

# Enantioselective Synthesis of Cyclic Sulfamidates via Pd-Catalyzed Hydrogenation

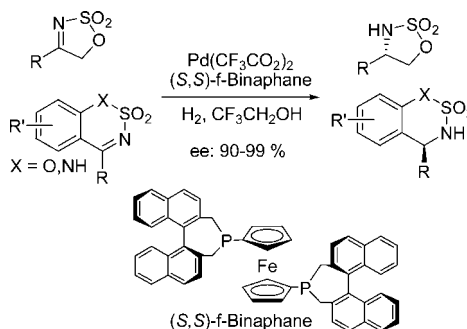
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Received March 13, 2008

## ABSTRACT



Using Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>/(S,S)-f-binaphane as the catalyst, an efficient enantioselective synthesis of cyclic sulfamidates was developed via asymmetric hydrogenation of the corresponding cyclic imines in 2,2,2-trifluoroethanol at room temperature with high enantioselectivities (up to 99% ee).

Chiral amines are ubiquitous in natural products and drugs and serve as building blocks, chiral ligands, and chiral auxiliaries in asymmetric synthesis.<sup>1</sup> Accordingly, the development of efficient synthetic methods for chiral amines is one of the most challenging tasks for organic chemists. 1,2- and 1,3-cyclic sulfamidates have served as useful and versatile precursors for the synthesis of various chiral amines possessing heteroatomic functional groups,<sup>2</sup> based on the established ability of this synthon to undergo nucleophilic displacement.<sup>3</sup> Typically, sulfamidates are prepared from chiral amino alcohols and diols in several steps.<sup>2,3</sup> Recently, the catalytic asymmetric intramolecular amidation of sulf-

amates esters has also been reported to afford chiral cyclic sulfamidates using chiral Ru(II) porphyrins, Mn(III) Schiff-

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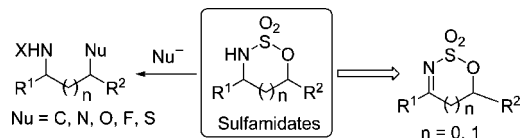
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base complexes, and dirhodium complexes with moderate to good enantioselectivity.<sup>4,5</sup> Development of new efficient methods for the synthesis of sulfamidates is still a challenge. According to the retrosynthetic analysis, we envisioned that direct asymmetric hydrogenation of the corresponding cyclic imines is the most convenient and efficient route to chiral cyclic sulfamidates (Scheme 1).

**Scheme 1.** Synthesis and Application of Sulfamidates



The catalytic asymmetric hydrogenation of imines has drawn much attention since it provides one of the most efficient routes for the synthesis of chiral amines,<sup>6,7</sup> and most of the catalysts are chiral Ir, Rh, and Ru complexes.<sup>6</sup> Recently, chiral palladium complexes<sup>8</sup> have been successfully applied to asymmetric hydrogenation of imines and

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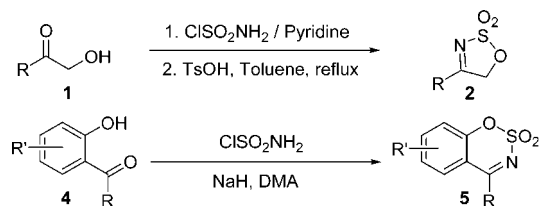
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functionalized ketones by us<sup>9</sup> and other groups,<sup>10</sup> and only activated imines gave high reactivity and enantioselectivity. In our ongoing efforts toward the development of asymmetric hydrogenation,<sup>9,11</sup> we became interested in exploring the practical synthesis of enantiopure cyclic sulfamidates via asymmetric hydrogenation. Herein, we present an efficient method for the enantioselective synthesis of cyclic sulfamidates by the asymmetric hydrogenation of activated imines **2** and **5** using Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>/(*S,S*)-f-binaphane as catalyst, and up to 99% ee was obtained.

Cyclic imines (**2**, **5**) can be conveniently prepared from hydroxy ketones (**1**, **4**) and sulfamoyl chloride by modified literature procedures<sup>12</sup> (Scheme 2).

**Scheme 2.** Synthesis of Cyclic Activated Imines



Imine **2a** is chosen as a model substrate for the optimization of reaction conditions, and the results are shown in Table 1. Based on our previous work on asymmetric hydrogenation of activated imines,<sup>9b,c</sup> initial experiments were carried out in trifluoroethanol (TFE) in the presence of 2.0 mol % of Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>/(*S,S*)-SynPhos. The product was isolated in quantitative yield with moderate enantioselectivity (44% ee). Several chiral bisphosphine ligands were examined (entries 1–4, Table 1). Fortunately, up to 97% ee was achieved using the (*S,S*)-f-binaphane ligand,<sup>13</sup> which was successfully developed by Zhang for asymmetric hydrogenation of imines. The absolute configuration of product **3a** was assigned by comparison of rotation sign with literature datum after the conversion<sup>14</sup> of **3a** into known *N*-benzyl derivatives.<sup>3a</sup> Next, different solvents were tested, and a strong solvent-dependent phenomenon was observed. CH<sub>2</sub>Cl<sub>2</sub>, THF, and MeOH led

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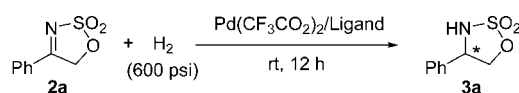
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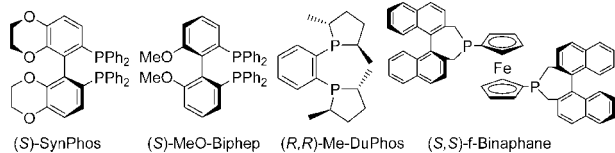
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**Table 1.** Optimization of Reaction Conditions<sup>a</sup>

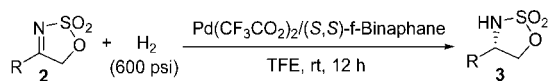
entry	ligand	solvent	convn <sup>b</sup>	ee <sup>c</sup>
1	( <i>S</i> )-SynPhos	TFE	>95	44 ( <i>R</i> )
2	( <i>S</i> )-MeO-Biphep	TFE	70	34 ( <i>R</i> )
3	( <i>R,R</i> )-Me-DuPhos	TFE	>95	59 ( <i>S</i> )
4	( <i>S,S</i> )-f-Binaphane	TFE	>95	97 ( <i>S</i> )
5	( <i>S,S</i> )-f-Binaphane	CH <sub>2</sub> Cl <sub>2</sub>	<5	-
6	( <i>S,S</i> )-f-Binaphane	THF	<5	-
7	( <i>S,S</i> )-f-Binaphane	MeOH	<5	-
8 <sup>d</sup>	( <i>S,S</i> )-f-Binaphane	TFE	>95	97 ( <i>S</i> )
9 <sup>e</sup>	( <i>S,S</i> )-f-Binaphane	TFE	>95	97 ( <i>S</i> )



<sup>a</sup> 0.25 mmol scale: Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> 2.0 mol %, ligand 2.4 mol %. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of the crude product. <sup>c</sup> ee was determined by HPLC analysis. <sup>d</sup> Reaction was run at 60 °C. <sup>e</sup> Reaction was run at 1000 psi of H<sub>2</sub>.

to very low reactivity; TFE was found to be the optimal solvent, which was in accordance with that in Pd-catalyzed asymmetric hydrogenation of imines and ketones.<sup>9,10a,b</sup> The hydrogen pressure and the reaction temperature had no apparent effect (entries 8 and 9, Table 1) on the enantioselectivity. It is noteworthy that low activity was observed using the corresponding Ir or Rh/bisphosphine complexes as the catalysts for asymmetric hydrogenation of **2a**.<sup>15</sup>

Under the optimal reaction conditions, a wide variety of imines **2** were tested to examine the reaction scope, as shown in Table 2. Substrates with electron-donating or electron-withdrawing aryl substituents (94–97% ee, entries 1–5, Table 2) can be successfully hydrogenated to give the corresponding cyclic sulfamidates in high ees. For alkyl-

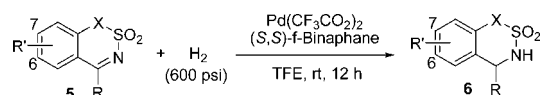
**Table 2.** Pd-Catalyzed Asymmetric Hydrogenation of Imines **2**<sup>a</sup>

entry	R of <b>2</b>	yield (%)	ee (%)	config <sup>b</sup>
1	Ph ( <b>2a</b> )	99	97	<i>S</i> -(+)
2	4-FC <sub>6</sub> H <sub>4</sub> ( <b>2b</b> )	95	97	<i>S</i> -(+)
3	4-MeC <sub>6</sub> H <sub>4</sub> ( <b>2c</b> )	96	96	<i>S</i> -(+)
4	3-MeOC <sub>6</sub> H <sub>4</sub> ( <b>2d</b> )	94	94	<i>S</i> -(+)
5	2-MeC <sub>6</sub> H <sub>4</sub> ( <b>2e</b> )	99	97	<i>S</i> -(+)
6	Me ( <b>2f</b> )	99	97	<i>S</i> -(+)
7	<i>t</i> -Bu ( <b>2g</b> )	98	94	<i>S</i> -(+)
8	<i>n</i> -C <sub>6</sub> H <sub>13</sub> ( <b>2h</b> )	97	96	<i>S</i> -(+)
9 <sup>c</sup>	Ph ( <b>2a</b> )	95	97	<i>S</i> -(+)

<sup>a</sup> 0.25 mmol scale: Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> 2.0 mol %, (*S,S*)-f-binaphane 2.4 mol %, isolated yields, and ee was determined by HPLC or GC. <sup>b</sup> Absolute configuration of 3b-i was determined by analogy. <sup>c</sup> Reaction was run in air.

substituted imines, high enantioselectivities and full conversions were also obtained (94–97% ee, entries 6–8, Table 2). It should be noted that the asymmetric hydrogenation of **2a** can be also operated in air with the same enantioselectivity and activity (entry 9, Table 2).

In addition to the five-membered ring imines **2**, we also explored the asymmetric hydrogenation of assorted six-membered ring benzo-fused imines **5**. As summarized in Table 3, the above Pd catalyst was also effective for a variety

**Table 3.** Pd-Catalyzed Asymmetric Hydrogenation of Imines **5**<sup>a</sup>

entry	X	R/R' of <b>5</b>	yield (%)	ee (%)
1	O	Me/H ( <b>5a</b> )	92	(–)–93
2	O	Me/6-F ( <b>5b</b> )	99	(–)–94
3 <sup>b</sup>	O	Me/7-F ( <b>5c</b> )	88	(–)–93
4	O	Me/6-Me ( <b>5d</b> )	99	(–)–94
5	O	Me/7-Me ( <b>5e</b> )	99	(–)–93
6	O	Et/H ( <b>5f</b> )	99	(–)–91
7	O	<i>n</i> -C <sub>6</sub> H <sub>11</sub> /7-Me ( <b>5g</b> )	97	(–)–90
8	O	Ph/H ( <b>5h</b> )	99	(–)–98
9	O	Ph/7-OMe ( <b>5i</b> )	99	(–)–97
10	O	Ph/6-Me ( <b>5j</b> )	99	(–)–98
11	O	Ph/7-Me ( <b>5k</b> )	99	(–)–98
12	O	<i>p</i> -FC <sub>6</sub> H <sub>4</sub> /7-Me ( <b>5l</b> )	99	(–)–99
13	O	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> /7-Me ( <b>5m</b> )	99	(–)–98
14	O	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub> /7-Me ( <b>5n</b> )	99	(–)–99
15	O	<i>o</i> -MeC <sub>6</sub> H <sub>4</sub> /7-Me ( <b>5o</b> )	99	(–)–99
16	NH	Ph/H ( <b>5p</b> )	99	(–)–97
17	NH	4-MeC <sub>6</sub> H <sub>4</sub> /H ( <b>5q</b> )	96	(–)–96
18	NH	3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub> /H ( <b>5r</b> )	98	(+)–98

<sup>a</sup> 0.25 mmol scale: Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> 2.0 mol %, (*S,S*)-f-binaphane 2.4 mol %, isolated yields, and ee was determined by HPLC or GC. <sup>b</sup> Conversion is 92%.

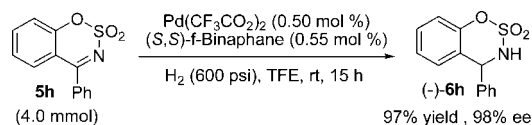
of imines **5** to give the corresponding chiral benzo-fused oxathiazinanes with 90–99% ee. For the R groups at 4-position of **5**, alkyl groups gave 90–94% ee regardless of the chain length (entries 1–7, Table 3), and aryl groups gave slightly higher ee (97–99% ee, entries 8–15, Table 3). Substituents at the 6- or 7-position could be well tolerated.

Furthermore, several nitrogen analogues of **5a**, 1*H*-2,1,3-benzothiadiazine 2,2-dioxides (**5p–5r**), prepared conveniently from their corresponding *o*-aminobenzophenones and sulfamoyl chloride,<sup>31</sup> can be successfully hydrogenated to give the products (**6p–6r**)<sup>16</sup> in 96–98% ee (entries 16–18, Table 3).

To test the practicality of the current method, the asymmetric hydrogenation of cyclic imine **5h** on a gram scale (1.037 g, 4.0 mmol of **5h**) was carried out with 0.5 mol % of Pd catalyst in TFE at room temperature (Scheme 3), and chiral product **6h** was obtained in 97% isolated yield with 98% ee.

(15) For the detailed experiments, see the Supporting Information.

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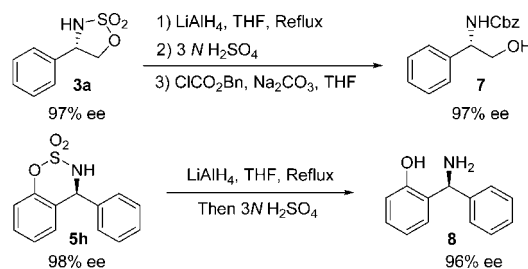
**Scheme 3.** Asymmetric Hydrogenation of **5h** on a Gram Scale

To demonstrate the utility of the current methodology, the nucleophilic ring opening of these sulfamidate heterocycles were carried out to synthesize enantiopure amino alcohol and 2-(amino(phenyl)methyl)phenol. The chiral amino alcohols and 2-aminomethyl phenols are important building blocks in organic synthesis and as well as structural units of agricultural and pharmaceuticals agents.<sup>17</sup> With  $\text{LiAlH}_4$  as the nucleophilic reagent, **3a** and **5h** were converted to  $\beta$ -amino alcohol **7** and 2-[amino(phenyl)methyl]phenol **8**,<sup>18</sup> respectively, without the loss of the optical purity (Scheme 4).

In conclusion, three series of cyclic imines, readily synthesized from hydroxyketones and sulfamoyl chloride,

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**Scheme 4.** Oxathiazinane Ring-Opening Reactions Using  $\text{LiAlH}_4$ 

can be hydrogenated using  $\text{Pd}(\text{CF}_3\text{CO}_2)_2/(S,S)$ -f-binaphane/TFE as the catalyst with high enantioselectivity. The present method provides a new efficient route to the synthesis of enantiopure cyclic sulfamidates.

**Acknowledgment.** Financial support from the National Natural Science Foundation of China (20532005 & 20060608) and the Chinese Academy of Sciences.

**Supporting Information Available:** Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL800591U