Supporting Information

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General:

^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on Bruker AV300M (300 MHz) spectrometer. Chemical shift of ^{1}H NMR was expressed in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$) in $CDCl_3$. Significant ^{1}H NMR data were tabulated in the following order: multiplicity (s: singlet; d: doublet; t: triplet; q: quartet; br: broad; m: multiplet) and coupling constants (*J*) are reported (Hz). Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ as an internal standard ($\delta =$ 77.0) in $CDCl_3$. Chemical shifts of ^{31}P NMR were expressed in parts per million downfield from 85% H_3PO_4 as an external standard ($\delta = 0$) in $CDCl_3$.

Analytical thin layer chromatography (TLC) was performed on a glass plates pre-coated with silica-gel (Merck Kieselgal 60 F_{254}, layer thickness 0.25 mm). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$. Column chromatography was performed on KANTO Silica Gel 60N (spherical, neutral).

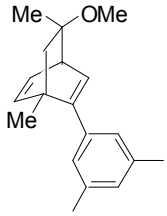
Capillary gas chromatographic analysis (GC) was conducted on Shimadzu GC-14B instrument equipped with FID detector and capillary column coated with PEG-20 M by using N_2 as a carrier gas. Peak area was calculated by Shimadzu C-R6A as an automatic integrator. CP-Chirasil-Dex CB (i.d. 0.25 mm x 25 m, CHROMPACK; GL Science) was used as a chiral column.

Optical rotations were measured on a JASCO DIP-370.

IR spectra were measured on a JASCO FT/IR-4200 spectrometer.

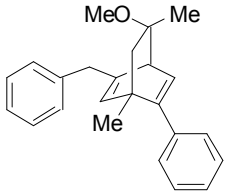
Elemental analyses were measured on a LECO CHNS-932 (Center for Advanced Materials Analysis in Tokyo Institute of Technology).

C_1-diene (2)



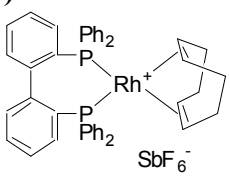
To a mixture of 3,5-dimethylphenylboronic acid (112.5 mg, 0.75 mmol) and trifluoromethanesulfonic acid 8-methoxy-1,8-dimethyl-bicyclo[2.2.2]octa-2,5-dien-2-yl ester[1] (156.2 mg, 0.5 mmol) in THF (8.0 mL) and 2.0M K_2CO_3/H_2O (8.0 mL) was added $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol). The reaction mixture was refluxed for 18 h. After cooling to room temperature, THF was evaporated under reduced pressure. The solution was extracted with ether 3 times. The organic layer was washed with brine, and then dried over $NaSO_4$. After evaporated under reduced pressure, the residue was purified by silica-gel chromatography (hexane/ethyl acetate = 10/1) to give diene **2** (yield 82%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.320 (s, 3H), 1.324 (d, J = 11.7 Hz, 1H), 1.34 (s, 3H), 1.65 (d, J = 11.7, 1H), 2.32 (s, 6H), 3.24 (s, 3H), 3.64 (td, J = 6.3, 1.2 Hz, 1H), 6.16 (td, J = 6.0, 1.2 Hz, 2H), 6.39 (t, J = 6.9 Hz, 1H), 6.78 (s, 2H), 6.90 (s, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 21.24, 21.71, 24.77, 45.33, 47.59, 49.86, 50.70, 84.09, 126.23, 128.09, 130.85, 134.06, 136.94, 139.49, 141.71, 150.05.
$[\alpha]_D^{20}$ = -22.3 (c = 0.36 in $CHCl_3$).

C_2'-diene (3)[2]



The titled compound was prepared according to the reported procedure.[2]
^{1}H NMR (300 MHz, $CDCl_3$) δ1.34 (s, 3H), 1.36 (s, 3H), 1.50 (d, J = 12.0 Hz, 1H), 1.63 (d, J = 12.0 Hz, 1H), 3.29 (s, 3H), 3.40 (dd, J = 6.6, 1.8 Hz, 1H), 3.52 (dd, J = 15.9, 1.8 Hz, 1H), 3.77 (d, J = 15.9 Hz, 1H), 5.85 (s, 1H), 6.07 (d, J = 6.6 Hz, 1H), 7.11-7.14 (m, 2H), 7.20-7.37 (m, 8H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 22.09, 25.13, 41.12, 45.18, 50.40, 50.87, 51.22, 84.07, 126.06, 126.72, 127.88, 128.12, 128.35, 129.32, 131.61, 133.35, 139.67, 147.14, 152.02.
Anal. Calcd for $C_{14}H_{26}O$: C, 87.23; H, 7.93%. Found: C, 87.09; H, 8.22%.

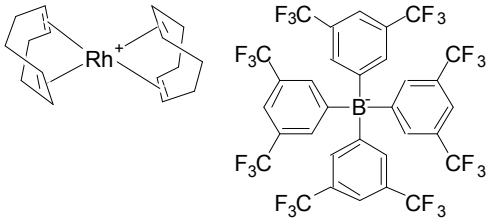
[Rh(biphep)(cod)](SbF$_6$) (1a-Rh/cod)



To a mixture of $[Rh(cod)_2]SbF_6$ and BIPHEP **1a** (1.0 eq.) was added dry dichloromethane under argon atmosphere, and stirred for 1 h at room temperature. After evaporation under reduced pressure, the resultant residue was washed with a few ml of Et_2O 3 times and dried *in vacuo* to give the titled compound quantitatively as orange powder.
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (m, 2H), 2.19 (m, 2H), 2.51 (m, 2H), 2.76 (m, 2H), 4.62

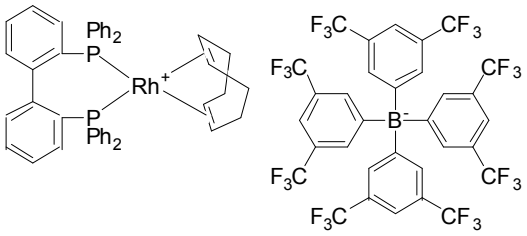
(m, 2H), 4.70 (m, 2H), 6.34 (m, 2H), 6.80-7.20 (m, 8H), 7.44-7.70 (m, 18H).
^{31}P NMR (121 MHz, $CDCl_3$) δ 24.8 (d, J_{Rh-P} = 145.0 Hz).

[Rh(cod)$_2$](BAr$_F$)



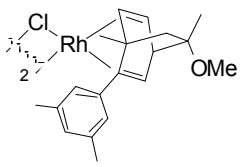
To a solution of $[Rh(cod)Cl]_2$ (100 mg, 0.2 mmol) in dry dichloromethane (3.0 mL) was added solid $NaBAr_F$ (363 mg, 0.41 mmol). Addition of 1,5-cyclooctadiene (0.075 ml, 0.6 mmol) to the orange reaction mixture resulted in immediate formation of a dark red suspension, which was stirred for 30 min at room temperature, and then filtered through a plug of Celite®. Evaporation of the volatiles afforded 387 mg of the complex (81% yield). The dark red solid was recrystallized from dichloromethane/hexane to give 320 mg of dark red needles (67% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 16H), 5.11 (s, 8H), 7.54 (s, 4H), 7.69 (s, 8H).
Anal. Calcd for $C_{48}H_{36}BF_{24}Rh$: C, 48.62; H, 3.07%. Found: C, 48.76; H, 3.07%.

[Rh(biphep)(cod)](BAr$_F$) (1a-Rh/cod)



The titled compound was prepared from $[Rh(cod)_2]BAr_F$ and BIPHEP **1a** according to the procedure as described for $[Rh(biphep)(cod)](SbF_6)$.
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01-2.12 (m, 4H), 2.44-2.70 (m, 4H), 4.45-4.56 (m, 2H), 4.72-4.80 (m, 2H), 6.34-6.40 (m, 2H), 6.98-7.07 (m, 4H), 7.16-7.27 (m, 4H), 7.28-7.39 (m, 6H), 7.42-7.62 (m, 18H), 7.75 (s, 8H).
^{31}P NMR (121 MHz, $CDCl_3$) δ 24.3 (d, J_{Rh-P} = 145.2 Hz).
Anal. Calcd for $C_{76}H_{52}BF_{24}P_2Rh$: C, 57.16; H, 3.28%. Found: C, 57.28; H, 3.24%.

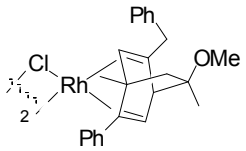
[RhCl(2)]$_2$



A mixture of chiral diene **2** (53.6 mg, 0.2 mmol) and $[RhCl(ethylene)_2]$ (42.8 mg, 0.11 mmol) in dry benzene (4.0 mL) was stirred for 24 h at room temperature under argon atmosphere, and then the reaction mixture was filtered through Celite®. After the filtrate was evaporated under reduced pressure, the yellow residue was washed with ether twice. Prolonged evacuation of the product at 100 °C gave the solvent free complex (yield 90%).[3]
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.68 (d, J = 13.8 Hz, 1H), 1.04 (s, 3H), 1.13 (d, J = 13.8, 1H), 1.65 (br s, 3H), 2.26 (br s, 6H), 3.22 (s, 3H), 3.32 (br s, 1H), 3.64 (br s, 1H), 3.71 (br m, 1H),

4.25 (br t, J = 6.0 Hz, 1H), 6.80 (br s, 1H), 7.32 (br s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 21.40, 21.53, 21.82, 48.22, 49.22, 49.31, 50.23 (d, J_{Rh-C} = 2.5 Hz), 51.55 (d, J_{Rh-C} = 11.0 Hz), 57.00 (d, J_{Rh-C} = 10.9 Hz), 71.26 (br s), 77.19, 80.90 (d, J_{Rh-C} = 2.5 Hz), 128.77, 128.85, 136.14, 137.37.
Anal. Calcd for $C_{38}H_{48}Cl_2O_2Rh_2$: C, 56.10; H, 5.95%. Found: C, 55.41; H, 5.95%.
$[\alpha]_D^{28}$ = -13.8 (c = 1.36 in $CHCl_3$).

[RhCl(3)]$_2$



The titled compound was prepared from chiral diene **3** and [RhCl(ethylene)$_2$] according to the procedure as described for [RhCl(**2**)]$_2$ (yield 88%). The product was diastereomer mixture (2.5 : 1 ratio).
^{1}H NMR (300 MHz, $CDCl_3$) *major diastereomer* δ 0.89 (d, J = 13.8 Hz, 1H), 1.09 (d, J = 13.8 Hz, 1H), 1.14 (s, 3H), 1.78 (s, 3H), 2.91 (d, J = 15.9 Hz, 1H), 3.00 (d, J = 15.9 Hz, 1H), 3.07 (s, 3H), 3.30 (s, 1H), 3.40-3.42 (m, 1H), 4.06 (d, J = 5.4 Hz, 1H), 7.22-7.39 (m, 6H), 7.95-8.00 (m, 4H).
^{1}H NMR (300 MHz, $CDCl_3$) *minor diastereomer* δ 0.85 (d, J = 14.1 Hz, 1H), 1.03 (d, J = 14.1 Hz, 1H), 1.14 (s, 3H), 1.63 (s, 3H), 3.05 (s, 3H), 3.21-3.30 (m, 3H), 3.36 (s, 1H), 4.12 (d, J = 6.3 Hz, 1H), 7.22-7.39 (m, 4H), 7.52-7.47 (m, 2H), 7.79-7.81 (m, 2H), 7.95-8.00 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) *major diastereomer* δ 21.80, 41.21, 46.22 (d, J_{Rh-C} = 10.9 Hz), 47.68, 49.56, 49.76 (d, J_{Rh-C} = 3.6 Hz), 53.13 (d, J_{Rh-C} = 2.9 Hz), 55.85 (d, J_{Rh-C} = 10.8 Hz), 70.84 (d, J_{Rh-C} = 12.1 Hz), 71.46 (d, J_{Rh-C} = 11.2 Hz), 77.24, 81.10, 126.22, 127.12, 128.15, 130.41, 130.85, 131.12, 137.66, 138.39.
^{13}C NMR (75 MHz, $CDCl_3$) *mainor diastereomer* δ 21.90, 41.31, 44.90 (d, J_{Rh-C} = 11.6 Hz), 47.58, 49.46, 54.12, 55.01 (d, J_{Rh-C} = 10.1 Hz), 71.74 (d, J_{Rh-C} = 11.2 Hz), 81.03, 120.33, 127.20, 130.92, 137.72, 138.49.
Anal. Calcd for $C_{48}H_{52}Cl_2O_2Rh_2 \cdot 2H_2O$: C, 57.10; H, 5.99; Cl, 6.82%. Found: C, 57.10; H, 5.99; Cl, 7.02%.
$[\alpha]_D^{27}$ = -76.2 (c = 1.22 in $CHCl_3$).
FT-IR (KBr pellet, cm^{-1}) 2964, 2824, 1599, 1448, 1260, 1071, 800, 700.

Preparation of BIPEHPs-Rh/diene Complexes
1) Thermodynamic Chirality Control

To a mixture of BIPHEP-Rh/cod(SbF_6) (**1a-Rh**/cod) (9.7 mg, 0.01 mmol) and chiral diene **2** (2.8 mg, 0.0105 mmol) was added dry $(CH_2Cl)_2$ (1.0 mL) under argon atmosphere, and stirred for 24 or 48 h at 80 °C. After removing solvent under reduced pressure, the desired complex was washed with Et_2O, and then dried in *vacuo*. Diastereomer ratio and undesired by-product were confirmed by ^{31}P NMR analysis.

2) Kinetic Chirality Control[4]

To a mixture of [RhCl(**2**)]$_2$ or [RhCl(**3**)]$_2$ (0.01 mmol) and silver salt (0.019 mmol) was added dry dichloromethane (1.0 mL) under argon atmosphere, and stirred for 6 h or 24 h at room temperature. Then, a solution of BIPHEP **1a** or DM-BIPHEP **1b** (0.019 mmol) in dry dichloromethane (1.0 mL), previously prepared in another Schlenk tube, was added to the reaction mixture *via* cannula. After stirring for 2 h, the AgCl precipitate was removed by filtration under argon atmosphere through a bed of Celite®. The complexes **1a-Rh**/**2** or

1b-Rh/3 were isolated by concentrating the mixture in *vacuo*, addition of a few ml of Et_2O, removal supernatant liquid via syringe, washing with Et_2O, and drying in *vacuo*. The diastereomer ratio and undesired by-product were confirmed by ^{31}P NMR analysis.

The diastereomer mixture (59:41) of **1a-Rh/2** was heated in dry $CDCl_3$ at 50 °C for 62 h (Figure S1).

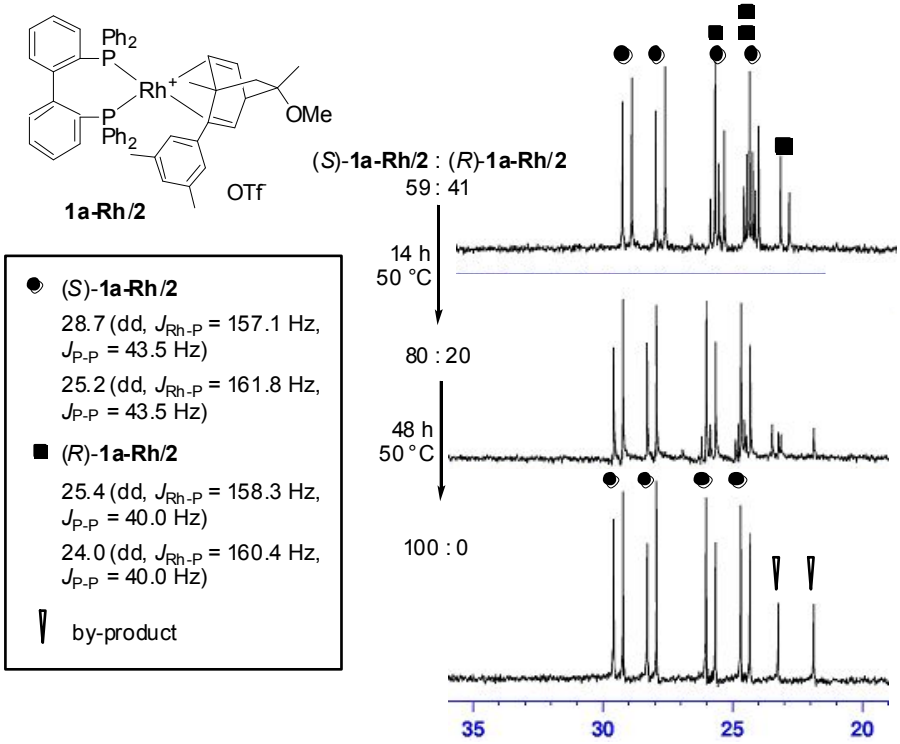


Figure S1

[Rh(biphep)(2)](OTf) (1a-Rh/2)

^1H NMR (300 MHz, $CDCl_3$) (*S*)-**1a-Rh/2** δ 0.72 (d, *J* = 13.2 Hz, 1H), 0.99 (s, 3H), 1.04 (d, *J* = 13.2 Hz, 1H), 1.54 (s, 3H), 1.85 (s, 6H), 3.21 (s, 3H), 3.46 (m, 1H), 3.60 (m, 1H), 4.55 (m, 1H), 4.82 (m, 1H), 6.05-6.08 (m, 2H), 6.80-7.78 (m, 29H).

^1H NMR (300 MHz, $CDCl_3$) (*R*)-**1a-Rh/2** δ 0.76 (d, *J* = 13.2 Hz, 1H), 1.03 (s, 3H), 1.23 (d, *J* = 13.2 Hz, 1H), 1.57 (s, 3H), 2.33 (s, 6H), 3.23 (s, 3H), 4.24 (m, 1H), 4.78 (m, 2H), 4.97 (m, 1H), 6.29-6.32 (m, 2H), 6.80-7.78 (m, 29H).

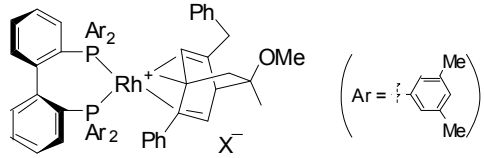
^{31}P NMR (121 MHz, $CDCl_3$) (*S*)-**1a-Rh/2** δ 28.7 (dd, J_{Rh-P}, J_{P-P} = 157.1, 43.5 Hz), 25.2 (dd, J_{Rh-P}, J_{P-P} = 161.8, 43.5 Hz); (*R*)-**1a-Rh/2** δ 25.4 (dd, J_{Rh-P}, J_{P-P} = 158.3, 40.0 Hz), 24.0 (dd, J_{Rh-P}, J_{P-P} = 160.4, 40.0 Hz).

[Rh(biphep)(2)](SbF$_6$) (1a-Rh/2)[4]

^1H NMR (300 MHz, $CDCl_3$) (*S*)-**1a-Rh/2** δ 0.73 (d, *J* = 13.2 Hz, 1H), 0.99 (s, 3H), 1.02 (d, *J* = 13.2 Hz, 1H), 1.54 (s, 3H), 1.86 (s, 6H), 3.21 (s, 3H), 3.42 (br s, 1H), 3.75 (m, 1H), 4.56 (br s, 1H), 4.80 (br s, 1H), 6.05-6.08 (m, 2H), 6.80-7.78 (m, 29H).

^{31}P NMR (121 MHz, $CDCl_3$) (*S*)-**1a-Rh/2** δ 28.8 (dd, J_{Rh-P}, J_{P-P} = 157.3, 43.9 Hz), 25.1 (dd, J_{Rh-P}, J_{P-P} = 162.0, 43.9 Hz).

[Rh{(*S*)-dm-biphep}(3)](X) ((*S*)-1b-Rh/3)



X = BF_4, ClO_4, PF_6, OTf, SbF_6

X = BF_4

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.60 (d, *J* = 13.2 Hz, 1H), 0.66 (d, *J* = 13.2 Hz, 1H), 0.91 (s, 3H), 1.69 (s, 3H), 2.17 (s, 6H), 2.20 (s, 3H), 2.31 (s, 6H), 2.34 (s, 6H), 2.46 (s, 6H), 2.82 (d, *J* = 14.1 Hz, 1H), 3.52 (d, *J* = 15.9 Hz, 1H), 3.71 (d, *J* = 15.9 Hz, 1H), 4.28 (m, 1H), 4.62 (d, *J* = 6.3 Hz, 1H), 5.86-5.89 (m, 1H), 6.00-6.03 (m, 1H), 6.66-7.55 (m, 27H), 7.87-7.93 (m, 1H).
^{31}P NMR (121 MHz, $CDCl_3$) δ 21.7 (dd, J_{Rh-P}, J_{P-P} = 157.9, 46.0 Hz), 27.4 (dd, J_{Rh-P}, J_{P-P} = 161.8, 46.0 Hz).
Anal. Calcd for $C_{68}H_{70}BF_4OP_2Rh{\cdot}2CH_2Cl_2$: C, 63.46; H, 5.63%. Found: C, 63.71; H, 5.58%.
$[\alpha]_D^{27}$ = +34.0 (c = 0.08 in $CHCl_3$).
FT-IR (KBr pellet, cm^{-1}) 2972, 1420, 1260, 1032, 759, 476.

X = ClO_4

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.63 (d, *J* = 13.2 Hz, 1H), 0.69 (d, *J* = 13.2 Hz, 1H), 0.92 (s, 3H), 1.68 (s, 3H), 2.16 (s, 6H), 2.17 (s, 3H), 2.30 (s, 6H), 2.35 (s, 6H), 2.46 (s, 6H), 2.80 (d, *J* = 14.1 Hz, 1H), 3.49 (d, *J* = 14.1 Hz, 1H), 3.56 (d, *J* = 14.1 Hz, 1H), 4.33 (m, 1H), 4.74 (d, *J* = 6.0 Hz, 1H), 5.85-5.88 (m, 1H), 6.00-6.04 (m, 1H), 6.73-7.57 (m, 27H), 7.89-7.95 (m, 1H).
^{31}P NMR (121 MHz, $CDCl_3$) δ 21.5 (dd, J_{Rh-P}, J_{P-P} = 157.7, 46.0 Hz), 27.4 (dd, J_{Rh-P}, J_{P-P} = 161.5, 46.0 Hz).
Anal. Calcd for $C_{68}H_{70}ClO_5P_2Rh{\cdot}3/2CH_2Cl_2$: C, 64.46; H, 5.68%. Found: C, 64.65; H, 5.42%.
$[\alpha]_D^{28}$ = +23.5 (c = 0.18 in $CHCl_3$).
FT-IR (KBr pellet, cm^{-1}) 2920, 1602, 1458, 1428, 1095, 758, 623.

X = PF_6

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.63 (d, *J* = 13.2 Hz, 1H), 0.69 (d, *J* = 13.2 Hz, 1H), 0.92 (s, 3H), 1.67 (s, 3H), 2.17 (s, 6H), 2.23 (s, 3H), 2.30 (s, 6H), 2.33 (s, 6H), 2.46 (s, 6H), 2.82 (d, *J* = 14.1 Hz, 1H), 3.52 (d, *J* = 16.2 Hz, 1H), 3.71 (d, *J* = 16.2 Hz, 1H), 4.35 (m, 1H), 4.67 (d, *J* = 6.3 Hz, 1H), 5.85-5.89 (m, 1H), 6.02-6.06 (m, 1H), 6.66-7.55 (m, 27H), 7.90-7.96 (m, 1H).
^{31}P NMR (121 MHz, $CDCl_3$) δ 21.3 (dd, J_{Rh-P}, J_{P-P} = 157.4, 45.7 Hz), 27.6 (dd, J_{Rh-P}, J_{P-P} = 161.5, 45.7 Hz).
Anal. Calcd for $C_{68}H_{70}F_6OP_3Rh{\cdot}3/2CH_2Cl_2$: C, 62.27; H, 5.49%. Found: C, 62.58; H, 5.37%.
$[\alpha]_D^{25}$ = +35.3 (c = 0.09 in $CHCl_3$).
FT-IR (KBr pellet, cm^{-1}) 2963, 1600, 1262, 1070, 840, 801, 695.

X = OTf

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.66 (br s, 2H), 0.90 (s, 3H), 1.69 (s, 3H), 2.15 (s, 6H), 2.20 (s, 3H), 2.29 (s, 6H), 2.34 (s, 6H), 2.47 (s, 6H), 2.86 (d, *J* = 14.1 Hz, 1H), 3.34 (d, *J* = 15.0 Hz, 1H), 3.70 (d, *J* = 15.0 Hz, 1H), 4.20 (m, 1H), 4.40 (d, *J* = 6.3 Hz, 1H), 5.88-5.91 (m, 1H), 6.00-6.03 (m, 1H), 6.67-7.58 (m, 27H), 7.82-7.88 (m, 1H).
^{31}P NMR (121 MHz, $CDCl_3$) δ 21.4 (dd, J_{Rh-P}, J_{P-P} = 157.4, 46.1 Hz), 27.1 (dd, J_{Rh-P}, J_{P-P} = 161.3, 46.1 Hz).
Anal. Calcd for $C_{69}H_{70}F_3O_4P_2RhS{\cdot}4CH_2Cl_2$: C, 56.31; H, 5.05; S, 2.06%. Found: C, 56.46; H, 4.76; S, 2.11%.
$[\alpha]_D^{27}$ = +14.2 (c = 0.05 in $CHCl_3$).
FT-IR (KBr pellet, cm^{-1}) 2962, 1602, 1261, 1029, 799.

X = SbF$_6$

^{31}P NMR (121 MHz, $CDCl_3$) δ 21.4 (dd, J_{Rh-P}, J_{P-P} = 157.7, 45.7 Hz), 27.6 (dd, J_{Rh-P}, J_{P-P} = 161.5, 45.7 Hz).
$[\alpha]_D^{26}$ = +12.5 (c = 0.13 in $CHCl_3$).
FT-IR (KBr pellet, cm^{-1}) 2921, 1602, 1459, 1125, 850, 660.

Typical Experiment Procedure of Asymmetric Hydrogenation by (*S*)-1b-Rh/3

To a mixture of (*S*)-**1b-Rh/3** (11.5 mg, 0.01 mmol) prepared by kinetic chirality control described above and 2-acetamidoacrylic acid methyl ester **5** (7.2 mg, 0.05 mmol) in 10 mL Schlenk tube was added dry dichloromethane (0.5 mL) under argon atmosphere. A mixture was charged with hydrogen gas using balloon (1 atm), then stirred for 24 h at 0 °C. The solvent was concentrated under reduced pressure. The product **6** was isolated by flash chromatography using dichloromethane/MeOH (19:1). *Ee* values was determined by chiral GC analysis; GC (column: CP Chirasil Dex CB, i.d. 0.32 mm x 25 m, CHROMPACK; carrier gas: nitrogen 75 kPa; column temperature: 100 °C; injection and detection temperature: 130 °C), t_R (*S* isomer) = 10.9 min, t_R of (*R* isomer) = 11.7 min.

It was confirmed by ^{31}P NMR analysis after the reaction that racemization of DM–BIPHEP moiety and decomposition of complex didn't occur during the course of reaction (Figure S2).

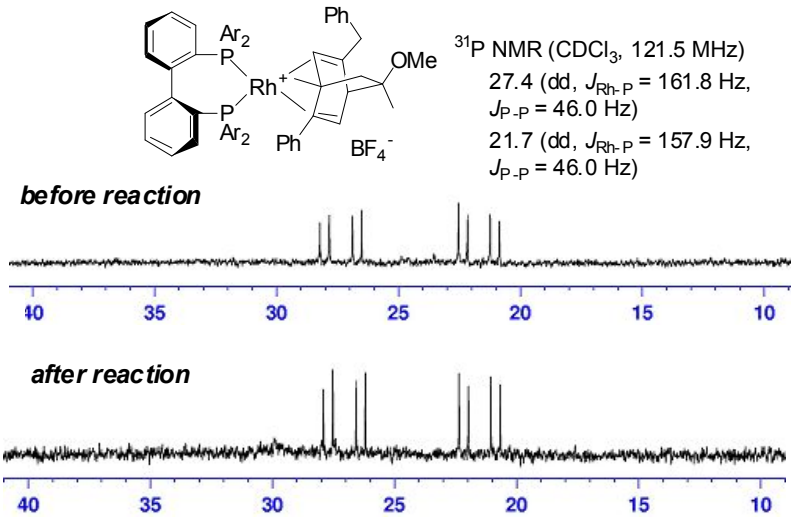
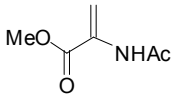


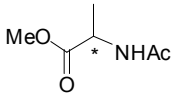
Figure S2

2-Acetamidoacrylic acid methyl ester (5)



The titled compound is commercially available.
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.13 (s, 3H), 3.85 (s, 3H), 5.88 (s, 1H), 6.60 (s, 1H), 7.74 (br s, 1H).

2-Acetamidopropionic acid methyl ester (6)[5]



^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (d, *J* = 6.9 Hz, 2H), 2.00 (s, 3H), 3.74 (s, 3H), 4.59 (qd, *J*

= 6.9, 6.9 Hz, 1H), 6.16 (br s, 1H).
GC (column, CP Chirasil Dex CB, i.d. 0.32 mm x 25 m, CHROMPACK, GL Sciences Inc.; carrier gas, nitrogen 75 kPa; column, 100 °C; injection and detection temp, 130 °C), t_R of minor-isomer 10.9 min(*S*), t_R of major-isomer 11.7 min(*R*).

B3LYP optimized geometry and energy
Basis sets used are SDD on Rh and 6-31G(d) on H, C, and P atoms.

(*S*)-**1a-Rh/3'**
Favored

E(B3LYP) = -2994.10114956 au
Zero-point vibrational energy = 555.11265 (Kcal/Mol)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-0.324132	-0.497442	-0.099982
2	15	0	1.837964	-0.285820	0.874328
3	15	0	-0.370716	1.796560	-0.680737
4	6	0	2.120581	1.312833	1.783391
5	6	0	2.187893	1.331401	3.185663
6	6	0	2.374549	2.517852	3.895300
7	6	0	2.509849	3.719114	3.205936
8	6	0	2.466861	3.714459	1.813626
9	6	0	2.268766	2.533812	1.078925
10	6	0	1.247402	2.468437	-1.302723
11	6	0	1.422662	2.767565	-2.663180
12	6	0	2.639125	3.236778	-3.159089
13	6	0	3.710182	3.426399	-2.291059
14	6	0	3.544083	3.158177	-0.934280
15	6	0	2.331886	2.676399	-0.413933
16	6	0	-1.556650	2.073047	-2.077042
17	6	0	-2.647894	2.948873	-1.982870
18	6	0	-3.553101	3.074860	-3.042035
19	6	0	-3.379885	2.335083	-4.210600
20	6	0	-2.301451	1.450848	-4.313791
21	6	0	-1.407974	1.311878	-3.252961
22	6	0	-0.507811	-2.742493	-0.798886
23	6	0	-0.746198	-2.611882	0.567531
24	6	0	-2.203264	-2.358206	0.938064
25	6	0	-2.541572	-1.044036	0.243411
26	6	0	-2.253740	-1.095789	-1.112991
27	6	0	-1.774212	-2.453451	-1.605000

28	1	0	2.113324	0.406052	3.742419
29	1	0	2.424094	2.492984	4.980118
30	1	0	2.658758	4.652227	3.741365
31	1	0	2.580981	4.647275	1.269710
32	1	0	0.595700	2.656040	-3.352511
33	1	0	2.737423	3.460439	-4.217456
34	1	0	4.664238	3.792050	-2.659295
35	1	0	4.371916	3.317353	-0.250020
36	1	0	-2.800506	3.539516	-1.086885
37	1	0	-4.391706	3.758934	-2.948262
38	1	0	-4.079816	2.440607	-5.034351
39	1	0	-2.160467	0.864830	-5.217784
40	1	0	-0.591699	0.598323	-3.333628
41	1	0	-2.341899	-2.298694	2.020340
42	1	0	-1.602752	-2.451160	-2.680792
43	1	0	-0.058957	-2.983106	1.316608
44	1	0	-2.639913	-0.364511	-1.812887
45	6	0	3.334299	-0.399147	-0.192142
46	6	0	4.603720	-0.070116	0.315848
47	6	0	3.218768	-0.814603	-1.523924
48	6	0	5.732960	-0.167529	-0.495348
49	1	0	4.709305	0.266579	1.343409
50	6	0	4.351553	-0.907195	-2.336105
51	1	0	2.243555	-1.066049	-1.925931
52	6	0	5.608258	-0.585826	-1.823867
53	1	0	6.709603	0.086017	-0.092536
54	1	0	4.247839	-1.232231	-3.367239
55	1	0	6.489319	-0.657743	-2.455395
56	6	0	-0.858202	3.038895	0.589047
57	6	0	-0.808196	4.414349	0.301555
58	6	0	-1.266252	2.624271	1.862959
59	6	0	-1.182450	5.349335	1.265400
60	1	0	-0.473928	4.755246	-0.674464
61	6	0	-1.635448	3.562364	2.829652
62	1	0	-1.273670	1.565524	2.101190
63	6	0	-1.599640	4.924413	2.530410
64	1	0	-1.145397	6.409457	1.030978
65	1	0	-1.945811	3.228417	3.815734
66	1	0	-1.888899	5.654707	3.280743
67	6	0	-3.453955	-0.026408	0.893460
68	1	0	-3.430807	0.902334	0.312878
69	1	0	-3.088615	0.207800	1.899061
70	6	0	-4.888179	-0.534618	0.996410
71	6	0	-5.727391	-0.529599	-0.126856
72	6	0	-5.389761	-1.025211	2.208514
73	6	0	-7.034937	-1.008103	-0.040944
74	1	0	-5.357874	-0.138108	-1.072256
75	6	0	-6.697952	-1.507088	2.297294

76	1	0	-4.756745	-1.021719	3.093479
77	6	0	-7.523119	-1.501606	1.171795
78	1	0	-7.675306	-0.990233	-0.918567
79	1	0	-7.072527	-1.879847	3.246591
80	1	0	-8.541903	-1.872075	1.239776
81	6	0	0.659755	-3.414888	-1.413869
82	6	0	0.912829	-3.313098	-2.795854
83	6	0	1.523140	-4.219709	-0.644537
84	6	0	1.987361	-3.979211	-3.382710
85	1	0	0.272005	-2.701268	-3.422594
86	6	0	2.598484	-4.882801	-1.231086
87	1	0	1.341707	-4.347106	0.417169
88	6	0	2.836566	-4.766469	-2.602613
89	1	0	2.156406	-3.888673	-4.452090
90	1	0	3.243535	-5.505118	-0.617401
91	1	0	3.668878	-5.293250	-3.060155
92	6	0	-3.067088	-3.505682	0.313703
93	6	0	-2.843271	-3.530533	-1.217718
94	1	0	-2.761755	-4.452160	0.773201
95	1	0	-4.119625	-3.344241	0.561169
96	1	0	-2.503596	-4.514576	-1.557935
97	1	0	-3.770097	-3.301529	-1.754337
98	6	0	2.096652	-1.582438	2.172294
99	6	0	3.205909	-2.440051	2.175924
100	6	0	1.118465	-1.746076	3.172006
101	6	0	3.340270	-3.423879	3.161015
102	1	0	3.969313	-2.348514	1.412109
103	6	0	1.259908	-2.719077	4.160446
104	1	0	0.237132	-1.109145	3.172350
105	6	0	2.374311	-3.563571	4.156601
106	1	0	4.207569	-4.077990	3.147425
107	1	0	0.499745	-2.821178	4.929985
108	1	0	2.484419	-4.324966	4.923298

(*R*)-**1a-Rh/3'**
Disfavored

E(B3LYP) = -2994.09331395 au
Zero-point vibrational energy = 555.04815 (Kcal/Mol)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.384089	-0.485295	0.015721

2	15	0	-1.726862	-0.460001	-0.983741
3	6	0	-2.893876	0.058668	0.347372
4	15	0	0.131344	1.865898	0.536573
5	6	0	0.993272	-2.584467	-0.362343
6	6	0	0.593194	-2.556415	0.980990
7	6	0	-1.881912	0.655613	-2.445545
8	6	0	-2.435714	-1.982734	-1.771493
9	6	0	-3.429919	-0.960186	1.157191
10	6	0	-3.112342	1.408477	0.715058
11	6	0	-1.224892	2.947153	-0.162688
12	6	0	1.678030	2.800552	0.150751
13	6	0	-0.128900	2.121311	2.347895
14	6	0	2.480458	-2.333732	-0.577786
15	6	0	1.747935	-2.118833	1.887004
16	6	0	-0.591454	-3.251404	1.540260
17	6	0	-3.132336	1.059955	-2.935391
18	6	0	-0.727977	0.961127	-3.180553
19	6	0	-1.607262	-2.668651	-2.676977
20	6	0	-3.771240	-2.392511	-1.643998
21	6	0	-4.217624	-0.671309	2.269176
22	6	0	-3.916864	1.674364	1.838159
23	6	0	-2.594545	2.608853	-0.015613
24	6	0	-0.901476	4.170661	-0.771826
25	6	0	2.552840	3.240175	1.155611
26	6	0	2.042482	2.997572	-1.194562
27	6	0	-0.294619	3.416035	2.870492
28	6	0	-0.193256	1.024655	3.216905
29	6	0	2.701546	-0.932754	-0.023372
30	6	0	3.283595	-3.360673	0.287888
31	6	0	2.252845	-0.813085	1.281782
32	6	0	2.876803	-3.197337	1.772616
33	6	0	-1.288192	-4.219004	0.788666
34	6	0	-1.020203	-3.014303	2.860592
35	6	0	-3.221065	1.776812	-4.127603
36	6	0	-0.819580	1.671690	-4.379906
37	6	0	-2.086164	-3.760566	-3.400575
38	6	0	-4.248807	-3.487972	-2.367784
39	6	0	-4.472594	0.655945	2.607163
40	6	0	-3.566285	3.504278	-0.491957
41	6	0	-1.883273	5.039952	-1.247859
42	6	0	3.757971	3.866833	0.823078
43	6	0	3.235904	3.638883	-1.522428
44	6	0	-0.496868	3.603708	4.237013
45	6	0	-0.400708	1.214198	4.585555
46	6	0	3.623220	0.030417	-0.735432
47	6	0	-2.371361	-4.908025	1.330673
48	6	0	-2.099531	-3.707302	3.405341
49	6	0	-2.065983	2.083487	-4.852541

50	6	0	-3.408227	-4.181146	-3.238910
51	6	0	-3.226338	4.704138	-1.111255
52	6	0	4.100723	4.072046	-0.513285
53	6	0	-0.547845	2.503109	5.097829
54	6	0	5.037207	-0.527971	-0.851294
55	6	0	-2.782173	-4.657198	2.642481
56	6	0	5.893645	-0.524168	0.259268
57	6	0	5.505825	-1.059492	-2.059163
58	6	0	7.184922	-1.043685	0.165365
59	6	0	6.798201	-1.580993	-2.156630
60	6	0	7.640116	-1.576565	-1.043715
61	1	0	0.423597	-3.111637	-1.116709
62	1	0	-3.225398	-1.998619	0.924438
63	1	0	2.757476	-2.401464	-1.632269
64	1	0	1.445262	-1.989122	2.925592
65	1	0	-4.038384	0.813659	-2.388925
66	1	0	0.241840	0.631270	-2.814424
67	1	0	-0.588572	-2.328990	-2.841699
68	1	0	-4.451707	-1.860102	-0.989436
69	1	0	-4.620584	-1.484192	2.865587
70	1	0	-4.087862	2.710229	2.114981
71	1	0	0.134111	4.469366	-0.868076
72	1	0	2.298302	3.102186	2.200880
73	1	0	1.384878	2.659267	-1.990526
74	1	0	-0.267822	4.278307	2.210618
75	1	0	-0.101037	0.023010	2.809649
76	1	0	4.355263	-3.197102	0.147190
77	1	0	3.053732	-4.368187	-0.075991
78	1	0	2.524203	0.027822	1.913721
79	1	0	3.726789	-2.870032	2.380993
80	1	0	2.517167	-4.140813	2.196822
81	1	0	-0.972283	-4.451081	-0.222084
82	1	0	-0.513563	-2.275854	3.472638
83	1	0	-4.193768	2.090809	-4.495523
84	1	0	0.080557	1.898065	-4.945042
85	1	0	-1.429674	-4.275676	-4.096308
86	1	0	-5.285626	-3.791668	-2.253310
87	1	0	-5.086917	0.900408	3.468825
88	1	0	-4.613021	3.239105	-0.373992
89	1	0	-1.590377	5.976615	-1.713224
90	1	0	4.423071	4.201055	1.614346
91	1	0	3.494538	3.794601	-2.566037
92	1	0	-0.618812	4.609132	4.629874
93	1	0	-0.453119	0.355223	5.248994
94	1	0	3.644076	0.981846	-0.200142
95	1	0	3.234765	0.230234	-1.741155
96	1	0	-2.885238	-5.653293	0.730560
97	1	0	-2.403763	-3.508243	4.429034

98	1	0	-2.140083	2.635352	-5.785177
99	1	0	-3.783744	-5.031701	-3.800354
100	1	0	-4.004787	5.369348	-1.473411
101	1	0	5.033930	4.565227	-0.768906
102	1	0	-0.708330	2.652242	6.161777
103	1	0	-3.617212	-5.205479	3.069085
104	1	0	5.549168	-0.103790	1.201841
105	1	0	4.860026	-1.055618	-2.934841
106	1	0	7.838192	-1.027564	1.033464
107	1	0	7.147237	-1.984630	-3.103046
108	1	0	8.646305	-1.978825	-1.118343

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