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Tetrahedron: *Asymmetry* 18 (2007) 705–709

Enantioselective hydrosilylation of ketimines catalyzed by Lewis basic C_2-symmetric chiral tetraamide

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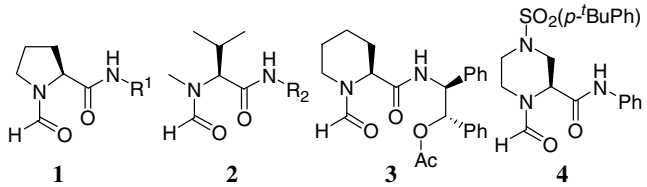
Received 28 November 2006; revised 3 March 2007; accepted 7 March 2007

Abstract—L-Proline derived C_2-symmetric chiral tetraamide **5b** was found to behave as an effective Lewis basic catalyst in the enantioselective hydrosilylation of ketimines, affording high isolated yields (up to 95%) and moderate to high enantioselectivities (up to 86% ee) for a broad range of ketimines. A clear synergistic effect of the two identical diamide units of **5b** was observed for asymmetric induction.

1. Introduction

Chiral amides have recently been developed as efficient Lewis basic organocatalysts for the asymmetric hydrosilylation of imines with trichlorosilane ($HSiCl_3$).[1–5] Matsumura first reported that L-proline derived amide **1** (Fig. 1) could catalyze this transformation with high yield and low to moderate enantioselectivity (<66% ee).[2a] Later, Malkov and Kocovsky disclosed that when L-valine derived amide catalyst **2** was used as the catalyst, significantly improved enantioselectivities (<92% ee) were obtained.[3a] In our recent report, we presented the first highly enantioselective Lewis basic amide catalyst **3** which displayed a broad substrate spectrum, promoting the hydrosilylation of a wide range of ketimines with up to 96% ee values.[4a] Very recently, we successfully developed another highly enantioselective amide catalyst **4**, of which the substrate scope is complementary to that of **3**.[4b]



1 **2** **3** **4**

a, R^1 = Ph **b**, R^1 = 1-Naphthyl

a, R^2 = Ph **b**, R^2 = 3,5-$Me_2C_6H_3$

Figure 1.

A common feature of the molecular structures of catalysts **1**–**4** is that they all contain two closely positioned amide functionalities (a diamide unit), including an *N*-formamide. The chelation of the oxygen atoms of these two amide groups with the central silicon atom of $HSiCl_3$ was believed to be a prerequisite for the operation of the catalyst over the course of the reaction.[2a,3] We were recently interested in designing new, structurally simple C_2-symmetric catalysts bearing two such identical diamide units and evaluating their efficacies for the asymmetric hydrosilylation of imines. The two identical diamide units could either function cooperatively or separately and thus endow the resulting C_2-symmetric tetraamide catalysts with different reactivities and/or enantioselectivities compared with the diamide catalysts. The results might shed some light on the mechanism of the Lewis base catalyzed asymmetric hydrosilylation, of which the transition state models in the literature are still debatable.[2,3a,5b,c] Thus we prepared a set of α-amino acid derived C_2-symmetric chiral tetraamide catalysts **5**–**8** (Fig. 2) and tested their effects in the hydrosilylation of *N*-aryl ketimines. Herein, we report the results, which reveal for the first time that the C_2-symmetric chiral tetraamide **5b**[6] behaved as an efficient enantioselective Lewis basic catalyst, affording up to 95% yield and 86% ee value.

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doi:10.1016/j.tetasy.2007.03.008

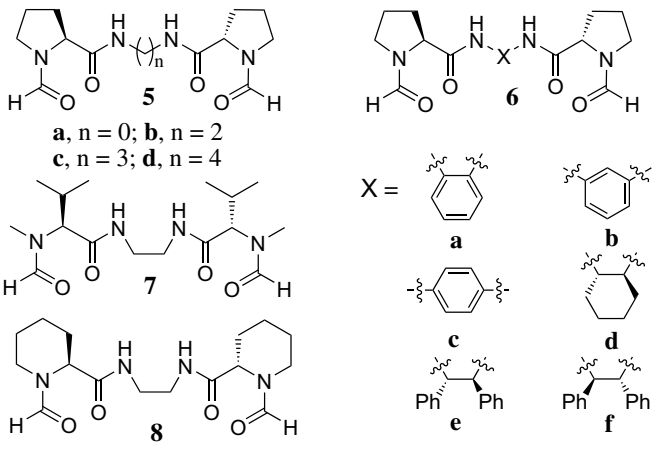


Figure 2.

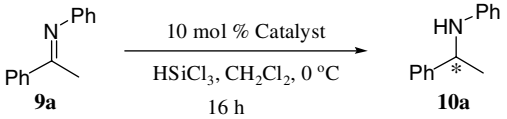
2. Results and discussion

Catalysts **5** and **6** were easily prepared by starting from the readily available *N*-Boc-L-proline and the corresponding diamines according to Scheme 1. Catalysts **7** and **8** were prepared similarly starting from the corresponding *N*-Boc protected amino acids and ethylenediamine.

With these catalysts in hand, we next tested their catalytic efficiencies in the hydrosilylation of **9a** with $HSiCl_3$ at 0 °C in CH_2Cl_2. As illustrated in Table 1, the linkage of the two proline diamide units proved to have significant impacts on the enantioselectivity of catalysts **5** and **6**. For catalysts **5**, the two-carbon linkage seems to be the best. Catalyst **5b** gave an ee of 77% (entry 2), whereas **5a**, **5c**, and **5d** with either a shorter or longer linkage afforded much lower enantioselectivities (entries 1, 3, and 4). Aromatic linkages in **6a**–**c** were found to be unfavorable (entries 5–7), so were the substituted two-carbon linkages in **6d**–**f** (entries 8–10).

Interestingly, while both the L-valine backbone and the L-pipecolinic acid backbone have proven to be superior to the L-proline backbone in the diamide catalyst system for asymmetric induction,[3,4a] in the C_2-symmetric tetraamide catalyst system, a completely different scenario was observed. Catalysts **7** and **8** with the L-valine backbone and the L-pipecolinic acid backbone, respectively, both exhibited much lower enantioselectivity than the L-proline derived catalyst **5b** under identical conditions (entries 11 and 12 vs entry 2).

Table 1. Asymmetric hydrosilylation of imine **9a** with different catalysts



Entry	Catalyst	Yield[a] (%)	ee[b] (%)	Configuration[c]
1	**5a**	51	<10	(*R*)
2	**5b**	93	77	(*R*)
3	**5c**	87	43	(*R*)
4	**5d**	64	25	(*R*)
5	**6a**	84	47	(*R*)
6	**6b**	70	11	(*R*)
7	**6c**	77	19	(*R*)
8	**6d**	82	24	(*R*)
9	**6e**	77	<10	(*R*)
10	**6f**	82	<10	(*S*)
11	**7**	64	16	(*S*)
12	**8**	97	<10	(*S*)
13	**11**	68	38	(*R*)
14	**12**	92	20	(*R*)

[a] Isolated yield based on the imine.
[b] Determined using chiral HPLC.
[c] Identified by comparison of the HPLC data with the literature data.

To explore if the two identical diamide units of the most effective C_2-symmetric tetraamide catalyst **5b** are dependent upon each other for the asymmetric induction, the truncated molecules **11** and **12** (Fig. 3) were synthesized and tested as catalysts in the hydrosilylation of **9a**. Interestingly, both **11** and **12** displayed dramatically decreased enantioselectivities compared with **5b** under identical conditions (entries 13 and 14 vs entry 2, Table 1), clearly indicating a synergistic effect of the two L-prolyl diamide units of **5b**.

Catalyst **5b** was also found to be effective for the asymmetric hydrosilylation of a broad range of other ketimines **9a**–**k** (Table 2), including aromatic and aliphatic ones. In the

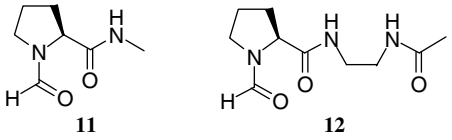
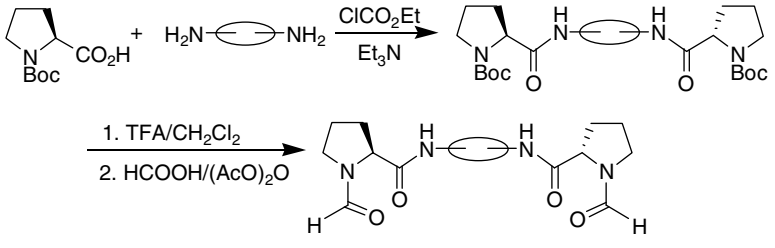
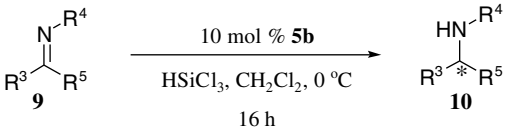


Figure 3.



Scheme 1.

Table 2. Asymmetric hydrosilylation of various imines catalyzed by **5b**



Entry	Imine	R	Yield[a] (%)	ee[b] (%)
1	**9a**	C_6H_5	93	77
2	**9b**	4-BrC_6H_4	95	74
3	**9c**	4-$NO_2C_6H_4$	88	74
4	**9d**	4-$MeOC_6H_4$	82	75
5	**9e**	2-Np	90	70
6	**9f**	6-MeONp	82	70
7	**9g**	*c*-C_6H_{11}	74	61
8	**9h**	4-ClC_6H_4	95	68
9	**9i**	4-$MeOC_6H_4$	77	73
10	**9j**	Et	93	78
11	**9k**	^{n}Pr	88	80
12	**9l**	^{n}Bu	87	79
13	**9m**	^{i}Bu	78	86

[a] Isolated yield based on the imine.
[b] Determined using chiral HPLC.

presence of 10 mol % **5b**, 74–95% yields and 61–86% ee values were obtained.

On the basis of the above experimental data, we propose that the **5b**-catalyzed hydrosilylation of ketimines occurred via either transition state **I** or **II**,[7] both of which could reasonably explain the synergistic effects of the two diamide units and the absolute configuration of the product as well (Fig. 4).

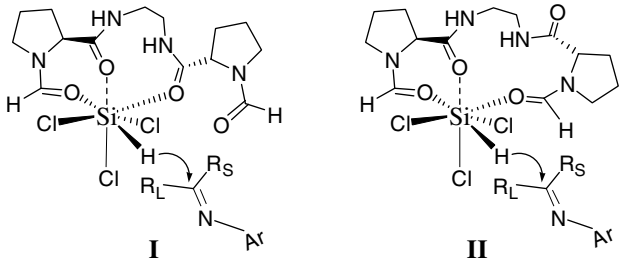


Figure 4.

3. Conclusions

In conclusion, we have shown that structurally simple C_2-symmetric tetraamides could work as effective Lewis basic catalysts for the asymmetric hydrosilylation of ketimines. Compound **5b**, easily prepared by starting from L-proline, catalyzed the hydrosilylation of a broad range of *N*-aryl ketimines in high isolated yield with good enantioselectivity. The two identical diamide units of the catalyst proved to work cooperatively for the asymmetric induction.

4. Experimental

4.1. General procedure for the synthesis of catalysts

To a solution of Boc-L-amino acid (10.0 mmol) and TEA (1.0 g, 10.0 mmol) in THF (40 mL) was added ethyl chloroformate (1.1 g, 10.0 mmol) dropwise at 0 °C. After stirring for 0.5 h, diamine (5.0 mmol) was introduced. The resulting solution was continued to stir at 0 °C for 1 h, at room temperature for 16 h, and then at reflux for 3 h. The reaction was then cooled down to room temperature and diluted with ethyl acetate. After filtration and removal of solvents under reduced pressure, the residue was purified through column chromatography on silica gel to give the *N*,*N*′-di-Boc protected diamide, which was then treated with 20 vol % TFA in CH_2Cl_2 (40 mL). After stirring for 1 h, the solution was concentrated under reduced pressure. The residue was dissolved in formic acid (1.5 mL) and the solution was then cooled down to 0 °C. Acetic anhydride (1 mL) was added dropwise at the same temperature. The mixture was warmed to room temperature and allowed to stir overnight. After removal of solvents under reduced pressure, the residue was purified though column chromatography on silica gel to give pure product.

4.1.1. *N*,*N*′-Di-(*N*-formyl-L-prolyl)-hydrazine 5a. Viscous liquid, yield: 63%, $[\alpha]_D^{20} = -137.0$ (*c* 0.108, EtOH); ^{1}H NMR (300 MHz, CD_3OD): $\delta = 1.89$–2.30 (m, 4H), 3.30–3.35 (m, 2H), 4.38–4.54 (m, 1H), 8.25 (s, 1H); ^{13}C NMR (150 MHz, CD_3OD): $\delta = 22.5$, 23.6, 29.6, 30.2, 44.0, 46.7, 56.4, 58.8, 162.1, 162.9, 171.4, 171.7. ESI HRMS exact mass calcd for $(C_{12}H_{18}N_4O_4+Na)^+$ requires *m*/*z* 305.1220; found, 305.1226.

4.1.2. *N*,*N*′-Di-(*N*-formyl-L-prolyl)-ethane-1,2-diamine 5b. Viscous liquid, yield: 75%; $[\alpha]_D^{20} = -81.25$ (*c* 0.16, EtOH). The major conformer, ^{1}H NMR (600 MHz, CD_3OD): $\delta = 1.87$–2.29 (m, 8H), 3.31–3.36 (m, 4H), 3.64–3.71 (m, 4H), 4.26–4.30 (m, 2H), 8.25 (s, 2H); ^{13}C NMR (150 MHz, MeOD): $\delta = 22.5$, 23.67, 29.63, 29.7, 38.6, 38.9, 44.0, 46.8, 58.2, 60.2, 162.3, 162.4, 172.9, 173.2; ESI HRMS exact mass calcd for $(C_{14}H_{22}N_4O_4+Na)^+$ requires *m*/*z* 333.1533; found, 333.1522.

4.1.3. *N*,*N*′-Di-(*N*-formyl-L-prolyl)-propane-1,3-diamine 5c. Viscous liquid, yield: 73%, $[\alpha]_D^{20} = -89.0$ (*c* 0.132, EtOH). The major conformer, ^{1}H NMR (300 MHz, CD_3OD): $\delta = 1.69$–2.30 (m, 5H), 3.17–3.23 (m, 2H), 3.53–3.69 (m, 2H), 4.30–4.46 (m, 1H), 8.26 (s, 1H); ^{13}C NMR (150 MHz, CD_3OD): $\delta = 22.5$, 23.7, 28.6, 29.8, 30.2, 36.1, 36.3, 44.0, 46.8, 58.2, 60.2, 162.3, 162.9, 172.7, 172.9. ESI HRMS exact mass calcd for $(C_{15}H_{24}N_4O_4+Na)^+$ requires *m*/*z* 347.1690; found, 347.1673.

4.1.4. *N*,*N*′-Di-(*N*-formyl-L-prolyl)-butane-1,4-diamine 5d. White solid, yield: 70%, mp 146.0–148.0 °C, $[\alpha]_D^{20} = -111.0$ (*c* 0.136, EtOH); ^{1}H NMR (600 MHz, DMSO-d_6): $\delta = 1.36$–1.38 (m, 2H), 1.73–1.90 (m, 3H), 2.07–2.14 (m,

1H), 3.02–3.07 (m, 2H), 3.48–3.6 (m, 1H), 3.57–3.61 (m, 1H), 4.14–4.16 (m, 1H), 8.19 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): $\delta = 23.0$, 24.0, 26.8, 26.9, 30.3, 30.6, 38.6, 38.8, 44.2, 46.7, 57.8, 59.7, 161.5, 161.9, 171.4, 171.8. ESI HRMS exact mass calcd for $(C_{16}H_{24}N_4O_4+Na)^+$ requires m/z 361.1846; found, 361.1826.

4.1.5. *N*,*N*′-Di-(*N*-formyl-L-prolyl)-benzene-1,2-diamine 6a. White solid, yield: 67%, mp 63.0–69.0 °C, $[\alpha]_D^{20} = -69.5$ (c 0.154, EtOH); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.87$–2.40 (m, 8H), 3.56–3.66 (m, 4H), 4.65 (t, $J = 6.12$ Hz, 2H), 7.07–7.16 (m, 2H), 7.58 (m, 2H), 8.26 (s, 2H), 9.20 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 23.1$, 24.3, 28.7, 30.6, 44.4, 47.2, 58.7, 61.1, 124.9, 125.9, 130.0, 161.8, 170.1. ESI HRMS exact mass calcd for $(C_{18}H_{22}N_4O_4+Na)^+$ requires m/z 381.1533; found, 381.1540.

4.1.6. *N*,*N*′-Di-(*N*-formyl-L-prolyl)-benzene-1,3-diamine 6b. White solid, yield: 65%, mp 113.0–117.0 °C, $[\alpha]_D^{20} = -160.0$ (c 0.14, EtOH); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.83$–2.24 (m, 8H), 3.47–3.68 (m, 4H), 4.56 (t, $J = 6.48$ Hz, 2H), 6.95 (t, $J = 8.16$ Hz, 1H), 7.21 (d, $J = 7.68$ Hz, 2H), 7.70 (s, 1H), 8.26 (s, 2H), 9.77 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 24.3$, 29.2, 47.1, 47.2, 58.8, 110.7, 115.0, 129.0, 138.4, 161.7, 161.8, 169.9, 171.1. ESI HRMS exact mass calcd for $(C_{18}H_{22}N_4O_4+Na)^+$ requires m/z 381.1533; found, 381.1534.

4.1.7. *N*,*N*′-Di-(*N*-formyl-L-prolyl)-benzene-1,4-diamine 6c. White solid, yield: 68%, mp 206.0–208.0 °C, $[\alpha]_D^{20} = -194.0$ (c 0.1, EtOH); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.89$–2.37 (m, 4H), 3.64–3.75 (m, 2H), 4.63 (t, $J = 6.15$ Hz, 1H), 7.28 (s, 2H), 8.35 (s, 1H), 9.51 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 24.3$, 28.3, 47.3, 58.7, 119.7, 120.0, 134.3, 161.8, 168.7. ESI HRMS exact mass calcd for $(C_{18}H_{22}N_4O_4+Na)^+$ requires m/z 381.1533; found, 381.1536.

4.1.8. *N*,*N*′-Di-(*N*-formyl-L-prolyl)-(1*S*,2*S*)-cyclohexane-1,2-diamine 6d. White solid, yield: 62%, mp 240.0–241.0 °C, $[\alpha]_D^{20} = -148.3$ (c 0.160, EtOH); ^{1}H NMR (600 MHz, CD_3OD): $\delta = 1.29$–1.39 (m, 4H), 1.78–2.27 (m, 12H), 3.45–3.71 (m, 6H), 4.25–4.44 (m, 2H), 8.23 (s, 2H); ^{13}C NMR (150 MHz, CD_3OD): $\delta = 22.5$, 23.7, 24.4, 29.7, 30.2, 31.7, 44.0, 46.7, 52.7, 52.8, 58.2, 60.6, 162.2, 163.3, 172.7, 172.4. ESI HRMS exact mass calcd for $(C_{12}H_{18}N_4O_4+Na)^+$ requires m/z 305.1220; found, 305.1226. ESI HRMS exact mass calcd for $(C_{18}H_{28}N_4O_4+Na)^+$ requires m/z 387.2003; found, 387.2001.

4.1.9. *N*,*N*′-Di-(*N*-formyl-L-prolyl)-(1*R*,2*R*)-1,2-diphenyl-ethane-1,2-diamine 6e. White solid, yield: 52%, mp 222.0–225.0 °C, $[\alpha]_D^{20} = -127.9$ (c 0.104, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6): $\delta = 1.47$–2.10 (m, 8H), 3.18–3.61 (m, 4H), 4.17–4.38 (m, 2H), 5.21–5.31 (m, 2H), 7.11–7.22 (m, 10H), 7.94 and 7.91 (s, 1H), 8.25 and 8.23 (s, 1H), 8.44 and 8.39 (d, $J = 7.44$ Hz, 1H), 8.71 and 8.59 (d, $J = 6.78$ Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): $\delta = 22.9$, 23.9, 29.9, 30.3, 30.6, 44.2, 46.7, 57.2, 57.8, 59.6, 127.2, 127.3, 127.4, 127.5, 127.6, 128.2, 128.3, 140.4, 140.5, 161.8, 162.1, 171.3, 171.8. ESI HRMS exact mass calcd for $(C_{26}H_{30}N_4O_4+Na)^+$ requires m/z 485.2159; found, 385.2137.

4.1.10. *N*,*N*′-Di-(*N*-formyl-L-prolyl)-(1*S*,2*S*)-1,2-diphenyl-ethane-1,2-diamine 6f. White solid, yield: 55%, mp 139.0–143.0 °C, $[\alpha]_D^{20} = -61.5$ (c 0.104, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6): $\delta = 1.20$–2.00 (m, 8H), 3.22–3.30 (m, 2H), 3.39–3.53 (m, 2H), 4.13–4.18 (m, 1H), 4.35 (m, 3.18 Hz, 1H), 5.32 (d, $J = 7.8$ Hz, 1H), 5.40 (d, $J = 7.44$ Hz, 1H), 7.13–7.32 (m, 10H), 7.90 and 7.91 (s, 1H), 8.14 and 8.15 (s, 1H), 8.28 (d, $J = 7.86$ Hz, 1H), 8.41 (d, $J = 8.82$ Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): $\delta = 22.8$, 23.9, 29.8, 30.5, 44.1, 46.6, 56.8, 57.2, 57.7, 59.6, 127.2, 127.2, 127.3, 127.4, 127.5, 127.5, 128.2, 128.3, 140.4, 140.6, 161.3, 161.9, 171.2, 171.5. ESI HRMS exact mass calcd for $(C_{26}H_{30}N_4O_4+Na)^+$ requires m/z 485.2159; found, 485.2137.

4.1.11. *N*,*N*′-Di-(*N*-methylformyl-L-valinyl)-ethane-1,2-diamine 7. White solid, yield: 48%, $[\alpha]_D^{20} = -71.1$ (c 0.242, CH_3OH); ^{1}H NMR (300 MHz, CD_3OD); $\delta = 0.84$ (d, $J = 6.57$ Hz, 6H), 1.19–1.24 (m, 1H), 2.97 (s, 3H), 3.29–3.47 (m, 2H), 4.07–4.28 (m, 1H), 8.08 (s, 1H); ^{13}C NMR (150 MHz, CD_3OD): $\delta = 13.5$, 17.5, 18.2, 18.3, 26.4, 26.5, 30.5, 38.4, 38.9, 39.7, 61.0, 68.1, 164.1, 164.5, 170.3, 170.4. ESI HRMS exact mass calcd for $(C_{16}H_{30}N_4O_4+Na)^+$ requires m/z 365.2159; found, 365.2148.

4.1.12. *N*,*N*′-Di-(*N*-formyl-L-piperidyl)-ethane-1,2-diamine 8. Viscous liquid, yield: 51%, $[\alpha]_D^{20} = -114.4$ (c 0.104, EtOH), ^{1}H NMR (600 MHz, CD_3OD): $\delta = 1.38$–1.67 (m, 8H), 2.25–2.33 (m, 3H), 2.80–2.85 (m, 1H), 3.27–3.39 (m, 4H), 3.62–3.64 (d, $J = 13.08$ Hz, 2H), 4.24–4.26 (m, 1H), 4.32–4.34 (m, 1H), 4.90–4.92 (m, 2H), 8.11 (s, 2H); ^{13}C NMR (150 MHz, CD_3OD): $\delta = 20.7$, 20.8, 24.18, 25.2, 25.9, 27.0, 39.1, 39.1, 44.4, 51.3, 57.6, 163.5, 171.1, 171.5; ESI HRMS exact mass calcd for $(C_{16}H_{26}N_4O_4+Na)^+$ requires m/z 361.1846; found, 361.1856.

4.2. General procedure for the synthesis of imines

A mixture of $NaHCO_3$ (50 mmol), amine (10 mmol), ketone (10 mmol) and activated molecular 4 Å sieves (8.0 g) in anhydrous toluene (10 mL) was heated at 80 °C for 12 h under an argon atmosphere. The mixture was filtered through Celite. The filtrate was then evaporated in vacuo and the product crystallized from appropriate solvents or purified by distillation to give pure imine.

4.3. General procedure for catalytic hydrosilylation of imines

Under an argon atmosphere, trichlorosilane (40 μL, 0.4 mmol) was added dropwise to a stirred solution of imine **9** (0.20 mmol) and catalyst **5b** (6.2 mg, 0.02 mmol) in anhydrous CH_2Cl_2 at 0 °C. The mixture was allowed to stir at the same temperature for 16 h. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (5 mL) and was extracted with EtOAc. The combined extracts were washed with brine and dried over anhydrous $MgSO_4$. Solvents were evaporated. The crude product was purified by column chromatography (silica gel, hexane/EtOAc) to afford pure amine **10**. The ee values were determined by using established HPLC techniques with chiral stationary phases.

Acknowledgement

We are grateful for the financial supports from the National Natural Science Foundation of China (Projects 20402014 and 20672107).

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