Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Catalytic Dehydrative Allylation of Alcohols

Hajime Saburi, Shinji Tanaka, and Masato Kitamura

Contribution from the Research Center for Materials Science and the Department of Chemistry, Nagoya University

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(1) Instruments

Nuclear magnetic resonance (NMR) spectra were recorded on JEOL JNM-ECA-600 spectrometer. The chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane or in ppm relative to $CHCl_3$ and CHD_2COCD_3 (δ 7.26 and 2.05 in ^1H NMR and δ 77.0 and 29.8 in ^{13}C NMR). Signal patterns of ^1H NMR are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal. Infrared (IR) spectra were measured on a PERKIN ELMER SPECTRUM 2000 by use of KBr or polytetrafluoroethylene (PTFE) film. X-ray crystallographic analysis was conducted on a Rigaku Saturn 70 CCD system, and the structure was solved by direct methods using the CrystalStructure crystallographic software. High-resolution mass spectra (HRMS) were measured on a PE Biosystems Mariner system. Gas chromatography analyses were performed on Shimazu GC-14B and GC-17A instruments. Conditions are as follows: capillary column, J&W Scientific DB-WAX (0.25 mm x 15 m); column temperature, 50–250 °C; rate of temperature increase, 10 °C/min (condition **A**), or capillary column, J&W Scientific DB-5 (0.25 mm x 30 m); column temperature, 50–250 °C; rate of temperature increase, 10 °C/min (condition **B**). In all cases the detection temperature, the carrier gas, the column pressure, and the flow rate were set to 250 °C, helium, 50 kPa, and 3.5 mL/sec, respectively. High performance liquid chromatography analyses were performed on a Shimazu LC-10Avp instrument.

(2) Materials

Gas: Argon gas was purified by being passed through a column of the BASF R3-11 catalyst at 80 °C and then through a column of granular calcium sulfate.

Solvents: Acetone-d_6 was distilled from MS 4A. Dichloromethane was distilled from calcium hydride (250 mg/100 mL). Methanol was dried and degassed at the reflux

temperature in the presence of magnesium (250 mg/100 mL) under argon stream for 6 h and distilled into Schlenk flasks. All of the solvents were degassed by three freeze–thaw cycles before use.

Silica gel: Flash column chromatography was performed using Daiko AP 300 or nacalai tesque Silica Gel 60 (spherical, neutral).

Ligands and catalyst precursor: The following compounds that were used for the investigation of the ligand acceleration effect were purchased and used without further purification: 2-Quinolinecarboxylic acid (quinaldic acid, **10**), 1-isoquinolinecarboxylic acid, 3-isoquinolinecarboxylic acid, 2-pyridinecarboxylic acid (picolinic acid), methyl 2-pyridinecarboxylate, 2-(hydroxymethyl)pyridine, and (±)-2-piperidinecarboxylic acid. Diphenylphosphinoacetic acid was synthesized according to the literature.[1] The catalyst precursor $[CpRu(CH_3CN)_3]PF_6$ (**9**) was purchased and used without further purification.

Alcohol Substrates: 2-Phenylethan-1-ol (**1a**) and cyclohexanol (**1b**) were purchased from Kisida, indan-2-ol (**1c**), 1,1-dimethyl-2-phenylethan-1-ol (**1d**), 5-hexen-1-ol (**1e**), phenol (**1f**), and geraniol (**1g**) were purchased from TCI, (*S*)-glycidol (**11a**) and 2,3,4,6-*tetra*-*O*-benzyl-D-glucopyranose (**12a)** were purchased from Aldrich, and 2,3-*O*-isopropylidene-D-ribofuranose (**13a)** was purchased from Lancaster. 6-Benzyloxyhexan-1-ol (**1h**),[2] 6-benzoyloxyhexan-1-ol (**1i**)[3], 6-(methoxymethyloxy)hexan-1-ol (**1j**),[4] 6-(*tert*-butyldiphenylsilyloxy)hexan-1-ol (**1k**),[5] and dipeptide **14a**[6] were synthesized according to the literature. All of the alcohol substrates except for 2,3,4,6-*tetra*-*O*-benzyl-D-glucopyranose (**12a**) and 2,3-*O*-isopropylidene-D-ribofuranose (**13a)** were purified by distillation or recrystallization.

(3) Catalytic allylation

General procedure: No solvent system: 2-Phenylethan-1-ol (**1a**) (1.22 g, 10 mmol) and 2-propen-1-ol (**2**) (0.58 g, 10 mmol) were placed in a 20-mL Schlenk tube equipped with Young's tap, and the whole mixture was degassed three times by freeze-thaw method. $[CpRu(CH_3CN)_3]PF_6$ (**9**) (2.2 mg, 5.0 μmol) and methanol (0.45 mL) were placed in another 20-mL Schlenk tube equipped with Young's tap under argon stream. A 100 mM methanol solution of 2-quinolinecarboxylic acid (**10**) (0.05 mL, 5.0 μmol) was added to the mixture. After being stood for 30 min at 30 °C, the reddish brown solution was concentrated under vacuum. To this was added the **1a** and **2** mixture by use of a cannula under an argon stream. The yellow homogeneous mixture was stirred at 70 °C for 6 h. The GC analysis determined the yield of allyl 2-phenylethyl ether (**3a**) to be 90% (condition **A**; t_R of **1a**, 6.0 min; t_R of **3a**, 4.0 min). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.90 (t, 2H, J = 6.89 Hz, $C_6H_5CH_2$), 3.65 (t, 2H, J = 6.89 Hz, CH_2CH_2O), 3.99 (d, 2H, J = 5.51 Hz, CH_2=CHCH_2), 5.16 (d, 1H, J = 11.0 Hz, CH=CHH), 5.25 (d, 1H, J = 17.2 Hz, CH=CHH), 5.87–5.93 (m, 1H, CH=CH_2), 7.19–7.30 (m, 5H, aromatic). ^{1}H NMR data was consistent with the reported value.[7]

CH_2Cl_2 system: 2-Phenylethan-1-ol (**1a**) (0.12 g, 1.0 mmol) and 2-propen-1-ol (**2**) (58 mg, 1.0 mmol) and CH_2Cl_2 (1.8 mL) were placed in a 20-mL Schlenk tube equipped with Young's tap, and the whole mixture was degassed three times by freeze-thaw method. $[CpRu(CH_3CN)_3]PF_6$ (**9**) (0.87 mg, 2.0 μmol) and methanol (0.18 mL) were placed in another 20-mL Schlenk tube equipped with Young's tap under argon stream. A 100 mM methanol solution of 2-quinolinecarboxylic acid (**10**) (20 μL, 2.0 μmol) was added to the mixture. After being stood for 30 min at 30 °C, the reddish brown solution was concentrated under vacuum. To this was added the **1a** and **2** solution by use of a cannula under an argon stream. The yellow homogeneous solution was stirred for 3 h in 70 °C oil bath. The GC analysis determined the yield of allyl 2-phenylethyl

ether (**3a**) to be 93% (condition **A**).

Listed below are the reaction scale, the yield of allyl ether product, and the physical property. The values in the parentheses are those obtained in CH_2Cl_2 system. The GC conditions and the retention times (t_R) of substrate and product were shown in Table S1.

Cyclohexanol (**1b**): 10 mmol (1.0 mmol); 76% (90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.19–1.92 (br, 10H, $(CH_2)_5$), 3.26–3.30 (m, 1H, C*H*OCH_2), 4.01 (d, 2H, *J* = 5.51, OCH_2), 5.14 (dd, 1H, *J* = 1.38, 10.3 Hz, CH=CH*H*), 5.27, (dd, 1H, *J* = 1.38, 17.2 Hz, CH=C*H*H), 5.90–5.96 (m, 1H, C*H*=CH_2). ^{1}H NMR data was consistent with the reported value.[8]

Indan-2-ol (**1c**): 14.3 mmol (1.0 mmol); 84% (92%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.00 (dd, 2H, *J* = 4.82, 15.8 Hz, CH*H*CHO), δ 3.17 (dd, 2H, *J* = 6.20, 15.8 Hz, C*H*HCHO), 4.05 (d, 2H, CH_2O), 4.38–4.42 (m, 1H, CH_2C*H*O), 5.18 (d, 1H, *J* = 10.3 Hz, CH=CH*H*), 5.30 (d, 1H, *J* = 17.2 Hz, CH=C*H*H), 5.89–5.98 (m, 1H, C*H*=CH_2), 7.14–7.21 (m, 4H, aromatic). ^{1}H NMR data was consistent with the reported value.[9]

1,1-Dimethyl-2-phenylethan-1-ol (**1d**): 5.0 mmol (1.0 mmol); 29% (30%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.16 (s, 6H, $(CH_3)_2$C), 2.81 (s, 2H, CCH_2), 4.00 (d, 2H, *J* = 4.13 Hz, OCH_2), 5.14 (d, 1H, *J* = 10.3 Hz, CH=CH*H*), 5.29 (d, 1H, *J* = 11.7 Hz, CH=C*H*H), 5.90–5.98 (m, 1H, C*H*=CH_2), 7.20–7.33 (m, 5H, aromatic). ^{1}H NMR data was consistent with the reported value.[10]

5-Hexen-1-ol (**1e**): 8.3 mmol (2.0 mmol); 90% (97%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.44–1.49 (m, 2H, CH_2C*H*$_2$$CH_2$$CH_2$), 1.58–1.63 (m, 2H, $CH_2$$CH_2$C*H*$_2$$CH_2$), 2.07 (q, 2H, *J* = 6.89 Hz, CH_2=CHC*H*$_2$$CH_2$), 3.43 (t, 2H, *J* = 6.89 Hz, OC*H*$_2$$CH_2$), 3.96 (d, 2H, *J* = 6.20 Hz, CH_2=CHC*H*$_2$O), 4.95 (d, 1H, *J* = 10.3, C*H*H=CH$CH_2$$CH_2$), 5.01 (dd, 1H, *J* = 1.38, 10.3 Hz, CH*H*=CH$CH_2$$CH_2$), 5.17 (d, *J* = 10.3 Hz, C*H*H=CHCH_2O), 5.27 (dd, *J* = 1.38, 17.2 Hz, CH*H*=CHCH_2O), 5.78–5.84 (m, 1H, CH_2=C*H*$CH_2$$CH_2$), 5.89–5.95 (m, 1H, CH_2=C*H*CH_2O). ^{1}H NMR data was consistent with

the reported value.[11]

Phenol (**1f**): 14 mmol (1.0 mmol); 24% (62%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.54 (d, 2H, *J* = 4.13 Hz, OCH_2), 5.29 (d, 1H, *J* = 12.4 Hz, CH=C*H*H), 5.42 (d, 1H, *J* = 17.2 Hz, CH=CH*H*), 6.03–6.10 (m, 1H, CH), 6.83 (d, 1H, *J* = 7.57 Hz, aromatic), 6.91–6.96 (m, 2H, aromatic), 7.23–7.30 (m, 2H, aromatic). ^{1}H NMR data was consistent with the commercially available authentic sample.

Geraniol (**1g**): 5.0 mmol (1.0 mmol); 92% (91%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.60 (s, 3H, CH_3CCH_3), 1.67 (s, 3H, CH_3CCH_2), 1.68 (s, 3H, CH_3CCH_3), 2.04 (t, 2H, *J* = 6.89 Hz, CH_3CCH_2), 2.11 (dt, 2H, *J* = 6.89, 7.57 Hz, $CH_3CCH_2CH_2$), 3.97 (d, 2H, *J* = 5.51 Hz, CH_2=CHCH_2O), 4.00 (d, 2H, *J* = 6.89 Hz, C=CHCH_2O), 5.10 (t, 1H, *J* = 6.20 Hz, CH_3C=C*H*CH_2O), 5.18 (d, 1H, *J* = 10.3 Hz, CH=CH*H*), 5.28 (d, 1H, *J* = 17.2 Hz, CH=C*H*H), 5.36 (t, 1H, *J* = 6.89 Hz, C*H*=$(CH_3)_2$), 5.90–5.97 (m, 1H, C*H*=CH_2). ^{1}H NMR data was consistent with the reported value.[12]

6-Benzyloxyhexan-1-ol (**1i**): 3.8 mmol (0.71 mmol); 90% (94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.33–1.43 (m, 4H), 1.56–1.66 (m, 4H), 3.42 (t, 2H, *J* = 6.89 Hz, CH_2O), 3.47 (t, 2H, *J* = 6.89 Hz, CH_2O), 3.96 (d, 2H, *J* = 5.51 Hz, CH_2=CHCH_2), 4.50 (s, 2H, $C_6H_5CH_2O$), 5.16 (d, 1H, *J* = 10.3 Hz, CH=C*H*H), 5.26 (d, 1H, *J* = 17.2 Hz, CH=CH*H*), 5.88–5.95 (m, 1H, C*H*=CH_2), 7.25–7.30 (m, 1H, aromatic), 7.32–7.36 (m, 4H, aromatic); ^{13}C NMR (151 MHz, $CDCl_3$) δ 26.0(1), 26.0(48), 29.7, 70.3, 71.8, 72.8, 117, 127.(4), 127.(6), 128, 135, 139; IR (PTFE film) 3065, 3030, 2936, 2917, 2859, 2792, 1719, 1647, 1496, 1479, 1455, 1431, 1362, 1307, 1273, 1203, 1101, 1028, 995.7, 922.9, 817.4, 735.6, 697.7, 611.4, 463.0 cm^{-1}; HRMS *m*/*z* (MH^+) obsd 249.17825, calcd 249.18491.

6-Benzoyloxyhexan-1-ol (**1i**): 5.0 mmol (0.73 mmol); 92% (94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.41–1.51 (m, 4H), 1.62 (tt, 2H, *J* = 6.89, 6.89 Hz, CH_2), 1.78 (tt, 2H, *J* = 6.89, 6.89 Hz, CH_2), 3.44 (t, 2H, *J* = 6.89 Hz, CH_2O), 3.96 (d, *J* = 5.51 Hz, CH_2=CHCH_2),

4.32 (t, 2H, *J* = 6.89 Hz, CH_2O), 5.16 (d, 1H, *J* = 10.3 Hz, CH=C*H*H), 5.27 (d, 1H, *J* = 17.2 Hz, CH=CH*H*), 5.88–5.95 (m, 1H, C*H*=CH_2), 7.44 (t, 2H, *J* = 7.57 Hz, aromatic), 7.55 (t, 1H, *J* = 7.57, aromatic), 8.04 (d, 2H, *J* = 8.22 Hz, aromatic); ^{13}C NMR (151 MHz, $CDCl_3$) δ 25.8(7), 25.9, 28.7, 29.6, 64.9, 70.2, 71.8, 117, 128, 129, 130, 133, 135, 167; IR (PTFE film) 3070, 2939, 2915, 2862, 2847, 1720, 1647, 1602, 1585, 1452, 1388, 1347, 1315, 1275, 1177, 1111, 1071, 1027, 992.5, 924.2, 807.2, 712.4, 687.8, 675.2 cm^{-1}; HRMS *m*/*z* (MH^+) obsd 263.16197, calcd 263.16417.

6-(Methoxymethyloxy)hexan-1-ol (**1j**): 5.0 mmol (0.70 mmol); 93% (92%); ^1H NMR (600 MHz, $CDCl_3$) δ 1.39 (tt, 4H, *J* = 3.44 Hz, CH_2CH_2), 1.60 (tt, *J* = 6.89 Hz, CH_2CH_2), 3.36 (s, 3H, CH_3O), 3.43 (t, 2H, J = 6.89 Hz, CH_2O), 3.52 (t, 2H, *J* = 6.89 Hz, CH_2O), 3.96 (d, 2H, J = 5.51 Hz, CH_2=CHC*H*$_2$), 4.62 (s, 2H, OCH_2O), 5.17 (d, 1H, *J* = 10.3 Hz, CH=C*H*H), 5.27 (d, 1H, *J* = 17.2 Hz, CH=CH*H*), 5.88–5.95 (m, 1H, C*H*=CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ 26.0, 26.1, 29.6(5), 29.6(8), 55.1, 67.7, 70.3, 71.8, 96.4, 117, 135; IR (PTFE film) 3080, 2936, 2916, 2861, 2848, 1647, 1456, 1387, 1347, 1217, 1151, 1111, 1047, 995.9, 920.0, 729.9, 561.3 cm^{-1}; HRMS *m*/*z* (MH^+) obsd 203.16607, calcd 203.16417.

6-(*tert*-Butyldiphenylsilyloxy)hexan-1-ol (**1k**): 2.0 mmol (0.64 mmol); 91% (97%); ^1H NMR (600 MHz, $CDCl_3$) δ 1.04 (s, 9H, $(CH_3)_3$), 1.30–1.40 (m, 4H, CH_2), 1.54–1.60 (m, 4H, CH_2), 3.40 (t, 2H, *J* = 6.89 Hz, CH_2OSi), 3.65 (t, 2H, *J* = 6.20 Hz, $CH_2CH_2OCH_2$), 4.00 (d, 2H, *J* = 6.20 Hz, CH_2OCH_2CH), 5.16 (d, 1H, *J* = 10.3 Hz, CH=CH*H*), 5.26 (d, 1H, *J* = 17.2 Hz, CH=C*H*H), 5.88–596 (m, 1H, C*H*=CH_2), 7.37 (t, 4H, *J* = 7.57 Hz, aromatic), 7.42 (t, 2H, *J* = 7.57 Hz, aromatic), 7.66 (t, 4H, *J* = 6.20 Hz, aromatic). ^1H NMR data was consistent with the reported value.[13]

(*S*)-Glycidol (**11a**): – (4.2 mmol of (*S*)-glycidol in 98% *ee*); – (87%, 98% *ee*); ^1H NMR (600 MHz, $CDCl_3$) δ 2.62 (dd, 1H, *J* = 2.75, 4.82 Hz, CH*H*OCH), 2.81 (t, 1H, *J* = 4.82 Hz C*H*HOCH), 3.17 (br, 1H, CH_2OCH), 3.41 (dd, 1H, *J* = 6.20, 11.4 Hz, $CH_2OCHHCHCH_2O$),

3.73 (dd, 1H, *J* = 2.75, 11.4 Hz, $CH_2OCHHCHCH_2O$), 4.01–4.09 (m, 2H, $CH_2CH{=}CH_2$), 5.20 (d, 1H, *J* = 10.3 Hz, CH=CH*H*), 5.30 (dd, 1H, 1.38, 17.2 Hz, CH=C*H*H), 5.88–5.95 (m, 1H, $CH{=}CH_2$). ^{1}H NMR data was consistent with the commercially available authentic sample. The *ee* of the allyl ether **11b** was determined by the HPLC analysis (conditions: column, CHIRALPAK AD-H; eluent, a 99:1 hexane–2-propanol mixture; flow rate, 0.5 mL/min; detection, 205-nm light). Figure S1 shows the chromatograph.

2,3,4,6-*tetra*-*O*-Benzyl-D-glucopyranose (**12a**): – (0.19 mmol); – (91% isolated yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.44–3.81 (m, 5H, C*HCHCHCHCH*), 3.99–4.16 (m, 2H, $CH_2CH{=}CH_2$), 4.43–5.00 (m, 10H, $OCHCH_2O$, $C_6H_5CH_2$), 5.20 (d, 1H, CH=CH*H*), 5.29–5.36 (m, 1H, CH=C*H*H), 5.89–6.00 (m, 1H, $CH{=}CH_2$), 7.12–7.35 (m, 20H, aromatic). ^{1}H NMR data was consistent with the reported value.[14]

2,3-*O*-Isopropylidene-D-ribofuranose (**13a**): – (0.59 mmol); – (90% isolated yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.43–3.50 (m, 2H, CH_2OCH_2CHO), 3.95 (dd, 1H, J = 5.51, 12.7 Hz, CH*H*OCH), 4.01 (m, 1H, CH_2OCH_2CHO), 4.16 (dd, 1H, *J* = 5.51, 12.9 Hz, C*H*HOCH), 4.34 (t, 1H, OCH_2CHO), 4.63 (d, 1H, *J* = 5.51 Hz, CHC*H*CHCH), 4.69 (d, 1H, *J* = 6.20 Hz, CHCHC*H*CH), 5.11 (s, 1H, CH_2OCH), 5.18 (d, 2H, J = 10.3 Hz, CH*H*CHCH$_2$O), 5.27 (d, 2H, J = 17.2 Hz, CH=C*H*H), 5.84–5.93 (m, 2H, $CH{=}CH_2$). ^{1}H NMR data was consistent with the reported value.[15]

Dipeptide **14a**: – (0.10 mmol); – (98%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.40 (s, 9H, $C(CH_3)_3$), 3.10 (d, 2H, *J* = 5.96 Hz, $CHCH_2C_6H_5$), 3.50 (t, 1H, *J* = 8.25 Hz, CHC*H*HOCH$_2$), 3.87 (d, 1H, *J* = 5.96 Hz, CHCH*H*OCH$_2$), 4.01 (br, 2H, $COOCH_2CH$), 4.22 (t, 1H, *J* = 6.87 Hz, CH), 4.32 (br, 1H, CH), 4.38 (d, 2H, *J* = 6.87 Hz, $CH_2CH{=}CH_2$), 4.73 (dt, 1H, *J* = 5.96, 7.33 Hz, CH), 5.19 (d, 1H, *J* = 10.5 Hz, CH=C*H*H), 5.25 (d, 1H, *J* = 17.4 Hz, CH=CH*H*), 5.69 (d, 1H, *J* = 5.50 Hz, NH), 5.80–5.88 (m, 1H, $CH{=}CH_2$), 7.05 (d, 1H, *J* = 5.50 Hz, NH), 7.16 (d, 2H, *J* = 6.87 Hz, aromatic), 7.21–7.33 (m, 5H, aromatic), 7.40 (t, 2H, *J* =

7.33 Hz, aromatic), 7.59 (d, 2H, J = 6.87 Hz, aromatic), 7.76 (d, 2H, J = 7.33 Hz, aromatic). ^{1}H NMR data was consistent with the reported value.[6]

(4) ^{1}H NMR experiment

Ten-mM solution of $[CpRu(CH_3CN)_3]PF_6$ (**9**) in acetone-d_6 (1.0 mL, 10 μmol) was added to a 3 mL Schlenk tube equipped with Young's tap containing 2-quinolinecarboxylic acid (**10**) (1.7 mg, 10 μmol) under argon stream. The solution was transferred to a 5-mm NMR tube equipped with Young's tap, which was connected to an argon line on a dual manifold vacuum-argon system via an adapter. The NMR tube was sealed by closing the Young's tap, and the ^{1}H NMR spectrum was taken (Figure S2, spectrum **b**). The tube was connected to vacuum-argon system again. To the solution was added 200 mM solution of **2** in acetone-d_6 (50 μL, 10 μmol) via a syringe under an argon stream. The tube was sealed, and then the ^{1}H NMR spectrum was taken (Figure S2, spectrum **c**). The tube was connected to vacuum-argon system again. To the solution was added 200 mM solution of **2** in acetone-d_6 (500 μL, 100 μmol) and 200 mM solution of **1a** in acetone-d_6 (500 μL, 100 μmol) via a syringe under an argon stream, and the system was sealed by closing the Young's tap. The reaction mixture was refluxed in 70 °C oil bath for 30 min, cooled to 27 °C, then was subjected to the ^{1}H NMR measurement (Figure S2, spectrum **d**).

(5) Conformational analysis of **7** (R = 5,6-$(CH)_4$) in solution

The conformation of π-allyl complex **7** (R = 5,6-$(CH)_4$) was deduced from observation of a nuclear Overhauser effect (nOe) between CpHs, π-allyl H_{anti}, $H_{anti'}$, H_{syn}, $H_{syn'}$, and H_{center}, and quinoline C(8)H in a 1D sense. The complex **7** (R = 5,6-$(CH)_4$) (5.2 mg, 10 μmol) was placed in a 5-mm NMR tube equipped with a Young's tap under

argon stream, and acetone-d_6 (1 mL) was introduced by use of cannula. The tube was sealed by closing Young's tap, and the mixture was sonicated for 10 min to make a clear yellow solution. The ^{1}H-NMR spectrum is shown in **a** of Figure S3. Each signal at δ 6.55 (CpHs), 4.75 (H_{anti}), 8.25 (C(8)H), and 4.40 and 4.44 (H_{syn} and $H_{syn'}$) was irradiated at the level of 55 dB, and the four difference spectra were measured to give **b**-**e** in Figure S3. The observed nOes between protons and the intensities (CpH-H_{anti}, 1.8-2%; CpH-$H_{anti'}$, 4.5%; CpH-C(8)H, 3.3%; C(8)H-H_{syn}, 7.8-9%; H_{syn}-H_{anti}, 20-25%; $H_{syn'}$-$H_{anti'}$ and $H_{syn'}$-H_{center}, 43%) indicate that the complex takes an endo-π-allyl conformation as illustrated in Figure S4.

(6) X-ray crystallographic analysis of π-allyl complex **7** (R = 5,6-$(CH)_4$)

[CpRu$(CH_3CN)_3$]PF_6 (21 mg, 49 μmol) and CH_2Cl_2 (4.9 mL) were placed in 20-mL schlenk tube under argon stream. 2-Quinolinecarboxylic acid (**10**) (8.5 mg, 49 μmol) was added to the mixture. After being stirred for 10 min, to the reddish brown solution was added a 100 mM solution of **2** in dichloromethane (490 μL, 49 μmol). The yellow solution was filtered with argon pressure to another 20-mL schlenk tube with stirring and heating to 40 °C. The filtrate was stand at 27 °C for 40 h and –30 °C for 24 h, giving pale yellow crystals in 30% yield. ^{1}H NMR (600 MHz, acetone-d_6) δ 4.40 (dd, 1H (syn), J = 2.75, 5.85 Hz), 4.44 (dd, 1H (syn'), J = 2.75, 6.20 Hz), 4.75 (d, 1H (anti), J = 9.64 Hz), 4.96 (d, 1H (anti')), 4.96–5.20 (m, 1H (center)), 6.55 (s, 5H, Cp), 7.99 (t, 1H, J = 7.57 Hz, aromatic), 8.10–8.17 (m, 2H, aromatic), 8.25 (d, 1H, J = 8.95 Hz, aromatic), 8.32 (d, 1H, J = 8.26 Hz, aromatic), 8.93 (d, 1H, J = 8.26 Hz, aromatic); ^{13}C NMR (151 MHz, acetone-d_6) δ 65.6, 72.1, 97.4, 104, 125, 129.(6), 130.(5), 131, 133, 134, 145, 149, 153, 172; mp 166 °C (dec); IR (KBr) 3134, 3093, 3026, 2362, 1978, 1752, 1674, 1600, 1568, 1519, 1475, 1459, 1440, 1423, 1397, 1369,

1333, 1287, 1264, 1236, 1209, 1180, 1157, 1119, 1071, 1061, 1031, 1017, 1003, 899.6, 880.0, 842.5, 800.1, 768.2, 740.2, 622.6, 611.2, 590.0, 557.7, 508.0, 470.6, 455.9 cm^{-1}; HRMS *m/z* ($C_{18}H_{16}NO_2Ru^+$) obsd 380.0405, calcd 380.0225. CCDC 251818 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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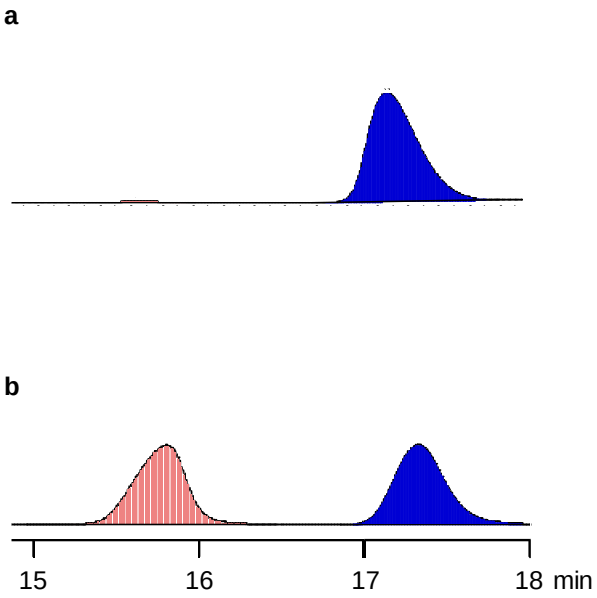

Figure S1. HPLC charts of allyl glycidyl ether (**11b**) (conditions: column, CHIRALPAK AD-H; eluent, a 99:1 hexaneŠ2-propanol mixture; flow rate, 0.5 mL/min; detection, 205-nm light). **a**: The product obtained by the present catalytic allylation of (*S*)-glycidol (**11a**) in 98% *ee*. **b**: authentic racemic sample.

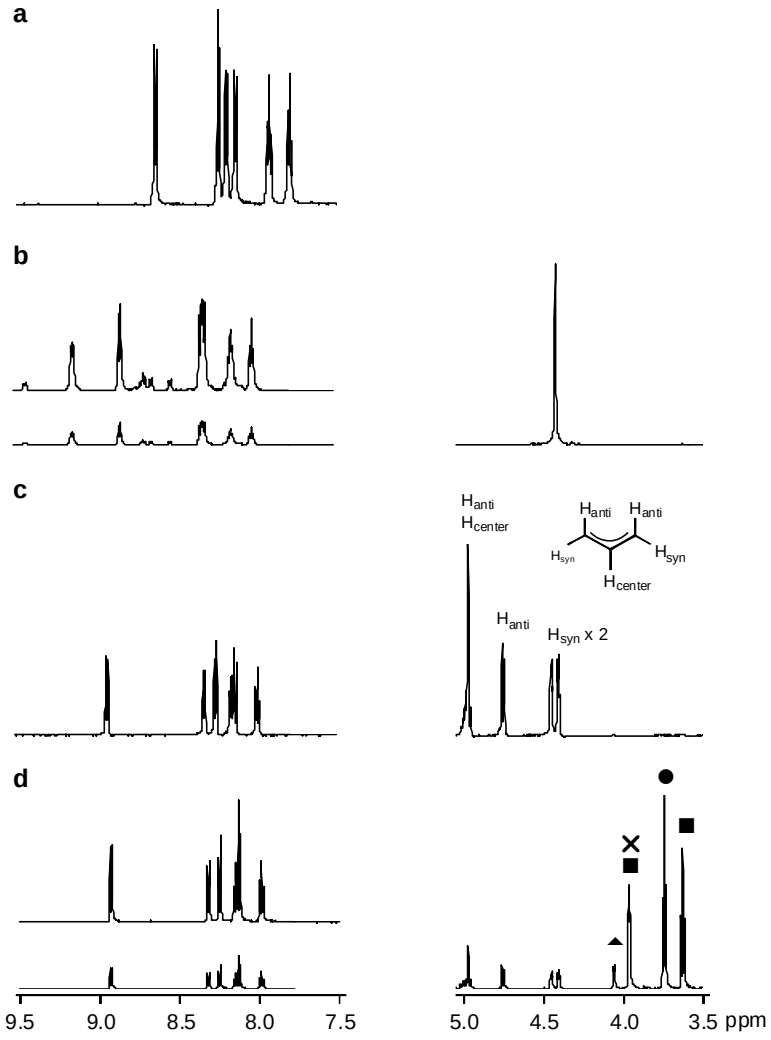

Figure S2. ^{1}H NMR spectra change of CpRu-2-quinolinecarboxylic acid combined catalyst in the allylation of 2-phenylethan-1-ol (**1a**) by use of 2-propen-1-ol (**2**). **a**: 2-quinolinecarboxylic acid (**10**) (10 mM, acetone-d_6). **b**: Addition of 1 mol amt $[CpRu(CH_3CN)_3]PF_6$ (**9**) (27 ?C, 15 min). **c**: Addition of 1 mol amt of **2** (27 ?C, 5 min). **d**: Addition of 10 mol amt **1a** and **2** (reflux, 30 min). ● = **1a**, ■ = allyl 2-phenylethyl ether (**3a**), ▲ = **2**, ✕ = diallyl ether.

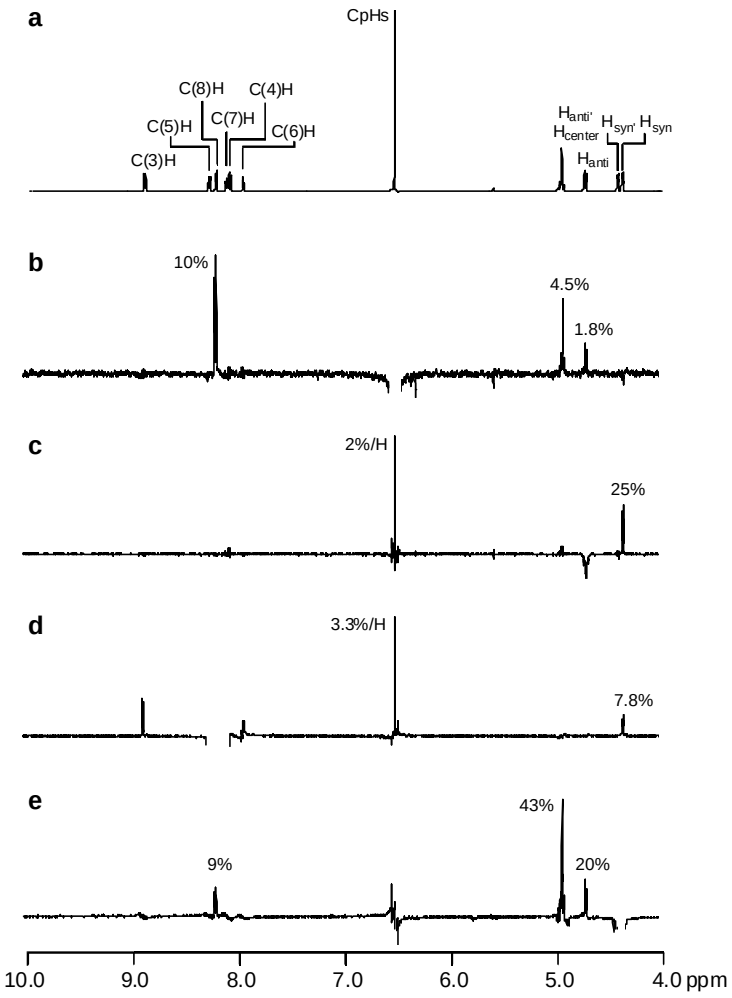

Figure S3. ^{1}H NMR spectrum of π-allyl Ru complex **7** (R = 5,6-$(CH)_4$) (**a**) and the difference spectra obtained under irradiation at δ 6.55 (CpHs) (**b**), at δ 4.75 (H_{anti}) (**c**), at δ 8.25 (quinoline C(8)H) (**d**), and at δ 4.40 and 4.44 (H_{syn} and $H_{syn'}$) (**e**) (acetone-d_6, 27 ?C).

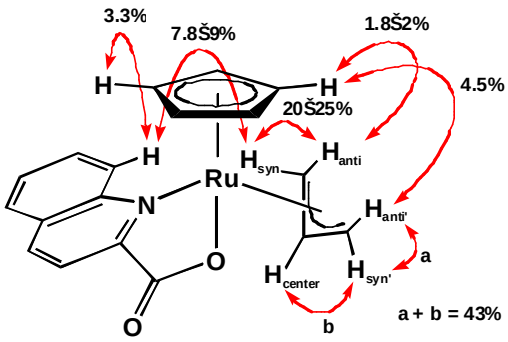

Figure S4. Conformational analysis of π-allyl Ru complex **7** (R = 5,6-$(CH)_4$) on the basis of nOe observation.

Table S1: Retention Times and Condition in GC Analysis.

	t_R, min		
Compound	**1**	**3**	Condition[a]
a	6.0	4.0	**A**
b	7.8	10	**B**
c	8.0	6.1	**A**
d	13	16	**B**
e	7.3	9.5	**B**
f	6.3	2.8	**A**
g	5.8	4.1	**A**
h	14	12	**A**
i	12	10	**A**
j	7.1	5.1	**A**
k	16	15	**A**

[a] See, (1) Instruments.