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New chiral biscarboline *N,N′*-dioxide derivatives as catalyst in enantioselective reduction of ketoimines with trichlorosilane

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ABSTRACT

New axial *N,N′*-dioxide secondary amide derived from L-tryptophan was synthesized and firstly employed in catalytic enantioselective reduction of ketoimines with trichlorosilane. It was found that **4f** was an effective catalyst with excellent reactivity and good enantioselectivity. Possible mechanism for the catalytic procedure was tentatively proposed.

Introduction

Chiral amines are key components in numerous bioactive molecules found in nature products, drugs, pharmaceutical, and agrochemical active compounds.[1–7] Catalytic asymmetric reduction of ketoimines is an efficient and straightforward method to afford different chiral amines, and it represents a powerful and widely used transformation for the synthesis of new stereogenic center with a new formed C—N bond. Most of the effective catalysis is conducted in the presence of transition metals.[8–20] Recently, much attention has been paid to the reduction using metal-free catalysts which could be readily synthesized and is environment-friendly. Chiral phosphoric acid employed as a catalyst in conjunction with Hantzsch esters as reductive reagents could afford high yields and good stereoselectivities in this reduction.[21–23] Chiral Lewis base in conjunction with trichlorosilane also performed well in this enantioselective reduction.[24]

Since Kobayashi and co-workers[25] reported that DMF could activate trichlorosilane toward the reduction of aldehydes, aldimines, and ketones, great efforts have been paid in this area and tremendous progress has been achieved.[26–29] However, catalysts with N—O structures have been rarely reported in the asymmetric hydrosilylation of imines with trichlorosilane. In our recent study, a *N,N′*-dioxide biscarboline was synthesized and utilized in asymmetric additions of trichlorosilanes to aldehydes affording the corresponding chiral alcohols with up to 99% ee. We hope to develop a series of biscarboline amides with *N,N′*-dioxide and to investigate their application in enantioselective reduction of ketoimines with trichlorosilanes. To the best of our knowledge, such chiral biscarboline amides have yet been studied as catalysts in enantioselective reduction of ketoimines with trichlorosilane.

Results and discussions

Ligands **4a**–**4f** were synthesized from **1** which can be readily obtained from tryptophan (Scheme 1).[30a] Resolution of (+)-**4** from (−)-**4** was performed through a chiral column with eluents DCM/MeOH (*V*/*V* = 85/15 to 95/5, 2 to 2.5 ml/min). Optically active compounds **4a**–**f** with positive optical rotation values should have the (*R*)-configuration and the resolution conditions are similar to our previous reports.[30b] As a Lewis base, the oxygen of N—O could coordinate with trichlorosilane, which may be applied for the enantioselective reduction of ketoimines. We carried out the initial experiment with compound **4b** (10 mol %) as a catalyst. It exhibited high reactivity (yield of 99%) and moderate enantioselectivity (35%) in the enantioselective reduction of **5a**. Encouraged by the result, **4a** to **4f** were investigated and the results are summarized in Table 1.

It was found that catalyst bearing cyclic amides such as (*R*)-**4b**, **f** gave much higher ee than acyclic amides (entries 1, 3–5). And, almost quantitative conversions were observed with all ligands

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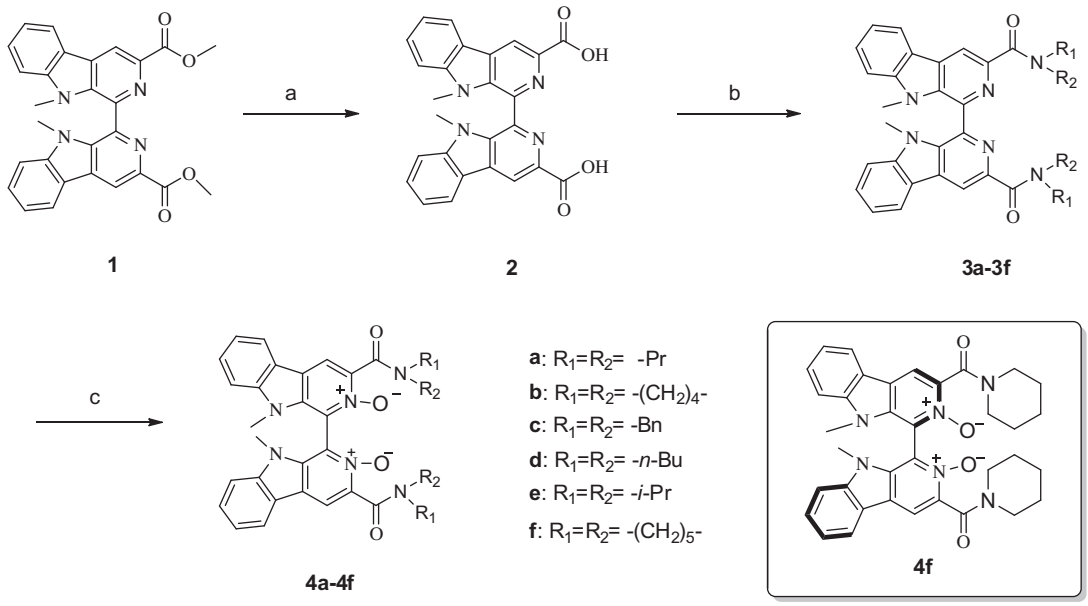
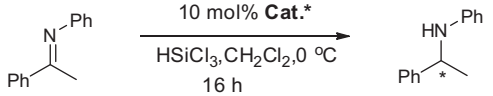


Scheme 1. Synthesis of chiral ligands **4a**–**4f**. Reaction conditions: (a) NaOH, H_2O, MeOH, 60 °C; (b) (i) isobutyl-chloroformate (2.4 equiv), Et_3N (2.4 equiv), DCM, 0 °C, 20 min, (ii) amine (2.2 equiv), rt, 12 h; (c) DCM, *m*-CPBA (6 equiv), rt, 12 h.

Table 1
Enantioselective hydrosilylation of ketoimine **5a** catalyzed by **4a**–**4f**



Entry	Ligand	Yield[b] (%)	Ee[c] (%)	Config.[d]
1	**4a**	99	47	*S*
2	**4b**	99	57	*S*
3	**4c**	99	50	*S*
4	**4d**	99	57	*S*
5	**4e**	>99	42	*S*
6	**4f**	>99	77	*S*

[a] All reactions were performed using **5a** (0.1 mmol) and $HSiCl_3$ (2 equiv) in the presence of **4f** at 0 °C for 16 h.
[b] Isolated yield.
[c] Determined by HPLC.
[d] The configuration was determined by comparing the sign of specific rotation value with the literature value.

(entries 1–6). Absolute configuration of *N*-(1-phenylethyl)aniline (**6a**) was assigned as (*S*) via comparing with previous experimental results and our recent study.[30b,31]

Influence of the catalyst loading for the reduction was then examined (Table 2). Surprisingly, when the catalyst amount increased to 20 mol %, the ee% was lower than that with 10 mol % of catalyst (entries 1 and 2). When it decreased to 1 mol %, the ee was improved to 83% without slowing down the reaction (Table 2, entries 2–4). However, if the catalyst was further reduced to 0.5 mol % or lower, both reactivity and enantioselectivity were significantly decreased (entry 5). Therefore, 1 mol % of **4f** was optimized in the standard conditions.

Effects of solvents and temperatures on the enantioselectivity were examined as well (Table 3). Good ee were observed (83%) at 0 °C. Neither higher nor lower temperature could increase the enantioselectivity (entries 1–6). Furthermore, dichloromethane was selected among chloroform, dichloroethane, toluene, acetonitrile, and THF (entries 6–10). The enantioselectivity in acetonitrile was only 13% (entry 9). Interestingly, no reactivity and enantioselectivity were observed when ethanol was used as the solvent (entry 12).

After the reaction conditions were optimized, a range of *N*-aryl ketoimines were investigated in the standard conditions by trichlorosiliane in the presence of 1 mol % of catalyst **4f** in dichloromethane at 0 °C. All the reductions using *N*-aryl ketoimines afforded excellent yield up to 99% (Table 4). Ketoimines **5b** and

Table 2
Influence of the amount of **4f** on the ee% in the reductions using **5a**

Entry	**4f** (%)	Time	Yield[b] (%)	ee[c] (%)
1	20	16	>99	75
2	10	16	>99	77
3	5	16	98	83
4	1	16	97	83
5	0.5	16	37	35

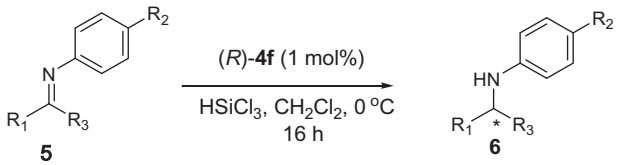
[a] All reactions were performed using **5** (0.1 mmol) and $HSiCl_3$ (2 equiv) in the presence of **4f** at 0 °C for 16 h.
[b] Isolated yield.
[c] Determined by HPLC.

Table 3
Effect of solvents and temperatures on the enantioselective reduction of ketoimine **5a**[a]

Entry	Solvent	*T* (°C)	Yield[b] (%)	ee[c] (%)
1	DCM	24	>99	51
2	DCM	10	>99	49
3	DCM	5	>99	60
4	DCM	0	>99	83
5	DCM	−10	95	71
6	DCM	−20	95	25
7	THF	0	97	82
8	$CHCl_3$	0	99	73
9	CH_3CN	0	90	13
10	CH_2ClCH_2Cl	0	99	76
11	Toluene	0	95	69
12	CH_3CH_2OH	0	—	—
13	DMF	0	70	0

[a] All reactions were performed using **5a** (0.1 mmol) and $HSiCl_3$ (2 equiv) in the presence of **4f** at 0 °C for 16 h.
[b] Isolated yield.
[c] Determined by HPLC.

Table 4
Enantioselective reduction of ketoimines **5a–l** with trichlorosilane catalyzed by (*R*)-**4f**



Entry	**5**, R_1, R_2, R_3	Yield[a] (%)	ee[b] (%)	OR[c]	Config.[d]
1	**5a**: Ph, H, Me	97	83	−12.0	*S*
2	**5b**: 4-F-Ph, H, Me	98	68	−12.8	*S*
3	**5c**: 4-Cl-Ph,H, Me	97	71	−8.2	*S*
4	**5d**: 4-Br-Ph, H, Me	96	80	14.5	*S*
5	**5e**: 4-NO_2-Ph,H,Me	96	67	31.9	*R*
6	**5f**: 4-MeO-Ph,H,Me	95	85	−15.3	*S*
7	**5g**: Ph, MeO, Me	97	75	−4.3	*S*
8	**5h**: Ph, EtO, Me	97	82	−15.8	*S*
9	**5i**: Ph, Me, Me	99	84	4.6	*R*
10	**5j**: Ph, Et, Me	97	71	−1.7	*S*
11	**5k**: Ph, Br, Me	98	71	25.1	*R*
12	**5l**: Ph, H, Et	95	81	−34.3	*S*

Unless specified, all reactions were carried out with 2 equiv of $HSiCl_3$, 1% (*R*)-**4f** in 1.5 ml CH_2Cl_2 at 0 °C for 16 h.
[a] Isolated yield.
[b] Determined by HPLC.
[c] The OR is measured by OR machine.
[d] The configuration was determined by comparing the sign of specific rotation value with the literature value.

5e with electron-withdrawing functional groups gave relatively moderate stereoselectivities with 68% and 67% ee (entries 2, 5). However, ketoimines **5f** and **5h** with the electron-donating group gave higher stereoselectivities (85%, 82% ee, entries 6, 8).

Because it was the first time that biscarboline *N*–O amides were employed in the enantioselective reductions, it is worth to discuss its plausible mechanism. It should be different from the one that the chiral catalysts contained a free –OH.[30b] In this case, the proton of –OH could chelate with the N atom of the C=N group and then the hydride on Si could transfer to imine carbon.

Firstly, the N—O group is necessary in the enantioselective hydrosilylation. If this group did not exist, such as **3a**, the product was only formed with a very low yield (less 20%) and less than 5% ee under the same conditions.

In our previous study, it was found that the two N—O oxygens were *trans* and therefore independent from each other in the presence of two five-membered rings in the structure of 9,9′-dimethyl-3,3′-di(pyrrolidine-1-carbonyl)-9*H*,9′*H*-[1,1′-bipyrido[3,4-*b*] indole] 2,2′-dioxide. This geometry can affect the following transition state structures and lead the product to different configurations.[30c] Presumably, the designed catalyst with six-membered ring skeleton could process a similar geometry to the five-membered-ring skeleton.

After conformational searches using MMFF94S force field, it was found that this catalyst with a six-membered ring has very similar geometry (Fig. 1, up) with that of five-membered ring although the reported catalyst with five-membered ring can catalyze enantioselective allylation of aldehydes with allyltrichlorosilanes. The transition state (TS) in the reduction of ketoimine with $HSiCl_3$ was thereby proposed as illustrated in Fig. 1 (down).

In the conformation with the lowest energy, the N—O oxygens were independent from each other in the presence of the two six-membered rings (Fig. 1, up). When the first $SiHCl_3$ approached to the catalyst, it would chelate with one of the two O—N groups. Then, the oxygen of amide C=O will chelate to the same silicon center and form the intermediate **7** (only half structure illustrated for clarity in Fig. 1). After this chelation, the second $SiHCl_3$ and PhC(Me)=NPh will bind with the intermediate **7** forming a 6-membered ring with two Ph groups orientated at *equatorial* position (pre-*S* configuration, TS structure **8**). The hydride of the first $HSiCl_3$ will attack the C=N and, the complex **8** will dissociate to the active catalyst **7** and the addition product **9**. Finally, this reaction can be quenched with saturated aqueous solution of NH_4Cl, and afford (*S*)-**6a** as the expected product.

Conclusion

In summary, we have developed a new chiral axial amide with *N*,*N*′-dioxide moiety and firstly utilized in enantioselective reduction of *N*-aryl ketoimines with trichlorosilane. This catalyst afforded high yields and good enantioselectivities under mild reaction conditions. A six-membered transition state responsible for the stereoselectivity was proposed in this catalysis.

Experimental section

All reactions were monitored by TCL. Flash chromatography was performed using silica gel (200–300 mesh). ^{1}H NMR was recorded with 400 or 600 MHz in $CDCl_3$ or DMSO with tetramethylsilane (TMS) as a reference. HPLC analysis was performed with chiral columns. Optical rotations were recorded using Na 589 nm.

Experimental procedure for preparation of 3e–4f *N*,*N*,*N*′,*N*′-tetraisopropyl-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-*b*]indole-3,3′-dicarboxamide (3e)

To a solution of **2** (0.45 g, 1 mmol) in anhydrous CH_2Cl_2 were added Et_3N (0.33 ml, 2.4 mmol) and isobutyl-chloroformate dropwise (0.31 ml, 2.4 mmol) at 0 °C. Piperidine (0.22 ml, 2.2 mmol) was added after 30 min. The reaction was slowly warmed to room temperature and detected with TLC. After the reaction finished, HCl aqueous solution (1 mol/L) was added to quench the reaction. Saturated $NaHCO_3$ aqueous solution was used to adjust pH to 7–8 and washed with brine, dried with over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the residue was purified with silica gel to get a yellow solid. Yield of 88%. IR (KBr, cm^{-1}), 3428, 2969, 1639, 1445, 1392, 1312, 1237, 1131, 1006, 748. MS-ESI, *m*/*z* 616 $[M+H]^+$. HR-MS *m*/*z* calcd for $C_{42}H_{52}N_6O_2$ 616.3530, found 616.3526. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1 H×2), 8.17 (d, J = 7.8 Hz, 1 H×2), 7.58 (t, J = 7.6 Hz, 1 H×2), 7.35 (m, 2 H×2), 3.42 (s, 3 H×2), 3.25 (m, 4 H×2), 1.74–1.40 (m, 2 H×2), 1.39–1.10 (m, 2 H×2), 0.98 (t, J = 7.3 Hz, 3 H×2), 0.85 (t, J = 7.3 Hz, 3 H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 145.7, 137.2, 128.6, 122.3, 121.0, 120.6, 116.0, 109.8, 47.0, 44.8, 30.8, 29.9, 28.2, 20.3, 19.8, 14.0.

(9,9′-Dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-*b*]indole-3,3′-diyl)bis(piperidin-1-ylmethanone) (3f)

Following the general procedure above, **3f** was obtained as yellow solid yield 67%. IR (KBr) n = 3425, 2931, 1615, 1541, 1439, 1408, 1266, 1131, 1044, 756 cm^{-1}. MS-ESI, *m*/*z* 584 $[M+H]^+$. HR-MS *m*/*z* calcd for $C_{36}H_{36}N_6O_2$ 584.2900, found 584.2886. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1 H×2), 8.22 (d, J = 13.4 Hz, 1 H×2), 7.64 (t, J = 7.3 Hz, 1 H×2), 7.38 (dd, J = 14.2, 7.7 Hz, 2 H×2), 4.15-3.36 (m, 4 H×2), 3.23 (s, 3 H×2), 1.87–1.13 (m, 4 H×2), 0.91 (m, 2 H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 143.1, 135.9, 129.6, 122.0, 120.8, 115.8, 109.9, 48.7, 43.7, 31.8, 26.6, 25.5, 24.5.

3,3′-Bis(diisopropylcarbamoyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-*b*]indole 2,2′-dioxide (4e)

To a stirred solution of **3e** (0.29 g, 0.5 mmol) in CH_2Cl_2 (25 ml) was added *m*-chlorobenzoperoxoic acid (*m*-CPBA) (75%, 1.5 mmol)

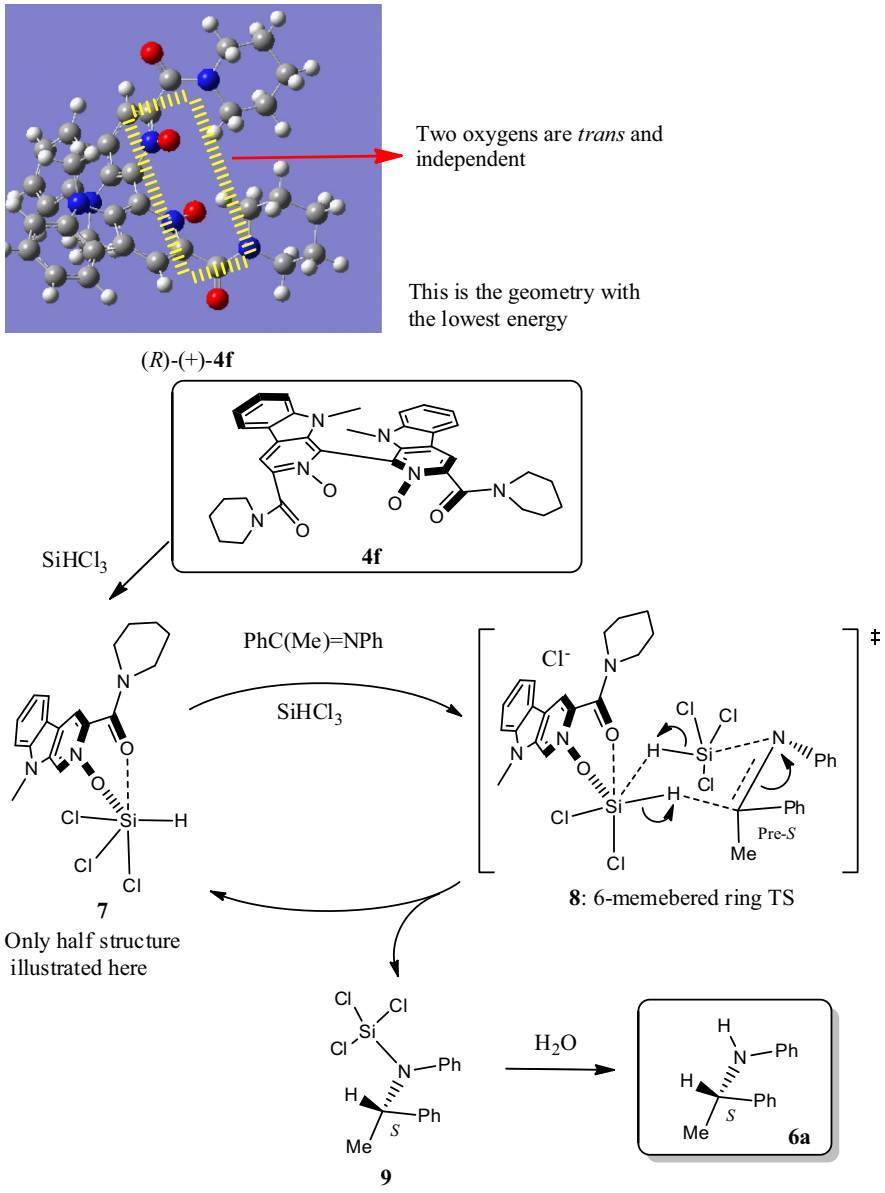


Figure 1. The structure of free ligand (up, color picture) and the plausible transition state structures for the formation of (*S*)-**6a** from **5a**.

at 0 °C. The reaction was quenched with saturated $NaHCO_3$ and washed with brine after completion. The organic layer was concentrated and the residue was purified through silica gel chromatography (DCM/MeOH = 50:1) to afford **4e** as yellow solid, yield 65%. IR (KBr) n = 3428, 2969, 1639, 1445, 1392, 1312, 1237, 1131, 1006, 748 cm^{-1}. MS-ESI, m/z 649 $[M+H]^+$. HR-MS m/z calcd for $C_{38}H_{44}N_6O_4$ 616.3424, found 616.3417. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1 H×2), 8.06 (d, J = 16.4 Hz, 1 H×2), 7.59 (t, J = 7.4 Hz, 1 H×2), 7.42–7.31 (m, 1 H×2), 3.84 (dt, J = 12.6, 6.3 Hz, 1 H×2), 3.60 (dt, J = 13.5, 6.8 Hz, 1 H×2), 3.44 (s, 3 H×2), 1.63 (d, J = 6.7 Hz, 3 H×2), 1.59 (d, J = 6.7 Hz, 3 H×2), 1.31 (d, J = 6.4 Hz, 3 H×2), 1.14 (d, J = 5.8 Hz, 3 H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 143.6, 138.3, 128.4, 124.5, 121.8, 121.1, 120.9, 114.6, 109.8, 51.5, 46.2, 29.5, 21.3, 21.1, 20.6, 19.8. $[\alpha]_D$ +568 (c 0.28, $CHCl_3$).

9,9′-Dimethyl-3,3′-di(piperidine-1-carbonyl)-9*H*,9′*H*-1,1′-bipyrido[3,4-*b*]indole 2,2′-dioxide (4f)

Following the general procedure, a yellow power was obtained, yield 63%. IR (KBr) n = 3441, 1634, 1446, 1392, 1335, 1256, 1132, 1006, 749 cm^{-1}. MS-ESI, m/z 617$[M+H]^+$. HR-MS m/z calcd for $C_{36}H_{36}N_6O_4$ 616.2798, found 616.2778. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1 H×2), 7.98 (d, J = 7.8 Hz, 1 H×2), 7.49 (t, J = 7.5 Hz, 1 H×2), 7.33–7.21 (m, 2 H×2), 3.36 (s, 3 H×2), 3.30 (t, 4 H×2), 1.63–1.17 (m, 6 H×2).^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 143.5, 137.9, 128.4, 124.6, 121.5, 121.3, 120.9, 120.8, 116.1, 109.8, 47.7, 42.9, 29.5, 26.2, 25.3, 24.4. $[\alpha]_D$ +492 (c 0.98, $CHCl_3$).

General procedure for enantioselective reduction of ketimines with trichlorosilane

To a stirred solution of **4f** (1 mol %) in anhydrous CH_2Cl_2, the imine was added under nitrogen at 0 °C. After 30 min, trichlorosilane (2 equiv) was added to the mixture dropwise and the reaction was allowed to stir at the same temperature for 16 h. The reaction was quenched by saturated $NaHCO_3$ (2 ml) and allowed to warm up to room temperature. The mixture was extracted by CH_2Cl_2 three times. The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated with reduced pressure. The crude product was purified by column chromatography (silica gel, hexane/EtOAc) to afford pure amine **6**.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.03.100.

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