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Doubly Stereocontrolled Asymmetric Aza-Henry Reaction with *in situ* Generation of *N*-Boc-Imines Catalyzed by Novel Rosin-Derived Amine Thiourea Catalysts

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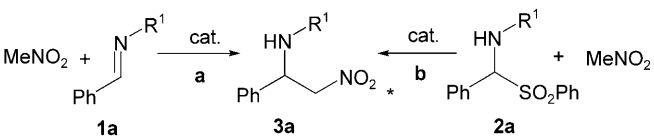
Abstract: The doubly stereocontrolled organocatalytic aza-Henry reaction of nitroalkanes to *N*-Boc-imines generated *in situ* from a variety of substituted α-amido sulfones was investigated for the first time, in general, affording the corresponding products with high to excellent yields (up to 93% yield) and enantioselectivities (up to 98% *ee*), and satisfactory diastereoselectivies (*anti*/*syn* up to 98:2). Furthermore, these organocatalysts based on rosin have been proved to be the very effective promoters for this catalytic asymmetric process along side the *Cinchona* alkaloid-derived catalysts.

Keywords: α-amido sulfones; asymmetric synthesis; aza-Henry reaction; imines; rosin-derived thiourea

The catalytic asymmetric aza-Henry reaction[1] constitutes one of the most versatile and attractive approaches for accessing optically active chiral β-nitroamines, which can be readily converted into valuable synthetic building blocks or biologically active vicinal diamines[2] and α-amino carbonyl compounds,[3] and could effectively be obtained by only two asymmetric catalytic ways to date (**a**: starting from *N*-protected imines; **b**: starting from α-amido sulfones, Scheme 1). Since Shibasaki reported the first catalytic asymmetric aza-Henry reaction of nitromethane to *N*-protected imines,[4] impressive progress has been made on the development of more selective and efficient catalytic systems involving metallic[5] and organic[6] catalysts for this asymmetric version. However, the preparation of these imines, such as *N*-carbamoylimines requires harsh conditions and their purification and storage are rather troublesome because of their inherent instability. To the best of our knowledge, only the two groups of Palomo[7a] and Ricci[7b] have independently reported catalytic asymmetric aza-Henry reactions with *in situ* generation of carbamate-protected imines from α-amido sulfones using the same chiral quaternary ammonium salt catalyst based on a *Cinchona* alkaloid by phase-transfer catalysis (PTC). Nevertheless, this more convenient and useful catalytic version remains a much less developed field and a practical asymmetric aza-Henry reaction with *in situ* generation of carbamate-protected imines catalyzed by other catalysts based on new chiral scaffolds has not yet been reported. Furthermore, except for a recently reported example,[8] *Cinchona* alkaloid derivatives were employed as exclusive efficient catalysts in all of the related asymmetric Mannich reactions with *in situ* generation of carbamate-protected imines from α-amido sulfones.[9]



Scheme 1. Two asymmetric catalytic ways.

We recently reported[10] a new class of thiourea-derived bifunctional catalysts[11,12] based on rosin, which have successfully been applied to the doubly stereocontrolled synthesis of γ-nitro heteroaromatic ketones. Herein, we describe our contribution to the progress of the catalytic asymmetric aza-Henry reaction and report the first doubly stereocontrolled

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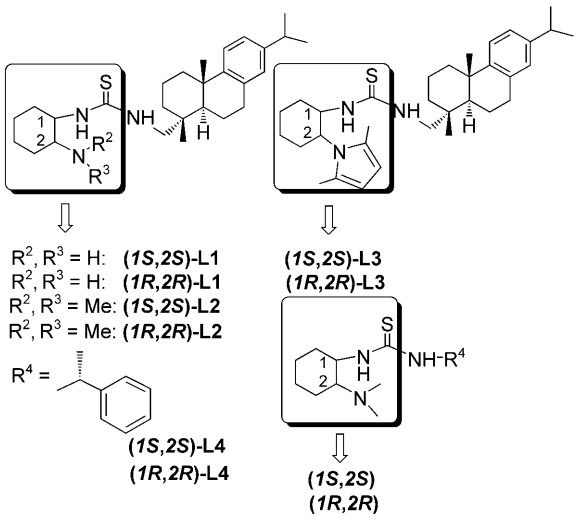
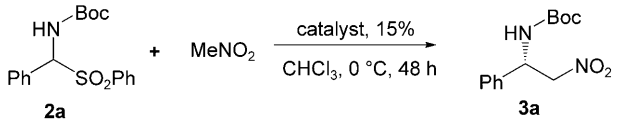


Figure 1. Structure of thiourea catalysts.

asymmetric aza-Henry reaction with *in situ* generation of *N*-carbamate imines catalyzed by novel organocatalysts based on rosin. Undoubtedly, the scope of catalytic asymmetric Mannich reactions with *in situ* generation of *N*-carbamate imines (especially, the catalytic aza-Henry version) and the application of rosin derivatives as well as thiourea will be considerably expanded by our work. In background studies, novel thiourea catalysts based on rosin **(1*R*,2*R*)-L2**, **L3** and **(1*S*,2*S*)-L2**, **L3** were designed and synthesized (Figure 1). Subsequently, the effects of the catalysts were investigated in comparison with other thiourea catalysts and *N*-Boc protected α-amido sulfones (Boc = *tert*-butyloxycarbonyl) were employed as substrates considering the easy removal of the *N*-Boc protecting group.

A model reaction of nitromethane with α-amido sulfone **2a** was performed in the presence of 15 mol% of thiourea catalysts at 0 °C under different conditions (Table 1). We initially screened a range of inorganic bases in the presence of 15 mol% **(1*S*,2*S*)-L2** in $CHCl_3$ (entries 1–8). We found that inorganic base and the solvent were crucial to obtain high reaction efficiency. While the desirable product could be obtained in the absence of an amount of water, only moderate enantioselectivity was observed in the reaction employing 1.0 equivalent of KOH (entry 1) and other cases afforded the racemic products (entries 2 and 3). In comparison, the reactions furnished the adducts with moderate to excellent enantioselectivities (69–93%, entries 4–8) and high to excellent yields (81–92%) in the biphasic solvent. These results indicated that a substantial change of inorganic bases did not have a significant effect on the yield, however, the impact of these bases appeared to be different for stereoselection. The best result was observed when the reaction was conducted with 1.0 equivalent of

Table 1. Screening of bases and thiourea catalysts in reaction of α-amido sulfone **2a** with nitromethane.[a]



Entry	Catalyst	Base[b]	Yield [%][c]	*ee* [%][d]
1[e]	**(1*S*,2*S*)-L2**	KOH	76	68 (*S*)
2[e]	**(1*S*,2*S*)-L2**	K_2CO_3	72	0
3[e]	**(1*S*,2*S*)-L2**	Cs_2CO_3	70	0
4	**(1*S*,2*S*)-L2**	CsOH	85	69 (*S*)
5	**(1*S*,2*S*)-L2**	NaOH	92	72 (*S*)
6	**(1*S*,2*S*)-L2**	KOH	90	80 (*S*)
7	**(1*S*,2*S*)-L2**	Na_2CO_3	81	78 (*S*)
8	**(1*S*,2*S*)-L2**	K_2CO_3	86	93 (*S*)
9	**(1*R*,2*R*)-L2**	K_2CO_3	88	87 (*R*)
10	**L1**	K_2CO_3	n.d.	n.d.
11	**L3**	K_2CO_3	n.d.	n.d.
12	**(1*S*,2*S*)-L4**	K_2CO_3	70	78 (*S*)
13	**(1*R*,2*R*)-L4**	K_2CO_3	72	80 (*R*)

[a] Unless noted, the reaction was conducted with **2a** (0.1 mmol) and nitromethane (0.3 mmol) in $CHCl_3$ (1.0 mL) and H_2O (1.0 mL) at 0 °C for 48 h.
[b] Base (1.0 equiv.).
[c] Isolated yield.
[d] The *ee* values were determined by HPLC, and the configuration was assigned by comparison of HPLC date and specific rotation with literature data.[6b]
[e] In $CHCl_3$ (1.0 mL).

K_2CO_3 in the biphasic solvent (86% yield and 93% *ee*, entry 8). Gratifyingly, **(1*R*,2*R*)-L2** also exhibited superior catalytic activity with an opposite sense of asymmetric induction (88% yield and 87% *ee*, entry 9). The effects of other catalysts were tested next (entries 10–13). Thiourea catalyst **L4** also gave the desired products with good yields and enantioselectivities (entries 12 and 13). The reaction also showed a dramatic ligand effect and those thiourea catalysts **L1** and **L3** proved to be essentially inactive for this transformation (entries 10 and 11). In contrast, thiourea catalyst **L2** is found to be the best one for this doubly stereocontrolled organocatalytic asymmetric process under these mild conditions. We have disclosed that the stereochemical control of the reaction is mainly provided by the 1,2-diaminocyclohexane moiety of the thiourea in the heterogeneous catalytic reaction.[10] In this biphasic catalytic system, the above results suggest that the cyclohexyl scaffold of the thiourea catalyst would also play a crucial role on the stereochemical control of the reaction (nitroalkane after deprotonation as the nitronate anion could coordinate to a tertiary amino group of cyclohexyl scaffold). The observed absolute configuration (*S*) or (*R*) of the adduct was explained by the attack of the nitronate

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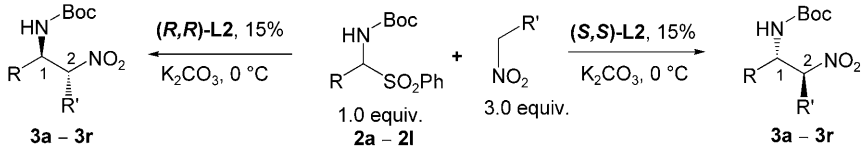
Table 2. Aza-Henry reaction of nitroalkanes to *N*-Boc-imines generated *in situ* from α-amido sulfones[a]



Entry	R	R′	Yield [%] (1*S*/1*R*)[b]	*ee* [%] (1*S*/1*R*)[c]	*dr* (*anti*/*syn*) (1*S*/1*R*)[d]
1	Ph	H	86/88	93/87	
2	1-naphthyl	H	82/80	93/82	
3	2-naphthyl	H	83/82	84/82	
4	4-ClC_6H_4	H	89/87	95/91	
5	4-FC_6H_4	H	83/86	98/93	
6	2-FC_6H_4	H	92/86	92/84	
7	2-ClC_6H_4	H	85/83	91/97	
8	3-ClC_6H_4	H	85/90	89/81	
9	2-$MeOC_6H_4$	H	81/81	95/89	
10	3-$MeOC_6H_4$	H	80/82	93/93	
11[e]	2-furyl	H	81/85	81/94	
12[e]	cyclohexyl	H	15/10	n.d.	
13	Ph	Me	85/82	85/81	88:12/85:15
14	4-ClC_6H_4	Me	93/83	95/87	78:22/93:7
15	2-ClC_6H_4	Me	86/85	85/78	98:2/98:2
16	2-FC_6H_4	Me	90/87	92/81	86:14/90:10
17	4-$MeOC_6H_4$	Me	82/80	91/80	85:15/96:4
18[e]	2-furyl	Me	82/83	88/85	98:2/88:12

[a] The reaction was conducted with α-amido sulfone (0.1 mmol), nitroalkane (0.3 mmol) and K_2CO_3 (1.0 equiv.) in $CHCl_3$ (1.0 mL) and H_2O (1.0 mL) for 48 h.
[b] Isolated yield.
[c] The *ee* values were determined by HPLC, and the configuration was assigned by comparison of HPLC date and specific rotation with literature data.[6b]
[d] Determined by 400 MHz ^1H NMR.
[e] The reaction was stirred for 56 h.

anion to the corresponding *si*-face or *re*-face of the activated amido sulfones.

The results of experiments under the optimized conditions that probe the scope of the reaction are summarized in Table 2. The doubly stereocontrolled catalytic aza-Henry reaction of nitroalkanes to *N*-Boc-imines generated *in situ* from a variety of substituted α-amido sulfones was examined. The results showed that, except for the cyclohexyl-substituted α-amido sulfone (entry 12), all reactions with nitromethane and aromatic/heterocyclic amido sulfones proceeded cleanly affording the desired products of the (*S*) or (*R*) configuration with high to excellent enantioselectivities [(1*S*)-adducts, 81–98% *ee*; (1*R*)-adducts, 81–97% *ee*, entries 1–11] and yields [(1*S*)-adducts, 80–92%; (1*R*)-adducts, 81–90%, entries 1-11]. As expected, nitroethane has proven to be an excellent substrate for the generation of two contiguous nitrogen-bearing stereogenic centers. The reactions afforded *anti*-diastereoselective adducts (*anti*/*syn* up to 98:2) with high to excellent enantioselectivities and yields in a doubly stereocontrolled manner for all of the α-amido sulfones tested (entries 13–18).

In conclusion, we have developed a new class of rosin-derived thiourea catalysts, which has been successfully applied to the doubly stereocontrolled asymmetric aza-Henry reaction with *in situ* generation of *N*-carbamate imines firstly. These organocatalysts based on rosin have been proved to be the very effective promoters for this catalytic asymmetric process along side the *Cinchona* alkaloid-derived catalysts. Especially, the reaction could be achieved under the mild conditions in a doubly stereocontrolled manner. Further investigations and mechanistic studies are ongoing in our laboratories.

Experimental Section

Procedure for the Synthesis of Rosin-Derived Amine Thiourea Catalysts

Using the reported procedures,[13] the pure dehydroabietic amine as a white solid was obtained in 45% yield. Carbon disulfide (4.0 mL) and *N,N′*-dicyclohexylcarbodiimide (10 mmol) were added to a solution of dehydroabietic

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amine (10 mmol) in dry ether (35 mL) at 0 °C. The reaction mixture was allowed to warm slowly to room temperature over a period of 3 h and then was stirred for a further 12 h at room temperature. After separation of the precipitated thiourea by filtration, the solvent was removed under reduced pressure. After column chromatography on silica gel eluted with 25% ethyl acetate in hexanes, the corresponding isothiocyanate as a white solid was isolated in 92% yield.

Under an argon atmosphere, to a solution of the above isothiocyanate (9.17 mmol) in dry dichloromethane (80 mL) was added *N,N*-dimethyl-*trans*-diaminocyclohexane (10 mmol). The reaction mixture was stirred for 12 h at room temperature and was concentrated under vacuum. After column chromatography on silica gel (ethyl acetate/hexane = 2/1 as eluent), the thiourea **L1** as a white solid was isolated in 83% yield.

1-[(1*R*,2*R*)-2-(Dimethylamino)cyclohexyl]-3-{[(1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl]methyl}thiourea (1*R*,2*R*)-L2: $[\alpha]_D^{20}$: +2 (*c* 2.0, $CHCl_3$); mp 82 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14–7.17 (d, *J* = 8.1 Hz, 1H), 6.97–6.99 (m, 1H), 6.88 (s, 1H), 6.45 (br, 1H), 3.68–3.70 (m, 1H), 3.35 (m, 1H), 2.79–2.91 (m, 3H), 2.39–2.45 (m, 1H), 2.20–2.34 (m, 7H), 1.67–1.88 (m, 8H), 1.43–1.50 (m, 2H), 1.21–1.38 (m, 16H), 0.85–1.64 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.1, 145.7, 134.7, 126.8, 124.1, 123.8, 67.1, 56.3, 55.4, 45.6, 40.3, 38.3, 37.8, 37.4, 36.6, 33.4, 33.1, 30.0, 25.2, 25.1, 24.5, 24.0, 23.9, 22.1, 19.1, 18.6, 18.5; IR: ν = 3437, 3259, 3066, 2928, 2248, 2122, 1550, 1452, 1380, 1058, 1029, 913, 822, 759, 624 cm^{-1}; ESI-MS: *m/z* = 470 [M^+]; HR-MS-ESI: *m/z* = 470.3573, calcd. for $C_{29}H_{47}N_3S$ [M + H]$^+$: 470.3563.

Typical Procedure for the Asymmetric Aza-Henry Reaction of Nitroalkanes to *N*-Boc-Imines Generated *in situ* from α-Amido Sulfones

To a stirred solution of **(1*R*,2*R*)-L2** or **(1*S*,2*S*)-L2** (0.015 mmol, 7 mg), α-amido sulfone **2a** (0.1 mmol, 34.7 mg) in the biphasic solvent of $CHCl_3$ (1.0 mL) and H_2O (1.0 mL), K_2CO_3 (0.1 mmol, 13.8 mg) was added. Subsequently, nitromethane (0.3 mmol, 16.1 μL) was added under argon. The solution was stirred at 0 °C. After the reaction was completed (the course of the reaction was monitored by means of thin-layer chromatography, TLC), the mixture was extracted with $CHCl_3$ (10 mL × 4) and dried with sodium sulfate. Concentration and flash chromatography on silica gel (eluent, ethyl acetate/hexane 1:8) afforded the optical active product (*S*)-**3a**; yield: 22.8 mg (86%) or (*R*)-**3a**; yield: 23.4 mg (88%). The enantiomeric purity of the product was determined by using HPLC (Chiralpak AD column, λ = 210 nm, *i*-PrOH/hexane 10:90, 0.6 mL min^{-1}): (*S*)-**3a** *ee* = 93%, t_{major} = 16.88 min, t_{minor} = 17.91 min; (*R*)-**3a** *ee* = 87%, t_{minor} = 17.07 min, t_{major} = 17.91 min.

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