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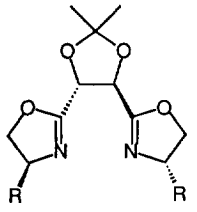
Novel C_2-Symmetric Chiral Bisoxazoline Ligands in Rhodium(I)-Catalyzed Asymmetric Hydrosilylation[1,2]

Yoshitane Imai, Wanbin Zhang, Toshiyuki Kida, Yohji Nakatsuji and Isao Ikeda*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Abstract: Novel C_2-symmetric chiral bisoxazoline ligands with four asymmetric centers were readily synthesized from the two enantiomers of tartaric acid and several aminoacids *via* the corresponding bis(β-hydroxylamide)s and dimesylates as successive intermediates. With these novel chiral bisoxazoline ligands, rhodium(I)-catalyzed hydrosilylation of acetophenone was carried out and the effects of the combination of the four asymmetric centers as well as the substituent on oxazoline ring of the ligands on the reaction were studied.

Chiral oxazolines derived from readily available aminoacids have found widespread use as chiral ligands in asymmetric catalytic reactions.[3] In this article, we report the preparation of a new kind of C_2-symmetric chiral bisoxazoline ligands **1** and **2** from two chiral sources, tartaric acid and aminoacids, and their application to the enantioselective hydrosilylation of acetophenone.



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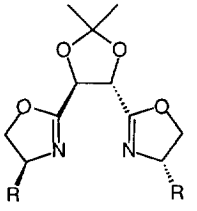

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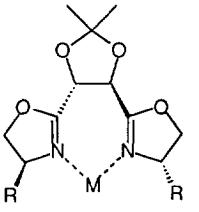

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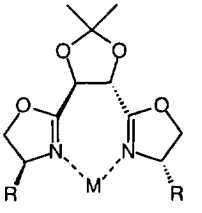

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Our design for this new kind of ligand is such that it is possible to let them possess a number of structural features which make them effective for the stereocontrol in metal-catalyzed reactions. First, they possess four asymmetric centers, two from tartaric acid and two from an aminoacid (Figure 1). By changing the combinations of the enantiomers of these starting materials, the stereochemistry of the four asymmetric centers is adjustable. Secondly, the bulkiness of the substituent on oxazoline ring is also adjustable by changing the aminoacid. Therefore, by proper selection of the stereochemistry of the four asymmetric centers and the bulkiness of the substituent on oxazoline ring, the best structure of this kind of ligand for the specific requirement of a particular reaction may be obtained.

In addition, on coordination of the ligand to metal, the tetra-cyclic complexes **3** and **4** are formed. Since

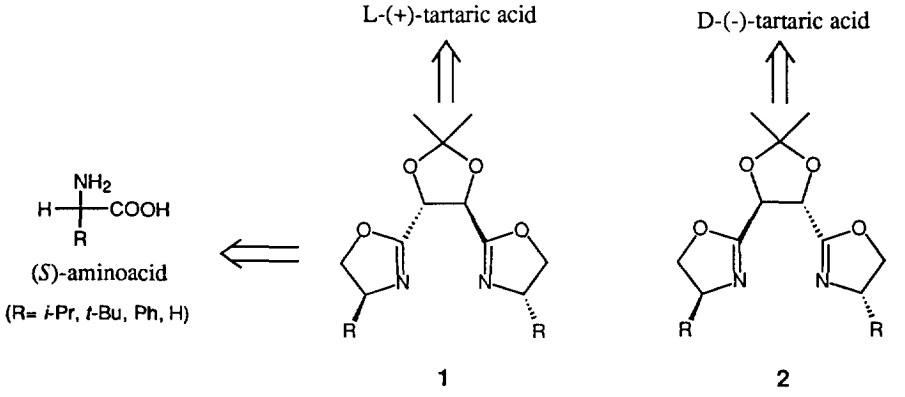
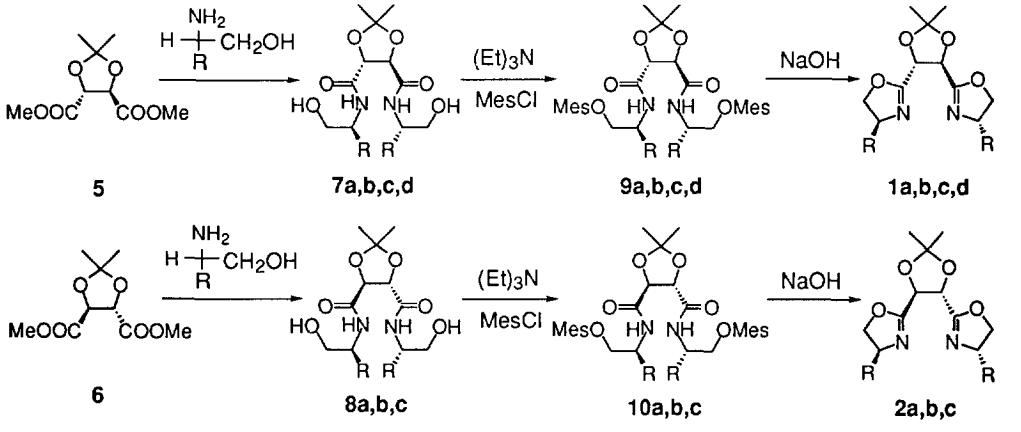


Figure 1

these complex structures are very rigid, higher enantiomeric excess may be induced.[3,4] Furthermore, the seven-membered coordination ring in complexes **3** and **4** makes the two substituents on the oxazoline rings closer to coordinated and incoming substrates than five- and six-membered coordination rings, suggesting a larger influence on the catalysis and to higher enantiomeric excess. All of these structural features may offer us an opportunity to develop novel effective ligands for asymmetric catalysis.

There are several methods[5] reported for the preparation of oxazoline compounds from carbonyl compounds and most of them are operated under acidic conditions. In the case of preparing **1** and **2**, however, these methods can not be adopted because of the presence of acid-sensitive 1,3-dioxolane groups in the compounds. Recently, we[1,6] and Denmark[7] independently reported an improved method for the preparation of oxazoline compounds *via* the corresponding mesylates. With this convenient and effective method, **1** and **2** were readily synthesized in high yields from dimethyl esters **5** and **6** and enantiomerically pure aminoalcohols under basic conditions (Scheme 1). Thus, **5** and **6** prepared from (L)-tartaric acid and (D)-tartaric acid[8] were

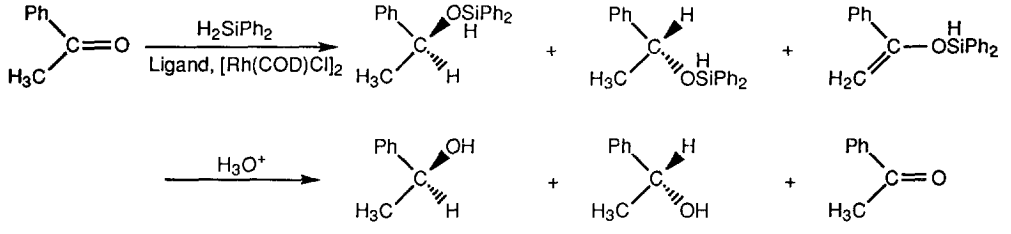


a, R = *i*-Pr; **b**, R = *t*-Bu; **c**, R = Ph; **d**, R = H

Scheme 1

heated with 2.1 equivalents of aminoalcohol at 120 ℃ for 3 h to give almost quantitatively bis(β-hydroxylamide)s **7** and **8**, respectively. Compounds **7** and **8** were further converted to dimesylates **9** and **10** by treatment with 2.5 equivalents of methanesulfonyl chloride in dichloromethane in the presence of 6 equivalents of triethylamine for 1 h at 0 ℃ and then for 3 h at room temperature. Reaction of **9** and **10** with 3 equivalents of pulverized sodium hydroxide in tetrahydrofuran for 72 h at room temperature afforded **1** and **2** in maximum 87% overall yield based on **5** and **6**, respectively.

In recent years, rhodium-catalyzed hydrosilylation of ketones, especially acetophenone, as an important asymmetric catalytic reaction has been investigated by Brunner,[9] Nishiyama,[10] Helmchen,[11] and Uemura[12] using oxazoline compounds as chiral ligands (Scheme 2). With the present new kind of bisoxazoline ligands in hand, we also investigated the rhodium-catalyzed hydrosilylation of acetophenone (Table 1).



Scheme 2

Table 1 Enantioselective Rh(I)-Catalyzed Hydrosilylation of Acetophenone [a]

Run	Ligand	Solvent	Time h	Temp °C	Yield, %[b]	ee, %[c]	Abs config[d]
1	**1a**	$PhCH_3$	120	-30	8	n.d	n.d
2	**1a**	CCl_4	72	-5	90	64	R
3	**1a**	CCl_4	48	rt	86	58	R
4	**2a**	CCl_4	72	-5	72	49	R
5	**1b**	CCl_4	72	-5	84	65	R
6	**2b**	CCl_4	72	-5	86	49	R
7	**1c**	CCl_4	72	-5	81	44	R
8	**2c**	CCl_4	72	-5	82	25	R
9	**1d**	CCl_4	120	-5	56	12	R

a) Conditions: Ligand (0.08 mmol), $[Rh(COD)Cl]_2$ (0.01 mmol), PhCOMe (2 mmol), Ph_2SiH_2 (3.2 mmol), $PhCH_3$ (0.5 ml) or CCl_4 (0.1 ml). Consumption of acetophenone was checked by TLC examination. b) The chemical yield was determined by ^{1}H-NMR studies using 1,1,2,2-tetrachloroethane as internal standard. c) The enantiomeric excess (% ee) was determined by HPLC analysis using a DAICEL CHIRALCEL OB column. d) The absolute configuration was determined by optical rotation.

With **1a** as a ligand, we first examined the effect of temperature on the catalytic reaction (run 1-3). At -30 ℃, the reaction proceeded very slowly and only 8% phenethyl alcohol was obtained after 120 h (run 1). As the temperature was raised to -5 ℃, acetophenone was completely consumed within 72 h and phenethyl alcohol

was obtained in 90% yield with 64% ee (run 2). When the temperature was raised to room temperature, the reaction was accelerated further but the ee was slightly down (run 3). Therefore, the ideal reaction temperature was -5 ℃ and at this temperature the reaction with **1b-d** and **2a-c** as ligands was carried out (run 4-9). From the experimental results, it was shown that **1a-c** and **2a-c** derived from two opposite enantiomers of tartaric acid gave the same chiral sense of enantioselection. Therefore, the chiral sense of enantioselection was determined only by the chirality of oxazoline ring derived from aminoacid. The ee with **1a-c** was higher than that with the corresponding **2a-c**, showing that the chirality of the dioxolane backbone derived from tartaric acid affected the degree of enantiomeric excess of the product. From Figure 2, it was clear that the steric environments of the

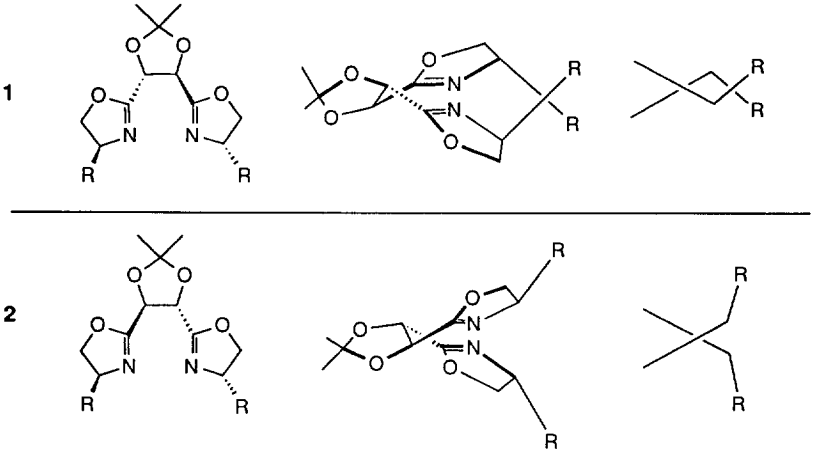


Figure 2

reaction site of ligands **1** and **2** were very different and the substituent on the oxazoline ring of ligand **1** was placed nearer to the reaction center than that of **2**, and therefore had a bigger effect on the enantioselectivity. It was also known from Table 1 that the bulkiness of the substituent on the oxazoline ring affected the enantioselectivity. Thus, the *tert*-butyl group gave the best ee while a phenyl group gave the worst ee.

It was noted that ligand **1d** with no substituent on the oxazoline ring also gave enantiomeric discrimination, though the ee of the product was very low. In this case, the stereocontrol of the reaction was determined by the chirality of the dioxolane backbone of the ligand.

In conclusion, we have developed new bisoxazolines with four asymmetric centers derived from two chiral sources, tartaric acid and aminoacids. With these compounds as chiral ligands, the rhodium-catalyzed asymmetric hydrosilylation of acetophenone was carried out. The effects of four asymmetric centers and the substituent on oxazoline ring of ligands on the reaction were studied and the best structure, **1b**, of this kind of ligand for the hydrosilylation of acetophenone was found. A study on the potential of this kind of ligand for other metal-catalyzed asymmetric reactions is now in progress.

Experimental Section

General methods: Melting points were measured on a Yanagimoto Micromelting Point Apparatus and have not been corrected. Optical rotations were measured on a Digital Polarimeter JASCO DIP-181. ^{1}H-

NMR spectra were recorded on a Bruker AM-600 (600 MHz) Spectrometer and the chemical shifts were referenced to $CHCl_3$ (δ 7.27) in $CDCl_3$. IR spectra were obtained on a Perkin-Elmer 1600 Series FT-IR. The fast atom bombardment mass spectra (FAB-MASS) were obtained on a JEOL JMS-DX303HF Spectrometer. Elemental analyses were performed on a Yanagimoto CHN-Corder. HPLC analyses were performed with a HITACHI L-6050 Pump, L-6250 Intelligent Pump, L-4200 UV-VIS Detector, D-2500 Chromato-Integrator, and a DAICEL CHIRALCEL OB column. Merck Art 7734 silica gel was used for column chromatography. Analytical TLC was performed on Merck Art 5735 precoated silica gel plates (0.25 mm).

(4*R*, 5*R*)-Bis(methoxycarbonyl)-2,2-dimethyl-1,3-dioxolane **5** was prepared from L-(+)-tartaric acid dimethyl ester and 2,2-dimethoxypropane, while (4*S*, 5*S*)-bis(methoxycarbonyl)-2,2-dimethyl-1,3-dioxolane **6** was prepared from D-(-)-tartaric acid, 2,2-dimethoxypropane and methanol with reported method.[8] Aminoalcohols were prepared by reduction of the corresponding commercially available aminoacids with lithium aluminium hydride as reducing agent in tetrahydrofuran. All of the other chemicals used in synthetic procedures were of reagent grade.

(4*R*,5*R*)-Bis[*N*-(1'*S*)-(1'-isopropyl-2'-hydroxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 7a: (*S*)-Valinol (5.0 g, 48.5 mmol) and dimethyl ester **5** (5.0 g, 22.9 mmol) were heated at 120 ℃ for 3 h under argon, while generated methanol was removed through a distillation equipment. After removal of the unreacted materials in vacuo, product **7a** was obtained as a white solid in 96% yield (7.9 g, 22.0 mmol). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 0.97 (d, 6H, *J* 6.9 Hz, CH_3), 0.99 (d, 6H, *J* 6.8 Hz, CH_3), 1.53 (s, 6H, O_2CCH_3), 1.70 (brs, 2H, OH), 1.94 (m, 2H, Me_2CH), 3.66 (dd, 2H, *J* 6.7, 11.2 Hz, OCH), 3.76 (dd, 2H, *J* 3.5, 11.2 Hz, OCH), 3.80 (m, 2H, NCH), 4.60 (s, 2H, NOCCH), 7.20 (d, 2H, *J* 8.3 Hz, NH). IR (KBr, cm^{-1}): 1650 (C=O), 1537 (N-H). FAB-MS (m/z): 361.

(4*R*,5*R*)-Bis[*N*-(1'*S*)-(1'-*tert*-butyl-2'-hydroxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 7b: Following the same procedure as described above, **7b** (8.5 g, 22.0 mmol) was obtained as a white solid in 96% yield from (*S*)-*tert*-leucinol (6.3 g, 53.8 mmol) and dimethyl ester **5** (5.0 g, 22.9 mmol). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 0.99 (s, 18H, CH_3), 1.55 (s, 6H, O_2CCH_3), 3.55 (q, 2H, *J* 8.6, 11.2 Hz, OCH), 3.87 (ddd, 2H, *J* 3.4, 7.8, 8.6 Hz, NCH), 3.93 (dd, 2H, *J* 3.4, 11.2 Hz, OCH), 4.62 (s, 2H, NOCCH), 7.28 (d, 2H, *J* 7.8 Hz, NH). IR (KBr, cm^{-1}): 1670(C=O), 1532 (N-H). FAB-MS (m/z): 389.

(4*R*,5*R*)-Bis[*N*-(1'*S*)-(1'-phenyl-2'-hydroxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 7c: Following the same procedure as described above, **7c** (9.0 g, 21.1 mol) was obtained as a white solid in 92% yield from (*S*)-phenylglycinol (6.5 g, 47.5 mmol) and dimethyl ester **5** (5.0 g, 22.9 mmol). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.54 (s, 6H, O_2CCH_3), 3.87 (dd, 2H, *J* 6.3, 11.4 Hz, OCH), 3.92 (dd, 2H, *J* 4.1, 11.4 Hz, OCH), 4.69 (s, 2H, NOCCH), 5.16 (ddd, 2H, *J* 4.1, 6.3, 7.9 Hz, NCH), 7.34 (m, 10H, Ph-H), 7.69 (d, 2H, *J* 7.9 Hz, NH). IR (KBr, cm^{-1}): 1668 (C=O), 1531 (N-H). FAB-MS (m/z): 429.

(4*R*,5*R*)-Bis[*N*-(2'-hydroxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 7d: Following the same procedure as described above, **7d** (5.6 g, 20.3 mmol) was obtained as a white solid in 89% yield from 2-aminoethanol (3.0 g, 49.1 mmol) and dimethyl ester **5** (5.0 g, 22.9 mmol). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.49 (s, 6H, O_2CCH_3), 3.42 (m, 2H, NCH), 3.48 (m, 2H, NCH), 3.71 (m, 4H, OCH), 4.57 (s, 2H, NOCCH), 7.40 (t, 2H, *J* 5.6 Hz, NH). IR (KBr, cm^{-1}): 1650 (C=O), 1537 (N-H). FAB-MS (m/z): 277.

(4*S*,5*S*)-Bis[*N*-(1'*S*)-(1'-isopropyl-2'-hydroxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 8a: Following the same procedure as described above, **8a** (8.1 g, 22.6 mmol) was obtained as a white solid in 98% yield from (*S*)-valinol (5.0 g, 48.5 mmol) and **6** (5.0 g, 22.9 mmol). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 0.95 (d, 6H, *J* 6.9 Hz, CH_3), 0.98 (d, 6H, *J* 6.8 Hz, CH_3), 1.53 (s, 6H, O_2CCH_3), 1.92 (m, 2H, Me_2CH), 3.65 (dd, 2H, *J* 6.5, 11.5 Hz, OCH), 3.74 (dd, 2H, *J* 3.6, 11.5 Hz, OCH), 3.80 (m, 2H, NCH), 4.57 (s, 2H, NOCCH), 7.03 (d, 2H, *J* 8.8 Hz, NH). IR (KBr, cm^{-1}): 1662 (C=O), 1558 (N-H). FAB-MS (m/z): 361.

(4*S*,5*S*)-Bis[*N*-(1'*S*)-(1'-*tert*-butyl-2'-hydroxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 8b: Following the same procedure as described above, **8b** (8.7 g, 22.5 mmol) was obtained as a white solid in 98% yield from (*S*)-*tert*-leucinol (6.4 g, 54.4 mmol) and dimethyl ester **6** (5.0 g, 22.9 mmol). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 0.97 (s, 18H, CH_3), 1.54 (s, 6H, O_2CCH_3), 3.57 (m, 2H, NCH), 3.86 (m, 4H, OCH), 4.59 (s, 2H, NOCCH), 7.04 (d, 2H, *J* 9.1 Hz, NH). IR (KBr, cm^{-1}): 1661(C=O), 1558 (N-H). FAB-MS (m/z): 389.

(4*S*,5*S*)-Bis[*N*-(1'*S*)-(1'-phenyl-2'-hydroxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 8c: Following the same procedure as described above, **8c** (9.7 g, 22.7 mmol) was obtained as a white solid in 99% yield from (*S*)-phenylglycinol (6.6 g, 48.2 mmol) and dimethyl ester **6** (5.0 g, 22.9 mmol). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.47 (s, 6H, O_2CCH_3), 2.34 (brs, 2H, OH), 3.85 (dd, 2H, *J* 6.7, 11.5 Hz, OCH), 3.91 (dd, 2H, *J* 4.1, 11.5 Hz, OCH), 4.66 (s, 2H, NOCCH), 5.16 (ddd, 2H, *J* 4.1, 6.7, 8.1 Hz, NCH), 7.34 (m, 10H, Ph-H), 7.56 (d, 2H, *J* 8.1 Hz, NH). IR (KBr, cm^{-1}): 1674 (C=O), 1530 (N-H). FAB-MS (m/z): 429.

(4*R*,5*R*)-Bis[*N*-(1'*S*)-(1'-isopropyl-2'-mesyloxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 9a: A solution of methanesulfonyl chloride (6.5 g, 56.7 mmol) in dry dichloromethane (30 ml) was added dropwise over 1 h to a solution of **7a** (7.9 g, 22.0 mmol) and triethylamine (20.0 ml, 143.5 mmol) in dry dichloromethane (120 ml) with stirring at -5 ℃. After stirred for 3 h at room temperature, cold water was added to the reaction solution. The organic layer was separated and washed with brine, dried over magnesium sulfate, and then concentrated in vacuo to give the crude product **9a** (11.6 g) as a light yellow solid. This material was directly used in the next reaction without further purification. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.00 (d, 6H, *J* 6.8 Hz, CH_3), 1.02 (d, 6H, *J* 6.7 Hz, CH_3), 1.53 (s, 6H, O_2CCH_3), 1.96 (m, 2H, Me_2CH), 3.04 (s, 6H, SCH_3), 4.01 (m, 2H, NCH), 4.28 (dd, 2H, *J* 3.7, 10.6 Hz, OCH), 4.35 (dd, 2H, *J* 5.2, 10.6 Hz, OCH), 4.56 (s, 2H, NOCCH), 7.11 (d, 2H, *J* 8.9 Hz, NH). IR (KBr, cm^{-1}): 1674 (C=O), 1529 (N-H). FAB-MS (m/z): 517.

(4*R*,5*R*)-Bis[*N*-(1'*S*)-(1'-*tert*-butyl-2'-mesyloxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 9b: Following the same procedure as described above, **9b** (11.7 g) was obtained from **7b** (8.5 g, 22.0 mmol) and methanesulfonyl chloride (6.3 g, 55.0 mmol) as a light yellow solid. This material was directly used in the next reaction without further purification. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.00 (s, 18H, CH_3), 1.53 (s, 6H, O_2CCH_3), 3.02 (s, 6H, SCH_3), 4.11 (m, 2H, NCH), 4.20 (q, 2H, *J* 7.6, 10.7 Hz, OCH), 4.42 (dd, 2H, *J* 3.6, 10.7 Hz, OCH), 4.55 (s, 2H, NOCCH), 7.18 (d, 2H, *J* 9.8 Hz, NH). IR (neat, cm^{-1}): 1678 (C=O), 1526 (N-H). FAB-MS (m/z): 545.

(4*R*,5*R*)-Bis[*N*-(1'*S*)-(1'-phenyl-2'-mesyloxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 9c: Following the same procedure as described above, **9c** (11.1 g) was obtained from **7c** (9.0 g,

21.1 mmol) and methanesulfonyl chloride (6.0 g, 52.4 mmol) as a light yellow solid. This material was directly used in the next reaction without further purification. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.56 (s, 6H, O_2CCH_3), 2.95 (s, 6H, SCH_3), 4.44 (dd, 2H, *J* 6.4, 10.8 Hz, OCH), 4.55(dd, 2H, *J* 4.4, 10.8 Hz, OCH), 4.63 (s, 2H, NOCCH), 5.41 (m, 2H, NCH), 7.36 (m, 10H, Ph-H), 7.70 (d, 2H, *J* 8.4 Hz, NH). IR (neat, cm^{-1}): 1672 (C=O), 1528 (N-H). FAB-MS (m/z): 585.

(4*R*,5*R*)-Bis[*N*-(2'-mesyloxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 9d: Following the same procedure as described above, **9d** (8.7 g) was obtained from **7d** (5.6 g, 20.3 mmol) and methanesulfonyl chloride (6.0 g, 52.4 mmol) as a light yellow solid. This material was directly used in the next reaction without further purification. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.51 (s, 6H, O_2CCH_3), 2.79 (s, 6H, SCH_3), 3.66 (m, 4H, NCH), 4.35 (m, 4H, OCH), 4.59 (s, 2H, NOCCH), 7.37 (t, 2H, *J* 5.8 Hz, NH). IR (neat, cm^{-1}): 1670 (C=O), 1534 (N-H). FAB-MS (m/z): 433.

(4*S*,5*S*)-Bis[*N*-(1'*S*)-(1'-isopropyl-2'-mesyloxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 10a: Following the same procedure as described above, **10a** (11.5 g) was obtained from **8a** (8.1 g, 22.6 mmol) and methanesulfonyl chloride (6.5 g, 56.7 mmol) as a light yellow solid. This material was directly used in the next reaction without further purification. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 0.99 (d, 6H, *J* 6.55 Hz, CH_3), 1.02 (d, 6H, *J* 6.45 Hz, CH_3), 1.52 (s, 6H, O_2CCH_3), 1.52 (s, 6H, SCH_3), 1.97 (m, 2H, Me_2CH), 4.00 (m, 2H, NCH), 4.29 (dd, 2H, *J* 5.27, 10.35 Hz, OCH), 4.32 (dd, 2H, *J* 4.06, 10.57 Hz, OCH), 4.59 (s, 2H, NOCCH), 7.17 (d, 2H, *J* 9.00 Hz, NH). IR (KBr, cm^{-1}): 1678 (C=O), 1530 (N-H). FAB-MS (m/z): 517.

(4*S*,5*S*)-Bis[*N*-(1'*S*)-(1'-*tert*-butyl-2'-mesyloxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 10b: Following the same procedure as described above, **10b** (11.8 g) was obtained from **8b** (8.7 g, 22.5 mmol) and methanesulfonyl chloride (6.5 g, 56.7 mmol) as a light yellow solid. This material was directly used in the next reaction without further purification. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 0.99 (s, 18H, CH_3), 1.50 (s, 6H, O_2CCH_3), 3.02 (s, 6H, SCH_3), 4.10 (m, 2H, NCH), 4.21 (dd, 2H, *J* 7.4, 10.6 Hz, OCH), 4.30 (dd, 2H, *J* 3.5, 10.6 Hz, OCH), 4.59 (s, 2H, NOCCH), 7.28 (d, 2H, *J* 8.5 Hz, NH). IR (neat, cm^{-1}): 1677 (C=O), 1529 (N-H). FAB-MS (m/z): 545.

(4*S*,5*S*)-Bis[*N*-(1'*S*)-(1'-phenyl-2'-mesyloxyethyl)-amido]-2,2-dimethyl-1,3-dioxolane 10c: Following the same procedure as described above, **10c** (12.9 g) was obtained from **8c** (9.7 g, 22.7 mmol) and methanesulfonyl chloride (6.5 g, 56.7 mmol) as a light yellow solid. This material was directly used in the next reaction without further purification. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.49 (s, 6H, O_2CCH_3), 2.95 (s, 6H, SCH_3), 4.46 (m, 2H, OCH), 4.53(m, 2H, OCH), 4.66 (s, 2H, NOCCH), 5.40 (m, 2H, NCH), 7.35 (m, 10H, Ph-H), 7.69 (d, 2H, *J* 8.4 Hz, NH). FAB-MS (m/z): 585. IR (neat, cm^{-1}): 1673 (C=O), 1530 (N-H). FAB-MS (m/z): 585.

(4*R*,5*R*)-Bis[(4'*S*)-isopropyloxazolin-2'-yl]-2,2-dimethyl-1,3-dioxolane 1a: The mixture of crude compound **9a** (11.6 g) and pulverized sodium hydroxide (3.0 g, 72.0 mmol) in tetrahydrofuran (150 ml) was stirred for 72 h at room temperature. After removal of solid material by filtration and solvent by evaporation, the remaining oily material was dissolved in dichloromethane. The solution was washed with water and brine, dried over magnesium sulfate and then the solvent was evaporated. The residue was distilled under reduced pressure to give **1a** (6.0 g, 18.6 mmol) as a colorless viscous liquid (155 ℃ / 0.08 mmHg). Overall yield from **7a** was 85%. $[\alpha]_D^{17}$ = -143.0 (c 1.0, CH_2Cl_2). ^{1}H-NMR (600 MHz, $CDCl_3$): δ

0.88 (d, 6H, *J* 6.7 Hz, CH_3), 0.96 (d, 6H, *J* 6.9 Hz, CH_3), 1.52 (s, 6H, O_2CCH_3), 1.78 (m, 2H, Me_2CH), 3.97 (m, 2H, NCH), 4.06 (dd, 2H, *J* 8.7, 9.6 Hz, OCH), 4.33 (dd, 2H, *J* 7.7, 8.7 Hz, OCH), 4.95 (s, 2H, NOCCH). IR (neat, cm^{-1}): 1675 (C=N). FAB-MS (m/z): 325. Anal. Calcd. for $C_{17}H_{28}N_2O_4$: C, 62.94; H, 8.70; N, 8.64. Found: C, 62.86; H, 8.84; N, 8.77.

(4*R*,5*R*)-Bis[(4'*S*)-*tert*-butyloxazolin-2'-yl]-2,2-dimethyl-1,3-dioxolane 1b: The mixture of crude compound **9b** (11.7 g) and pulverized sodium hydroxide (3.0 g, 72.0 mmol) in tetrahydrofuran (150 ml) was stirred for 72 h at room temperature. After removal of solid material by filtration and solvent by evaporation, **1b** (6.1 g, 17.4 mmol) was obtained by recrystallization from ether as white needles. Overall yield from **7b** was 79%. mp: 86-88 ℃. $[\alpha]_D^{17}$ = -151.0 (c 0.5, CH_2Cl_2). ^{1}H-NMR (600 MHz, $CDCl_3$): δ0.90 (s, 18H, CH_3), 1.52 (s, 6H, O_2CCH_3), 3.91 (q, 2H, *J* 8.2, 10.0 Hz, OCH), 4.16 (q, 2H, *J* 8.2, 8.6 Hz, OCH), 4.27 (q, 2H, *J* 8.6, 10.0 Hz, NCH), 4.98 (s, 2H, NOCCH). IR (KBr, cm^{-1}): 1679 (C=N). FAB-MS (m/z): 353. Anal. Calcd. for $C_{19}H_{32}N_2O_4$: C, 64.75; H, 9.15; N, 7.95. Found: C, 64.70; H, 9.18; N, 7.92.

(4*R*,5*R*)-Bis[(4'*S*)-phenyloxazolin-2'-yl]-2,2-dimethyl-1,3-dioxolane 1c: The mixture of crude compound **9c** (11.1 g) and pulverized sodium hydroxide (3.0 g, 72.0 mmol) in tetrahydrofuran (150 ml) was stirred for 72 h at room temperature. After removal of solid material by filtration and solvent by evaporation, **1c** (6.9 g, 17.6 mmol) was obtained by recrystallization from ether as white needles. Overall yield from **7c** was 84%. mp: 90-92 ℃. $[\alpha]_D^{17}$ = -126.3 (c 0.5, CH_2Cl_2). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.59 (s, 6H, O_2CCH_3), 4.23 (t, 2H, *J* 8.5 Hz, OCH), 4.76 (q, 2H, *J* 8.5, 9.4 Hz, OCH), 5.19 (s, 2H, NOCCH), 5.29 (q, 2H, *J* 8.5, 9.4 Hz, NCH), 7.30 (m, 10H, Ph-H). IR (KBr, cm^{-1}): 1071 (C=N). FAB-MS (m/z): 393. Anal. Calcd. for $C_{23}H_{24}N_2O_4$: C, 70.39; H, 6.16; N, 7.14. Found: C, 70.33; H, 6.14; N, 7.15.

(4*R*,5*R*)-Bis(oxazolin-2'-yl)-2,2-dimethyl-1,3-dioxolane 1d: The mixture of crude compound **9d** (8.7 g) and pulverized sodium hydroxide (2.5 g, 60.0 mmol) in tetrahydrofuran (150 ml) was stirred for 72 h at room temperature. After removal of solid material by filtration and solvent by evaporation, the remaining oily material was dissolved in dichloromethane. The solution was washed with water and brine, dried over magnesium sulfate and then the solvent was evaporated. The residue was distilled under reduced pressure to give **1d** (4.8 g, 19.9 mmol) as a colorless viscous liquid (120 ℃ / 1.00 mmHg). Overall yield from **7d** was 98%. $[\alpha]_D^{17}$ = -51.6 (c 1.0, CH_2Cl_2). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.50 (s, 6H, O_2CCH_3), 3.91 (t, 4H, *J* 9.6 Hz, OCH), 4.35 (t, 4H, *J* 9.6 Hz, NCH), 4.96 (s, 2H, NOCCH). IR (neat, cm^{-1}): 1668 (C=N). FAB-MS (m/z): 241. Anal. Calcd. for $C_{11}H_{16}N_2O_4$: C, 54.99; H, 6.71; N, 11.66. Found: C, 54.81; H, 6.85; N, 11.48.

(4*S*,5*S*)-Bis[(4'*S*)-isopropyloxazolin-2'-yl]-2,2-dimethyl-1,3-dioxolane 2a: The mixture of crude compound **10a** (11.5 g) and pulverized sodium hydroxide (3.0 g, 72.0 mmol) in tetrahydrofuran (150 ml) was stirred for 72 h at room temperature. After removal of solid material by filtration and solvent by evaporation, **2a** (5.9 g, 18.1 mmol) was obtained by recrystallization from ether as white needles. Overall yield from **8a** was 80%. mp: 65-66 ℃. $[\alpha]_D^{17}$ = -41.4 (c 0.5, CH_2Cl_2). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 0.88 (d, 6H, *J* 6.6 Hz, CH_3), 0.96 (d, 6H, *J* 6.9 Hz, CH_3), 3.04 (s, 6H, O_2CCH_3), 1.79 (m, 2H, Me_2CH), 4.00 (m, 2H, NCH), 4.08 (t, 2H, *J* 8.2 Hz, OCH), 4.34 (t, 2H, *J* 9.1 Hz, OCH), 4.97 (s, 2H, NOCCH). IR (KBr, cm^{-1}): 1675 (C=N). FAB-MS (m/z): 325. Anal. Calcd. for $C_{17}H_{28}N_2O_4$: C, 62.94; H, 8.70; N, 8.64. Found: C, 62.90; H, 8.75; N, 8.65.

(4*S*,5*S*)-Bis[(4'*S*)-*tert*-butyloxazolin-2'-yl]-2,2-dimethyl-1,3-dioxolane 2b: The mixture of crude compound **10b** (11.8 g) and pulverized sodium hydroxide (3.0 g, 72.0 mmol) in tetrahydrofuran (150 ml) was stirred for 72 h at room temperature. After removal of solid material by filtration and solvent by evaporation, **2b** (6.3 g, 18.0 mmol) was obtained by recrystallization from ether as white needles. Overall yield from **8b** was 80%. mp: 103-105 ℃. $[\alpha]_D^{17}$ = -44.6 (c 0.5, CH_2Cl_2). ^{1}H-NMR (600 MHz, $CDCl_3$): δ0.90 (s, 18H, CH_3), 1.52 (s, 6H, O_2CCH_3), 3.93 (q, 2H, *J* 8.3, 10.0 Hz, OCH), 4.16 (q, 2H, *J* 8.3, 8.7 Hz, OCH), 4.29 (q, 2H, *J* 8.7, 10.0 Hz, NCH), 4.98 (s, 2H, NOCCH). IR (KBr, cm^{-1}): 1674 (C=N). FAB-MS (m/z): 353. Anal. Calcd. for $C_{19}H_{32}N_2O_4$: C, 64.75; H, 9.15; N, 7.95. Found: C, 64.69; H, 9.15; N, 7.95.

(4*S*,5*S*)-Bis[(4'*S*)-phenyloxazolin-2'-yl]-2,2-dimethyl-1,3-dioxolane 2c: The mixture of crude compound **10c** (12.9 g) and pulverized sodium hydroxide (3.0 g, 72.0 mmol) in tetrahydrofuran (150 ml) was stirred for 72 h at room temperature. After removal of solid material by filtration and solvent by evaporation, the residue was purified by silica gel column chromatography with ethylacetate-benzene-triethylamine (70 : 30 : 1) as eluent to give **2c** (7.0 g, 16.4 mmol) as a colorless viscous liquid. Overall yield from **8c** was 73%. Rf = 0.5 (ethylacetate-benzene-triethylamine, 70 : 30 : 1). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.54 (s, 6H, O_2CCH_3), 4.23 (t, 2H, *J* 8.3 Hz, OCH), 4.76 (dd, 2H, *J* 8.3, 10.4 Hz, OCH), 5.19 (s, 2H, NOCCH), 5.29 (dd, 2H, *J* 8.3, 10.4 Hz, NCH), 7.30 (m, 10H, Ph-H). IR (neat, cm^{-1}): 1666 (C=N). FAB-MS (m/z): 393. $[\alpha]_D^{17}$ = +5.1 (c 1.5, CH_2Cl_2). Anal. Calcd. for $C_{23}H_{24}N_2O_4$: C, 70.39; H, 6.16; N, 7.14. Found: C, 70.27; H, 6.15; N, 7.14.

Typical procedure for the rhodium-catalyzed hydrosilylation of acetophenone: A solution of **1a** (26 mg, 0.08 mmol), $[Rh(COD)Cl]_2$ (5 mg, 0.01 mmol), and acetophenone (240 mg, 2 mmol) in tetrachloromethane (0.1 ml) was stirred for 1 h at room temperature under argon atmosphere. After diphenylsilane (590 mg, 3.2 mmol) was added to the solution at -5 ℃, the reaction mixture was stirred at the temperature until acetophenone disappeared by TLC analysis (Rf = 0.2, hexane-ether, 5 : 1). The reaction solution was quenched with methanol (0.4 ml), and then 1 N hydrochloric acid (2.0 ml) at 0 ℃ to give a mixture of phenethyl alcohol and a small amount of acetophenone. Chemical yield was determined by ^{1}H-NMR spectra of the reaction mixture with 1,1,2,2,-tetrachloroethane as an internal standard. After purification by column chromatography on silica gel with hexane-isopropanol (9 : 1), the configuration of the product was determined by optical rotation and enantiomeric excess was determined by HPLC analysis using a DAICEL CHIRALCEL OB column (eluent, hexane-isopropanol (9 : 1); flow rate, 0.5 ml /min).[13]

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References and Notes

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