluoroethanol and screened a series of mixed solvents (see Supporting Information, Table S2). When the reaction was conducted in a mixed solvent

Scheme 2. Substrate Scope of Ni-Catalyzed Asymmetric Hydrogenation of β -Acetylamino Acrylosulfones^a



^aAll reactions were carried out with a $\text{Ni}(\text{OAc})_2/(\text{S})\text{-Binapine}$ /substrate (0.2 mmol) ratio of 1:1.1:20 in 1 mL of mixture solvents ($\text{MeOH}/\text{CF}_3\text{CH}_2\text{OH} = 1:9$) at 50°C under H_2 (50 atm) for 12 h. All yields were isolated yields. Enantiomeric excess was determined by HPLC analysis using a chiral stationary phase.

Scheme 3. Gram-Scale Reaction and S/C Evaluation



of methanol and trifluoroethanol with a 1:9 volume ratio, the best result was obtained, affording chiral β -amido sulfone **2a** with a 88% yield and 99% ee (Table 1, entry 11).

Subsequently, a variety of diphosphine ligands (Figure 2) were evaluated, and the results reveal that (S)-Binapine is superior to all the other ligands tested, giving chiral β -amido sulfone **2a** with 88% yield and 99% ee (Table 2, entry 2). Most of the other diphosphine ligands, whether they were P chiral ligands, planar chiral phosphine ligands, or phosphine ligands with a chiral center, failed to give the target product (Table 2, entries 1–12). When the reaction was conducted with a lower hydrogen pressure or shorter reaction time, the yield dropped slightly, but without any loss in enantioselectivity (Table 2, entries 13–14). The reaction was totally inhibited when the temperature was decreased to room temperature (Table 2, entry 15).

With the optimal conditions in hand, the substrate scope of this reaction was investigated. As shown in Scheme 2, the reaction exhibited good tolerance to the substrates, and various β -aryl substituted β -acylamino vinylsulfones could be hydrogenated very efficiently, giving β -acylamino sulfones with good yields and excellent enantioselectivities (**2a–2k**). When R^1 was changed to a heteroaryl group, the reaction proceeded smoothly, albeit the yield decreased slightly (**2l**). Replacing R^2 by a phenyl group, the yield increased slightly while the enantioselectivity remained the same (**2m**). It is worth noting that β -alkyl substituted β -acylamino vinylsulfones, poor substrates for rhodium-catalyzed asymmetric hydrogenation, are well tolerated in the nickel-catalyzed system (**2n** and **2o**).

To demonstrate the potential utility of this methodology, the Z/E mixture (1:1) of **1m** was used directly to investigate the compatibility of this catalytic system. Fortunately, the Z/E isomeric mixture of β -amido sulfones, a kind of incompatible substrate for rhodium catalytic system,¹¹ proceeded very smoothly in the nickel/(S)-Binapine catalytic system, giving the desired product in 85% yield with 97% ee (Scheme 3, eq 1). In addition, the asymmetric hydrogenation of alkyl substituted β -amido sulfones, a kind of incompatible substrate for rhodium catalytic system,¹¹ proceeded very smoothly in the nickel/(S)-Binapine catalytic system, giving the desired product in 85% yield with 97% ee (Scheme 3, eq 1). In addition, the asymmetric hydrogenation of (Z)-**1m** was conducted on a gram scale in the presence of a 0.2 mol % catalyst loading, affording **2m** in 90% yield with unchanged enantioselectivity (99% ee) (Scheme 3, eq 2). These results declare that the nickel/(S)-Binapine catalytic system can work as well as or even better than the Rh-catalyzed system on the compatibility of Z/E mixtures and alkyl substituted β -amido sulfones.

In conclusion, nickel-catalyzed asymmetric hydrogenation of β -acylamino vinylsulfones has been achieved, affording β -acylamino sulfones with high yields and excellent enantioselectivities. This protocol provides an efficient access to chiral β -amido sulfones. More importantly, the $\text{Ni}(\text{OAc})_2/(\text{S})\text{-Binapine}$ catalytic system exhibited better performance than the precious catalyst in asymmetric hydrogenation of alkyl substituted β -acylamino vinylsulfones and in asymmetric hydrogenation of the Z/E mixture of β -acylamino vinylsulfones. Further investigations on nickel-catalyzed asymmetric hydrogenation are 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/acs.orglett.8b02579.

Experimental details and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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