Asymmetric Synthesis of β-Hydroxy Acid *via* Stereoselective Dirhodium(II)-Catalyzed C–H Insertion of α-Alkoxydiazoketone

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A new methodology for the asymmetric synthesis of β-hydroxy acid was developed. Dirhodium(II)-catalyzed C–H insertion of α-alkoxydiazoketone (3), which was prepared from primary alkyl halide (1) and readily available chiral α-hydroxy acid (2), gave stereoselectively 2,5-*cis*-disubstituted 3(2*H*)-furanone (4). The Baeyer-Villiger reaction of 4 followed by treatment with an acid afforded chiral β-hydroxy acid (6) with high optical purity.

Key words β-hydroxy acid; α-alkoxydiazoketone; C–H insertion; dirhodium(II); 3(2*H*)-furanone

The development of new methodologies for the synthesis of chiral β-hydroxy acids is highly desired because of their utility in organic synthesis.[1—3] We have been investigating a new strategy for the synthesis of chiral β-hydroxy acids, which is based on the stereoselective dirhodium(II)-catalyzed C–H insertion[4—8] of α-alkoxydiazoketone, and report herein our preliminary results.

Our strategy is outlined in Chart 1. Primary alkyl halide (**1**) is easily transformed into α-alkoxydiazoketone (**3**) by treatment with α-hydroxy acid (**2**), which can be prepared from α-amino acid in an optically active form, followed by diazomethylation. The dirhodium(II)-catalyzed reaction of **3** stereoselectively affords the 2,5-*cis*-disubstituted 3(2*H*)-furanone (**4**).[9—11] Oxidation of **4** with *m*-chloroperbenzoic acid (*m*-CPBA) regio- and stereoselectively gives protected β-hydroxy acid (**5**), which is easily converted into β-hydroxy acid by treatment with an acid and is also an important intermediate for the synthesis of *syn*- and *anti*-1,3-diols.[12,13] The chirality of the resultant β-hydroxy acid is transferred from that of the used α-hydroxy acid (**2**). From the literature,[9—11] we expected that the reaction of α–alkoxydiazoketone having a bulky group at α-position would give good *cis*-selectivity in the formation of 2,5-disubstituted 3(2*H*)-furanone. Thus, we investigated the C–H insertion reaction of **3** which has an isopropyl group at the α-position of the keto group (R^1=*i*-Pr). The requisite α-hydroxy acid **2** (R^1=*i*-Pr, R^2=H) can be easily obtained in both optically active forms from valine.[14]

First, we investigated the reactions of racemic diazoketones (**3**) with catalytic amounts of various dirhodium(II) catalysts. The results are shown in Table 1. Starting diazoketones (**3a** and **3b**) were prepared from α-alkoxyester (**7**) by a standard manner.[15] After hydrolysis of **7** into the corresponding carboxylic acid, the acid was converted into its mixed anhydride using ethyl chloroformate, and then treated with excess diazomethane to afford **3** (Chart 2).

α-Benzyloxydiazoketone (**3a**) was reacted with 1 mol% of dirhodium(II) tetraacetate [$Rh_2(OAc)_4$] in CH_2Cl_2 (0.017 M) at room temperature for 10 min. The only 2-isopropyl-5-phenyldihydrofuran-3-one (**4a**) was isolated in 30% yield as a 1.4 : 1 mixture of *cis* and *trans* isomers (Entry 1).[16] Both chemical yield and diastereoselectivity were influenced by the ligand of dirhodium(II) catalyst. Treatment of **3a** with dirhodium(II) tetraoctanoate [$Rh_2(oct)_4$] gave **4a** in 39% yield with high *cis*-selectivity (17 : 1) (Entry 3). However, the use of dirhodium(II) tetra(triphenylacetate) [$Rh_2(TPA)_4$] having bulkier ligand than that of $Rh_2(oct)_4$ decreased *cis*-selectivity to 3.8 : 1 (Entry 2). The stereostructure of the major product was deduced from differential nuclear Overhauser effect (NOE) experiments: positive NOEs were observed between 2-H and 5-H. The reaction of butoxy derivative (**3b**) with $Rh_2(oct)_4$ in CH_2Cl_2 (0.017 M) gave exclusively *cis*-**4b** in 53% yield (Entry 4). A low concentration (0.005 M) gave a slight increase in the yield (Entry 5). In benzene, the reaction at room temperature gave a higher yield (Entry 6) and the best result (70% yield) was obtained in the reaction at high temperature (Entry 7).

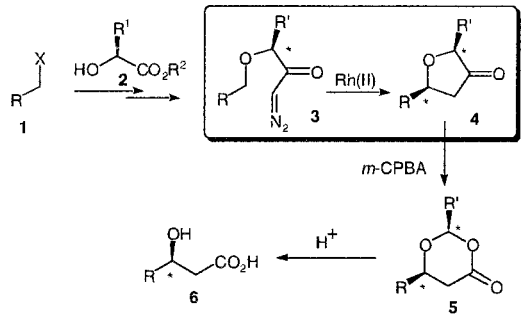

Chart 1

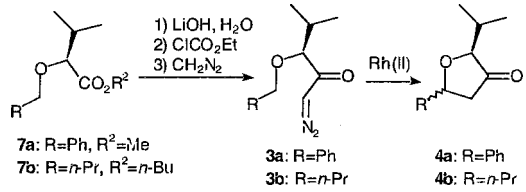

Chart 2

Table 1. Dirhodium(II)-Catalyzed Reaction of **3**[a]

Entry	3	Rh(II)	Solvent	Temp.	Yield (%)	*cis* : *trans*[b]
1	**a**	$Rh_2(OAc)_4$	CH_2Cl_2	rt	30	1.4 : 1
2	**a**	$Rh_2(TPA)_4$	CH_2Cl_2	rt	39	3.8 : 1
3	**a**	$Rh_2(oct)_4$	CH_2Cl_2	rt	39	17 : 1
4	**b**	$Rh_2(oct)_4$	CH_2Cl_2	rt	53	*cis*
5[c]	**b**	$Rh_2(oct)_4$	CH_2Cl_2	rt	59	*cis*
6	**b**	$Rh_2(oct)_4$	benzene	rt	62	*cis*
7	**b**	$Rh_2(oct)_4$	benzene	reflux	70	*cis*

a) Reactions were carried out in 0.017 M solution. All reactions were completed in 10 min. *b*) Determined by ^{1}H-NMR. *c*) Concentration was 0.005 M.

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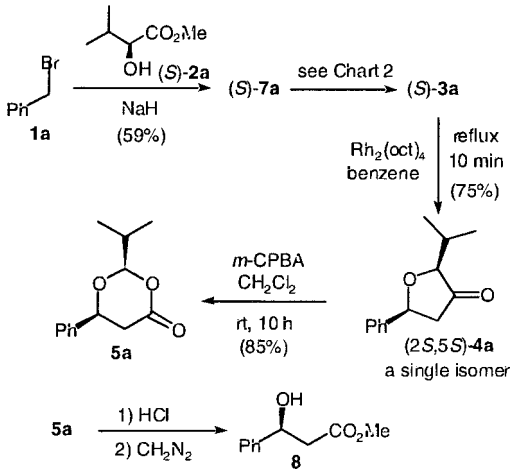

Chart 3

On the basis of the above mentioned results, we attempted the asymmetric synthesis of a chiral β-hydroxy acid (Chart 3). Treatment of benzyl bromide with methyl (*S*)-2-hydroxy-3-methylbutanoate [(*S*)-**2a**][14] in the presence of sodium hydride in dimethylformamide (DMF) gave (*S*)-**7a**[14,17] in an optically active form (90.8% ee) in 59% yield. Conversion of (*S*)-**7a** into (*S*)-**3a** was performed using the same procedure as that for racemic **7a**. Fortunately, the dirhodium(II)-catalyzed reaction of (*S*)-**3a** in refluxing benzene gave excellent stereoselectivity and a high yield. Thus, (*S*)-**3a** was reacted with 1 mol% of $Rh_2(oct)_4$ in benzene (0.017 M) under reflux for 10 min to afford (2*S*,5*S*)-**4a** as a single isomer in 75% yield. Then, treatment of (2*S*,5*S*)-**4a** with *m*-CPBA in CH_2Cl_2 at room temperature for 10 h gave the protected β-hydroxy acid (**5a**) in 85% yield. The *cis* configuration of **5a** was determined by NOE experiments. The absolute configuration of **5a** was confirmed by conversion into known chiral β-hydroxy-ester (**8**) *via* treatment with hydrochloric acid, followed by esterification with diazomethane. The spectroscopic data and the specific rotation of **8** were identical with those of an authentic sample[18] and the optical purity (90.4% ee) was determined by HPLC analysis using Chiralcel ADH (hexane/EtOH, 95/5, 1 ml/min).

In summary, we showed a new methodology for the synthesis of chiral β-hydroxy acid from primary alkyl halide employing stereoselective dirhodium(II)-catalyzed C–H insertion as a key step. The chirality of the resultant β-hydroxy acid was effectively transferred from that of the used α-hydroxy acid.

Experimental

Melting points are uncorrected. IR spectra were recorded using a JASCO FT/IR-410 spectrophotometer. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75.4 MHz) spectra were determined with a JEOL JNM-AL 300 spectrometer, using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. All ^{13}C-NMR spectra were determined with complete proton decoupling. High resolution MS were determined with JEOL JMS-SX 102A (FAB-MS) and JEOL JMS-BU 20 (EI- and CI-MS) instruments. Optical rotations were measured with a JASCO DIP-360 polarimeter. Column chromatography was performed on Silica gel 60 (0.063—0.200 mm) (MERCK).

3-Benzyloxy-1-diazo-4-methylpentan-2-one (3a) Lithium hydroxide monohydrate (404 mg, 9.63 mmol) was added to a solution of known methyl 2-benzyloxy-3-methylhexanoate (**7a**)[14] (855 mg, 3.85 mmol) in MeOH (30 ml) and H_2O (6.2 ml) and the mixture was stirred at room temperature overnight. The resulting mixture was concentrated under reduced pressure, then 10% hydrochloric acid was added until pH was 2. The mixture was extracted with Et_2O and the extract was dried ($MgSO_4$) and concentrated to give crude 2-benzyloxy-3-methylhexanoic acid. According to the procedure of Seebach *et al.*,[15] a solution of the crude acid in THF (20 ml) was cooled to −15 °C and Et_3N (400 mg, 3.96 mmol) and $ClCO_2Et$ (430 mg, 3.96 mmol) were added. After 30 min, the suspension was allowed to warm to 0 °C and stirred for further 30 min. Then a solution of CH_2N_2 in Et_2O was added at the same temperature until a strong yellow color persisted. The suspension was allowed to warm to room temperature and stirred for 5 h. The excess of CH_2N_2 was destroyed by the addition of a few drops of AcOH. The mixture was diluted with H_2O, and extracted with Et_2O. The organic layer was washed with aqueous saturated $NaHCO_3$ solution, aqueous saturated NH_4Cl solution and brine, and dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel (5% EtOAc in hexane) to give **3a** (551 mg, 62% in 3 steps) as a yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, d, J=6.8 Hz), 0.98 (3H, d, J=6.8 Hz), 1.93—2.09 (1H, m), 3.58 (1H, d, J=5.7 Hz), 4.44 (1H, ABq, J=11.6 Hz), 4.64 (1H, ABq, J=11.6 Hz), 5.71 (1H, s), 7.21—7.39 (5H, m). IR (neat) cm^{-1}: 2104, 1634. FAB-MS *m/z*: 233.1286 (Calcd for $C_{13}H_{17}N_2O_2$: 233.1290).

Butyl 2-Butoxy-3-methylbutanoate (7b) A solution of 2-hydroxy-3-methylbutanoic acid (1 g, 8.47 mmol) in DMF (20 ml) was added to a suspension of NaH (447 mg, 18.6 mmol) in DMF (10 ml) at 0 °C under nitrogen atmosphere and the mixture was stirred for 30 min at the same temperature. A solution of 1-bromobutane (2.79 g, 20.3 mmol) in DMF (10 ml) and tetrabutylammonium iodide (313 mg, 0.85 mmol) were added. After 30 min, the mixture was allowed to warm to room temperature and stirred overnight. The mixture was quenched with H_2O, and extracted with Et_2O. The extract was washed with H_2O and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (5% EtOAc in hexane) to give **7b** (639 mg, 33%) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 0.91 (3H, t, J=7.3 Hz), 0.94 (3H, t, J=7.2 Hz), 0.95 (3H, d, J=6.6 Hz), 0.96 (3H, d, J=6.6 Hz), 1.32—1.48 (4H, m), 1.52—1.69 (4H, m), 1.95—2.11 (1H, m), 3.29 (1H, dt, J=9.2, 6.6 Hz), 3.53 (1H, d, J=5.9 Hz), 3.57 (1H, dt, J=9.2, 6.4 Hz), 4.08—4.22 (2H, m). IR (neat) cm^{-1}: 1749. CI-MS *m/z*: 231.1954 (Calcd for $C_{13}H_{27}O_3$: 231.1960).

3-Butoxy-1-diazo-4-methylpentan-2-one (3b) According to a procedure similar to that described for the preparationo of **3a**, **3b** (320 mg, 34% in 3 steps) was obtained from **7b** (1.1 g, 4.8 mmol) as a yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 0.93 (3H, t, J=7.3 Hz), 0.94 (3H, d, J=6.8 Hz), 0.96 (3H, d, J=6.8 Hz), 1.33—1.48 (2H, m), 1.52—1.62 (2H, m), 1.87—2.03 (1H, m), 3.35 (1H, dt, J=9.2, 6.6 Hz), 3.41 (1H, d, J=5.5 Hz), 3.55 (1H, dt, J=9.2, 6.4 Hz), 5.67 (1H, s). IR (neat) cm^{-1}: 2104, 1638. FAB-MS *m/z*: 199.1453 (Calcd for $C_{10}H_{19}N_2O_2$: 199.1447).

General Procedure for the Dirhodium(II)-Catalyzed C–H Insertion of α-Alkoxydiazoketone A solution of **3** (0.2 mmol) in an appropriate solvent (2 ml) was added to a solution of dirhodium(II) catalyst (0.002 mmol) in an appropriate solvent (10 ml) at room temperature or under reflux, and the mixture was stirred for 10 min at the same temperature and the reaction mixture was concentrated. The residue was chromatographed on silica gel.

Dirhodium(II)-Catalyzed C–H Insertion of 3a Entry 1: According to the general procedure, **3a** (47 mg, 0.2 mmol) was treated with $Rh_2(OAc)_4$ (1 mg, 0.002 mmol) in CH_2Cl_2 (12 ml) and the crude material was chromatographed on silica gel (10% EtOAc in hexane) to give a 1.4 : 1 mixture of *cis* and *trans* isomers of **4a** (12 mg, 30%) as a colorless oil. The ratio of *cis*-**4a** and *trans*-**4a** was estimated to be 1.4 : 1 by integration of the intensities of the peak heights of the signals due to the methine proton at 5-position which appeared at δ 5.11 (dd) and 5.42 (t), respectively.

Entry 3: According to the general procedure, **3a** (47 mg, 0.2 mmol) was treated with $Rh_2(oct)_4$ (2 mg, 0.002 mmol) in CH_2Cl_2 (12 ml) and the crude material was chromatographed on silica gel (10% EtOAc in hexane) to give a 17 : 1 mixture of *cis* and *trans* isomers of **4a** (16 mg, 39%) as a colorless oil. The mixture was re-chromatographed on silica gel (5% EtOAc in hexane) to give pure (2*S**,5*S**)-2-isopropyl-5-phenyldihydrofuran-3-one (*cis*-**4a**) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.02 (3H, d, J=7.0 Hz), 1.13 (3H, d, J=7.0 Hz), 2.11—2.27 (1H, m), 2.39 (1H, dd, J=17.8, 11.2 Hz), 2.82 (1H, dd, J=17.8, 5.7 Hz), 3.81 (1H, d, J=3.7 Hz), 5.11 (1H, dd, J=11.2, 5.7 Hz), 7.32—7.45 (5H, m). ^{13}C-NMR ($CDCl_3$) δ: 17.0, 19.0, 30.3, 46.6, 76.8, 86.0, 126.0, 128.2, 128.6 (3), 140.4, 215.7. IR (neat) cm^{-1}: 1756. CI-MS *m/z*: 205.1234 (Calcd for $C_{13}H_{17}O_2$: 205.1228). The ^{1}H-NMR spectrum of the mixture of *cis* and *trans* isomers of **4a** exhibited the following signals of the *trans*-**4a**, δ: 1.01 (3H, d, J=6.9 Hz), 1.09 (3H, d, J=6.9 Hz), 2.05—2.20 (1H, m), 2.63 (1H, dd, J=18.2, 6.4 Hz), 2.89 (1H, dd, J=18.2, 7.7 Hz), 3.87 (1H, d, J=5.1 Hz), 5.42 (1H, t, J=7.2 Hz), 7.32—7.49 (5H, m).

Dirhodium(II)-Catalyzed C–H Insertion of 3b According to the general procedure, **3b** (20 mg, 0.1 mmol) was treated with $Rh_2(oct)_4$ (1 mg, 0.001 mmol) in refluxing benzene (6 ml) and the crude material was chromatographed on silica gel (5% EtOAc in hexane) to give (2*S**,5*R**)-2-isopropyl-5-propyldihydrofuran-3-one (*cis*-**4b**) (12 mg, 70%) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 0.90 (3H, d, J=6.8 Hz), 0.97 (3H, t, J=7.3 Hz), 1.03 (3H, d, J=7.0 Hz), 1.32—1.84 (4H, m), 1.97—2.13 (1H, m), 2.04 (1H, dd, J=17.7, 10.9 Hz), 2.49 (1H, dd, J=17.7, 5.4 Hz), 3.62 (1H, d, J=3.9 Hz), 4.02—4.16 (1H, m). ^{13}C-NMR ($CDCl_3$) δ: 14.1, 16.8, 18.6, 18.8, 30.1, 37.7, 44.3, 75.2, 85.6, 217.0. IR (neat) cm^{-1}: 1754. CI-MS *m*/*z*: 171.1391 (Calcd for $C_{10}H_{19}O_2$: 171.1385).

Methyl (*S*)-2-Benzyloxy-3-methylhexanoate [(*S*)-7a] A solution of methyl (*S*)-2-hydroxy-3-methylbutanoate [(*S*)-**2a**] (125 mg, 0.95 mmol), which was prepared from L-valine,[14] in DMF (0.5 ml) was added to a suspension of NaH (18 mg, 0.75 mmol) in DMF (1 ml) at 0 °C under nitrogen atmosphere and the mixture was stirred for 45 min at the same temperature. A solution of benzyl bromide (162 mg, 0.95 mmol) in DMF (0.5 ml) was added and stirred at 0 °C for 2 h. The mixture was quenched with saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was washed with H_2O and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (20% EtOAc in hexane) to give the starting hydroxyester (26 mg, 21%) and (*S*)-**7a**[14] (99 mg, 47%, 59% based on recovery of starting material) as a colorless oil. $[\alpha]_D^{24}$ −72.0° (c=1.61, CH_2Cl_2), $[\alpha]_D^{23}$ −73.5° (c=2.44, $CHCl_3$). [lit.[17] for (*R*)-**7a**, $[\alpha]_D^{20}$ +77.3° (c=2.44, $CHCl_3$)]. HPLC: t_R (*R*)-**7a**, 4.01 min (4.6%); t_R (*S*)-**7a**, 7.27 min (95.4%) (Chiralcel OJ; hexane/*i*-PrOH, 90/10; flow rate 1 ml/min; UV 254 nm). The spectroscopic properties (^{1}H-NMR and IR) were identical with those of the authentic sample.[14,17]

(*S*)-3-Benzyloxy-1-diazo-4-methylpentan-2-one [(*S*)-3a] According to the procedure for the conversion of racemic **7a** into **3a**, (*S*)-**3a** was obtained from (*S*)-**7a** as a colorless oil. $[\alpha]_D^{23}$ −106.1° (c=0.95, $CHCl_3$). The spectroscopic properties (^{1}H-NMR and IR) were identical with those of racemic sample.

Dirhodium(II)-Catalyzed C–H Insertion of (*S*)-3a According to the general procedure, (*S*)-**3a** (200 mg, 0.86 mmol) was treated with $Rh_2(oct)_4$ (7 mg, 0.009 mmol) in refluxing benzene (51 ml) and the crude material was chromatographed on silica gel (10% EtOAc in hexane) to give (2*S*,5*S*)-**4a** (131 mg, 75%) as a colorless oil. $[\alpha]_D^{23}$ −185.3° (c=0.77, $CHCl_3$). The spectroscopic properties (^{1}H-NMR and IR) were identical with those of racemic sample.

(2*R*,3*S*)-2-Isopropyl-6-phenyl-1,3-dioxan-4-one (5a) A suspension of (2*S*,5*S*)-**4a** (131 mg, 0.64 mmol), *m*-CPBA (221 mg, 1.28 mmol), and $NaHCO_3$ (54 mg, 0.64 mmol) in CH_2Cl_2 (6 ml) was stirred at room temperature for 10 h. The mixture was washed with saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (10% EtOAc in hexane) to give **5a** (120 mg, 85%) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.07 (3H, d, J=7.0 Hz), 1.08 (3H, d, J=6.8 Hz), 2.02—2.18 (1H, m), 2.71 (1H, dd, J=17.6, 10.8 Hz), 2.94 (1H, dd, J=17.6, 4.4 Hz), 4.93 (1H, dd, J=10.8, 4.4 Hz), 5.28 (1H, d, J=4.2 Hz), 7.33—7.44 (5H, m). ^{13}C-NMR ($CDCl_3$) δ: 16.06, 16.13, 32.8, 38.1, 75.6, 106.5, 125.4, 128.6, 128.8 (3), 139.2, 167.6. IR (neat) cm^{-1}: 1747. CI-MS *m*/*z*: 220.1098 (Calcd for $C_{13}H_{16}O_3$: 220.1099). $[\alpha]_D^{23}$ −75.4° (c=0.37, $CHCl_3$).

Methyl (*S*)-3-Hydroxy-3-phenylpropanoate (8) A 10% HCl solution (2 ml) was added to a solution **5a** (60 mg, 0.27 mmol) in Et_2O (2 ml) and the mixture was vigorously sttired for 1 h. The organic layer was dried ($MgSO_4$) and concentrated. The residue was dissolved in Et_2O and treated with excess CH_2N_2. The solution was allowed to warm to room temperature and stirred for 30 min. The excess of CH_2N_2 was destroyed by the addition of few drops of AcOH. The mixture was diluted with H_2O, and extracted with Et_2O. The organic layer was washed with aqueous saturated $NaHCO_3$ solution and brine, and dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel (20% EtOAc in hexane) to give **8** (20 mg, 41% in 2 steps) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 2.71 (1H, dd, J=16.2, 4.4 Hz), 2.78 (1H, dd, J=16.2, 8.4 Hz), 3.20 (1H, br s), 3.73 (3H, s), 5.14 (1H, dd, J=8.4, 4.4 Hz), 7.24—7.50 (5H, m). ^{13}C-NMR ($CDCl_3$) δ: 43.1, 51.9, 70.3, 125.6 (2), 127.8, 128.5 (2), 142.5, 172.8. IR (neat) cm^{-1}: 3422, 1734. EI-MS *m*/*z*: 180.0788 (Calcd for $C_{10}H_{12}O_3$: 180.0786). $[\alpha]_D^{23}$ −21.5° (c=1.00, EtOH). [lit.[18] $[\alpha]_D^{24}$ −18.8° (c=4.735, EtOH)]. HPLC:[19] t_R (*R*)-**8**, 21.96 min (4.8%); t_R (*S*)-**8**, 24.33 min (95.2%) (Chiralcel ADH; hexane/EtOH, 95/5; flow rate 1 ml/min; UV 254 nm).

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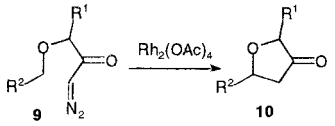

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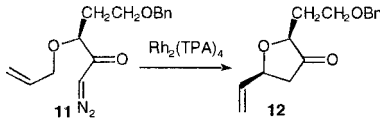

11 **12**

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