Tetrahedron 68 (2012) 1371–1375

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Highly efficient and convenient asymmetric hydrosilylation of ketones catalyzed with zinc Schiff base complexes

Shuai Liu, Jiajian Peng *, Hu Yang, Ying Bai, Jiayun Li, Guoqiao Lai *

Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, 222 Wenyi Rd, Hangzhou 310012, China

ARTICLE INFO

Article history:
Received 20 September 2011
Received in revised form 13 December 2011
Accepted 20 December 2011
Available online 28 December 2011

Keywords:
Asymmetric catalysis
Ketones
Hydrosilylation
α-Amino acids based Schiff base

ABSTRACT

Several chiral Schiff base ligands derived from α-amino acids were prepared, and zinc complexes with these chiral Schiff base ligands prepared were tested for the catalytic asymmetric hydrosilylation of ketones, and the results showed that excellent ee values were obtained, which are the prominent examples of catalytic asymmetric hydrosilylation of ketones catalyzed with zinc complexes in the presence of readily available and inexpensive α-amino acids based Schiff base ligands.

1. Introduction

Chiral secondary alcohols are important chiral building blocks in synthetic organic chemistry, especially in the preparations of pharmaceuticals, flavor and fragrance, and agrochemicals.[1–3] As regards the preparation of chiral secondary alcohols, in comparison with other major catalytic methods for the reduction of carbonyl groups, i.e., hydrogenation and hydrogen transfer, asymmetric hydrosilylation (AHS) presents the advantages of simplicity of the procedure combined with the use of inexpensive and stable silanes as reducing agents.[4] Asymmetric hydrosilylation of prochiral ketones has been known since the early 1970s, and chiral rhodium phosphines, or nitrogen complexes,[5,6] titanium complexes coordinated by chiral diamines[7] or binaphthol,[8] and chiral ammonium fluoride[9] etc. had been proved to be effective catalysts. Recently, the use of copper hydride in the hydrosilylation of aryl ketones with excellent results has been reported by Lipschutz.[10] Zinc complexes of chiral secondary amines were introduced by Mimoun as chiral catalysts for the enantioselective hydrosilylation of ketones.[3] Most frequently used chiral secondary amines include derivatives of 1-phenylethylamine, *trans*-1,2-diaminocyclohexane, *trans*-1,2-diaminocyclopentane, and 1,2-diphenyl-1,2-diaminoethane. Introduction of two chiral centers into the ligand gave rise to synergistic effects, leading to an increase of the enantioselectivity of hydrosilylation reaction.[11,12] Recent work in the enantioselective hydrosilylation of ketones reported by Gajewy and co-workers has demonstrated that an efficient enantioselective catalyst can be prepared from Zinc–Macrocyclic Oligoamine Complexes, with enantioselectivities up to 89% ee.[13] These procedures usually make the use of inexpensive, easily handled, non-toxic, and air and moisture stable polymethylhydrosiloxane (PMHS) or monomeric silanes as the reducing agents.[14] One of the main goal of current studies on AHS is the development of catalytic systems that would comply with the criteria of high efficiency (yield, enantioselectivity), low cost and feasibility of recovery of the catalyst as well as with possible environmental friend.[15] Herein we reported that enantioselective reduction of ketones by $HSi(OEt)_3$ was catalyzed with diethylzinc coordinated with Schiff bases ligands derived from substituted salicylaldehydes and inexpensive chiral α-amino acids **1**–**9** (see Fig. 1).

2. Results and discussion

2.1. Asymmetric hydrosilylation

The effect of the volume ratio of THF/*tert*-butanol and the reaction temperature on the catalytic activity and enantioselectivity are summarized in Table 1. The optical purity of product alcohol was largely influenced by addition of *tert*-butanol as co-solvent. Thus, the ee values of product were varied from 78% to 96% along with the increasing volume of *tert*-butanol added from 0 mL to 0.4 mL (entries 1–5, Table 1). It was found that the best result was obtained when the ratio of THF/*tert*-butyl alcohol (v/v) was 3:0.4

* Corresponding authors. Fax: +86 571 28865135; e-mail addresses: jjpeng@hznu.edu.cn (J. Peng), gqlai@hznu.edu.cn (G. Lai).

0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2011.12.054

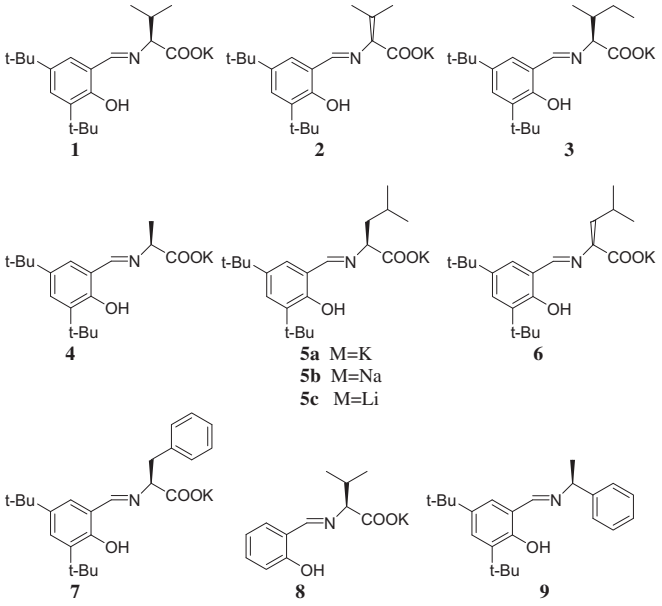


Fig. 1. Structures of Schiff base ligands prepared.

Table 1
Effect of the volume ratio of THF/*tert*-butanol and the reaction temperature on the catalytic activity and enantioselectivity[a]

Entry	Solvent (THF/*tert*-butanol, v/v)	*T* (°C)	Yield[c] (%)	ee[b] (%)
1	3.4:0	−40	77	78
2	3:0.1	−40	76	80
3	3:0.2	−40	73	85
4	3:0.3	−40	72	89
5	3:0.4	−40	71	96
6	3:0.5	−40	62	96
7	3:0.4	25	91	65
8	3:0.4	0	88	71
9	3:0.4	−10	82	77
10	3:0.4	−20	79	80
11	3:0.4	−30	74	89
12	3:0.4	−40	71	96
13	3:0.4	−50	52	97

[a] Reaction conditions: $(EtO)_3SiH$ 2.5 equiv, $ZnEt_2$ 3 mol %, chiral ligand 1, 3 mol %, 30 h.
[b] Enantiomeric excess (ee) determined by GC analysis with a CP-ChiralSil-Dex CB column.
[c] Isolated yields.

(entry 5, Table 1). Additionally, lower reaction temperature, for example, −40 °C, was need to achieve higher ee hydrosilylation product (entry 6, Table 1). Elevating the reaction temperature from −40 °C to 25 °C (entries 6–10, Table 1) caused a significant loss of enantioselectivity.

The ligands **1**–**7** were readily obtained from simple condensation of 3,5-di-*tert*-butylsalicyldehyde with the corresponding α-amino acid via established methods. According to the general procedures described for the enantioselective hydrosilylation of prochiral ketones,[3,12] acetophenone was treated with 3 mol % of diethylzinc, and 3 mol % of the chiral ligand in THF solvent in the presence of 2.5 equiv of $(EtO)_3SiH$ −40 °C for 30 h, and the results are summarized in Table 2.

The results listed in Table 2 indicated that the ligand plays an important role on the catalytic activity and the enantioselectivity. Meanwhile, substituents attached on aromatic ring of substituted salicylaldehyde have a great impact on ee values. Interestingly, we investigated other carboxylate such as −COONa and −COOLi derived from L-leucine it was found that ee values decreased to 30% and 15%,

Table 2
Asymmetric hydrosilylation of acetophenone with $HSi(OEt)_3$[a]

Entry	Ligands (see Fig. 1)	Yield[c] (%)	ee[b] (%)
1	**1**	71	96(*S*)
2	**2**	72	92(*R*)
3	**3**	75	88(*S*)
4	**4**	75	68(*S*)
5	**5a**	80	87(*S*)
6	**5b**	82	30(*S*)
7	**5c**	75	15(*S*)
8	**6**	85	86(*R*)
9	**7**	67	87(*S*)
10	**8**	70	70(*S*)
11	**9**	Trace	—

[a] Reaction conditions: $(EtO)_3SiH$ 2.5 equiv, $ZnEt_2$ 3 mol %, chiral ligand 3 mol %, THF/*tert*-butanol(v/v, 3:0.4), −40 °C, 30 h.
[b] Enantiomeric excess determined by GC analysis with a CP-ChiralSil-Dex CB column.
[c] Isolated yields.

respectively. Meanwhile, by comparison ligands **1**–**8** with **9**, it showed that −COOK group plays crucial operation on the catalytic properties.

In order to investigate the scope and limitation of such catalyst system for catalytic asymmetric hydrosilylation of prochiral ketones, the hydrosilylation of substituted aryl ketones with $(EtO)_3SiH$ in the presence of **1**/$ZnEt_2$ was conducted, and the results were summarized in Table 3. However, lower yields as well as enantioselectivity were obtained when aryl ethyl ketone or benzylideneacetone was used as substrate (entries 1 and 2, Table 3). It can be seen that excellent ee values were obtained when aryl ketones with either electron-donating or electron withdrawing substituents were used as substrates (entries 3–6, Table 3). The experimental results showed that substituents on the aromatic ring have little effect on the enantioselective. Nevertheless, the yields achieved from the aryl ketones with electron withdrawing substituents were higher than that of aryl ketones with electron-donating substituents. *o*-Substituents on the aromatic ring have a certain extent effect on the enantioselective (entry 11, Table 3). This may be due to *o*-substituents steric hindrance resulting enantioselective decrease.

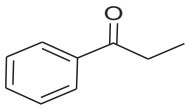
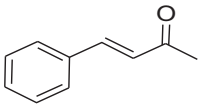
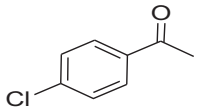
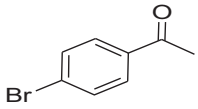
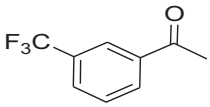
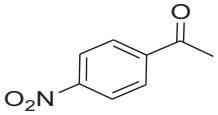
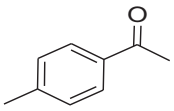
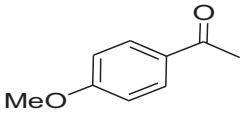
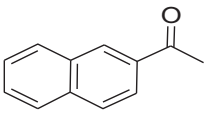
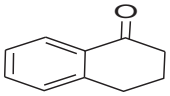
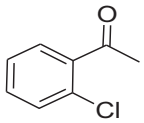
2.2. Mechanistic insights

Herein, the reaction mechanism was proposed as follows (Scheme 1).

Complexation of $ZnEt_2$ by the Schiff base ligand to form **A**, complex **A** reacted with $(EtO)_3SiH$ to give ZnH active species **B**, which contacted carbonyl group to form the four-membered metallacycle intermediate **C** and then to the five-membered metallacycle intermediate **D**, in which zinc achieved the tetracoordination including Zn–N and Zn–O bond. Since alkoxo ligands easily transfer from zinc to silicium,[3] thus formation of hydrosilylation product $(EtO)_3SiOCHR_1R_2$ and recycle of catalytic species **B** were undertaken when **D** was contacted with $(EtO)_3SiH$. Though this proposed mechanism is not relevant to the enantioselective hydrosilylation, the key operation of −COOM group containing in Schiff base ligands on the catalytic properties may be interpreted.

In conclusion, chiral Schiff base ligands **1**–**9** were used in the enantioselective hydrosilylation of prochiral ketones. It was found that the ligand plays an important role on the catalytic activity and the enantioselectivity. The substituents attached on aromatic ring of substituted salicylaldehyde have a great impact on ees. And the −COOK group derived from chiral α-amino acids plays crucial operation on the catalytic properties, and the reaction mechanism was proposed.

Table 3
Asymmetric hydrosilylation of various ketones with $HSi(OEt)_3$[a]

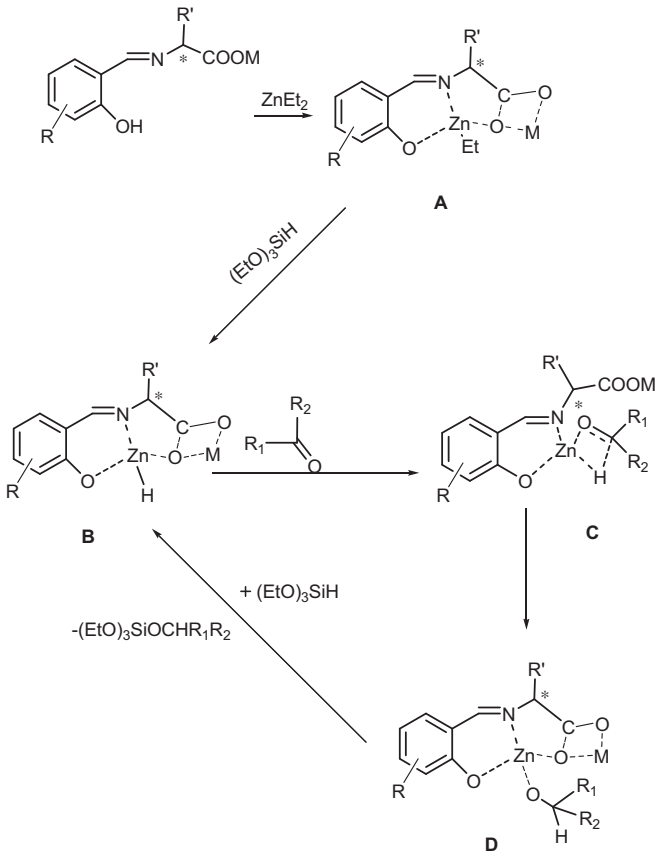
Entry	Ketones	Yield[d] (%)	ee (%)
1		55	87[b]
2		63	85[c]
3		82	94[b]
4		81	92[b]
5		90	92[b]
6		80	90[c]
7		59	93[b]
8		68	93[b]
9		70	93[c]
10		71	90[b]
11		85	81[b]

[a] Reaction conditions: $(EtO)_3SiH$ 2.5 equiv, $ZnEt_2$ 3 mol %, chiral ligand 3 mol %, THF/*tert*-butanol(v/v, 3:0.4), −40 °C, 30 h.
[b] Enantiomeric excess determined by GC analysis with a CP-ChiralSil-Dex CB column.
[c] The ee was determined by HPLC with a Chiralcel OD column.
[d] Isolated yields.

3. Experimental section

3.1. General

All reaction flask and solvent were dried according to standard methods prior to use. Flash column chromatography was performed over silica (100–200 mesh). NMR spectra were recorded on a 400 MHz spectrometer (Avance 400). ^{13}C NMR spectra were obtained with broadband proton decoupling. For spectra recorded in DMSO-d_6, unless otherwise noted, chemical shifts were recorded relative to the internal TMS (tetramethylsilane) reference signal. IR spectra were recorded on FT-IR apparatus (Nicolot 5700).



Scheme 1. Proposal mechanism of hydrosilylation of ketones catalyzed with $ZnEt_2$/Schiff base.

3.2. General procedure for the preparation of Schiff base ligands

*3.2.1. Ligands **1**–**7**.* Synthesis was adapted from a previously reported procedure.[16] To an argon purged methanolic solution (15 mL) of KOH (5.5 mmol), L-valine (5.5 mmol) was dissolved by agitation, and the solution was kept in ice-water bath. 3,5-Di-*tert*-butylsalicyldehyde (5 mmol) dissolved in methanol (10 mL) was then rapidly added to the ice-cooled alkaline solution of the amino acid, and the color of the solution immediately turned yellow. The reaction mixture was stirred for 3 h and then subjected to evaporation at rota-evaporator. A mixture of hexane (10 mL) and diethyl ether (10 mL) was added to the residue and then filtered to remove the remaining amino acid salt. Evaporation of the filtrate yielded the desired ligand, which was kept in a desiccator over $CaCl_2$.

*3.2.1.1. Ligand **1**.* Yellow powder, mp 102–103 °C; yield, 1.5 g (81%); ^1H NMR (DMSO-d_6, 400 MHz) δ 8.253 (s, 1H), 7.103–7.219 (d, 2H), 3.368–3.381 (d, J=5.2 Hz, 1H), 2.191–2.289 (m, 1H), 1.361 (s, 9H), 1.233 (s, 9H), 0.859 (br m, 3H), 0.841 (br m, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz), δ 173.14, 164.77, 162.48, 137.58, 137.01, 126.28, 117.54, 79.08, 35.04, 34.14, 31.77, 31.40, 29.78, 20.8, 18.92; IR (cm^{-1}, KBr): 3421, 3052, 2959, 1630, 1527, 1478, 1402, 1360, 1307, 1251, 1173, 1024, 911, 873, 803, 537. Anal. Calcd for $C_{20}H_{30}NO_3K$: C, 64.63; H, 8.06; N, 3.80; O, 12.95. Found: C, 64.65; H, 8.07; N, 3.77; O, 12.92.

3.2.1.2. Ligand **2**. Yellow powder, mp 105–106 °C; yield, 1.5 g (81%); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.251 (s, 1H), 7.102–7.218 (d, 2H), 3.367–3.380 (d, J=5.2 Hz, 1H), 2.191–2.289 (m, 1H) 1.360 (s, 9H), 1.232 (s, 9H), 0.859 (s, 3H), 0.841 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz), δ 173.12, 164.75, 162.49, 137.55, 137.01, 126.26, 117.53, 79.07, 35.04, 34.13, 31.76, 31.40, 29.76, 20.8, 18.92; IR (cm^{-1}, KBr): 3421, 3050, 2959, 1630, 1527, 1478, 1402, 1360, 1307, 1251, 1173, 1024, 911, 873, 803, 537. Anal. Calcd for $C_{20}H_{30}NO_3K$: C, 64.61; H, 8.01; N, 3.87; O, 12.98. Found: C, 64.65; H, 8.07; N, 3.77; O, 12.92.

3.2.1.3. Ligand **3**. Yellow powder, mp 112–115 °C; yield, 1.6 g (83%); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.267 (s, 1H), 7.106–7.219 (d, 2H), 3.450–3.464 (d, J=5.6 Hz, 1H), 1.978–2.040 (m, 1H), 1.358 (s, 9H), 1.232 (s, 9H), 1.025–1.069 (m, 2H), 0855 (m, 3H), 0.838 (m, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz), δ 173.45, 164.75, 162.33, 137.63, 136.97, 126.24, 117.60, 78.56, 38.05, 35.01, 34.09, 31.74, 29.78, 25.27, 16.94, 12.01; IR (cm^{-1}, KBr): 3410, 3052, 2961, 2874, 1630, 1478, 1402, 1361, 1250, 1202, 1174, 1025, 877, 802, 537. Anal. Calcd for $C_{21}H_{32}NO_3K$: C, 65.44; H, 8.31; N, 3.65; O, 12.48. Found: C, 65.42; H, 8.30; N, 3.63; O, 12.46.

3.2.1.4. Ligand **4**. Yellow powder, mp 113–115 °C; yield, 1.3 g (76%); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.335 (s, 1H), 7.106–7.222 (d, 2H), 3.748–3.765 (t, J=6.8 Hz, 1H), 1.358 (s, 9H), 1.358 (br m, 3H), 1.236 (s, 9H); ^{13}C NMR (DMSO-d_6, 100 MHz), δ 173.89, 164.19, 162.83, 137.44, 137.20, 126.61, 126.40, 117.42, 66.67, 35.04, 34.15, 31.77, 29.79, 20.92; IR (cm^{-1}, KBr): 3422, 3052, 2960, 2871, 1629, 1528, 1477, 1400, 1361, 1250, 1203, 1173, 1026, 877, 540. Anal. Calcd for $C_{18}H_{26}NO_3K$: C, 63.02; H, 8.56; N, 4.17; O, 13.92. Found: C, 62.95; H, 8.57; N, 4.07; O, 13.97.

3.2.1.5. Ligand **5**. Yellow powder, mp 121–123 °C; yield, 1.5 g (78%); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.342 (s, 1H), 7.136–7.222 (d, 2H), 3.684–3.718 (t, J_1=4.8 Hz, J_2=4 Hz, 1H), 1.572–1.731 (m, 2H), 1.468–1.571 (m, 1H), 1.354 (s, 9H), 1.233 (s, 9H), 0.870–0.887 (d, J=6.8 Hz, 3H), 0.834–0.850 (d, J=6.4 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz), δ 174.14, 164.76, 161.54, 137.97, 136.74, 126.30, 117.78, 71.30, 43.47, 34.99, 34.12, 31.76, 29.77, 25.07, 23.93, 22.12; IR (cm^{-1}, KBr): 3421, 3052, 2958, 2869, 1630, 1474, 1361, 1298, 1249, 1172, 1071, 926, 879, 826, 802, 540. Anal. Calcd for $C_{21}H_{32}NO_3K$: C, 65.43; H, 8.31; N, 3.65; O, 12.48. Found: C, 65.42; H, 8.30; N, 3.63; O, 12.45.

3.2.1.6. Ligand **6**. Yellow powder, mp 123–126 °C; yield, 1.6 g (83%); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.342 (s, 1H), 7.135–7.222 (d, 2H), 3.684–3.718 (d, J=4.8 Hz, 1H), 1.572–1.730 (m, 1H), 1.468–1570 (m, 1H), 1.354 (s, 9H), 1.233 (s, 9H), 0.870–0.887 (d, J=6.8 Hz, 3H), 0.833–0.849 (d, J=6.4 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz), δ 173.34, 164.77, 161.48, 137.58, 136.71, 126.30, 117.77, 71.30, 43.47, 34.98, 34.12, 31.75, 29.78, 25.06, 23.92, 22.12; IR (cm^{-1}, KBr): 3421, 3052, 2958, 2869, 1630, 1474, 1361, 1298, 1249, 1172, 1071, 926, 879, 826, 802, 540. Anal. Calcd for $C_{21}H_{32}NO_3K$: C, 65.44; H, 8.32; N, 3.62; O, 12.49. Found: C, 65.42; H, 8.30; N, 3.63; O, 12.45.

3.2.1.7. Ligand **7**. Yellow powder, mp 140–142 °C; yield, 1.5 g (73%); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.140 (s, 1H), 7.198–7.203 (d, 2H), 7.039–7.187 (m, 5H), 3.812–3.844 (d, J_1=4.4 Hz, J_2=4.8 Hz, 1H), 3.408–3.422 (m, 2H), 1.358 (s, 9H), 1.211 (s, 9H); ^{13}C NMR (DMSO-d_6, 100 MHz), δ 173.21, 165.22, 160.65, 140.68, 138.37, 136.49, 129.71, 128.42, 126.30, 126.21, 126.06, 117.94, 74.94, 35.03, 34.15, 31.78, 29.79; IR (cm^{-1}, KBr): 3421, 3052, 2957, 1628, 1527, 1478, 1399, 1361, 1251, 1202, 1173, 1088, 701, 495. Anal. Calcd for $C_{24}H_{30}NO_3K$: C, 68.74; H, 7.16; N, 3.37; O, 11.47. Found: C, 68.70; H, 7.15; N, 3.34; O, 11.44.

3.2.1.8. Ligand **8**. The ligand **8** was synthesized after introducing important modifications to the method described by Heinert and Martell. The L-valine was added to a solution of potassium hydroxide (1 mmol) in *i*-propanol. The amino acid was stirred with gentle warming until it had completely dissolved. The salicylaldehyde (1 mmol) was added and the reaction mixture was refluxed for 3 h. The mixture was then cooled and the product was filtered, and washed with ethanol and petroleum ether. The compounds were recrystallized from methanol and ether and dried in vacuo.[17,18] The product was obtained as a light yellow powder, mp 92–95 °C. Yield, 0.83 g (67%); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.291 (s, 1H), 6.611–7.302 (m, 4H), 3.432–3.444 (d, J=4.8 Hz, 1H), 2.226–2.307 (m, 1H), 0.859–0.864 (d, J=2 Hz, 3H), 0.843–0.847 (d, J=1.6 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz), δ 177.02, 171.92, 168.64, 137.95, 137.16, 123.92, 122.82, 120.72, 82.63, 36.19, 25.41, 23.37; IR (cm^{-1}, KBr): 3373, 3050, 2862, 1638, 1605, 1523, 1406, 1376, 1217, 1154, 1013, 890, 760, 739, 574, 537, 480. Anal. Calcd for $C_{12}H_{15}NO_3K$: C, 55.42; H, 5.55; N, 5.36; O, 18.60. Found: C, 55.56; H, 5.78; N, 5.40; O, 18.51.

3.2.1.9. Ligand **9**. (*S*)-(−)-α-Methylbenzylamine (0.61 g 5 mmol) and 3,5-di-*tert*-butylsalicyldehyde (1.175 g, 5 mmol) were dissolved in dry EtOH (25 mL) over molecular sieves for 2 h. The reaction mixture was refluxed and stirred for 6 h. The reaction was followed by TLC. The solution was filtered and the solvent was removed under reduced pressure to afford **9** ligand as a yellow oil.[19,20] Yield, 1.34 g, 75%; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 14.055 (s, 1H), 8.674 (s, 1H), 7.388–7.391 (m, 3H), 7.280–7.388 (m, 5H), 4.628–4.644 (q, J=6.4 Hz, 1H), 1.548–1.565 (d, J=6.8 Hz, 3H), 1.365 (s, 9H), 1.251 (s, 9H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 166.15, 157.86, 144.46, 140.18, 136.06, 129.09, 127.61, 127.00, 126.86, 126.69, 118.28, 67.39, 35.03, 34.32, 31.77, 29.76, 24.67; IR (cm^{-1}, KBr): 3421, 3052, 2960, 2867, 1630, 1443, 1250, 1172, 829, 765, 703. Anal. Calcd for $C_{23}H_{31}NO$: C, 81.85; H, 9.25; N, 4.15; O, 4.75. Found: C, 81.50; H, 9.26; N, 4.14; O, 5.10.

3.3. General procedure for the hydrosilylation of ketones

In a Schlenk flask $ZnEt_2$ (0.03 mL, 1 M in hexanes, 0.03 mmol) and chiral ligand (0.03 mmol) were dissolved in 3 mL of THF and stirred under nitrogen atmosphere for 30 min. Then the *tert*-butanol (0.4 mL) and the corresponding ketone (1 mmol) was added, and then $HSi(OEt)_3$ (5 mL, 2.5 mmol) was added slowly to the mixture. The reaction was kept at (−40 °C) for 30 h. The reaction mixture was poured on KOH 15% aqueous solution (5 mL) and extracted with CH_2Cl_2 (3 mL×3). The organic layer was washed with water (3 mL×2), dried over $MgSO_4$, and concentrated in vacuo. The product was purified by column chromatography on silica gel with hexane-EtOAc (10:1) as eluent.

3.4. Conditions for the analysis and assignment of configuration of the chiral secondary alcohol products from the enantioselective reductions

Chiral capillary GC: CP-ChiralSil-Dex CB column 25 m×0.25 mm×0.39 mm. Carrier gas H_2. Detector FID, 275 °C. Injector 250 °C.

Chiral HPLC: Chiralcel OD column, 254 nm UV detector.

Acknowledgements

We are grateful to the Fund of Zhejiang province (2008C14041) and the Fund of Zhejiang province (Y4100248) for financial support.

References and notes

1. (a) Ohkuma, T.; Noyori, R. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 2, pp 29–121; (b) Nishiyama,

H. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 2, pp 182–189; (c) Wishka, D. G.; Graber, D. R.; Seest, E. P.; Dolak, F. H.; Watt, W.; Morris, J. *J. Org. Chem.* **1998**, *63*, 7851–7859.
2. Astleford, B. A.; Weigel, L. O. In *Chirality in Industry II*; Collins, A. N., Ed.; Wiley: New York, NY, 1997; p 99.
3. Mimoun, H.; de saint Laumer, J. Y.; Giannini, L.; Scopelliti, R.; Floriani, C. *J. Am. Chem. Soc.* **1999**, *121*, 6158–6166.
4. Ojima, I. In *Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, NY, 1998; Vol. 2, pp 1687–1792.
5. (a) Ojima, I.; Li, Z.; Zhu, J. In *Recent Advances in the Hydrosilylation Reaction: Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, NY, 1998; Vol. 2; (b) Yamamoto, K.; Uramoto, Y.; Kumada, M. *J. Organomet. Chem.* **1971**, *31*, C9–C10.
6. (a) Brunner, H.; Becker, R.; Riepl, G. *Organometallics* **1984**, *3*, 1354–1359; (b) Nishiyama, H.; Yamaguchi, S.; Kondo, M.; Itoh, K. *J. Org. Chem.* **1992**, *57*, 4306–4309.
7. (a) Gade, L. H.; César, V.; Bellemin-Laponnaz, S. *Angew. Chem.* **2004**, *116*, 1036–1039; (b) César, V.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. *Chem.—Eur. J.* **2005**, *11*, 2862–2873.
8. Imma, H.; Mori, M.; Nakai, T. *Synlett* **1996**, 1229–1230.
9. Drew, M. D.; Lawrence, N. J.; Watson, W.; Bowles, S. A. *Tetrahedron Lett.* **1997**, *38*, 5857–5860.
10. Lipshutz, B. H.; Noson, K.; Chrisman, W. T. *J. Am. Chem. Soc.* **2001**, *123*, 12917–12918.
11. Bette, V.; Mortreux, A.; Savoia, D.; Carpentier, J.-F. *Tetrahedron* **2004**, *60*, 2837–2842.
12. Mastranzo, V. M.; Quintero, L.; de Parrodi, C. A.; Juaristi, E.; Walsh, P. J. *Tetrahedron* **2004**, *60*, 1781–1789.
13. Gajewy, J.; Kwit, M.; Gawrońskia, J. *Adv. Synth. Catal.* **2009**, *351*, 1055–1063.
14. Lawrence, N. J.; Drew, M. D.; Bushell, S. M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3381–3391.
15. (a) Diez-González, S.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 349–358; (b) Troepel, D.; Stohrer, J. *Coord. Chem. Rev.* **2011**, *13*, 1440–1459; (c) Hosokawa, S.; Ito, J.; Nishiyama, H. *Organometallics* **2010**, *22*, 5773–5775.
16. Chatterjee, D.; Basak, S.; Riahi, A.; Muzart, J. *J. Mol. Catal. A: Chem.* **2007**, *271*, 270–276.
17. Paredes-García, V.; Latorre, R. O.; Spodine, E. *Polyhedron* **2004**, *23*, 1869–1870.
18. Heinert, D. H.; Martell, A. T. *J. Am. Chem. Soc.* **1962**, *84*, 3257–3263.
19. Flores-López, L. Z.; Parra-Hake, M.; Somanathan, R.; Walsh, P. J. *Organometallics* **2000**, *19*, 2153–2160.
20. Iglesias, A. L.; Aguirre, G.; Somanathan, R.; Parra-Hake, M. *Polyhedron* **2004**, *23*, 3051–3062.