Tetrahedron 64 (2008) 9408–9412

Contents lists available at ScienceDirect

Tetrahedron

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

Felkin–Anh selectivity in Rh(bisoxazolinylphenyl)-catalyzed reductive aldol coupling reaction: asymmetric synthesis of stereotriads

Toru Hashimoto, Jun-ichi Ito, Hisao Nishiyama *

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan

ARTICLE INFO

Article history:
Received 11 June 2008
Received in revised form 22 July 2008
Accepted 22 July 2008
Available online 26 July 2008

Keywords:
Rhodium
Asymmetric catalysis
Reductive aldol reaction
Felkin–Anh
Bisoxazoline

ABSTRACT

The catalytic reductive aldol coupling of 2-phenylpropionaldehyde and acrylate derivatives with rhodium-bisoxazolinyl catalysts resulted in high Felkin–Anh selectivity (β,γ-*syn*) up to 98% accompanied by α,β-*anti* diastereoselectivity and high enantiomeric excesses up to 99%.

1. Introduction

The asymmetric reductive aldol coupling reaction initiated by hydride promoters has been recognized as a potent and versatile method for construction of α,β-stereogenic centers with α,β-unsaturated carbonyl compounds such as enones or acrylates as enolate precursors and aldehydes or imines as acceptors.[1] For example, Morken reported high α,β-*syn* selectivity of up to 90% in the coupling of methyl acrylate and α-benzyloxyacetoaldehyde with iridium-bisoxazolinylpyridine catalyst and Et_2MeSiH.[2] On the other hand, we observed high α,β-*anti* selectivity of up to 98% in the coupling of *tert*-butyl acrylate and benzaldehyde with rhodium-bisoxazolinylphenyl catalyst and $(EtO)_2MeSiH$.[3] These reactions have complementary stereoselectivity. Furthermore, Morken extended the reaction to double stereodifferentiation with (*R*)-α-benzyloxypropionaldehyde to observe α,β-*syn*-Felkin–Anh selectivity (i.e., β,γ-*syn*) (Scheme 1). Interestingly, no coupling was observed by use of the corresponding (*S*)-aldehyde, which is thought to be a mismatched acceptor under catalyst control. Recently, Krische reported high *anti*-Felkin–Anh selectivity (α,β-*syn*,β,γ-*anti*) up to 95% in the hydrogen-mediated coupling of methyl vinyl ketone and α-aminoaldehydes with rhodium catalyst.[4]

Asymmetric construction of α,β,γ-stereotriads is an important and challenging subject for organic synthesis, especially for total synthesis of macrolides or other large naturally occurring compounds.[5]

We report here study on asymmetric synthesis of stereotriads and β,γ-stereoselectivity, Felkin–Anh or *anti*-Felkin–Anh, as summarized in Scheme 2.

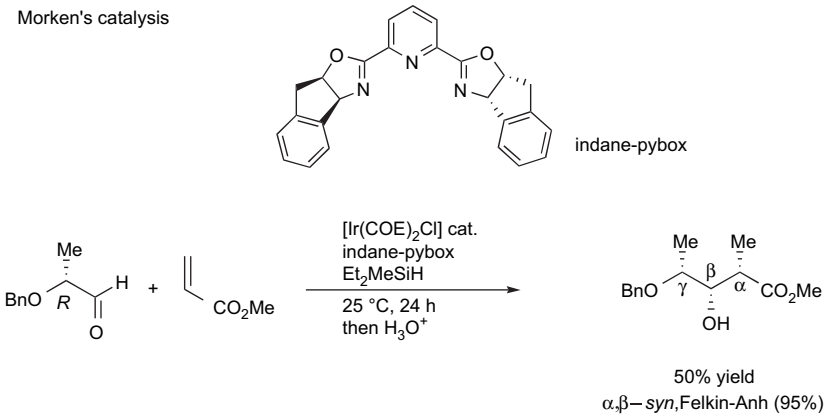
2. Results and discussion

The reductive coupling reaction of racemic 2-phenylpropanal (**5**) (1.0 mmol) and *tert*-butyl acrylate (**6**) (2.0 equiv) with achiral catalyst **1a** (1 mol %) in the presence of $(EtO)_2MeSiH$ (2.2 equiv) was carried out at 50 °C for 30 min in a toluene solution (Table 1). The reaction mixture was treated with KF (5 equiv) and TBAF to give the desired β-hydroxyester **7** in 84% yield with 69% α,β-*anti*,*syn* selectivity, i.e., selective formation of the Felkin–Anh product. The product of the second-highest diastereomer ratio (dr), 21%, was presumed to be α,β-*anti*,*anti*-Felkin–Anh product on the basis of catalyst control. The use of an optically active aldehyde (*S*)-**5** (92% ee) resulted in formation of the corresponding coupling product (2*R*,3*R*,4*S*)-**7** in 68% dr with 93% ee. Use of other silanes, such as Me_2PhSiH and $MePh_2SiH$, gave slightly high stereoselectivities of 74 and 79% drs with 91 and 93% ees, respectively.

We considered that Felkin–Anh selectivity (β,γ-*syn*) could be derived from differences in steric repulsion between Ph and Me groups and the 1,3-diaxial interaction between Ph/H and Me/H, via Zimmerman–Traxler type chair-like transition state of Rh-*E*(O)-enolate, which gives rise to α,β-*anti* diastereoselectivity (Fig. 1).[6,7]

* Corresponding author. Fax: +81 52 789 3209.
E-mail address: hnishi@apchem.nagoya-u.ac.jp (H. Nishiyama).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.07.092



Scheme 1. Example for asymmetric synthesis of stereotriads by reductive aldol coupling reactions.

Next, we examined the reaction of the chiral catalyst **1b** with racemic aldehyde **5**, which similarly provided the (2*R*,3*R*,4*S*)-*anti*-Felkin–Anh product in a diastereomer ratio with 76% ee (Table 2). Evidently, the (*S*)-aldehyde **5** was selectively captured to give (4*S*)-absolute configuration at the γ-carbon atom. When the chiral aldehyde (*S*)-**5** (92% ee) was employed, high diastereomer ratio of 88% was obtained for *anti*-Felkin–Anh product, and the enantiomeric excess was found to be 99%. It was thus clear that the (*S*,*S*)-catalyst and (*S*)-aldehyde could make a matched pair. Me_2PhSiH and $MePh_2SiH$ gave almost similar yields and stereoselectivities over 80% drs and 98% ees. On the other hand, when (*R*)-aldehyde (95% ee) was employed as an acceptor, *anti*-Felkin–Anh decreased to 20% and *anti*,*anti*-Felkin–Anh product was the main diastereomer in 71% ee.[8,9]

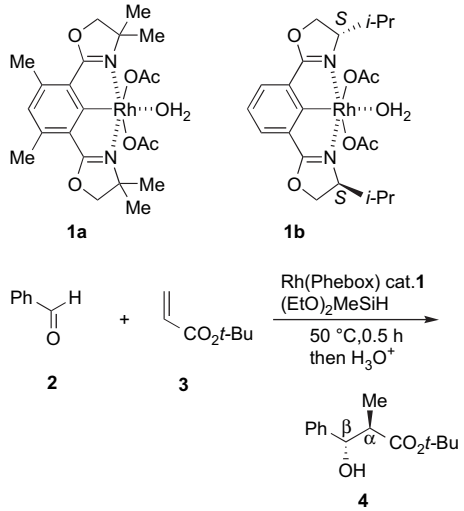
We believe that the catalyst-controlled reaction with the chiral catalyst can preferably direct *Si*-face of the generated enolate species **i** to the acceptor aldehyde rather than *Re*-face of the enolate **ii** (Fig. 2). In addition, if the (*R*)-aldehyde is captured by the intermediate rhodium enolate, the sterically unfavorable transition state **iii** forms *anti*,*anti*-Felkin–Anh product.

Finally, we employed three α,β-unsaturated esters, namely crotonate **8**, cinnamate **9**, and methacrylate **10**, for the coupling with (*S*)-2-phenylpropanal in the presence of chiral catalyst **1b** (Scheme 3). The crotonate and the cinnamate provided high diastereoselectivity (>98:2, >91:9) and enantioselectivity (98%, 97%) for *anti*-Felkin–Anh products. The methacrylate **10** also resulted in high β,γ-*syn* selectivity with high enantioselectivity of 91%.

A single crystal of the corresponding sulfonamide-ester **14** was derived from the enantiomer of **11** (Scheme 4). From this, the absolute configuration (2*R*,3*R*,4*S*) of **11** was confirmed by X-ray analysis (Fig. 3). On the basis of the absolute configuration of **14**, we propose a hypothetical transition state giving *anti*-Felkin–Anh product with 2*R*,3*R*,4*S* (Fig. 4).

3. Conclusion

We have found Felkin–Anh selectivity in reductive aldol coupling reaction of 2-phenylpropionaldehyde as a probe acceptor with several unsaturated esters by use of achiral and chiral Rh(Phebox) catalysts. These findings will provide an important means of catalytic construction of multiple stereocenters including asymmetric synthesis with transition metal complexes.

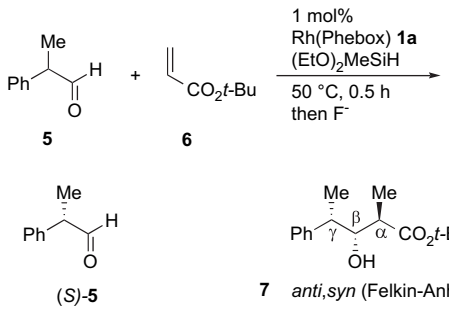


cat.	yield of **4**	*anti:syn*	ee of *anti*	ref.
1a	94%	96:4	-	3a
1b	91%	95:5	91%[a]	3b

[a] (2*R*,3*S*)

Scheme 2. Rh(Phebox) catalyzed reductive aldol coupling of benzaldehyde and acrylate (Refs. 3a and b).

Table 1
Coupling reaction of 2-phenylpropanal and *tert*-butyl acrylate with achiral Rh(Phebox) catalyst



Aldehyde	Yield of **7** (%)	dr	ee (%) of *anti*-Felkin–Anh
5	84	69[a]:21:7:3	Racemic
5[b]	93	72[a]:21:6:1	Racemic
5[c]	94	73[a]:19:7:1	Racemic
(*S*)-**5**[d]	84	68[a]:20:10:2	93[e]
(*S*)-**5**[d,b]	78	74[a]:18:7:1	91[e]
(*S*)-**5**[d,c]	73	79[a]:15:5:1	93[e]

[a] *anti*-Felkin–Anh.
[b] Me_2PhSiH.
[c] MPh_2SiH.
[d] 92% ee.
[e] (2*R*,3*R*,4*S*).

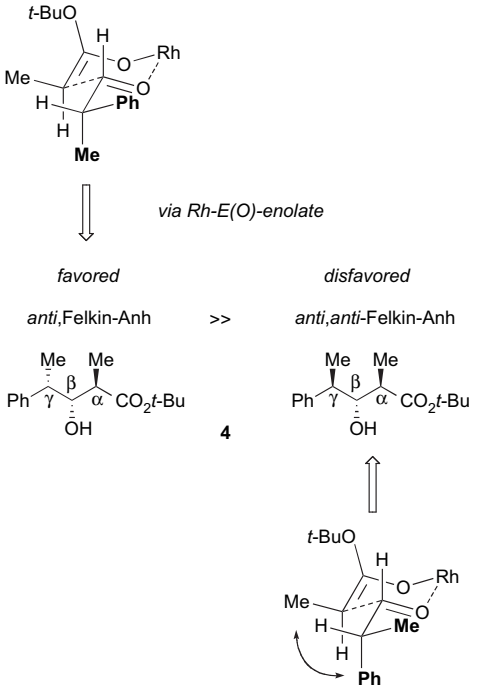


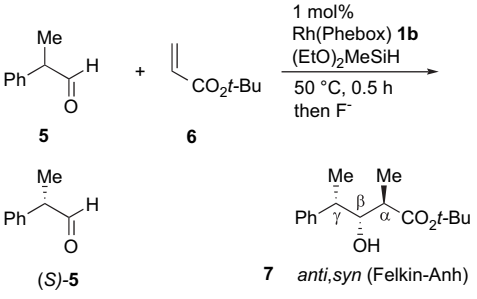
Figure 1. Hypothetical transition model for Rh(Phebox) catalyzed reductive coupling reaction.

4. Experimental

4.1. General

NMR spectra were obtained in $CDCl_3$ solution at 25 °C. ^1H NMR chemical shifts are reported in δ units, in parts per million relative to the singlet at 7.26 ppm for chloroform. IR spectra were recorded with a JASCO FT/IR-230 spectrometer. Rh(Phebox) catalysts were synthesized by the method reported previously.[3b,10]

Table 2
Coupling reaction of 2-phenylpropanal and *tert*-butyl acrylate with chiral Rh(Phebox) catalyst



Aldehyde	Yield of **7** (%)	dr	ee (%) of *anti*-Felkin–Anh
5	70	55[a]:35:8:2	76
(*S*)-**5**[b]	83	88[a]:4:7:1	99[c]
(*S*)-**5**[b,d]	81	80[a]:4:15:1	98[c]
(*S*)-**5**[b,e]	72	88[a]:2:9:1	98[c]
(*R*)-**5**[f]	75	20[a]:65[g]:14:1	71[g]

[a] *anti*-Felkin–Anh.
[b] 92% ee.
[c] (2*R*,3*R*,4*S*).
[d] Me_2PhSiH.
[e] MPh_2SiH.
[f] 95% ee.
[g] *anti*,*anti*-Felkin–Anh (2*R*,3*R*,4*R*).

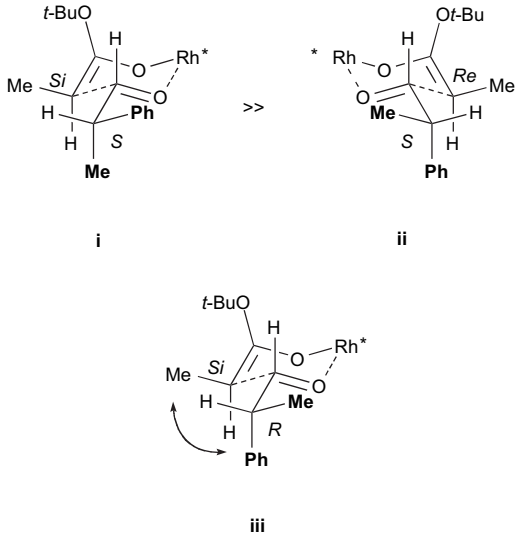
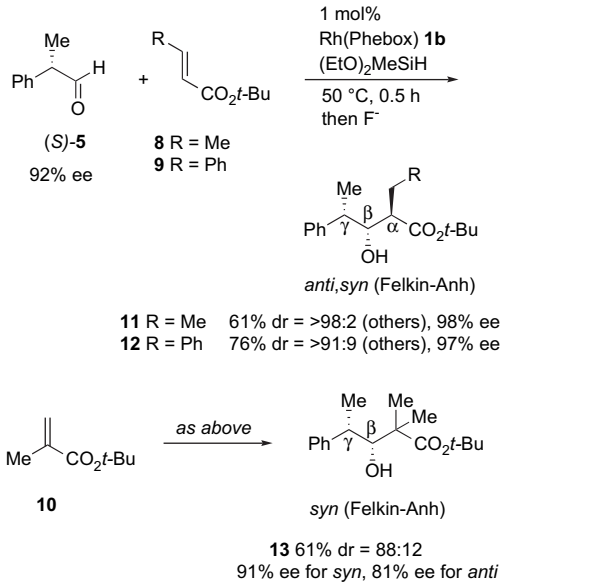


Figure 2. Hypothetical transition model for chiral Rh(Phebox) catalyzed reductive coupling reaction with chiral aldehydes.

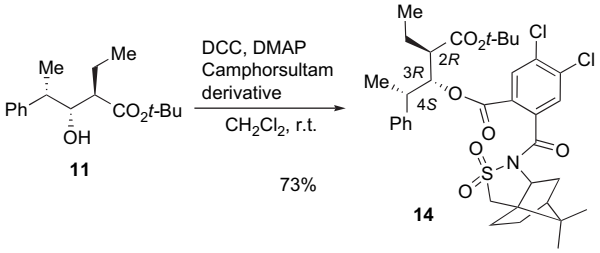


Scheme 3. Coupling reaction of (*S*)-2-phenylpropanal and other α,β-unsaturated esters with chiral Rh(Phebox) catalyst.

4.2. Typical reactions

4.2.1. The reaction of 2-phenylpropionaldehyde and tert-butyl acrylate with Rh(Phebox) ***1a***

In a 25 mL flask, Rh(Phebox) **1a** (5.4 mg, 0.01 mmol) was placed under argon atmosphere. After toluene (1.0 mL), 2-phenylpropionaldehyde (134 mg, 1.0 mmol), and *tert*-butyl acrylate (256 mg, 2.0 mmol) were added to the flask at room temperature,



Scheme 4. Synthesis of the sulfonamide-ester **14**.

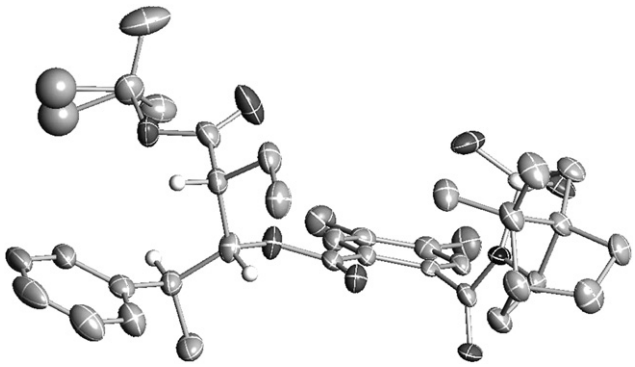


Figure 3. Molecular structure of **14**.

diethoxymethylsilane (295 mg, 2.2 mmol) was added at 50 °C. The mixture was stirred for 30 min at 50 °C. Water (1 mL), methanol (1 mL), KF (5 mmol), and TBAF (1 mL, 1 M in THF) were added, and the mixture was extracted with ethyl acetate. The extract was dried over magnesium sulfate, concentrated, and the residue was purified by silica gel column chromatography (ethyl acetate/hexane=20:1 as eluent) to give *tert*-butyl 3-hydroxy-2-methyl-4-phenylpentanoate **7** (222 mg, 0.84 mmol, 84%) as colorless oil; diastereomer ratio of 69:21:7:3 was determined by ^{1}H NMR (500 MHz, $CDCl_3$): for C*H*OH, δ 3.54 (m, *major*), 3.72 (m, *second major*), 4.03 (m, *minor*), 4.00 (m, *minor*); *anti*,*syn*, *anti*,*anti*, *syn*,*syn* (tentatively), *syn*,*anti* (tentatively).

4.2.2. The reaction of (S)-2-phenylpropionaldehyde and tert-butyl acrylate with Rh(Phebox) **1a**

(*S*)-2-phenylpropionaldehyde (134 mg, 1.0 mmol, 92% ee) was used, which was prepared by use of commercially available (*S*)-(+)-2-phenylpropionic acid via methyl esterification with $TMSCHN_2$ in MeOH, reduction with DIBAL at −78 °C followed by oxidation with IBX in DMSO at room temperature in ca. 70% yield in three steps. The reaction and purification were carried out as described above to give **7** (223 mg, 0.84 mmol, 84%); diastereomer ratio was 68:20:10:2.

4.2.3. The reaction of (S)-2-phenylpropionaldehyde and tert-butyl acrylate with Rh(Phebox) **1b**

The reaction with **1b** (5.4 mg, 0.01 mmol) was carried out as described. After the reaction was completed, the mixture was treated with DMF (2.5 mL), water (1 mL), KF (290 mg, 5.0 mmol), and TBAF (1 M in THF, 0.2 mL) at 50 °C for 9 h. After water (15 mL) was added, the mixture was extracted with ethyl acetate. After the residue concentrated, dried over magnesium sulfate, and purified by silica gel column chromatography (ethyl acetate/hexane=20:1 as eluent) to give **7** (219 mg, 0.83 mmol, 83%); diastereomer ratio was 88:4:7:1. Compound **7** (major, *anti*,*syn*): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20 (d, *J*=7.5 Hz, 3H), 1.37 (d, *J*=7.0 Hz, 3H), 1.47 (s, 9H), 2.28 (dq, *J*=4.5, 7.5 Hz, 1H), 2.84 (dq, *J*=7.0, 7.5 Hz, 1H), 3.55 (dd, *J*=4.5, 8.0 Hz, 1H), 7.17–7.23 (m, 3H), 7.28–7.32 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 15.6, 17.1, 28.1, 42.3, 44.5, 78.8, 81.1, 126.5, 127.6, 128.5, 144.7, 176.1; IR (neat) ν 3620–3300, 1727 cm^{-1}; FAB-HRMS: (M+H) *m*/*z*, found: 265.1806; calcd ($C_{16}H_{25}O_3^+$): 265.1798; LC: DAICEL CHIRALPAC AD-H, eluent=hexane/2-propanol (99:1, 0.7 mL/min), retention time=12.2 min (major), 14.7 min (minor), >99% ee; for second major (*anti*,*anti*), 17.0 min, 18.0 min. The corresponding methyl ester is a known compound in which α,β-*anti*,β,γ-*syn*-stereochemistry for the four diastereomers were determined; ^{1}H NMR spectra were measured in CCl_4.[11]

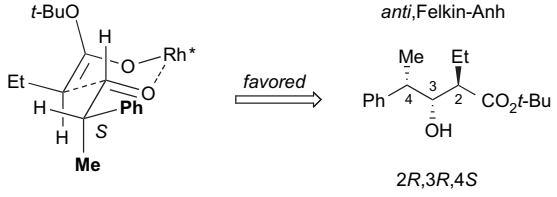


Figure 4. Hypothetical transition state.

4.2.4. The reaction of (S)-2-phenylpropionaldehyde and tert-butyl crotonate with Rh(Phebox) **1b**

The reaction with **1b** (5.4 mg, 0.01 mmol) and *tert*-butyl crotonate (284 mg, 2.0 mmol) was carried out as described above. After the reaction was completed, the mixture was treated with DMF (2.5 mL), water (1 mL), KF (290 mg, 5.0 mmol), and TBAF (1 M in THF, 0.2 mL) at 50 °C for 16 h. After water (15 mL) was added, the mixture was extracted with ethyl acetate. After the residue concentrated, dried over magnesium sulfate, and purified by silica gel column chromatography (ethyl acetate/hexane=20:1 as eluent) to give **11** (171 mg, 0.61 mmol, 61%); diastereomer ratio, 98:2 (others), determined by ^{1}H NMR. Compound **11** (major, *anti*,*syn*): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (t, *J*=7.5 Hz, 3H), 1.37 (d, *J*=6.5 Hz, 3H), 1.48 (s, 9H), 1.61 (m, 1H), 1.75 (m, 1H), 2.06 (m, 1H), 2.75 (m, 1H), 3.15 (d, *J*=9.5 Hz, 1H), 3.62 (m, 1H), 7.16 (m, 2H), 7.23 (m, 1H), 7.28–7.32 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 11.7, 18.0, 23.6, 28.2, 45.1, 49.3, 77.1, 81.3, 126.5, 127.6, 128.5, 144.6, 175.8; IR (neat) ν 3620–3300, 1704 cm^{-1}; FAB-HRMS: (M+H) *m*/*z*, found: 279.1962; calcd ($C_{17}H_{27}O_3^+$): 279.1955; LC: DAICEL CHIRALCEL OD-H, eluent=hexane/2-propanol (99:1, 0.7 mL/min), retention time=6.4 min (major), 7.4 min (minor), 98% ee.

4.2.5. The reaction of (S)-2-phenylpropionaldehyde and tert-butyl cinnamate with Rh(Phebox) **1b**

The reaction with **1b** (5.4 mg, 0.01 mmol) and *tert*-butyl cinnamate (408 mg, 2.0 mmol) was carried out as described above. The compound **12** was obtained in 76% yield (259 mg, 0.76 mmol); diastereomer ratio, 91:9 (others), determined by ^{1}H NMR; proportion of the other isomers could not determined, the stereochemistry of *anti*,*syn* was tentatively assigned based on the case of **7**. Compound **12** (major, *anti*,*syn*): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (s, 9H), 1.35 (d, *J*=7.0 Hz, 3H), 2.45 (m, 1H), 2.77 (m, 1H), 2.89 (m, 1H), 2.99 (m, 1H), 3.32 (d, *J*=10.0 Hz, 1H), 3.55 (m, 1H), 7.03–7.07 (m, 4H), 7.17–7.28 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 18.7, 27.9, 36.3, 45.4, 48.9, 76.4, 81.4, 126.3, 126.5, 127.5, 128.2, 128.5, 129.1, 138.4, 144.4, 175.1; IR (neat) ν 3620–3300, 1698 cm^{-1}; FAB-HRMS: (M+H) *m*/*z*, found: 341.2112; calcd ($C_{22}H_{29}O_3^+$): 341.2111; LC: DAICEL CHIRALPAC AD-H, eluent=hexane/2-propanol (99:1, 0.7 mL/min), retention time=22.8 min (minor), 27.8 min (major), 97% ee.

4.2.6. The reaction of (S)-2-phenylpropionaldehyde and tert-butyl methacrylate with Rh(Phebox) **1b**

The reaction with **1b** (5.4 mg, 0.01 mmol) and *tert*-butyl methacrylate (284 mg, 2.0 mmol) was carried out as described above. The compound **13** was obtained in 61% (169 mg, 0.61 mmol) as white solids; diastereomer ratio, 88:12, determined by ^{1}H NMR: for C*H*O, δ 3.72 (*syn*), 3.81 (*anti*) and for O*H*, δ 3.19 (*anti*), 3.23 (*syn*); *anti* and *syn* stereochemistry was tentatively assigned. Compound **13** (major, *syn*): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.14 (s, 3H), 1.16 (s, 3H), 1.26 (d, *J*=7.0 Hz, 3H), 1.47 (s, 9H), 2.96 (m, 1H, C*H*Ph), 3.23 (d, *J*=8.5 Hz, 1H, O*H*), 3.72 (m, 1H), 7.17–7.20 (m, 1H), 7.25–7.30 (m, 4H); (minor, *anti*): 1.14 (s, 3H), 1.20 (s, 3H), 1.31 (d, *J*=7.0 Hz, 3H), 1.32 (s, 9H), 2.92 (m, 1H), 3.19 (d, *J*=8.5 Hz, 1H), 3.81 (m, 1H), 7.17–7.20 (m, 1H), 7.25–7.30 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): 16.5, 21.8, 24.9, 27.9, 41.7, 47.3, 81.0, 81.2, 126.1, 127.6, 128.3, 146.9, 177.3; IR (KBr disk) ν 3620–3300, 1701 cm^{-1}; FAB-HRMS: (M+H) *m*/*z*, found: 279.1974; calcd ($C_{17}H_{27}O_3^+$): 279.1955; LC: DAICEL CHIRALPAC AD-H, eluent=hexane/2-propanol (99:1, 0.7 mL/min),

retention time: for *syn*, 20.0 min (major), 30.5 min (minor), 91% ee; for *anti*, 12.8 min (minor), 14.1 min (major), 81% ee.

4.3. Synthesis of sulfonamide-ester 14

To a solution of **11** (84 mg, 0.30 mmol, >98% ee) and *N*-(2-carboxy-4,5-dichlorobenzoyl)-(−)-10,2-camphorsultam (TCI-1683) (195 mg, 0.45 mmol) in dichloromethane (8 mL), DCC (93 mg, 0.45 mmol) and DMAP (5.5 mg) were added at 0 °C, and then the mixture was stirred for 6 days at room temperature. After filtration through Celite column, the filtrate was concentrated to give the crude product, which was purified by silica gel column chromatography (ethyl acetate/hexane as eluent) to give the corresponding sulfonamine ester (153 mg, 0.22 mmol, 73%). Compound **14**: white solids; mp: 117–118 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.069 (s, 1H), 0.74 (t, J=7.5 Hz, 3H), 0.97 (s, 3H), 1.20–1.23 (m, 6H), 1.30 (m, 1H), 1.47 (m, 1H), 1.51 (s, 9H), 1.64 (m, 1H), 1.95 (m, 3H), 2.15–2.26 (m, 2H), 2.53 (m, 1H), 3.33 (m, 1H), 3.39 (d, J=14.0 Hz, 1H), 3.43 (d, J=14.0 Hz, 1H), 4.10 (m, 1H), 5.37 (dd, J=11.0, 2.0 Hz, 1H), 7.20–7.25 (m, 1H), 7.28–7.35 (m, 4H), 7.53 (s, 1H), 8.21 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 1.0, 11.8, 19.1, 20.1, 20.8, 22.6, 26.5, 26.9, 28.2, 33.1, 37.7, 42.5, 44.7, 47.8, 48.5, 49.9, 53.0, 65.7, 79.3, 80.8, 126.9, 127.8, 128.0, 128.7, 131.1, 131.6, 134.6, 135.4, 137.0, 143.1, 162.7, 165.2, 171.1; IR (KBr disk) ν 1729, 1678 cm^{-1}; FAB-HRMS: (M+H) m/z, found: 692.2200; calcd ($C_{35}H_{44}Cl_2NO_7S^+$): 692.2210; $[\alpha]_D^{25}$ −42.6 (c 1.09, $CHCl_3$).

4.4. X-ray analysis of 14

Single crystals of **14** suitable for X-ray diffraction study were obtained from a hot hexane solution. The diffraction data were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo Kα radiation (λ=0.71073 Å). An empirical absorption correction was applied using SADABS. The structure was solved by direct method and refined by full-matrix least-square on F^2 using SHELXTL. All non-hydrogen atoms except the disordered atoms and the solvent molecule were refined with anisotropic displacement parameters. The disorders at C17 and C50–52 were refined in the ratio of 35:65 and 62:38, respectively. Crystallographic data for **14**: $C_{38}H_{50}Cl_2NO_7S$; M_r=735.75; temperature 133 K; monoclinic, $P2_12_12_1$; a=14.548(6), b=18.519(8), c=28.785(12) Å; V=7755(6) Å^3; Z=8; ρ_{calcd}=1.260 Mg/m^3; μ=0.269 mm^{-1}; reflections collected 55 697, independent reflections 18 068 [R(int)=0.0898]; data/restraints/parameters 18 068/46/874; goodness-of-fit on F^2: 0.992; final R indices [$I>2\sigma(I)$] R_1=0.0662, wR_2=0.1398; R indices (all data) R_1=0.1225, wR_2=0.1639; largest diff. peak/hole 0.471 and −0.478 e Å^{-3}. CCDC 690605 contains the supplementary crystallographic data. The data can be obtained free of charge via http://www.ccdc.cam.au.ac.uk or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; deposit@ccdc.cam.au.uk.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan (Concerto Catalysts, 460:18065011), the Japan Society for the Promotion of Science (18350049), G-COE in Chemistry (Nagoya University).

Supplementary data

Analysis for NMR, IR, and LC charts of the products are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.07.092.

References and notes

1. (a) Nishiyama, H.; Shiomi, T. Metal Catalyzed Reductive C–C Bond Formation. In *Topics in Current Chemistry*; Krische, M. J., Ed.; Springer: Berlin, Heidelberg, 2007; Vol. 279, p 105; (b) Iida, H.; Krische, M. J. Metal Catalyzed Reductive C–C Bond Formation. In *Topics in Current Chemistry*; Krische, M. J., Ed.; Springer: Berlin, Heidelberg, 2007; Vol. 279, p 77; (c) Motherwell, W. B. *Pure Appl. Chem.* **2002**, *74*, 135; (d) Jang, H.-Y.; Krische, M. J. *Acc. Chem. Res.* **2004**, *37*, 653; (e) Chiu, P. *Synthesis* **2004**, 2210.
2. Zhao, C.-X.; Duffey, M. O.; Taylor, S. J.; Morken, J. P. *Org. Lett.* **2001**, *3*, 1829.
3. (a) Nishiyama, H.; Shiomi, T.; Tsuchiya, Y.; Matsuda, I. *J. Am. Chem. Soc.* **2005**, *127*, 6972; (b) Ito, J.; Shiomi, T.; Nishiyama, H. *Adv. Synth. Catal.* **2006**, *348*, 1234; (c) Shiomi, T.; Ito, J.; Yamamoto, Y.; Nishiyama, H. *Eur. J. Org. Chem.* **2006**, 5594; (d) Hashimoto, T.; Shiomi, T.; Ito, J.; Nishiyama, H. *Tetrahedron* **2007**, *63*, 12883; (e) Nishiyama, H.; Ishikawa, J.; Shiomi, T. *Tetrahedron Lett.* **2007**, *48*, 7841.
4. Jung, C.-K.; Krische, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 17051.
5. For example: (a) Paterson, I.; Lyothier, I. *J. Org. Chem.* **2005**, *70*, 5494; (b) Guindon, Y.; Brazeau, J.-F. *Org. Lett.* **2004**, *6*, 2599; (c) Kiyooka, S.; Shahid, K. A.; Goto, F.; Okazaki, M.; Shuto, Y. *J. Org. Chem.* **2003**, *68*, 7967; (d) Dias, L. C.; de Oliveira, L. G.; de Sousa, M. A. *Org. Lett.* **2003**, *5*, 265; (e) Shahid, K. A.; Mursheda, J.; Okazaki, M.; Shuto, Y.; Goto, F.; Kiyooka, S. *Tetrahedron Lett.* **2002**, *43*, 6377; (f) Yang, H. W.; Zhao, C.; Romo, D. *Tetrahedron* **1997**, *53*, 16471; (g) For diastereofacial selectivity of aldol reactions, see: Paterson, I.; Franklin, A. S. *Tetrahedron Lett.* **1994**, *35*, 6925; (h) Roush, W. R. *J. Org. Chem.* **1991**, *56*, 4151.
6. (a) For Zimmerman–Traxler model, see: Zimmerman, H. E.; Traxler, M. D. *J. Am. Chem. Soc.* **1957**, *79*, 1920; (b) Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. *Organic Chemistry*; Oxford University Press: New York, NY, 2001; p 900.
7. For Felkin–Anh model: (a) Chérest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199; (b) Mengel, A.; Reiser, O. *Chem. Rev.* **1999**, *99*, 1191; Also see: (c) Smith, M. B.; March, J. *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*, 6th ed.; John Wiley & Sons: Hoboken, 2007; Chapter 4, p 169 and references cited therein; (d) Wyatt, P.; Warren, S. *Organic Synthesis, Strategy and Control*; John Wiley and Sons: Chichester, UK, 2007; Chapter 21, p 429 and Chapter 30, p 681.
8. Use of other hydrosilanes: Me_2PhSiH, 85% yield with **5**, 46:41:7:6 (major, 77% ee); $MePh_2SiH$, 75% yield with **5**, 50:36:10:4 (major, 80% ee).
9. When benzyl group was employed in place of isopropyl group of Rh(Phebox) **1b**, the yield of **7** with (*S*)-**5** was 72% with 84:5:8:3 diastereomer ratio and 99% ee for *anti*/*syn*.
10. Kanazawa, Y.; Tsuchiya, Y.; Kobayashi, K.; Shiomi, T.; Ito, J.; Kikuchi, M.; Yamamoto, Y.; Nishiyama, H. *Chem.—Eur. J.* **2006**, *12*, 63.
11. Matsumoto, T.; Hosoda, Y.; Mori, K.; Fukui, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3156.