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**Asymmetric Catalysis of Nozaki-Hiyama Allylation and Methallylation with
A New Tridentate Bis(oxazoliny)carbazole Ligand**

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General Information. ^1H and ^{13}C NMR spectra were recorded on a JEOL AL-400 and Bruker AVANCE 600 spectrometer. ^1H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. IR spectra were recorded on a JASCO FT/IR-8300. Optical rotations were measured using a 2 ml cell with a 1 dm path length on a JASCO DIP-1000. Chiral HPLC analysis was performed on a JASCO PU-980 and UV-970. Mass spectra and elemental analyses were provided at the Materials Characterization Central Laboratory, Waseda University.

Materials. DME and THF were distilled from sodium/benzophenone ketyl. Toluene was distilled from sodium. DMF was distilled from CaH_2 under reduced pressure. Liquid aldehydes were distilled from CaH_2 and stored under nitrogen. CrCl_2 was purchased from Aldrich. All other reagents were purchased from TCI, or Kanto Chemical co. Ltd.

3,6-diphenyl carbazole

PhB(OH)_2 (5.45 g, 44.7 mmol), Pd(OAc)_2 (0.164 g, 0.731 mmol), $(o\text{-tol})_3\text{P}$ (0.458 g, 1.50 mmol), $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ (14.1 g, 44.8 mmol) were successively added to a solution of 3, 6-diiodocarbazole* (6.26 g, 14.9 mmol) in DME (120 ml) and H_2O (20 ml). The resulting mixture was heated at 80 °C for 8 h, cooled to ambient temperature, and filtered to remove precipitates. The filtrate was concentrated under vacuum, extracted with CH_2Cl_2 (100 ml x 3), and the organic layer was dried over Na_2SO_4 . The organic layer was evaporated, and the residue was purified by flash chromatography (hexane/ CH_2Cl_2 =3/1). Recrystallization from hexane/ethyl acetate afforded pure 3 (4.58 g, 96%): mp 186 °C; IR (KBr) 3428, 1600, 1478, 1268, 1236, 818, 762, 696 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ =8.34 (dd, J =1.7, 0.7 Hz, 2H), 8.11 (s, 1H), 7.72 (ddd, J =7.3, 1.5, 1.5 Hz, 4H), 7.69 (dd, J =8.3, 1.7 Hz, 2H), 7.50 (dd, J =8.3, 0.7 Hz, 2H), 7.48 (dddd, J =7.3, 1.5, 1.5 Hz, 4H), 7.34

(tt, $J=7.3, 1.5$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): $\delta=141.9, 139.3, 133.1, 128.7, 127.2, 126.4, 125.5, 123.9, 118.8, 110.9$; Anal. Calcd for $\text{C}_{24}\text{H}_{17}\text{N}$: C, 90.25; H, 5.37; N, 4.39. Found: C, 89.94; H, 5.38; N, 4.31.

*reference: Beginn, C.; Gražulevičius, J. V.; Strohriegl, P. *Macromol. Chem. Phys.* **1994**, *195*, 2353-2370.

1, 8-diiodo-3, 6-diphenyl carbazole (4)

To a suspension of **3** (22.3 g, 69.8 mmol) in the mixed solvent of AcOH (1000 ml), H_2O (200 ml), and H_2SO_4 (30 ml) was added I_2 (17.7 g, 69.6 mmol), $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ (7.94 g, 34.9 mmol) successively. After stirring at 80 °C for 5 h, the reaction mixture was cooled to ambient temperature, and poured into H_2O (2000 ml). The precipitated crude product was partitioned between ethyl acetate (1000 ml) and saturated aqueous NaHCO_3 (300 ml), and the organic layer was washed with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (100 ml), and then brine (200 ml), dried over Na_2SO_4 . Evaporation and recrystallization of the residue from toluene affording pure **4** (26.8 g, 67%): mp 258-261 °C; IR (KBr) 3440, 1602, 1558, 1508, 1478, 1268, 1196, 870, 758, 690 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) $\delta=8.23$ (d, $J=1.5$ Hz, 2H), 8.16 (s, 1H), 8.07 (d, $J=1.5$ Hz, 2H), 7.66 (dddd, $J=7.3, 1.2, 1.2, 1.2$ Hz, 4H), 7.48 (dddd, $J=7.3, 7.3, 1.2, 1.2$ Hz, 4H), 7.37 (tt, $J=7.3, 1.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): $\delta=140.3, 140.3, 135.6, 134.3, 128.8, 127.2, 127.1, 124.6, 119.4, 76.4$; HRMS (FAB): m/z calcd for $\text{C}_{24}\text{H}_{15}\text{I}_2\text{N}$ 570.9294, found 570.9288.

1,8-bis[4'-(S)-isopropylloxazolin-2'-yl]-3,6-diphenyl carbazole (1)

CuCN (2.35 g, 26.2 mmol) was added to a solution of **4** (5.00 g, 8.75 mmol) in DMF (130 ml) under Ar atmosphere, and the resulting mixture was refluxed for 1.5 h. The reaction mixture was cooled to ambient temperature, filtered to remove precipitates, and the filtrate was poured into saturated aqueous NaCN (400 ml). The precipitated solid was filtered, and the filtrate was partitioned between ethyl acetate (700 ml) and H_2O (200 ml), and the organic layer was washed with brine (100 ml),

dried over Na_2SO_4 . Evaporation of the solvent and drying under vacuum afforded crude 1, 8-dicyano-3, 6-diphenyl carbazole 5. Crude 5 was dissolved in PhCl (100 ml) and to the solution was added L-valinol (2.71 g, 26.1 mmol) and ZnCl_2 (3.56 g, 26.2 mmol). The reaction mixture was refluxed for 72 h, then cooled to ambient temperature. After the addition of a solution of ethylenediamine (15 ml) in H_2O (100 ml) to the mixture, the mixture was stirred for 1 h. The resulting mixture was extracted with CH_2Cl_2 (200 ml), and the organic layer was dried over Na_2SO_4 , evaporated, and the residue was purified by flash chromatography (hexane/ CH_2Cl_2 =4/1-1/1). Recrystallization from hexane/ethyl acetate afforded pure ligand 1 (3.38 g, 71%, 2 steps from 4): $[\alpha]_D^{26} +85.7^\circ$ (c 1.13, CHCl_3); mp 174-177 $^\circ\text{C}$; IR (KBr): 3352, 2960, 1650, 1604, 1480, 1290, 1268, 1218, 1154, 762, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ =12.0 (s, 1H), 8.46 (d, J =1.5 Hz, 2H), 8.20 (d, J =1.5 Hz, 2H), 7.76 (dddd, J =7.3, 1.2, 1.2, 1.2 Hz, 4H), 7.48 (dddd, J =7.3, 7.3, 1.2, 1.2 Hz, 4H), 7.35 (tt, J =7.3, 1.2 Hz, 2H), 4.50 (dd, J =7.9, 7.2 Hz, 2H), 4.25 (m, 2H), 4.22 (dd, J =7.2, 7.2 Hz, 2H), 1.92 (m, 2H), 1.17 (d, J =6.6 Hz, 6H), 1.04 (d, J =6.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ =162.3, 141.3, 138.8, 132.4, 128.7, 127.2, 126.6, 125.2, 124.1, 121.8, 110.8, 72.9, 70.0, 33.5, 19.2, 18.7; Anal. Calcd for $\text{C}_{36}\text{H}_{35}\text{N}_3\text{O}_2$: C, 79.82; H, 6.51; N, 7.76. Found: C, 79.59; H, 6.48; N, 7.80.

Representative Procedure for the Enantioselective Allylation with Ligand (1)

(*S*)-1-phenyl-3-buten-1-ol (2a)

A mixture of ligand 1 (27.1 mg, 0.0500 mmol), CrCl_2 (6.3 mg, 0.0510 mmol), and Mn (53.8 mg, 0.979 mmol) was azeotroped three times with toluene and dried under high vacuum, and was suspended in THF (2 ml). The color of the suspension immediately turned to brown. To the stirred suspension was added DIPEA (0.026 ml, 0.15 mmol), and after 5 min to the resulting mixture was added allylbromide (0.086 ml, 0.99 mmol). After stirring for 30 min, the color of the mixture turned to greenish brown. To the stirred mixture was added benzaldehyde (0.050 ml, 0.49 mmol), TMSCl (0.125 ml, 0.985 mmol) successively at 0 $^\circ\text{C}$. After 12 h the color of the reaction mixture turned to reddish brown. The reaction was quenched with saturated aqueous NaHCO_3 (1 ml), filtered through Celite, and evaporated under vacuum. The crude product was dissolved in THF (2 ml), and the stirred mixture was treated with TBAF (1 ml, 1 M soln). The reaction was quenched with adding saturated aqueous NH_4Cl (2 ml), extracted with Et_2O (10 ml x 4), dried over Na_2SO_4 , and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford the known compound, (*S*)-1-phenyl-3-buten-1-ol 2a (64.7 mg, 93% ee, 89%): $[\alpha]_D^{27} - 46.2$ (c 0.94, benzene), (lit.^{19a} $[\alpha]_D - 43.7$ (c 6.7, benzene)); ee was determined by HPLC (254 nm); Daicel Chiral Cell OD-H 0.46 cm ϕ x 25 cm; hexane/isopropanol=19/1; flow rate=0.3 ml/min; retention time : 26.4 min for (*R*)-1-phenyl-3-buten-1-ol, 28.7 min for (*S*)-1-phenyl-3-buten-1-ol 2a.

(S)-1-phenyl-3-buten-1-ol (2a) (1st time recycling)

A mixture of ligand **1** (27.1 mg, 0.0500 mmol), CrCl_2 (6.5 mg, 0.053 mmol), and Mn (58.3 mg, 1.06 mmol) was azeotroped three times with toluene and dried under high vacuum, and was suspended in THF (2 ml). The color of the suspension immediately turned to brown. To the stirred suspension was added DIPEA (0.026 ml, 0.15 mmol), and after 5 min allylbromide (0.086 ml, 0.99 mmol) was added. After stirring for 30 min, the color of the mixture turned to greenish brown. To the stirred mixture was added benzaldehyde (0.050 ml, 0.49 mmol), TMSCl (0.126 ml, 0.993 mmol) successively at 0°C . After 12 h the color of the reaction mixture turned to reddish brown. The reaction was quenched with saturated aqueous NaHCO_3 (1 ml), filtered through Celite, and evaporated under vacuum. The crude product was dissolved in THF (2 ml), and the stirred mixture was treated with TBAF (1 ml, 1 M soln). The reaction was quenched with saturated aqueous NH_4Cl (2 ml), extracted with Et_2O (10 ml x 4), dried over Na_2SO_4 , and evaporated. The residue was purified by preparative TLC (hexane/ethyl acetate=4/1) to afford (S)-1-phenyl-3-butenol **2a** (64.8 mg, 93% ee, 89%). Ee was determined by HPLC under the same condition as described above.

The Cr-ligand **1** complex remained on the base line of the preparative TLC was eluted with CH_2Cl_2 /ethyl acetate=1/1, and the eluate was evaporated, dried under vacuum affording a pale yellow viscous oil. The oil was dissolved in CH_2Cl_2 (5 ml), washed with water (5 ml x 1), dried over Na_2SO_4 , and evaporated. A mixture of this recovered Cr-ligand **1** and Mn (54.1 mg, 0.985 mmol) was azeotroped with toluene and dried under high vacuum, and was suspended in THF (2 ml). Using this suspension the same operation as described in "Representative Procedure for the Enantioselective Allylation with Ligand **1**" was carried out. The reaction time needed 24h to afford (S)-1-phenyl-3-buten-1-ol **2a** (62.8 mg, 92% ee, 86%).

(S)-1-phenyl-3-buten-1-ol (2a) (second time recycling)

The second time recycling was also successfully carried out according to the same procedure as described in the first time recycling affording (S)-1-phenyl-3-buten-1-ol **2a** (57.4 mg, 79%, 93% ee).

(S)-1-*p*-bromophenyl-3-buten-1-ol (2b)

$[\alpha]_D^{23}$ - 26.1 (c 0.29, benzene), (lit.^{19b} $[\alpha]_D^{23}$ - 26.1 (c 1.1, benzene)); ee was determined by HPLC; Daicel Chiral Cell OD-H 0.46 cm ϕ x 25 cm; hexane/isopropanol=19/1; flow rate=0.15 ml/min; retention time : 46.1 min for (R)-1-*p*-bromophenyl-5-buten-3-ol, 51.3 min for (S)-1-*p*-bromophenyl-5-buten-3-ol **2b**.

***trans*-(*S*)-1-phenyl-1, 5-hexadien-3-ol (2c)**

$[\alpha]_D^{25} + 25.1$ (c 0.28, Et₂O), ((*R*)-form; lit.^{19a} $[\alpha]_D - 13.5$ (c 9.7, Et₂O)); ee was determined by HPLC; Dicel Chiral Cell OD-H 0.46 cm $\phi \times 25$ cm; hexane/isopropanol=19/1; flow rate=0.4 ml/min; retention time : 29.7 min for *trans*-(*R*)-1-phenyl-1, 5-butadien-3-ol, 52.4 min for *trans*-(*S*)-1-phenyl-1, 5-butadien-3-ol 2c.

(*R*)-1-phenyl-5-hexen-3-ol (2d)

$[\alpha]_D^{23} + 19.4$ (c 0.28, CHCl₃), (for (*S*)-form; lit.^{4f} $[\alpha]_D - 14.8$ (c 0.68, CHCl₃)); ee was determined by HPLC; Dicel Chiral Cell OD-H 0.46 cm $\phi \times 25$ cm; hexane/isopropanol=19/1; flow rate=0.3 ml/min; retention time : 28.4 min for (*S*)-1-phenyl-5-hexen-3-ol, 43.5 min for (*R*)-1-phenyl-5-hexen-3-ol 2d.

(*S*)-1-cyclohexyl-3-butene-1-ol (2e)

$[\alpha]_D^{24} - 6.56$ (c 0.43, EtOH), (for (*R*)-form; lit.^{19a} $[\alpha]_D + 8.2$ (c 0.6, EtOH)).

(*S*)-4-cyclohexyl-4-(3, 5-dinitrobenzoyloxy)-1-butene

To a solution of (*S*)-1-cyclohexyl-3-butene-1-ol 2e (29.0 mg, 0.188 mmol) in CH₂Cl₂ (1 ml) was added 4-*N*, *N*-dimethylaminopyridine (DMAP) (47.2 mg, 0.386 mmol), 3,5-dinitrobenzoylchloride (65.1 mg, 0.282 mmol) successively. After stirring for 3 h at room temperature under Ar, the reaction was quenched with saturated aqueous NH₄Cl (5 ml). The reaction mixture was extracted with CH₂Cl₂ (5 ml $\times$ 3), dried over Na₂SO₄, and evaporated. The obtained residue was purified by flash chromatography (hexane/ethyl acetate=12/1) to afford the corresponding 3,5-dinitrobenzoate (62.4 mg, 95%): ¹H NMR (400 MHz, CDCl₃): δ =9.22 (t, *J*=2.2 Hz, 1H), 9.13 (d, *J*=2.2 Hz, 2H), 5.78 (dddd, *J*=17.1, 10.0, 7.8, 6.3 Hz, 1H), 5.14 (ddd, *J*=8.1, 6.3, 4.4 Hz, 1H), 5.10 (ddd, *J*=17.1, 2.9, 1.5 Hz, 1H), 5.05 (ddd, *J*=10.0, 1.5, 1.0 Hz, 1H), 2.58-2.42 (m, 2H), 1.83-1.68 (m, 6H), 1.33-1.06 (m, 5H); ee was determined by HPLC; Dicel Chiral Cell OD-H 0.46 cm $\phi \times 25$ cm;

hexane/isopropanol=19/1; flow rate=0.3 ml/min); retention time : 34.3 min for (*R*)-4-cyclohexyl-4-(3, 5-dinitrobenzoyloxy)-1-butene, 36.2 min for (*S*)-4-cyclohexyl-4-(3, 5-dinitrobenzoyloxy)-1-butene.

(*R*)-1-nonene-4-ol (2f)

$[\alpha]_D^{30} + 4.9$ (c 0.37, CHCl_3), (lit. 19c $[\alpha]_D + 3.6$ (c 0.9, CHCl_3)).

(*R*)-4-(3, 5-dinitrobenzoyloxy)-1-nonene

(*R*)-1-nonene-4-ol 2f (32.9 mg, 0.231 mmol) was converted to the corresponding 3,5-dinitrobenzoate (61.7 mg, 79%) as described for (*S*)-1-cyclohexyl-3-butene-1-ol: ^1H NMR (400 MHz, CDCl_3): δ =9.23 (t, J =2.2, Hz, 1H), 9.14 (d, J =2.2 Hz 2H), 5.80 (dddd, J =17.1, 10.0, 7.1, 7.1 Hz, 1H), 5.28 (dddd, J =7.3, 7.1, 5.6, 5.4 Hz, 1H), 5.13 (ddd, J =17.1, 2.7, 1.5 Hz, 1H), 5.09 (ddd, J =10.0, 1.5, 1.0 Hz, 1H), 2.57-2.44 (m, 2H), 1.83-1.68 (m, 2H), 1.41-1.25 (m, 6H), 0.90-0.87 (m, 3H); ee was determined by HPLC; Dicel Chiral Cell AS-H 0.46 cm ϕ $\times$ 25 cm; hexane/isopropanol=19/1; flow rate=0.1 ml/min); retention time : 49.8 min for (*R*)-4-(3, 5-dinitrobenzoyloxy)-1-nonene, 52.3 min for (*S*)-4-(3, 5-dinitrobenzoyloxy)-1-nonene.

(*S*)-5-methyl-1-phenyl-5-buten-3-ol (2g)

$[\alpha]_D^{26} - 51.6$ (c 0.33, Et_2O), (lit. 19d $[\alpha]_D^{20} - 19.7$ (c 9.9, Et_2O)); ee was determined by HPLC; Dicel Chiral Cell OD-H 0.46 cm ϕ $\times$ 25 cm; hexane/isopropanol=14/1; flow rate=0.3 ml/min); retention time : 21.9 min for (*R*)-5-methyl-1-phenyl-5-buten-3-ol, 28.4 min for (*S*)-5-methyl-1-phenyl-5-buten-3-ol 2g.

***trans*-(*S*)-5-methyl-1-phenyl-1, 5-butadien-3-ol (2h)**

$[\alpha]_D^{23} - 2.9$ (c 0.435, Et_2O), (lit. 19e $[\alpha]_D - 1.48$ (c 2.43, Et_2O)); ee was determined by HPLC; Dicel Chiral Cell OD-H 0.46 cm ϕ $\times$ 25 cm; hexane/isopropanol=9/1; flow rate=0.5 ml/min); retention time : 15.5 min for *trans*-(*R*)-5-methyl-1-phenyl-1, 5-butadien-3-ol, 28.2 min for *trans*-(*S*)-5-methyl-1-phenyl-1, 5-butadien-3-ol 2h.

(S)-1-cyclohexyl-3-methyl-3-butene-1-ol (2i)

$[\alpha]_D^{26} + 3.0$ (c 0.67, CCl_4), (lit.^{19f} $[\alpha]_D^{20} + 3.8$ (c 1.36, CCl_4)).

(S)-4-cyclohexyl-4-(3, 5-dinitrobenzoyloxy)-2-methyl-1-butene

(S)-1-cyclohexyl-3-methyl-3-butene-1-ol **2i** (12.7 mg, 0.0755 mmol) was converted to the corresponding 3,5-dinitrobenzoate (20.2 mg, 74%) as described for (S)-1-cyclohexyl-3-butene-1-ol; ^1H NMR (400 MHz, CDCl_3): δ =9.22 (t, J =2.2, Hz, 1H), 9.13 (d, J =2.2 Hz 2H), 5.28 (ddd, J =9.5, 5.6, 3.7 Hz, 1H), 4.73-4.74 (m, 2H), 2.46 (dd, J =14.2, 9.5 Hz, 1H), 2.41 (dd, 14.2, 3.7 Hz, 1H), 1.83-1.67 (m, 6H), 1.78 (s, 3H), 1.33-1.07 (m, 5H); ee was determined by HPLC; Dicel Chiral Cell OD-H 0.46 cm ϕ $\times$ 25 cm; hexane/isopropanol=19/1; flow rate=0.2 ml/min; retention time : 42.5 min for (R)-4-cyclohexyl-4-(3, 5-dinitrobenzoyloxy)-2-methyl-1-butene, 46.2 min for (S)-4-cyclohexyl-4-(3, 5-dinitrobenzoyloxy)-2-methyl-1-butene.

(R)-2-methyl-1-nonene-4-ol (2j)

$[\alpha]_D^{35} + 13.5$ (c=0.61, benzene), (for (S)-form; lit.^{19f} $[\alpha]_D - 9.36$ (c=1.56, benzene)).

(R)-MTPA ester of 2-methyl-1-nonene-4-ol (2j)^{19g}

2-Methyl-1-nonene-4-ol **2j** (10.1 mg, 0.0646 mmol) was reacted with excesss (R)-MTPA-Cl (25.7 mg, 0.109 mmol) and 4-*N*, *N*-dimethylaminopyridine (DMAP) (14.2 mg, 0.116 mmol). Usual workup and purification by preparative TLC (hexane/ethyl acetate=4/1) afforded a mixture of (R)-4-[(R)-1-methoxy-1-(trifluoromethyl)phenylacetyloxy]-2-methyl-1-nonene (major) and (S)-4-[(R)-1-methoxy-1-(trifluoromethyl)phenylacetyloxy]-2-methyl-1-nonene (minor) (21.4 mg, 89%); ee was determined by ^1H NMR; ^1H NMR (400 MHz, CDCl_3): δ =4.82 (major) 4.72 (minor) (s, 1H), 4.76 (major) 4.65 (minor) (s, 1H).

reference : 19 (g) Ishihara, K.; Mouri, M.; Gao, Q.; Maruyama, T.; Furuta, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 11490-11495.

(R)-(+)-MTPA ester of *anti*-5 and *syn*-5^{4c}

2-Methyl-1-phenyl-3-butene-1-ol (a mixture of *anti*-5 and *syn*-5) (8.2 mg, 0.051 mmol) was reacted with excess (R)-MTPA-Cl (18.0 mg, 0.0761 mmol) and 4-*N*, *N*-dimethylaminopyridine (DMAP) (10.5 mg, 0.0859 mmol). Usual workup and preparative TLC (hexane/ethyl acetate=4/1) afforded a mixture of (R)-(+)-MTPA ester of *anti*-5 and *syn*-5 (13.8 mg, 71%); ee and absolute configuration were determined by ¹H NMR; ¹H NMR (600 MHz, CDCl₃): δ=3.52 (1*S*, 2*S*), 3.50 (1*S*, 2*R*), 3.44 (1*R*, 2*R*), 3.43 (1*R*, 2*S*) (dd, 3H), 1.09 (1*S*, 2*S*), 0.99 (1*R*, 2*R*), 0.88 (1*S*, 2*R*), 0.85 (1*R*, 2*S*) (d, 3H).

reference : 4 (e) Bandini, M.; Cozzi, P. G.; Umani-Ronchi, A. *Angew. Chem., Int. Ed.* 2000, 39, 2327-2330.

(1*R*, 5*S*, 6*R*, 9*R*)-9-[(1*R*, 3*S*)-1, 5-dimethyl-3-hydroxy-5-hexenyl]-1-methyl-5-phenylmethoxybicyclo[4.3.0]nonane (4) by the reaction with *ent*-ligand (1)

A mixture of *ent*-ligand 1 (16.9 mg, 0.0312 mmol), CrCl₂ (3.8 mg, 0.031 mmol), and Mn (34.4 mg, 0.626 mmol) was azeotroped three times with toluene and dried under high vacuum, and was suspended in THF (1 ml). The color of the suspension immediately turned to brown. To the stirred suspension was added DIPEA (0.027 ml, 0.16 mmol), and after 5 min was added methallylchloride (0.031 ml, 0.32 mmol). After stirring at room temperature for 30 min, the color of the mixture turned to greenish brown. To the stirred mixture was added a solution of aldehyde 3^{12a} (48.8 mg, 0.155 mmol) in THF (1 ml) via a canula, and then the washings (0.3 ml x 3). To the reaction mixture was added TMSCl (0.039 ml, 0.31 mmol) and the mixture was stirred at room temperature. After 18 h the color of the reaction mixture turned to reddish brown. The reaction was quenched with saturated aqueous NaHCO₃ (1 ml), filtered through Celite, and evaporated under vacuum. The crude product was dissolved in THF (2 ml), and the stirred mixture was treated with TBAF (1 ml, 1 M soln). The reaction was quenched with saturated aqueous NH₄Cl (2 ml), extracted with Et₂O (10 ml x 4), dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=20/1) to afford a mixture of the known compounds, (1*R*, 5*S*, 6*R*, 9*R*)-9-[(1*R*, 3*S*)-1, 5-dimethyl-3-hydroxy-5-hexenyl]-1-methyl-5-phenylmethoxybicyclo[4.3.0]nonane 4 and its diastereomer, (1*R*, 5*S*, 6*R*, 9*R*)-9-[(1*R*, 3*R*)-1, 5-dimethyl-3-hydroxy-5-hexenyl]-1-methyl-5-phenylmethoxybicyclo[4.3.0]nonane 4' (52.5 mg, 97% de, 91%); stereochemistry of 4 and de were determined by 600MHz ¹H-NMR comparing with the data of the authentic samples prepared by the literature methods^{12a, b}; ¹H-NMR (600 MHz, CDCl₃) : 4; δ=7.36-7.22 (m, 5H), 4.90 (br, 1H), 4.81 (br, 1H), 4.61 (d, *J*=12.3 Hz, 1H), 4.36 (d, *J*=12.3 Hz, 1H), 3.83-3.78 (m, 1H), 3.72-3.70 (m, 1H), 2.32-

2.26 (m, 1H), 2.07-1.94 (m, 3H), 1.90-1.66 (m, 3H), 1.77 (s, 3H), 1.57-1.52 (m, 1H), 1.48-1.05 (m, 10H), 0.98 (d, $J=6.4$ Hz, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta=142.9, 139.9, 128.0, 126.8, 126.7, 113.6, 76.6, 71.2, 67.3, 57.5, 52.8, 46.0, 43.5, 42.2, 40.8, 33.6, 29.3, 27.7, 22.8, 22.4, 19.4, 18.0, 13.7$; $[\alpha]_D^{25} +83.0^\circ$ (c 0.51, CHCl_3); IR (neat): 2940, 2868, 1648, 1498, 1454, 1376, 1358 cm^{-1} ; HRMS (FAB): m/z calcd for $\text{C}_{25}\text{H}_{37}\text{O}_2$ $[\text{M} - \text{H}]^+$ 369.2794, found 369.2809.
4'; $\delta=4.86$ (br, 1H), 4.78 (br, 1H).

reference : 12 (a) Johnson, W. S.; Chan, M. F. *J. Org. Chem.* **1985**, *50*, 2598-2600. (b) Nakada, M.; Urano, Y.; Kobayashi, S.; Ohno, M. *Tetrahedron Lett.* **1994**, *35*, 741-744.

4 and 4' by the reaction without ligand

A mixture of CrCl_2 (3.8 mg, 0.031 mmol) and Mn (32.0 mg, 0.582 mmol) was azeotroped three times with toluene and dried under high vacuum, and was suspended in THF (1 ml). To the stirred suspension was added methallylchloride (0.027 ml, 0.28 mmol) to the mixture. After stirring at room temperature for 30 min, to the stirred mixture was added a solution of aldehyde 3 (43.4 mg, 0.138 mmol) in THF (1 ml) via a canula, and then the washings (0.3 ml x 3). To the reaction mixture was added TMSCl (0.037 ml, 0.29 mmol) and the mixture was stirred at room temperature. After 30 h the reaction was quenched with saturated aqueous NaHCO_3 (1 ml), filtered through Celite, and evaporated under vacuum. The crude product was dissolved in THF (2 ml), and the stirred mixture was treated with TBAF (1 ml, 1 M soln). The reaction was quenched with adding saturated aqueous NH_4Cl (2 ml), extracted with Et_2O (10 ml x 4), dried over Na_2SO_4 , and evaporated. The residue was purified by preparative TLC (hexane/ethyl acetate=4/1) to afford a mixture of 4 and 4' (5.8 mg, -3% de, 27% at 41% conversion).