Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201700787

Link to VoR: http://dx.doi.org/10.1002/adsc.201700787

10.1002/adsc.201700787

COMMUNICATION

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Bifunctional Phase-Transfer Catalysts Catalyzed Diastereo- and Enantioselective Aza-Henry Reaction of β,γ-Unsaturated Nitroalkenes With Amidosulfones

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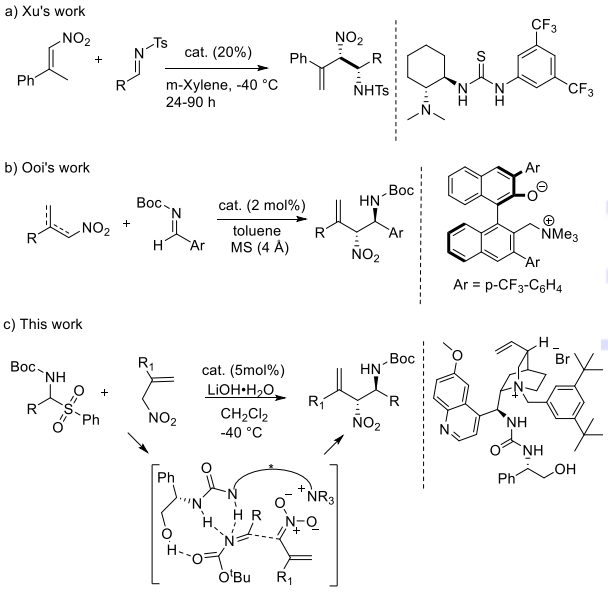
Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. An efficient diastereo- and enantioselective aza-Henry reaction of *β,γ*-unsaturated nitroalkenes with *N*-Boc amidosulfones has been realized under the catalysis of bifunctional chiral phase-transfer catalysts bearing multiple H-bonding donors, which was derived from cinchona alkaloids. This asymmetric catalytic protocol is suitable for a wide range of substrates, and give the corresponding products in high to excellent yields (up to 99%) with excellent diastereo- and enantioselectivities (up to >99:1 dr, up to >99% ee). Density functional theory (DFT) calculations are also performed and give the possible transition-state model to illustrate the mechanism of the developed reaction.

Keywords: asymmetric synthesis ; organocatalysis ; nitroalkenes ; phase-transfer catalysts ; aza-Henry reaction

The catalytic asymmetric aza-Henry (or nitro-Mannich) reaction is one of the most effective methods for constructing C-C bond, especially those involving in complex organic molecules that contain multiple chiral centers, and also of vital importance in organic syntheses.[1] In addition, nitro compounds play an important role in organic chemistry. For example, nitro functional groups can be converted into a variety of other useful functional groups, and this has attracted the attention of the organic chemists.[2] This synthetic strategy based on nitro transformation has been widely used in the synthesis of natural products and biologically active molecules.[3] Nitroalkenes, as a kind of nitro compounds, play a significant role in the construction of above-mentioned natural products and biologically active molecules. Especially, conjugated nitroolefins, due to high degree of electron-deficient character, has been extensively studied as a Michael receptor.[4] In addition, theoretically nitroolefins, especially those



Scheme 1. Asymmetric MBH Reaction and Aza-Henry Reaction of Imines with Nitroolefins

containing γ-H compounds, can be also used as a nucleophile in the presence of bases or organopho sphorus catalysts. However, nitroolefins easily performed electrophilic polymerization, though in the MBH (Morita–Baylis–Hillman) reaction has only limited applications.[5] In 2007, Shi and co-workers have solved the problem by introducing the β-alkyl group in the nitroalkenes.[6] Subsequently, the *β,β*-disubstituted nitroolefins as a nucleophile was applied to a variety of reactions.[7] The nucleophilic addition of conjugate nitroolefins to imines is one of them. However, the reaction between activated imines and nitroolefins is very rare, especially in chiral asymmetric synthesis. To the best of our knowledge, only two examples can be seen in the

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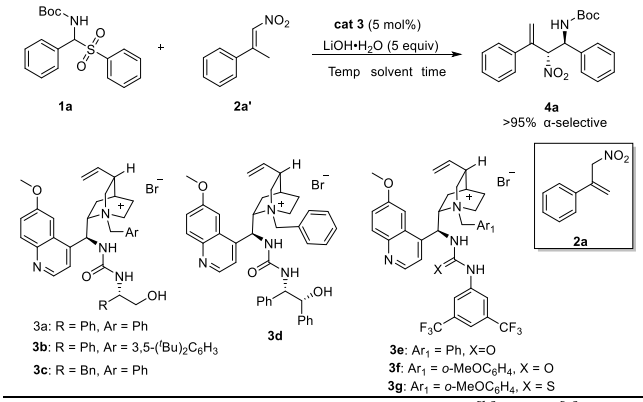
literature. In 2009, Xu et al. reported the first example of diastereo- and enantioselective aza-MBH-type reaction of N-tosylimines with *β,β*-disubstituted nitroolefins, which was catalyzed by (1*R*,2*R*)-diaminocyclohexane thiourea catalyst. The corresponding products were obtained in good yields with high diastereo- and enantioselectivities (Scheme 1a).[8] In 2012, Ooi et al. reported the aza-Henry reaction of *N*-Boc imines catalyzed by chiral ammonium betaines with good to excellent yields and high diastereo- and enantioselectivities (Scheme 1b).[9] In above mentioned reactions including aza-Henry reactions, Lewis bases such as organic amines and organic onium salts are mainly used as catalysts; the reaction mechanism is similar with that of MBH reaction, and the α-addition of conjugate niroolefins to a series of electrophiles is a major reaction. Compared with conjugate nitroolefins, nonconjugate nitroolefins such as *β,γ*-nitroolefins are also accessible and potential direct substrates which are prone to α-addition reactions under the catalysis of suitable inorganic bases. However, nonconjugated nitroolefins used as nucleophiles are rarely reported.

N-Boc aminosulfones, compared with *N*-Boc imines, have high stability, generality and practicality, which has been demonstrated in many asymmetric reactions.[10] Furthermore, the asymmetric phase-transfer catalysis is one of the most important methods in a class of organic catalytic processes and has been widely used in asymmetric catalysis.[11] In addition, it is well known that cinchona alkaloids are one of superior chiral skeleton, and amino acid derivatives are one of inexpensive and accessible chiral resources. Combining cinchona alkaloids with chiral amino alcohols, we can construct a variety of structurally variable chiral quaternary ammonium salts containing multiple hydrogen-bonding donors. In terms of their applicability, these novel quaternary ammonium salts may be a kind of effective phase transfer catalysts for some conventional and challenging asymmetric reactions by structural screening and optimization. Based on this design strategy, we have developed a series of bifuctional chiral phase transfer catalysts with multiple hydrogen bonding donors and successfully applied to asymmetric nitro-Mannich reactions of amidosulfones.[12] On basis of previous works, we envisioned that diastereo- and enantioselective aza-Henry reaction of *β,γ*-unsaturated nitroolefins to amidosulfones is suitable for asymmetric phase transfer catalysis, and the asymmetric catalytic reaction mechanism may be different from that of MBH reaction in the presence of inorganic bases. So far, direct asymmetric aza-Henry reaction of *β,γ*-unsaturated nitroalkenes with amidosulfones catalyzed by chiral phase transfer catalysts has not been reported. Herein, we would like to report bifunctional phase-transfer catalysts catalyzed-diastereo- and enantioselective aza-Henry reaction of *β,γ*-unsaturated nitroalkenes to amidosulfones.

Initially, we investigated the reaction between amidosulfone **1a** and *β,β*-disubstituted nitroolefin **2a'** in the presence of 5 equivalents of $LiOH·H_2O$ at -30 °C in $CHCl_3$ (Table 1) using compouds **3a-3g** as catalysts. As can be seen from Table 1, in all cases, all the catalysts had little effect on the yield of the reaction. The product **4a** was obtained in 33-40% yield with 80:20 to 92:8 dr (Table 1, entries 1-7). Among these catalysts, catalyst **3b** containing the L-phenylglycinol moiety and bulky *N*-3,5-di-*tert*-butylbenzyl moiety gave the best diastereo- and enantioselectivity (92:8 dr and 90% ee), but the yield needed to be further improved. The ensuing screening of bases indicated that $LiOH·H_2O$ was the best one (Table 1, entries 8-9). Next, the screening of the

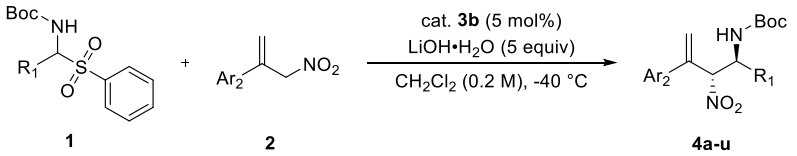
Table 1. Optimization of Reaction Conditions[a]



entry	cat.	solvent	*t* (h)	temp (□)	Yield[b] (%)	d.r.[c]	Ee[d]
1	**3a**	$CHCl_3$	24	-30	39	91:9	77/71
2	**3b**	$CHCl_3$	24	-30	36	92:8	90/90
3	**3c**	$CHCl_3$	24	-30	41	89:11	70/73
4	**3d**	$CHCl_3$	24	-30	43	85:15	80/78
5	**3e**	$CHCl_3$	24	-30	33	80:20	90/89
6	**3f**	$CHCl_3$	24	-30	45	73:27	60/62
7	**3g**	$CHCl_3$	24	-30	40	80:20	27/37
8[e]	**3b**	$CHCl_3$	24	-30	18	90:10	91/80
9[f]	**3b**	$CHCl_3$	24	-30	25	92:8	90/89
10	**3b**	$CHCl_3$	18	-20	41	89:11	70/73
11	**3b**	toluene	24	-30	30	90:10	66/74
12	**3b**	CH_2Cl_2	24	-30	54	87:13	87/84
13[g]	**3b**	CH_2Cl_2	24	-30	54	81:19	90/86
14[h]	**3b**	CH_2Cl_2	24	-30	95	94:6	98/96
15[h]	**3b**	$CHCl_3$	24	-30	92	87:13	98/95
16[h]	**3b**	CH_2Cl_2	21	-40	97	99:1	>99/-

[a] Unless otherwise noted, Reactions were carried out with 0.2 mmol of **1a**, 0.30 mmol of **2a'**, and 5 mol% of catalyst in 1.0 mL of solvent. [b]Yield of isolated product. [c] Diastereomeric ratios determined by ^1H NMR or HPLC. [d] Determined by HPLC using a chiral stationary phase. [e] 5 equiv K_2CO_3 was used. [f] 5 equiv Cs_2CO_3 was used. [g] An equimolar mixture of **2a** and **2a'** was used instead of pure **2a'**.h)**2a** was used instead of **2a'**.

Table 2. Substrate Scope of Aza-Henry Reaction by Using Catalyst **3b**[a]



1 **2** **4a-u**

>95% α-selective

entry	**1**	R_1	**2**	Ar_2	Time[b]	Yield[c]	d.r.[d]	Ee[e] (%)
1	**1a**	Ph	**2a**	Ph	21	97	99:1	99
2	**1b**	*o*-FC_6H_4	**2a**	Ph	24	93	94:6	99
3	**1c**	*o*-$MeOC_6H_4$	**2a**	Ph	23	99	99:1	99
4	**1d**	*m*-$MeOC_6H_4$	**2a**	Ph	24	99	96:4	93
5	**1e**	*m*-ClC_6H_4	**2a**	Ph	23	99	97:3	99
6	**1f**	*p*-$MeOC_6H_4$	**2a**	Ph	24	99	95:5	98
7	**1g**	*p*-MeC_6H_4	**2a**	Ph	24	97	99:1	95
8	**1h**	*p*-FC_6H_4	**2a**	Ph	23	99	96:4	98
9	**1i**	*p*-ClC_6H_4	**2a**	Ph	23	98	95:5	99
10	**1j**	*p*-BrC_6H_4	**2a**	Ph	23	85	95:5	99
11	**1k**	*p*-$CF_3C_6H_4$	**2a**	Ph	20	99	99:1	98
12	**1l**	2-furyl	**2a**	Ph	24	97	99:1	97
13	**1m**	2-thienyl	**2a**	Ph	24	96	97:3	84
14	**1n**	2-naphthyl	**2a**	Ph	24	99	97:3	99
15	**1o**	phenyl ethyl	**2a**	Ph	24	93	98:2	99
16	**1p**	ethyl	**2a**	Ph	22	94	89:11	98
17	**1q**	propyl	**2a**	Ph	22	96	91:9	99
18	**1r**	isobutyl	**2a**	Ph	22	92	87:13	99
19	**1a**	Ph	**2b**	*o*-FC_6H_4	20	90	99:1	99
20	**1a**	Ph	**2c**	*m*-ClC_6H_4	18	80	98:2	99
21	**1a**	Ph	**2d**	*p*-MeC_6H_4	24	90	99:1	99
22	**1a**	Ph	**2e**	*p*-ClC_6H_4	20	94	98:2	99
23	**1a**	Ph	**2f**	*p*-BrC_6H_4	18	86	98:2	99
24	**1a**	Ph	**2g**	2-naphthyl	24	80	98:2	97

[a] Unless otherwise noted, Reactions were carried out with 0.2 mmol of **1**, 0.30 mmol of **2**, and 5 mol% of **3b** in 1.0 mL of CH_2Cl_2. [b] Reaction time was determined by TLC. [c] Yield of isolated product. [d]Diastereomeric ratios determined by HPLC. [e] Determined by HPLC using a chiral stationary phase. Absolute and relative configurations of *anti*-isomers were determined by comparison to literature data.[9]

reaction temperature was performed. When the reaction temperature was raised to -20 °C, the yield increased slightly, but ee value decreased significantly (Table 1, entry 10). Then we examined the effect of the solvents on the reaction (Table 1, entries 11 and 12). Surprisingly, dichloromethane used as the solvent have a beneficial effect on the yield of adduct **4a**, and the yield increased from 30% to 54%. Meanwhile, we found that the raw material **2a'** could be slowly converted into non-conjugated **2a** by ^{1}H NMR (300 MHz) analysis. Thus, **2a** and **2a'** were prepared respectively, and their impact on the reaction were examined, respectively (Table 1, entries 12-14). Gratifyingly, when **2a** was used as a substrate, the yield of adduct **4a** could be greatly improved, and the yield increased from 54% to 95%; high levels of diastereo- and enantioselectivity were also obtained (Table 1, entry 14, 94:6 dr, 98% ee). In the subsequent optimization, chloroform in place of dichloromethane used as the solvent did not improve the outcomes (Table 1, entry 15); reducing the reaction temperature to -40 °C further improved the reaction results, and in this case catalyst **3b** showed excellent catalytic activity and diastereo- and enantiocontrol ability (Table 1, entry 16, 97% yield, 99:1 dr , >99% ee). Absolute and relative configurations of *anti*-isomers were determined by comparison to literature data.[9] After a series of screening and optimization, we chose *β,γ*-unsaturated nitroolefins and amidosulfones as substrates to construct compounds **4a** and its derivatives; accordingly, we chose catalyst **3b**, dichloromethane solvent, and the reaction temperature of -40 °C as the optimal reaction conditions.

With the optimal reaction conditions in hand, next, we investigated the substrate generality of this asymmetric aza-Henry protocol. Representative results obtained in the reaction of *β,γ*-unsaturated nitroalkenes **2** with a variety of amidosulfones **1** are summarized in Table 2. As shown in Table 2, in all

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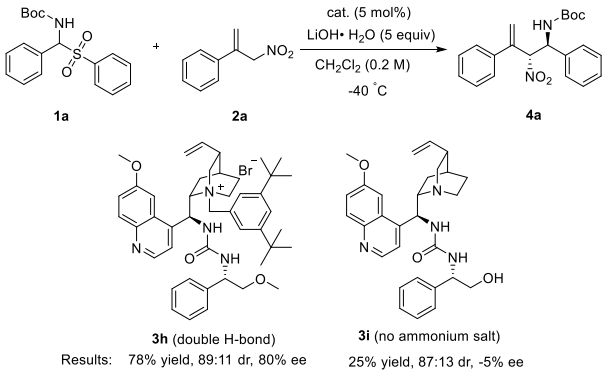
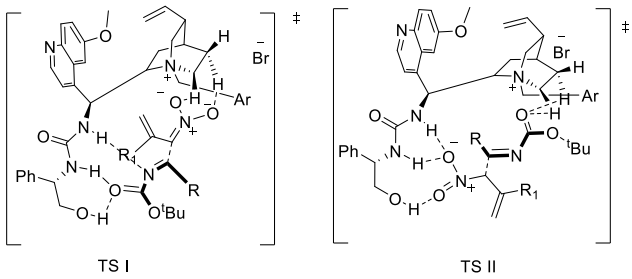
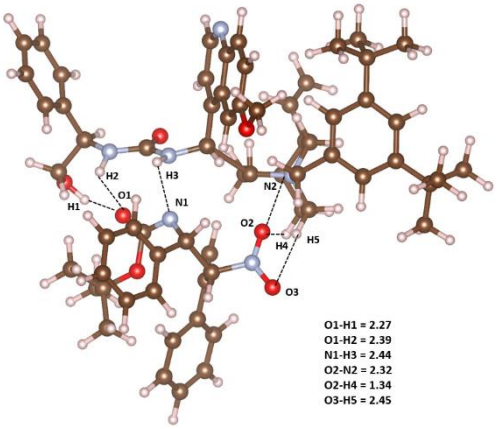
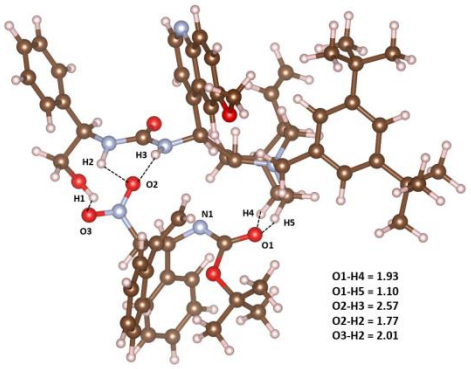


Scheme 2. Control Experiment for Mechanistic Study**.**





TS I: $\Delta G^{\ddagger}$ = 8.7; $\Delta E_{product}$ = -17.7



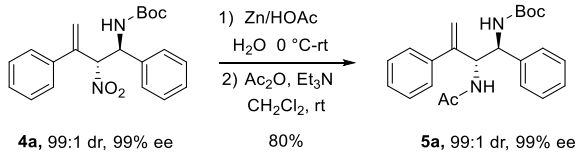
TS II: $\Delta G^{\ddagger}$ = 9.3; $\Delta E_{product}$ = -5.9

Figure 1. The C–C Bond Forming Transition States in the aza-Henry Reaction of **1a** and **2a** with the catalyst **3b**. All the Energies are in kcal•mol^{-1}, and the Bond Lengths are in Angstrom.

cases, high to excellent yields (80-99%) and excellent diastereo- and enantioselectivities (94:6-99:1 dr, 84-99% ee) were obtained across the series. Aromatic aldehyde-derived amidosulfones **1** with electron-withdrawing and electron-donating groups were well tolerated (Table 2, entries 1-11), and the position of the substituents seemed to have limited effect on the reaction (Table 2, entry 3 vs 4 and 6, 2 vs 8, 5 vs 9). Moreover, polycyclic aromatic and heteroaromatic substrates were also appeared to be a good candidate (Table 2, entries 12-14). In spite of this, the heteroaromatic amidosulfone **1m** derived from 2-thenaldehyde have a slight decrease in ee value (Table 2, entry 13, 84% ee). In addition, aliphatic amidosulfone also proved to be applicable to the catalytic protocol, excellent yield and high to excellent levels of diastereo- and enantioselectivity were obtained (Table 2, entries 15−18). Finally, we examined the generality of the reaction with other *β,γ*-unsaturated nitroalkenes (Table 2, entries 19-23). Unsurprisingly, in all cases, high to excellent yields (80-94%) and excellent diastereo- and enantioselectivities (≥98:2 dr, 99% ee) were obtained respectively. Pleasingly, 2-(3-nitroprop-1-en-2-yl)naphthalene **2g** as the substrate showed the same reactivity as **2a**, and the expected product **4x** with excellent stereocontrol was obtained (98:2 dr, 97% ee).

The significant role of the quaternary ammonium center and multiple H-bonding donors played in this system could be demonstrated through the control experiments using catalyst **3h** with two hydrogen-bonds, in which the hydroxyl group was protected by methylation, and **3i** without the quaternary ammonium center under the optimized reaction conditions. The corresponding results were presented in Table 2 (Scheme 2). Compared with catalyst **3b** (97% yield, 99:1 dr and 99% ee in Table 2, entry 1), modified catalysts **3h** and **3i** gave product **4a** in a lower yield with a lower diastereo-/enantioselectivity (Scheme 2). To identify the reaction mechanism and the transition state conformation intuitively, the reaction between compound **2a** and *N*-Boc imine (the resulting intermediate by the elimination of amidosulfone **1a** under basic conditions) to form **4a** in the presence of catalyst **3b** was investigated again by computational research and analysis (Figure 1). There are two reaction transition-state models containing multiple H-bonding interaction between catalyst **3b** and the *N*-Boc imine or **2a** (TS I and TS II). The theoretical caculation results show that both transition-state models indeed significantly reduce the reaction barriers about 10 kcal•mol^{-1} compared with the corresponding reaction without any catalyst. Although the activation free energies in TS I and II

are both in almost the same level, the adduct **4a** with **3b** was stabilized much more in energy (about 11.8 kcal•mol^{-1}). Obviously, this energy difference derived from the more effective multiple H-bonding interaction and embedded electrostatic interaction with little steric repulsion in TS I. The reaction via TS I is both kinetically stable and thermodynamically stable (See the SI for a detailed description of the theoretical calculations). These results supported cooperative catalysis of bifunctional catalysts and indicated that both the hydrogen-bonding sites of the phenylglycinol moiety and the quaternary ammonium center were crucial to achieve excellent catalytic activity and stereocontrol in this asymmetric aza-Henry reaction.



Scheme 3. Derivatization of the aza-Henry adduct **4a** to the corresponding 2,3-diamino alkene **5a**.

Finally, the applicability of this protocol was exemplified by the derivatization of the aza-Henry adduct. As demonstrated in Scheme 3, the optically active product such as **4a** was readily transformed into 2,3-diamino alkene **5a**, containing two different N-protected groups, which was obtained in good yield without loss of diastereo- and enantioselectivity by zinc-mediated reduction in two steps reaction.

In conclusion, we have developed a highly enantio- and diastereoselective aza-Henry reaction of *β,γ*-unsaturated nitroalkenes with amidosulfones catalyzed by easily available bifunctional chiral phase-transfer catalysts bearing multiple H-bonding donors derived from quinine. The strategy has a broad substrate scope, and corresponding products were obtained in high to excellent yields with high to excellent diastereo- and enantioselectivities under mild conditions. The density functional theory (DFT) calculations give the possible transition-state model and support the bifunctional catalytic mechanism. Further efforts to study the reaction mechanism and the application of these phase-transfer catalysts to other asymmetric transformations are under way in our laboratory.

Experimental Section

General procedure for enantio- and diastereoselective aza-Henry reaction: Without protection of inert gases, catalyst **3b** (5 mol%) and amidosulfones (0.20 mmol) were dissolved in dry CH_2Cl_2 (0.2 M), Nitroolefins (0.30 mmol, 1.5 eq.) was added, the mixture was cooled to –40 °C, freshly grounded $LiOH·H_2O$ (42.0 mg, 5 eq.) was added in one portion, the resulting suspention was vigorously stirred at –40 °C. The reaction stirred until complete by TLC, 3 mL sat. aq. NH_4Cl was added and the solution was allowed to warm to room temperature, the aqueous was extracted with ethylacetate (3×5 mL), then the organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (PE/EA = 10:1).

Acknowledgements

We give thanks for the financial support from the National Natural Science Foundation of China (No. 51373067), and Science and Technology Development Project of Jilin Province (No. 20140520085JH). We are grateful to Prof. Fuquan Bai from Institute of Theoretical Chemistry for useful discussion and enthusiastic help for the density functional theory (DFT) calculations.

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10.1002/adsc.201700787

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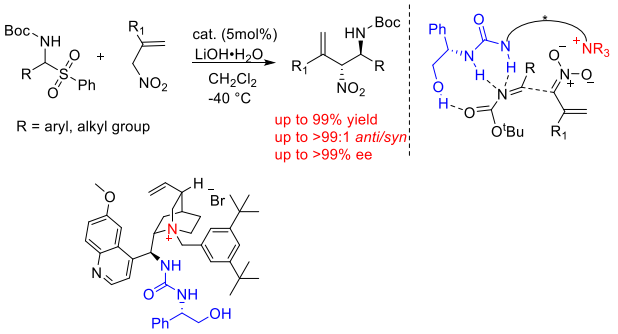
Bifunctional Phase-Transfer Catalysts Catalyzed Diastereo- and Enantioselective Aza-Henry Reaction of β,γ-Unsaturated Nitroalkenes With Amidosulfones



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