VIP Asymmetric Catalysis

DOI: 10.1002/anie.201002355

Catalytic Asymmetric Bromoamination of Chalcones: Highly Efficient Synthesis of Chiral α-Bromo-β-Amino Ketone Derivatives**

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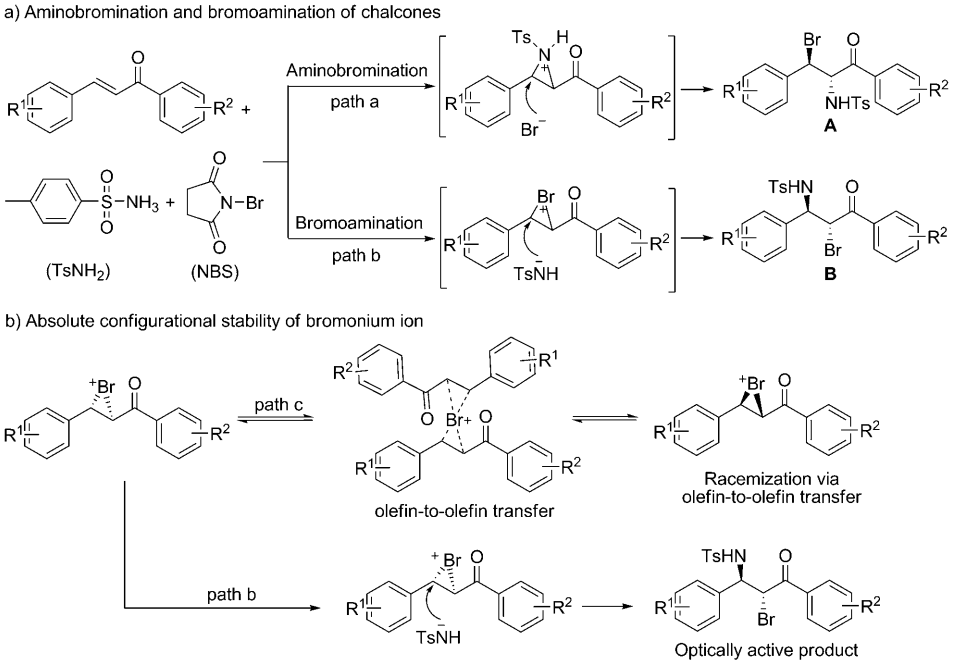
Catalytic asymmetric difunctionalization of carbon–carbon double bonds, such as dihydroxylation,[1] aminohydroxylation,[2] and diamination[3] has been broadly studied and has also matured to the extent that the transformations are routinely applied in organic synthesis. However, asymmetric electrophilic halofunctionalization reactions attract less attention, and still pose a great challenge.[4] Among them, bromoaminations[5] of chalcones are of great interest, because the resulting vicinal bromoamines are extremely versatile building blocks in organic and medicinal chemistry.[6] Moreover, optically active bromine-containing products can serve as key intermediates[7] for further manipulations.[8] Nonetheless, an efficient catalytic asymmetric bromoamination reaction to afford chiral α-bromo-β-amino ketone derivatives **B** (Scheme 1, path b) has been elusive. The main difficults are as follows:



Scheme 1. Regioselectivity and enantioselectivity of the bromoamination reaction.

1) The regioselectivity of the difunctionalization reaction: chalcones prefer an aminobromination process (Scheme 1, path a) probably through an aziridinium-based mechanism.[9a] Therefore, the catalytic aminobromination of chalcones to synthesize racemic amino-brominated products **A** (Scheme 1, path a) was widely reported in the literature.[9] While few examples involve a bromoamination procedure which generates α-bromo-β-amino ketone products **B** via a bromonium ion intermediate (Scheme 1, path b).
2) The enantioselectivity of the bromoamination reaction: the bromonium ion intermediate possibly suffers racemization through olefin-to-olefin transfer (Scheme 1, path c), which is competitive with intermolecular capture by anionic nucleophiles.[10]

Herein, we developed the first catalytic regio- and enantioselective bromoamination of chalcones by chiral *N*,*N*′-dioxide/scandium(III) complexes to afford α-bromo-β-amino ketone derivatives with excellent outcomes (up to 99% yield, 99% *ee*, and 99:1 d.r.) under mild reaction conditions.

In our initial study, the catalytic activity of a series of Lewis acids such as $Cu(OTf)_2$, $Fe(OAc)_2$, $Zn(OTf)_2$, $InBr_3$, $Zr(OiPr)_4$, $SnCl_2{\cdot}2H_2O$, $Mn(OAc)_2{\cdot}4H_2O$, and $Cd(OAc)_2{\cdot}2H_2O$ was examined in the bromoamination of chalcones with *p*-toluenesulfonamide ($TsNH_2$) and *N*-bromosuccinimide (NBS; for details, see the Supporting Information). However, no α-bromo-β-amino ketone derivatives **B** were obtained and only α-amino-β-bromo ketone deriva-

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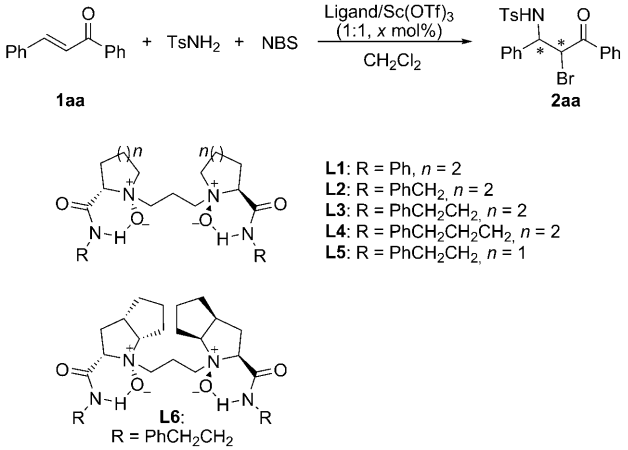
[**] We appreciate the financial support from the National Natural Science Foundation of China (Nos. 20732003 and 20872097), the PCSIRT (No. IRT0846), and the National Basic Research Program of China (973 Program; No. 2010CB833300). We also thank Sichuan University Analytical & Testing Center for NMR analysis.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201002355.

tives **A** were detected as the major product—this outcome is similar to previously reported results.[9] Further investigation of other Lewis acids showed that trace amounts of bromoaminated products **B** could be obtained by employing Yb(OTf)$_3$ or La(OTf)$_3$ as the catalyst. Pleaseingly, Sc(OTf)$_3$ gave the desired compound **B** as a major product in 31% yield. The addition of molecular sieves (M.S.; 4 Å) notably improved the yield to 70%.

Next, we carried out chiral Lewis acid catalyzed regio-, diastereo-, and enantioselective bromoamination of chalcones. In our previous studies, it was demonstrated that *N*,*N*′-dioxide/metal complexes exhibited an excellent ability to catalyze various asymmetric reactions.[11] Therefore, the catalytic activity of a series of *N*,*N*′-dioxide/Sc(OTf)$_3$ complexes was examined for the synthesis of chiral α-bromo-β-amino ketone derivatives. Initially, by coordination with Sc(OTf)$_3$ the chiral *N*,*N*′-dioxide ligand **L1** derived from (*S*)-pipecolic acid could catalyze the asymmetric bromoamination of chalcone **1aa**, and produced **2aa** in 34% yield with 85% enantiomeric excess (*ee*) and up to 99:1 diastereomeric ratio (d.r., Table 1, entry 1). Encouraged by this result, other amines and chiral backbone moieties of *N*,*N*′-dioxide ligands were investigated (Table 1, entries 2–6). It was found that phenylethanamine and (*S*)-pipecolic acid derived *N*,*N*′-dioxide **L3**/Sc(OTf)$_3$ was the most promising catalyst (70% yield, 91% *ee*, >99:1 d.r.; Table 1, entry 3). Then, the effect of temperature was examined, and the enantioselectivity was increased to 96% *ee* at 0°C (Table 1, entry 7). Remarkably, when M.S. (4 Å) were used as an additive, the yield was greatly improved to 95% with maintained stereoselectivity (Table 1, entry 8). Investigation of solvent effect showed that CH_2Cl_2 was the best solvent and higher concentration gave better yield (Table 1, entry 9). Pleaseingly, the catalytic activity of *N*,*N*′-dioxide **L3**/Sc(OTf)$_3$ catalyst was prominent, and the catalyst loading could be decreased from 10 mol% to 0.05 mol% without any loss in the yield and enantioselectivity (Table 1, entry 10). Exclusion of air and moisture was also unnecessary, and made the protocol more simple, convenient, and practical (Table 1, entry 11). Notably, further decreasing the catalyst loading to 0.001 mol% maintained the enantioselectivity with moderate yield (Table 1, entry 12). The stability test of the catalyst showed that the activity and selectivity could be maintained when using a solution of catalyst kept at room temperature for three months (Table 1, entry 13).

Table 1: Optimization of the reaction conditions in the asymmetric bromoamination of chalcone.



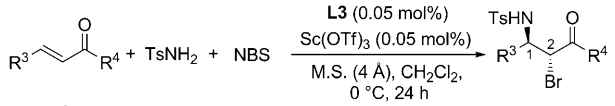
Entry[a]	Ligand	Catalyst loading [*x* mol%]	Yield [%][b]	*ee* [%][c]	d.r.[d]
1	**L1**	10	34	85	>99:1
2	**L2**	10	24	91	>99:1
3	**L3**	10	72	91	>99:1
4	**L4**	10	71	91	>99:1
5	**L5**	10	36	84	>99:1
6	**L6**	10	47	91	>99:1
7[e]	**L3**	10	59	96	>99:1
8[e,f]	**L3**	10	95	96	>99:1
9[e,f,g]	**L3**	10	99	96	>99:1
10[h]	**L3**	0.05	99	96	>99:1
11[h,i]	**L3**	0.05	99	96	>99:1
12[h,j]	**L3**	0.001	58	96	>99:1
13[h,i,k]	**L3**	0.05	99	96	>99:1

[a] Unless otherwise noted, all reactions were performed with ligand (10 mol%), Sc(OTf)$_3$ (10 mol%), **1aa** (0.1 mmol), TsNH$_2$ (0.11 mmol), and NBS (0.12 mmol) in CH_2Cl_2 (0.5 mL) under nitrogen at 35°C for 24 h. [b] Yield of isolated product. [c] Determined by HPLC on a chiral stationary phase using a Chiralcel AD-H column. [d] Determined by ^{1}H NMR spectroscopy and HPLC on a chiral stationary phase. [e] Reaction was performed at 0°C. [f] M.S. (4 Å, 20 mg) was added. [g] Only 0.2 mL of CH_2Cl_2 was used. [h] Catalyst (0.05 mol%, 25 μL, 0.002 M **L3**/Sc(OTf)$_3$ in THF), **1aa** (0.1 mmol), TsNH$_2$ (0.11 mmol), NBS (0.12 mmol), M.S. (4 Å, 20 mg) in CH_2Cl_2 (0.2 mL) under nitrogen at 0°C for 24 h. [i] Not under N_2. [j] The reaction was carried out on a 1 mmol scale with 0.001 mol% catalyst for 72 h. [k] Using the catalyst solution that was kept at room temperature for three months. THF = tetrahydrofuran.

Under the optimized reaction conditions (Table 1, entry 11), the substrate scope was extended. As summarized in Table 2, all substrates gave the desired α-bromo-β-amino ketone derivatives in excellent diastereoselectivity (>99:1 d.r.). The reaction performed well with β-phenyl-substituted chalcone derivatives, and gave the corresponding products in nearly quantitative yields with 90–97% *ee*—regardless of the electronic nature or the position of the benzoyl moiety (Table 2, entries 1–12). Moreover, the electronic nature and the position of the substituents on β-phenyl group also had little influence on yields and enantioselectivities (90–99% yield, 94–98% *ee*; Table 2, entries 16–27). Furthermore, fused-ring, multi-substituted, and heteroaromatic-substituted chalcones were also suitable substrates for the reaction, and delivered the corresponding products with up to 99% *ee* and over 99:1 d.r. (Table 2, entries 13–15, and 28). The substrate with a cinnamyl group still gave good yield with 99% *ee* (Table 2, entry 29). Finally, when rigid enones were subjected to the reaction, the desired vicinal bromoamines **2bd** and **2be**, which have a quarternary carbon center, were obtained in good yield with 97% *ee* and over 99:1 d.r., respectively (Scheme 2).

Next, the scope of the nucleophile was explored, and the results were shown in Table 3. In all cases, excellent enantioselectivity and diastereoselectivity were obtained regardless of the nature of substituents on the sulfonyl group. 4-Methylbenzenesulfonamide, 2-methylbenzenesulfonamide, and benzenesulfonamide equally gave the corresponding

Table 2: Substrate scope of chalcones when using $TsNH_2$ and NBS in the asymmetric bromoamination.

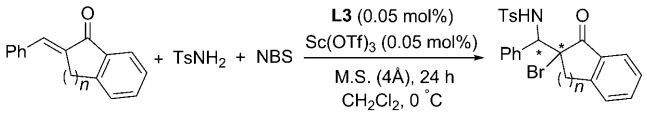


1 2

d.r. >99:1

Entry[a]	R^3	R^4	Product	Yield [%][b]	*ee* [%][c]
1	Ph	Ph	**2aa**	99	96
2	Ph	4-$CH_3C_6H_4$	**2ab**	98	96
3	Ph	3-$CH_3C_6H_4$	**2ac**	99	96
4	Ph	4-ClC_6H_4	**2ad**	99	97
5	Ph	3-ClC_6H_4	**2ae**	99	96
6	Ph	4-FC_6H_4	**2af**	99	97
7	Ph	4-BrC_6H_4	**2ag**	90	97
8	Ph	2-$CH_3OC_6H_4$	**2ah**	92	90
9	Ph	3-$CH_3OC_6H_4$	**2ai**	98	96
10	Ph	4-$CH_3OC_6H_4$	**2aj**	90	97
11	Ph	4-$NO_2C_6H_4$	**2ak**	91	95
12	Ph	3-$NO_2C_6H_4$	**2al**	99	95
13	Ph	2-naphthyl	**2am**	99	99
14	Ph	3,4-$Cl_2C_6H_3$	**2an**	98	95
15[d]	Ph	2-fural	**2ao**	99	98
16	2-$CH_3C_6H_4$	Ph	**2ap**	91	94
17	3-$CH_3C_6H_4$	Ph	**2aq**	97	96
18	4-$CH_3C_6H_4$	Ph	**2ar**	96	95
19	3-ClC_6H_4	Ph	**2as**	99	96
20	4-ClC_6H_4	Ph	**2at**	93	96
21	4-FC_6H_4	Ph	**2au**	97	96
22	4-BrC_6H_4	Ph	**2av**	94	96
23	3-$MeOC_6H_4$	Ph	**2aw**	93	95
24	3-$PhOC_6H_4$	Ph	**2ax**	97	96
25	4-PhC_6H_4	Ph	**2ay**	96	96
26	4-$NO_2C_6H_4$	Ph	**2az**	91	97
27	3-$NO_2C_6H_4$	Ph	**2ba**	90	99 (1*R*,2*R*)[e]
28	3,4-$Cl_2C_6H_3$	Ph	**2bb**	96	97
29[f]	PhCH=CH	Ph	**2bc**	80	99

[a] Unless specified, the reactions were performed with **1** (0.2 mmol), **L3**/Sc^{III} complex (0.05 mol%, 1:1), and M.S. (4 Å, 40 mg) in CH_2Cl_2 (0.4 mL) at 0°C for 5 min, then a mixture of $TsNH_2$ (0.22 mmol) and NBS (0.24 mmol) was added, and the reaction mixture was stirred at 0°C for 24 h. [b] Yield of isolated product. [c] Determined by HPLC using a chiral stationary phase (see the Supporting Information). [d] d.r. = 98:2. [e] Absolute configuration was determined by X-ray crystallography of **2ba** (see the Supporting Information). [f] d.r. = 96:4.

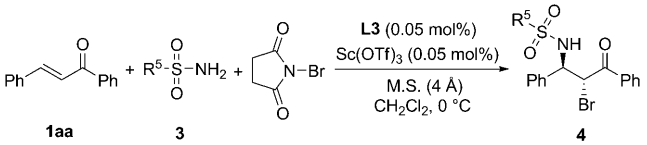


1bd *n* = 1 **2bd** 68% yield, 97% *ee*, >99:1 d.r.
1be *n* = 2 **2be** 78% yield, 98% *ee*, >99:1 d.r.

Scheme 2. Asymmetric bromoamination of rigid enones **1bd** and **1be** with NBS and $TsNH_2$.

vicinal bromoamines in nearly quantitative yields with 96–97% *ee* (Table 3, entries 1–3). Other benzenesulfonamides substituted with electron-donating or electron-withdrawing groups also gave excellent enantioselectivity and moderate yield (Table 3, entries 4–7). Meanwhile, methanesulfonamide

Table 3: Sulfonamide scope in the catalytic asymmetric bromoamination of chalcone.



1aa **3** **4**

Entry[a]	R^5	Product	*t* [h]	Yield [%][b]	*ee* [%][c]	d.r.[d]
1	4-$CH_3C_6H_4$	**2aa**	24	99	96	>99:1
2	2-$CH_3C_6H_4$	**4ab**	24	98	97	>99:1
3	Ph	**4ac**	24	97	97	>99:1
4[e]	2-ClC_6H_4	**4ad**	48	38	94	>99:1
5[e]	3-ClC_6H_4	**4ae**	48	70	93	>99:1
6[e]	4-ClC_6H_4	**4af**	48	46	95	>99:1
7[e]	4-$MeOC_6H_4$	**4ag**	48	66	97	>99:1
8[e]	Me	**4ah**	48	95	92	>99:1

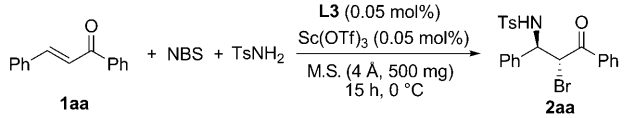
[a] Unless specified, the reactions were performed with **1aa** (0.2 mmol), **L3**/Sc^{III} complex (0.05 mol%, 1:1), and M.S. (4 Å, 40 mg) in CH_2Cl_2 (0.4 mL) at 0°C for 5 min, then a mixture of sulfonamide **3** (0.22 mmol) and NBS (0.24 mmol) was added. [b] Yield of isolated product. [c] Determined by HPLC on a chiral stationary phase (see the Supporting Information). [d] Determined by ^1H NMR spectroscopy and HPLC using a chiral stationary phase. [e] 0.5 mol% catalyst loading was used.

was still a suitable reagent for the reaction, and produced **4ah** in 95% yield with 92% *ee* (Table 3, entry 8).

In addition, α,β regioselectivity of the bromoaminated products has been completely controlled for all these cases. The regiochemistry was assigned on the basis of the high-resolution mass spectrometry (HRMS) analysis, which showed a prominent signal corresponding to the $[ArCHNHTs]^+$ ion fragment. The *anti* stereoselectivity was confirmed by converting the vicinal bromoamine **2aa** into the corresponding known *trans*-aziridine **5aa** ($J_{trans} = 4.0$ Hz; Scheme 3b). The absolute configuration (1*R*,2*R*) was unambiguously determined by the X-ray crystallographic analysis of **2ba**, which further confirmed the *anti* stereoselectivity and regiochemistry assignment.[12]

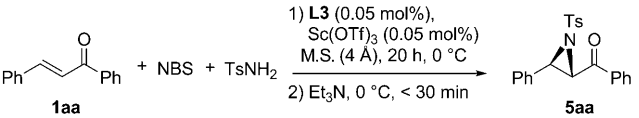
To show the synthetic utility of the catalyst system, bromoamination of chalcone **1aa** was expanded to gram-scale preparation. As shown in Scheme 3a, the desired synthesis of bromoamine **2aa** was accomplished in 96% yield with 96% *ee* using only 0.05 mol% of **L3**/$Sc(OTf)_3$ complex

a) Asymmetric bromoamination of chalcone on a gram scale



1aa (5.0 mmol, 1.04 g) **2aa** 2.18 g, 96% yield, 96% *ee*, >99:1 d.r.

b) One-pot conversion of **1aa** to chiral aziridine **5aa**



1aa **5aa** 97% yield, 96% *ee*, >99:1 d.r.

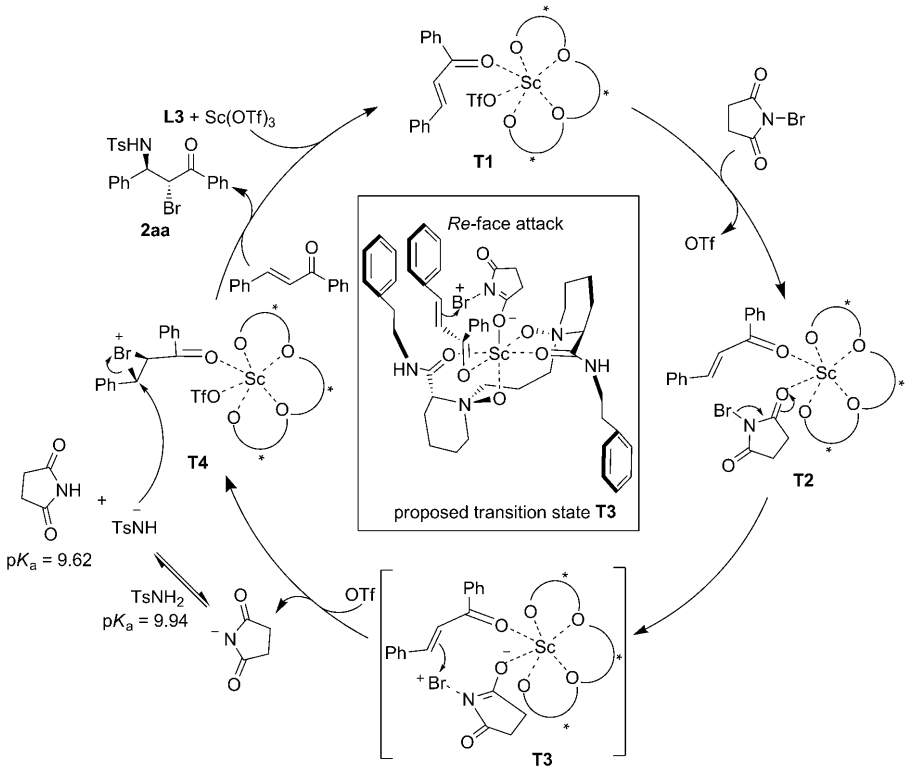
Scheme 3. The synthetic utility of this catalyst system.

catalyst. In addition, the α-bromo-β-amino ketone derivative **2aa** was easily transformed into the corresponding aziridine **5aa**, which is a versatile building block in organic synthesis,[13] by adding Et_3N directly to the reaction system. This protocol offers an efficient process for the synthesis of the chiral aziridine (97% yield, 96% *ee*, >99:1 d.r.; Scheme 3b).

Preliminary studies of the mechanism were carried out (see the Supporting Information). Firstly, Michael-type addition of $TsNH_2$ to the chalcone did not occur in this catalyst system, thus suggesting that a mechanism involving Michael-type addition should be excluded. Furthermore, the *trans*-α-bromo-β-amino products obtained indicated that the aziridinium-based mechanism[9a] was also unlikely. The observations of the high *anti* stereoselectivity and formation of trace amounts of dibromide product indicate that a possible bromonium intermediate[4,9e] is likely. Secondly, HRMS analysis on the catalyst structure showed that $[\mathbf{L3}/Sc(OTf)]^+$ was the main fragment ion, and nonlinear effects[14] were not observed, which indicates that the monomeric catalyst should be the main catalytically active species. In light of the X-ray structures of **2ba**[12] and the *N*,*N*′-dioxide/scandium(III) complex,[15] the oxophilic property of Sc^{III},[16] and the above experimental results, a proposed chiral-bromonium-based mechanism and the transition-state **T3** are proposed to explain the observed sense of asymmetric induction (Scheme 4).

In the initial step, two carbonyl oxygen atoms and the N-oxide oxygen atom of **L3**, the chalcone, and OTf coordinate with Sc^{III} to give the transition-state **T1**. Next, exchange of OTf with NBS forms the key intermediate **T2**. In **T2** the *Si* face of the chalcone was blocked by the bulky phenethyl group. Therefore, attack at the *Re* face relative to the bromine atom of NBS through **T3** yields the corresponding chiral bromonium ion **T4** and the negatively charged succinimide ion. Then, the negatively charged *p*-toluenesulfonamide would be generated from the negatively charged succinimide ion by reaction with $TsNH_2$. And immediately, intermolecular capture of a chiral bromonium ion by the nucleophilic *p*-toluenesulfonamide through an S_N2 mechanism led to the desired product **2aa** with excellent *anti* stereoselectivity. The regioselective outcome can be rationally explained by this bromonium-based mechanism, because the β position of the bromonium ion intermediate has more positive charge than its α position as a result of the stablization effect from phenyl ring. Furthermore, the observation that 3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one and 3-(2-methoxyphenyl)-1-phenylprop-2-en-1-one gave poor *ee* values (see the Supporting Information), can also be explained on the basis that electron-rich bromonuim ions may be more easily racemized through the bimolecular olefin-to-olefin pathway.[10b]

In conclusion, the first highly regio- and enantioselective bromoamination of chalcones has been developed which proceeds via an unusual bromonium-based mechanism and delivers important chiral α-bromo-β-amino ketone derivatives. Excellent results (up to 99% *ee*, >99:1 d.r., and nearly quantitative yields) were obtained using 0.05 mol% of the C_2-symmetric *N*,*N*′-dioxide **L3**/scandium(III) complex under mild reaction conditions. The remarkable features of the method, such as low catalyst loading, convenient operation, and simple procedure allow the practical asymmetric construction of difunctional molecules that are useful for further synthesis. The insight into the mechanism of the regioselective changes will provide interesting and useful information for realization of other asymmetric difunctionalization such as bromoamination of olefins.



Scheme 4. Proposed catalytic process for bromoamination of chalcone.

Experimental Section

A dry reaction tube was charged with 50 μL (0.05 mol% loading) of catalyst solution (0.002 M **L3**/$Sc(OTf)_3$ in THF). After the solvent was removed under vacuum, chalcone **1aa** (0.2 mmol) and M.S. (4 Å, 40 mg) were weighed into the tube before CH_2Cl_2 (0.4 mL) was added. The mixture was stirred at 35 °C for 5 min, and then cooled to 0 °C. Finally, a mixture of *p*-toluenesulfonamide (37.5 mg, 0.22 mmol) and *N*-bromosuccinimide (NBS, 42.7 mg, 0.24 mmol) was added while stirring. The reaction mixture was stirred at 0 °C for 24 h. The residue was purified by flash chromatography on silica gel to afford the desired product.

Received: April 21, 2010
Revised: June 11, 2010
Published online: July 20, 2010

Keywords: asymmetric catalysis · bromoamination · chalcones · scandium · sulfonamides

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