Supporting Information

Catalytic Enantioselective Allylation of Ketoimines

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Contents

General: NMR spectra were recorded on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for ^{1}H NMR, 125.65 MHz for ^{13}C NMR, 202.35 MHz for ^{31}P NMR, and 160.4 MHz for ^{11}B NMR. Chemical shifts were reported downfield from TMS (= 0) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to the solvent used as an internal reference. ^{11}P NMR was measured using H_3PO_4 (= 0 ppm) as an external standard. ^{11}B NMR was measured using $NaBH_4$ as an external standard (–61 ppm). Optical rotations were measured on a JASCO P-1010 polarimeter. Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM). The enantiomeric excess (ee) was determined by HPLC analysis. HPLC analysis was performed on JASCO HPLC systems consisting of the following: pump, 880-PU or PU-980; detector, 875-UV or UV-970, measured at 254 nm; mobile phase, hexane-2-propanol. GC analysis was performed on Shimadzu GC-14A with Varian Chirasil DEX CB column (0.25 mm x 25 m). In general, reactions were carried out in dry solvents under an argon atmosphere, unless noted otherwise. Toluene was distilled from benzophenone-ketyl. Normal glassware can be used to conduct the reactions in this manuscript. $CuF•3PPh_3•2EtOH$ was synthesized following the reported procedure.[1] $La(O^iPr)_3$ was purchased from Kojundo Chemical Laboratory Co., Ltd. (Fax: +81-492-84-1351). LiO^iPr was purchased from Aldrich chemical company. Pinacol 2–propenylboronic ester (**4**) was purchased from Lancaster Synthesis Ltd and used after distillation. (*R*,*R*)-^{i}Pr-DuPHOS and (*S*,*S*)–BICP were purchased from Strem Chemicals, Inc. ^{t}BuOH was used after distillation.

1. Catalytic Allylation of *N*-Benzyl Ketoimines

Preparation of *N*-Benzyl Ketoimines

N-Benzyl ketoimines were prepared from appropriate ketones and benzylamine (1.0-1.5 eq) under azeotropic conditions as shown in literatures[2]. Addition of catalytic amount of $ZnCl_2$ (1~5 mol %) accelerated the imine formation. These ketoimines were purified by distillation or recrystallization.

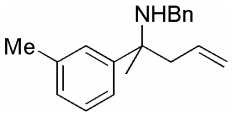
A typical procedure for catalytic allylation of *N*-benzyl ketoimines :

To a mixture of $CuF•3PPh_3$ (2.6 mg, 0.003 mmol) and $La(O^iPr)_3$ (22.5 μL, 0.2 M in THF, 0.0045 mmol) were added allylboronate **4** (141 μL, 0.75 mmol) and ketoimine **3a** (62.8 mg, 0.3 mmol). ^{t}BuOH (28.2 μL, 0.3 mmol) was added in one portion and stirred at 45 °C. After the starting material disappeared on TLC (2

h), H_2O was added to quench the reaction. The product was extracted with AcOEt, and the combined organic layer was washed with satd. NaCl aq. The organic layer was dried over Na_2SO_4. Filtration, evaporation, and purification through silica gel column chromatography (AcOEt/hexane =1/2 to 1/1) give **7a** in 94% yield (71.1 mg, white powder).

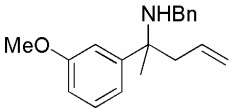
3a is a known compound.[3] Data of other products are as follows.

Benzyl-(1-methyl-1-(3-methylphenyl)-but-3-enyl)amine (7b)



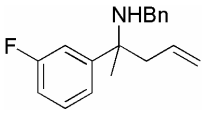
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.21 (m, 8H), 7.05 (d, *J* = 7.7 Hz, 1H), 5.73-5.65 (m, 1H), 5.09 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.06 (dd, *J* = 10.1, 1.5 Hz, 1H), 3.55 (d, *J* = 12.2 Hz, 1H), 3.45 (d, *J* = 12.2 Hz, 1H), 2.55 (d, *J* = 7.3 Hz, 2H), 2.38 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 141.3, 137.5, 134.4, 128.3, 128.1, 128.0, 127.1, 127.0, 126.7, 123.4, 118.1, 58.2, 47.3, 47.0, 25.7, 21.7; IR (neat) 2975, 1452, 914, 705 cm^{-1}; LR-MS [ESI(+)] *m/z* 266 $(M+H)^+$; HR-MS [FAB(+)] calcd for $C_{19}H_{24}N^+$ $(M+H)^+$: 266.1903. Found: 266.1910.

Benzyl-(1-methyl-1-(3-methoxylphenyl)-but-3-enyl)amine (7c)



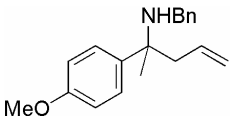
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.21 (m, 6H), 7.12-7.08 (m, 2H), 6.79 (dd, *J* = 8.2, 2.5 Hz, 1H), 5.69 (ddd, *J* = 15.9, 8.9, 7.4 Hz, 1H), 5.08 (d, *J* = 15.9 Hz, 1H), 5.06 (d, *J* = 8.9 Hz, 1H), 3.82 (s, 3H), 3.57 (d, *J* = 12.5 Hz, 1H), 3.47 (d, *J* = 12.5 Hz, 1H), 2.53 (d, *J* = 7.4 Hz, 2H), 1.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 148.6, 141.3, 134.2, 129.0, 128.3, 128.1, 126.7, 118.8, 118.1, 112.7, 111.3, 58.4, 55.1, 47.4, 46.9, 25.6; IR (neat) 2974, 1454, 915, 702 cm^{-1}; LR-MS [ESI(+)] *m/z* 282 $(M+H)^+$; HR-MS [FAB(+)] calcd for $C_{19}H_{24}NO^+$ $(M+H)^+$:282.1852. Found: 282.1850.

Benzyl-(1-methyl-1-(3-fluorophenyl)-but-3-enyl)amine (7d)



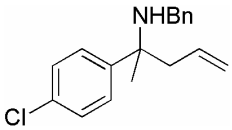
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.22 (m, 8H), 6.95-6.91 (m, 1H), 5.65 (ddd, *J* = 17.1, 10.4, 7.3 Hz, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 5.07 (d, *J* = 10.4 Hz, 1H), 3.57 (d, *J* = 12.5 Hz, 1H), 3.45 (d, *J* = 12.5 Hz, 1H), 2.51 (d, *J* = 7.3 Hz, 2H), 1.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1 (d, *J* = 248 Hz), 149.8, 141.0, 133.8, 129.5 (d, *J* = 7.2 Hz), 128.3, 128.1, 126.8, 121.9, 118.5, 113.5 (d, *J* = 22.9 Hz), 113.1 (d, *J* = 21.7 Hz), 58.3, 47.3, 46.9, 25.6; IR (neat) 2976, 1433, 917, 700 cm^{-1}; LR-MS [ESI(+)] *m/z* 270 $(M+H)^+$; HR-MS [FAB(+)] calcd for $C_{18}H_{21}FN^+$ $(M+H)^+$: 270.1653. Found: 270.1646.

Benzyl-(1-methyl-1-(4-methoxylphenyl)-but-3-enyl)amine (7e)



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.33-7.20 (m, 5H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.67 (m, 1H), 5.07 (d, *J* = 17.7 Hz, 1H), 5.05 (d, *J* = 11.3 Hz, 1H), 3.81 (s, 3H), 3.54 (d, *J* = 12.5 Hz, 1H), 3.44 (d, *J* = 12.5 Hz, 1H), 2.51 (d, *J* = 7.1 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 140.1, 133.2, 127.1, 126.9, 126.2, 125.5, 116.8, 112.2, 56.7, 54.0, 46.3, 45.6, 24.5, ; IR (neat) 2974, 1453, 915, 699 cm^{-1}; LR-MS [ESI(+)] *m/z* 278 $(M+H)^+$ 282; HR-MS [FAB(+)] calcd for $C_{19}H_{24}NO^+$ $(M+H)^+$: 282.1852. Found: 282.1854.

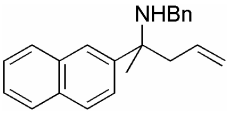
Benzyl-(1-methyl-1-(4-chlorophenyl)-but-3-enyl)amine (7f)



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ7.47-7.45 (m, 2H), 7.37-7.27 (m, 6H), 7.25-7.22 (m, 1H), 5.69-5.61 (m, 1H), 5.07 (d, *J* = 17.3 Hz, 1H), 5.06 (d, *J* = 11.0 Hz, 1H), 3.55 (d, *J* = 12.5 Hz, 1H), 3.42 (d, *J* = 12.5 Hz, 1H), 2.50 (d, *J* = 7.0 Hz, 2H), 1.51 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 141.0, 133.8, 132.1, 128.3, 128.2, 128.0, 127.9, 126.8, 118.6, 58.1, 47.4, 46.8, 25.5; IR (neat) 2976, 1638, 1491, 1093, 1011, 698 cm^{-1}; LR-MS

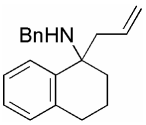
[ESI(+)] *m/z* $(M+H)^+$ 286; HR-MS [FAB(+)] calcd for $C_{18}H_{21}ClN^+$ $(M+H)^+$: 286.1357. Found: 286.1356.

Benzyl-(1-methyl-1-(*β*-naphthyl)-but-3-enyl)amine (7g)



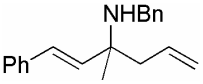
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.83 (m, 4H), 7.75 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.48-7.46 (m, 2H), 7.33-7.21 (m, 5H), 5.72-5.67 (m, 1H), 5.11 (d, *J* = 17.1 Hz, 1H), 5.06 (d, *J* = 10.1 Hz, 1H), 3.58 (d, J = 12.5 Hz, 1H), 3.45 (d, *J* = 12.5 Hz, 1H), 2.65 (d, *J* = 5.8 Hz, 2H), 1.64 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 141.3, 134.2, 133.2, 132.2, 128.3, 128.1, 128.0, 127.9, 127.4, 126.7, 125.8, 125.6, 125.0, 124.9, 118.3, 58.5, 47.2, 47.1, 25.5; IR (KBr) cm^{-1}; LR-MS [ESI(+)] *m/z* $(M+H)^+$ 302; HR-MS [FAB(+)] calcd for $C_{22}H_{24}N^+$ $(M+H)^+$: 302.1903. Found: 302.1903.

***N*-Benzyl-1-(but-3-enyl)-1,2,3,4-tetrahydro-1-naphthaleneamine (7h)**



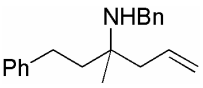
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ7.56 (d, *J* = 7.6 Hz, 1H), 7.33-7.28 (m, 4H), 7.24-7.09 (m, 4H), 5.83 (m, 1H), 5.09 (d, *J* = 17.1 Hz, 1H), 5.06 (d, *J* = 12.2 Hz, 1H), 3.64 (d, *J* = 12.5 Hz, 1H), 3.40 (d, *J* = 12.5 Hz, 1H), 2.82-2.75 (m, 2H), 2.58 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.44 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.10-2.06 (m, 1H), 1.93-1.86 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.54, 141.47, 138.2, 134.5, 128.9, 128.2, 128.1, 126.8, 126.6, 126.2, 125.8, 118.1, 57.5, 47.9, 46.8, 31.9, 30.1, 20.3; IR (neat) 2934, 1452, 913, 699 cm^{-1}; LR-MS [ESI(+)] *m/z* 278 $(M+Na)^+$; HR-MS [FAB(+)] calcd for $C_{20}H_{24}N^+$ $(M+H)^+$: 278.1903. Found: 278.1906.

***N*-Benzyl-(1-methyl-1-(1-phenyl-1*E*-vinyl)-but-3-enyl)amine (7i)**



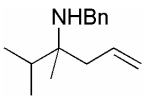
Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.27 (m, 8H), 7.25-7.22 (m, 2H), 6.48 (d, *J* = 16.5 Hz, 1H), 6.23 (d, *J* = 16.5 Hz, 1H), 5.89-5.84 (m, 1H), 5.14 (d, *J* = 17.1 Hz, 1H), 5.12 (d, *J* = 9.8 Hz, 1H), 3.70 (s, 2H), 2.43-2.39 (m, 2H), 1.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 137.3, 137.1, 134.1, 128.5, 128.46, 128.4, 128.2, 127.2, 126.7, 126.3, 118.2, 56.7, 47.1, 45.3, 24.4; IR (neat) 2975, 1450, 914, 694 cm^{-1}; LR-MS [ESI(+)] *m/z* 278 $(M+H)^+$; HR-MS [FAB(+)] calcd for $C_{20}H_{24}N^+$ $(M+H)^+$: 278.1903. Found: 278.1901.

***N*-Benzyl-(1-methyl-1-phenetyl-but-3-enyl)amine (7j)**



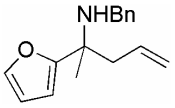
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.23 (m, 7H), 7.20-7.17 (m, 3H), 5.89 (ddd, *J* = 16.8, 10.4, 7.7 Hz, 1H), 5.14 (d, *J* = 16.8 Hz, 1H), 5.14 (d, *J* = 10.4 Hz, 1H), 3.73 (s, 2H), 2.68 (dddd, *J* =17.1, 11.6, 11.3, 5.8 Hz, 2H), 2.30 (ddd, *J* = 17.1, 13.8, 7.7 Hz, 2H), 1.75 (dddd, *J* = 18.3, 13.8, 11.6, 5.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 141.3, 134.5, 128.4, 128.3, 128.2, 126.8, 125.6, 117.8, 54.8, 46.2, 43.5, 40.9, 30.1, 24.8; IR (neat) 2928, 1453, 914, 698 cm^{-1}; LR-MS [ESI(+)] *m/z* 280 $(M+H)^+$; HR-MS [FAB(+)] calcd for $C_{20}H_{26}N^+$ $(M+H)^+$: 280.2060. Found: 280.2057.

***N*-Benzyl-(1-methyl-1-isopropyl-but-3-enyl)amine (7k)**



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.29 (m, 4H), 7.24-7.21 (m, 1H), 5.94-5.87 (m, 1H), 5.12 (d, *J* = 16.5 Hz, 1H), 5.11 (d, *J* = 10.7 Hz, 1H), 3.65 (s, 2H), 2.27 (d, *J* = 7.3 Hz, 2H), 1.85-1.81 (m, 1H), 0.97 (s, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 135.0, 128.2, 126.6, 117.3, 56.9, 45.7, 40.3, 33.9, 20.3, 17.4, 16.9; IR (neat) 2960, 1453, 912, 698 cm^{-1}; LR-MS [ESI(+)] *m/z* 218 $(M+H)^+$; HR-MS [FAB(+)] calcd for $C_{15}H_{24}N^+$ $(M+H)^+$: 218.1903. Found: 218.1904.

***N*-Benzyl-(1-methyl-1-(2-furyl)-but-3-enyl)amine (7l)**



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ7.38 (bs, 1H), 7.30-7.21 (m, 5H), 6.32-6.31 (m, 1H), 6.17 (bs, 1H), 5.74-5.68 (m, 1H), 5.07 (d, *J* = 16.2 Hz, 1H), 5.04 (d, *J* = 12.2 Hz, 1H), 3.53 (d, *J* = 12.2 Hz, 1H), 3.43 (d, *J* = 12.2 Hz, 1H), 1.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 140.0, 139.6, 132.6, 127.1, 127.0, 125.5, 116.7, 108.4, 105.1, 55.0, 46.4, 43.5, 21.9; IR (neat) 2978, 2360, 1454, 1157, 1013, 916, 735 11cm^{-1}; LR-MS [ESI(+)] *m/z* $(M+H)^+$ 242; HR-MS [FAB(+)] calcd for $C_{16}H_{20}NO^+$ $(M+H)^+$: 242.1539. Found: 242.1537.

2. Catalytic Enantioselective Allylation of Ketoimines

Benzyl-(1-methyl-1-phenyl-but-3-enyl)amine (7a)

$[\alpha]^{21}_D$ –8.8 (*c* = 0.94, $CHCl_3$) (89% ee); HPLC (DAICEL CHIRALPAK OD-H, hexane/2-propanol 1000/1, 1.0 mL/min) t_R: 12.1 min (major) and 16.1 min (minor).

Benzyl-(1-methyl-1-(3-methylphenyl)-but-3-enyl)amine (7b)

$[\alpha]^{19}_D$ –3.2º (*c* = 0.84, $CHCl_3$) (91% ee); HPLC (DAICEL CHIRALPAK OD-H, hexane/2-propanol 1000/1, 1.0 mL/min) t_R: 9.0 min (major) and 11.8 min (minor).

Benzyl-(1-methyl-1-(3-methoxylphenyl)-but-3-enyl)amine (7c)

$[\alpha]^{20}_D$ –10.2º (*c* = 0.93, $CHCl_3$) (93% ee); HPLC (DAICEL CHIRALPAK OD-H, hexane/2-propanol 1000/1, 1.0 mL/min) t_R: 21.1 min (major) and 25.1 min (minor).

Benzyl-(1-methyl-1-(3-fluorophenyl)-but-3-enyl)amine (7d)

$[\alpha]^{20}_D$ –7.9º (*c* = 0.90, $CHCl_3$) (87% ee); HPLC (DAICEL CHIRALPAK OD-H, hexane/2-propanol 1000/1, 1.0 mL/min) t_R: 10.0 min (major) and 12.5 min (minor).

Benzyl-(1-methyl-1-(4-methoxylphenyl)-but-3-enyl)amine (7e)

$[\alpha]^{23}_D$ –13.0º (*c* = 0.96, $CHCl_3$) (85% ee); HPLC (DAICEL CHIRALPAK OD-H, hexane/2-propanol 1000/1, 1.0 mL/min) t_R: 19.0 min (major) and 24.6 min (minor).

Benzyl-(1-methyl-1-(4-chlorophenyl)-but-3-enyl)amine (7f)

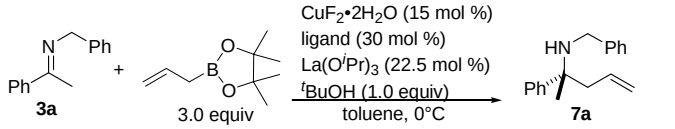
$[\alpha]^{19}_D$ –2.6º (*c* = 0.66, $CHCl_3$) (81% ee); HPLC (DAICEL CHIRALPAK OD-H, hexane/2-propanol 1000/1, 1.0 mL/min) t_R: 11.7 min (major) and 14.6 min (minor).

Benzyl-(1-methyl-1-(*β*-naphthyl)-but-3-enyl)amine (7g)

$[\alpha]^{23}_D$ –25.1º (*c* = 0.94, $CHCl_3$) (92% ee); HPLC (DAICEL CHIRALPAK OD-H, hexane/2-propanol/diethylamine 1000/1/1, 1.0 mL/min) t_R: 17.8 min (major) and 23.4 min (minor).

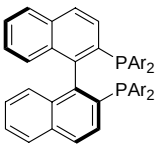
Results using other chiral ligands and La(O^{i}Pr)$_3$ as an metal alkoxide source is shown in Table S-1.

Table S-1. Screening of Chiral Ligands

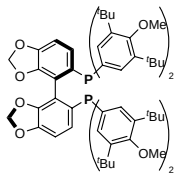


entry	ligand	time (h)	yield (%)	ee (%)
1	(*S*)-tol-BINAP	16	66	20
2	(*S*)-DM-BINAP	28	96	24
3	(*S*)-DTBM-SEGPHOS	3-17	71-92	32-60
4	(*R*,*R*)-^{i}Pr-DuPHOS	24	63-87	47-80
5[a]	(*R*,*R*)-3-pentyl-DuPHOS	20	54	53

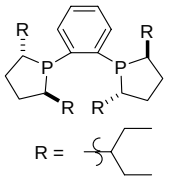
[a] LiO^{i}Pr was used instead of La(O^{i}Pr)$_3$



(*S*)–tol–BINAP : Ar = 4-Me-C_6H_4
(*S*)-DM-BINAP : Ar = 2,6-di-Me-C_6H_3



(*R*)-DTBM-SEGPHOS

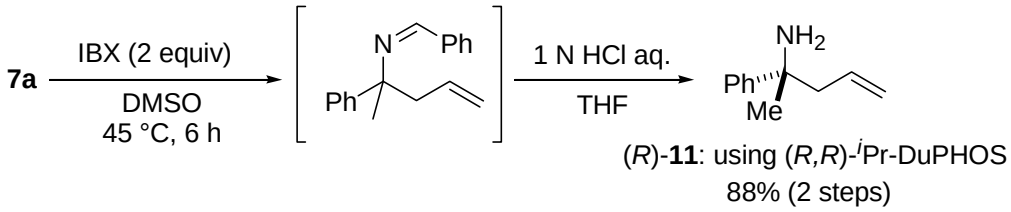


(*R*,*R*)-3-pentyl-DuPHOS

3. Removal of the Benzyl Group and Determination of the Absolute Configuration

Removal of the benzyl group was performed following a reported procedure:[4]
To a suspension of IBX (iodoxybenzoic acid) (125 mg, 0.44 mmol) in 0.6 mL DMSO was added a 0.4 mL DMSO solution of **7a** (obtained by using (*S*,*S*)-^{i}Pr-DuPHOS; 73% ee, 56.3 mg, 0.22 mmol) at ambient temperature. The resulting colorless solution was stirred at 45 °C for 6 h. Saturated $Na_2S_2O_3$ was added to quench the reaction, and the extraction was done using AcOEt. Combined organic layer washed with saturated NaCl aq., and dried over Na_2SO_4. Filtration and evaporation of the solvent gave a yellow oil. To this yellow oil, 0.5 mL THF and 1N HCl aq. were added successively, and the mixture was stirred at ambient temperature for 1 h. Solvent was evaporated, and the 1N NaOH aq. was added to adjust the PH over 8. The product was extracted with AcOEt, and the combined organic layer was washed with brine and dried over Na_2SO_4. Filtration, evaporation of solvent, and purification by silica gel chromatography gave the product amine (31.1 mg, 88% yield). $[\alpha]^{20}_{D}$ –32.9 (c = 0.51, CH_2Cl_2). By comparison to the reported optical rotations ($[\alpha]_D$ +45.8 (c = 0.86, CH_2Cl_2 for optically pure amine);[5] $[\alpha]_D$ +38.1 (c = 1.06, CH_2Cl_2 for 90% ee)[6], the absolute configuration was determined to be (*S*).

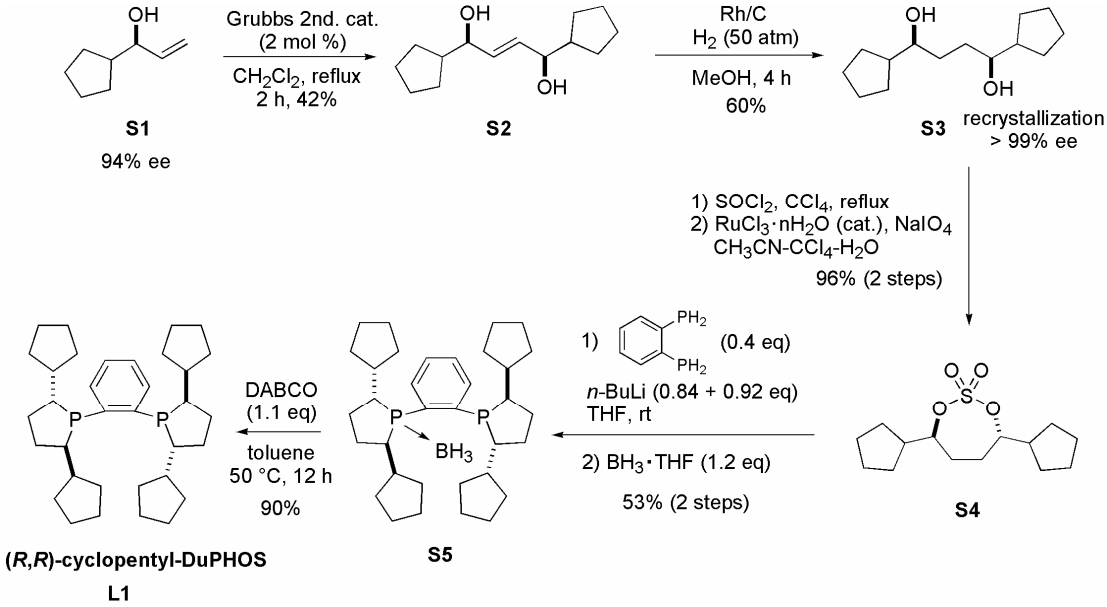
Scheme S-1. Removal of the Benzyl Group



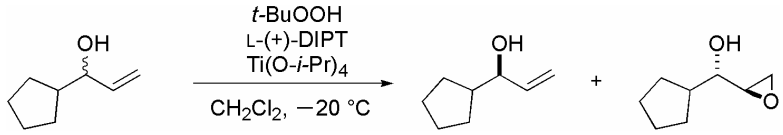
(*R*)-**11**: using (*R*,*R*)-^{i}Pr-DuPHOS
88% (2 steps)

4. The Preparation Method for (*R*,*R*)-Cyclopentyl-DuPHOS (L1)[7]

Scheme S-2. **Synthetic Scheme for (*R*,*R*)-cyclopentyl-DuPHOS**

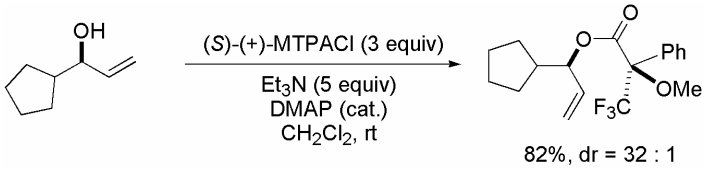


Preparation of optically active S1;



To a solution of L-(+)-diisopropyltartrate (24.0 g, 0.12 mol) in anhydrous toluene (120 mL), Ti(O-*i*-Pr)$_4$ (31.5 mL, 0.11 mol) was added at room temperature and stirred at 50 °C for 30 min. Then the solvent was pumped up. To the mixture anhydrous CH_2Cl_2 (300 mL) was added and the mixture was cooled to –20 °C. To the cooled mixture, racemic **S1** (12.2 g, 97 mmol) was added and after 30 min TBHP (5.5 M in decane, 9.7 mL, 53 mmol) was added. The mixture was allowed to stir at 20 °C for 48 h and quenched by the addition of H_2O (100 mL). The resulting precipitate was removed by filtration through celite pad. The mother liquid was extracted with CH_2Cl_2 (30 mL x 3) and washed with $Na_2S_2O_3$ aq. (20%, 50 mL) and brine. After drying over Na_2SO_4 the solvent was evaporated and the crude residue was purified by silica gel column chromatography to give **S1** (4.58 g, 36 mmol, 37% yield, 94% ee) as colorless oil; $[\alpha]^{21}{}_D$ –2.0º (*c* = 0.92, $CHCl_3$) (94% ee).

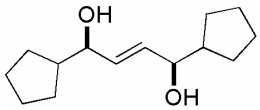
Determination of enantioselectivity of S1;



To the solution of **S1** (7.8 mg, 0.062 mmol) in CH_2Cl_2 (0.5 mL), Et_3N (43.2 □L, 0.31 mmol) and DMAP were added. (*S*)-(+)-α-Methoxy-α-trifluoromethylphenylacetyl chloride (34.7 mL, 0.18 mmol) was added to the mixture at room temperature. The mixture was stirred for 3 h and quenched by the addition of water. They were extracted with EtOAc (3 mL x 3), washed with brine and dried over Na_2SO_4. The solvent was

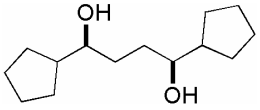
evaporated and the residue was purified by silica gel column chromatography to give **S1'** (17.4 mg, 0.051 mmol, 82% yield, dr = 32 : 1 (determined by ^{1}H NMR) as colorless oil.

(*R*,*R*)-1,4-Cyclopentyl-2-(*E*)-butene-1,4-diol (S2);

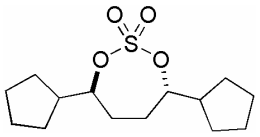


To a solution of optically active **S1** (2.97 g, 23.5 mmol, 94% ee) in degassed CH_2Cl_2 (120 mL), Grubbs 2nd catalyst (400 mg, 2 mol %) was added at room temperature. The reaction mixture was stirred at 40 °C for 2 h, and then solvent was evaporated. The obtained crude mixture was purified by silica gel column chromatography to give **S2** (1.12 g, 5.0 mmol, 42% yield) as brown solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.69-5.68 (m, 2H), 3.89 (br-s, 2H), 1.98-1.94 (m, 2H), 1.83-1.77 (m, 2H), 1.66 (m, 10H), 1.42-1.37 (m, 2H), 1.26 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.6, 45.7, 29.0, 28.8, 25.6; IR (KBr) 3302, 2951 cm^{-1}; LR-MS [ESI(+)] *m/z* $(M+Na)^+$ 247; HR-MS [FAB(+)] calcd for $C_{14}H_{23}O^+$ $(\tilde{M}OH)^+$: 207.1743. Found: 207.1744; $[\alpha]^{23}_D$ –4.9º (*c* = 0.98, $CHCl_3$) (94% ee)

(*R*,*R*)-1,4-Cyclopentyl-1,4-butanediol (S3);



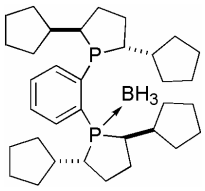
To a solution of **S2** (1.26 g, 5.6 mmol) in MeOH (30 mL), 5% Rh/C (231 mg, Rh = 2 mol %) was added at room temperature. The resulting mixture was put into autoclave and stirred vigorously under 50 atm pressure of hydrogen. After 4 h, Rh catalyst was filtered off through celite pad, and washed with MeOH thoroughly. Then solvent was evaporated under reduced pressure, followed by recrystallization from EtOAc to give optically pure **S3** (780 mg, 3.4 mmol, 60% yield) as colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43-3.40 (m, 2H), 1.90-1.47 (m, 18H), 1.37-1.33 (m, 2H), 1.24-1.18 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 46.6, 32.9, 29.2, 28.8, 25.7, 25.6; IR (KBr) 3304 cm^{-1}; LR-MS [ESI(+)] *m/z* $(M+Na)^+$ 249; HR-MS [FAB(+)] calcd for $C_{14}H_{27}O_2^+$ $(M+H)^+$: 227.2006. Found: 227.2009; $[\alpha]^{21}_D$ –5.7º (*c* = 0.65, $CHCl_3$) (>99% ee). Enantiomeric excess was determined by the corresponding Mosher ester.



Cyclic Sulfate (S4);

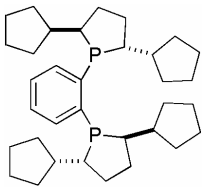
$SOCl_2$ (0.19 mL, 2.6 mmol) was added to the solution of chiral diol **S3** (450 mg, 2.0 mmol) in CCl_4 (4.0 mL) at room temperature. The resulting mixture was then heated at reflux for 2 h. After the complete consumption of **S3** on TLC, the solution was cooled to room temperature. Then excess $SOCl_2$ and solvent was evaporated under reduced pressure followed by the residue was pumped up *in vacuo*. To a brownish oily residue, CH_3CN (1.4 mL), CCl_4 (1.4 mL), H_2O (2.1 mL) were added. The resulting mixture was cooled to 4 °C. $RuCl_3$•*n*H_2O (5.3 mg, Ru = 1 mol %) and $NaIO_4$ (513 mg, 2.4 mmol) were added to the cooled mixture and allowed to stir at room temperature for 5 h. Then water was added to the mixture and they were extracted with Et_2O (5 mL x 3), washed with brine, and dried over Na_2SO_4. After evaporating the solvent, the residue was purified by silica gel column chromatography (hexane/EtOAc: 100/1 to 30/1) to give **S4** as colorless solid (552 mg, 1.9 mmol, 96% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.48-4.45 (m, 2H), 2.10-2.05 (m, 2H), 1.97-1.50 (m, 20H), 1.32-1.25 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 88.8, 44.4, 32.0, 29.2, 28.4, 25.6. 25.4; IR (KBr) 1359, 1197 cm^{-1}; LR-MS [ESI(+)] *m/z* $(M+Na)^+$ 311; HR-MS [FAB(+)] calcd for $C_{14}H_{25}O_4S^+$ $(M+H)^+$: 289.1468. Found: 289.1469; $[\alpha]^{21}_D$ –54.9º (*c* = 0.94, $CHCl_3$) (>99% ee)

(*R*,*R*)-cyclopentyl-DuPHOS monoborane complex (**S5**);



To a mixture of 1,2-bis(phosphino)benzene [10 wt% in hexane] (1.20 mL, 0.84 mmol) and degassed THF (13 mL), *n*-BuLi (1.57 N in hexane, 1.1 mL, 1.68 mmol) was added dropwise via syringe at room temperature. The pale yellow solution was stirred for 1 h. To the resulting mixture, cyclic sulfate **S4** (600 mg, 2.1 mmol) in degassed THF (3 mL) was added and stirred for 2 h. To the resulting mixture, *n*-BuLi (1.57 N in hexane, 1.2 mL, 1.85 mmol) was added dropwise via syringe at room temperature. The mixture was stirred for overnight, after which BH_3•THF (1.07 N in THF, 2.4 mL, 2.52 mmol) was added and stirred for 1 h. Excess borane and *n*-BuLi were quenched by 1N HCl aq. The mixture was extracted with Et_2O (5 mL x 2), washed with H_2O (5 mL) and brine (5 mL x 2), and dried over Na_2SO_4. After evaporating the solvent, the residue was purified by silica gel column chromatography (hexane/Et_2O = 50/1) to give **S5** (238 mg, 0.44 mmol, 53% yield) as colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ8.38-8.34 (m, 1H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.44-7.41 (m, 2H), 3.18-3.01 (m, 1H), 2.69-2.62 (m, 1H), 2.49-2.45 (m, 1H), 2.35-2.04 (m, 10 H), 1.91-0.97 (m, 27H), 0.88 (t, *J* = 7.0 Hz, 1H), 0.41-0.38 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2 (d, *J* = 34.2 Hz), 139.1 (m), 136.5 (m), 129.8 (d, *J* = 3.1 Hz), 128.8 (d, *J* = 13.5 Hz), 51.6 (d, *J* = 13.5 Hz), 49.4 (m), 49.1 (m), 47.7 (d, *J* = 16.6 Hz), 42.3 (d, *J* = 19.7 Hz), 41.8 (m), 41.1 (m), 40.8 (m), 33.3 (m), 32.4 (m), 31.8 (s), 31.5 (s), 29.5 (d, *J* = 8.3 Hz), 28.7 (s), 25.9 (s), 25.4 (s), 25.3 (s), 25.2 (s), 25.0 (s), 24.9 (s), 24.8 (s), 24.7 (s); ^{31}P NMR (202 MHz, $CDCl_3$) □ ̃ 7.2 (s); IR (KBr) 2949, 2861, 2357, 1449, 1061 cm^{-1}; LR-MS [ESI(+)] *m/z* 537 $(M+H)^+$; HR-MS [FAB(+)] calcd for $(M+H)^+$: 537.3945. Found: 537.3954; $[\alpha]^{23}_D$ –66.1º (*c* = 0.95, $CHCl_3$) (>99% ee).

1,2-bis[(*R*,*R*)-2,5-dicyclopentylphospholano]benzene ((*R*,*R*)-cyclopentyl-DuPHOS; L1);

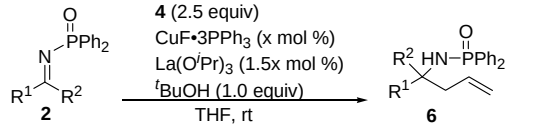


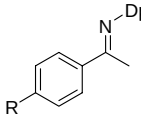
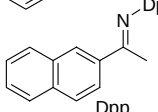
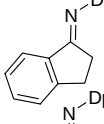
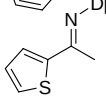
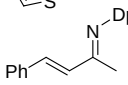
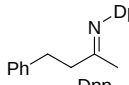
S5 (224 mg, 0.42 mmol) and DABCO (52 mg, 0.46 mmol) were mixed in toluene (4.2 mL, distilled from benzophenone-ketyl) under Ar atmosphere. The mixture was allowed to stir at 50 °C for 12 h. Then the mixture was cooled to room temperature and filtered through short pad alumina under Ar atmosphere. They were eluted thoroughly with degassed hexane/Et_2O = 10/1 eluent system. After the solvent was evaporated under Ar atmosphere, remaning solvent was removed by pump up. **L1** was obtained as colorless solid (198 mg, 0.38 mmol, 90% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.29-7.24 (m, 2H), 2.55-2.53 (m, 2H), 2.29-2.26 (m, 2H), 2.11-2.09 (m, 2H), 2.02-1.96 (m, 4H), 1.87-1.81 (m, 4H), 1.73-1.43 (m, 20H), 1.29-1.13 (m, 12H), 0.97-0.94 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9 (s), 133.7 (s), 127.5 (s), 48.1(m), 47.4 (s), 45.7(m), 41.1 (s), 34.5(m), 33.1(m), 32.0 (s), 31.7(m), 31.6 (s), 31.2(m), 25.4 (s), 25.31 (s), 25.25 (s), 24.9 (s); ^{31}P NMR (202 MHz, $CDCl_3$) δ –11.2 (s); IR (KBr) 2941, 2866, 2357, 1442, 747 cm^{-1}; LR-MS [ESI(+)] *m/z* 523 $(M+H)^+$; HR-MS [FAB(+)] calcd for $(M+H)^+$: 523.3617. Found: 523.3614.

5. Catalytic Allylation of Diphenylphosphinoyl (Dpp) Ketoimines

Dpp ketoimines can be also utilized as substrates in CuF-catalyzed allylation. However, enantioselectivity is unsatisfactory when applied to asymmetric reaction. Typical procedures and data of the products are shown below. Dpp-ketoimines were prepared using known procedures.[8]

Table S-2. Catalytic Allylation of Dpp Ketoimines

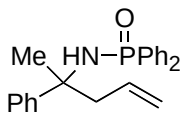


entry	substrate		x (mol %)	time (h)	yield [a] (%)
1		R = H (**2a**)	10	3	95
2		R = CH_3 (**2b**)	10	3	97
3		R = Cl (**2c**)	10	1	90
4		**2d**	10	24	80
5		**2e**	15	24	74
6		**2f**	10	3	91
7		**2g**	10	3	90
8		**2h**	10	3	81
9		**2i**	15	24	83

A typical procedure for catalytic allylboration of dpp-ketoimines :

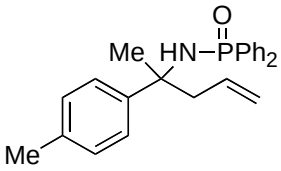
To a mixture of $CuF•3PPh_3$ (8.7 mg, 0.01 mmol) and $La(O^iPr)_3$ (75 μL, 0.2M in THF, 0.015 mmol) were added allylboronate **4** (47 μL, 0.25 mmol) and ketoimine **2a** (0.1 mmol). ^{t}BuOH (9.4 μL, 0.1 mmol) was added in one portion and stirred at ambient temperature. After the starting material disappeared on TLC (3 h), H_2O was added to quench the reaction. The product was extracted with AcOEt, and the combined organic layer was washed with satd. NaCl aq. The organic layer was dried over Na_2SO_4. Filtration, evaporation, and purification through silica gel column chromatography (AcOEt/hexane =1/2 to 1/1) give **6a** in 95% yield (34.4 mg, white powder).

***N*-(1-Methyl-1-phenyl-but-3-enyl)-diphenylphosphinamide (6a) (entry 1)**



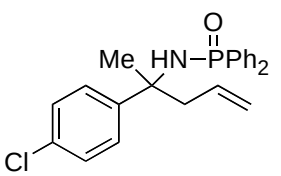
white powder; ^{1}H NMR ($CDCl_3$) δ1.60 (s, 3H), 2.81-2.82 (d, *J* = 7.4 Hz, 2H), 3.40-3.41 (d, *J* = 5.5 Hz, 1H), 5.03 (d, *J* = 1.5 Hz, 1H), 5.05 (d, *J* = 1.9 Hz, 1H), 5.16-5.45 (m,1H), 7.22-7.26 (m,1H), 7.31-7.47 (m,8H), 7.52-7.53 (d, *J* = 7.6 Hz, 2H), 7.87-7.92 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 23.4, 47.7, 58.5, 118.2, 124.1, 125.1, 126.8, 126.9, 127.0, 129.9, 129.9, 129.9, 129.9, 130.0, 130.4, 130.5, 132.3, 132.6, 133.0, 133.6, 134.0, 145.4, 145.4; ^{31}P NMR ($CDCl_3$) δ 19.65; IR (KBr) 3150, 3054, 2926, 2851, 1437, 1188, 724, 693, 536cm^{-1}; ESI-MS *m/z* 384 (M+Na$^+$); HRMS [FAB(+)] Calcd for $C_{23}H_{25}NOP^+$ (M+H$^+$) 362.1668. Found 362.1664.

***N*-(1-Methyl-1-(4-methylphenyl)-but-3-enyl)-diphenylphosphinamide (6b) (entry 2)**



white powder; ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 3H), 2.33 (s, 3H), 2.80-2.82, (d, *J* = 7.5 Hz, 2H), 3.35-3.36 (d, *J* = 5.2 Hz, 1H), 5.02-5.04 (d, *J* = 10.1 Hz, 1H), 5.15-5.18 (d, *J* = 17.1Hz, 1H), 5.43-5.51 (m, 1H), 7.12-7.13 (d, *J* = 7.9Hz, 2H), 7.36-7.48 (m, 8H), 7.87-7.91 (m,4H); ^{13}C NMR ($CDCl_3$) δ 19.2, 26.6, 47.5, 58.2, 117.9, 123.9, 126.6, 126.7, 126.8, 127.3, 129.7, 129.7, 129.8, 129.8, 130.3, 130.3, 132.3, 132.6, 133.0, 133.6, 134.0, 134.5, 142.3, 142.3; ^{31}P NMR ($CDCl_3$) δ 19.54; IR (KBr) 3158, 3074, 1638, 1451, 1177, 724, 700 cm^{-1}; ESI-MS *m/z* 398 (M+Na$^+$); HRMS [FAB(+)] Calcd for $C_{24}H_{27}NOP^+$ (M+H$^+$) 376.1825. Found 376.1817.

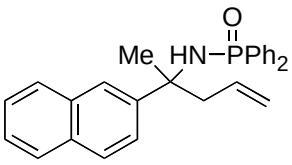
***N*-(1-Methyl-1-(4-chlorophenyl)-but-3-enyl)-diphenylphosphinamide (6c) (entry 3)**



white powder; ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 3H), 2.77, (d, *J* = 7.6 Hz, 2H), 3.37 (d, *J* = 5.5 Hz, 1H), 5.07 (d, *J* = 10.4 Hz, 1H), 5.19 (d, *J* = 17.1Hz, 1H), 5.40-5.47 (m, 1H), 7.27 (d, *J* = 9.0 Hz, 2H), 7.39-7.48 (m, 8H), 7.82-7.90 (m,4H); ^{13}C NMR

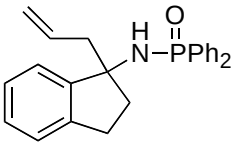
($CDCl_3$) δ 28.5, 49.5, 59.9, 120.5, 128.7, 128.7, 128.8, 128.8, 128.9, 131.8, 131.9, 131.9, 131.9, 132.0, 132.1, 132.2, 132.9, 133.7, 134.2, 134.7, 135.2, 135.7; 145.7 ^{31}P NMR ($CDCl_3$) δ 19.74; IR (KBr) 3145, 1436, 1183, 1121, 692, 530 cm^{-1}; ESI-MS *m/z* 418 ($M+Na^+$); HRMS [FAB(+)] Calcd for $C_{23}H_{24}ClNOP^+$ ($M+H^+$) 396.1279. Found 396.1280.

***N*-(1-Methyl-1-(2-naphthyl)-but-3-enyl)-diphenylphosphinamide (6d) (entry 4)**



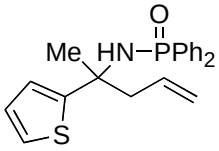
white powder; ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 3H), 2.92-2.93 (d, *J* = 7.4 Hz, 2H), 3.52-3.50 (d, *J* = 5.5 Hz, 1H), 5.03-5.05 (dd, *J* = 1.9, 10.1 Hz, 1H), 5.19-5.23 (dd, *J* = 1.6, 10.1 Hz, 1H), 5.42-5.49 (m, 1H), 7.35 (m, 2H), 7.44-7.48 (m, 6H), 7.69-7.71 (dd, *J* = 1.9, 8.9 Hz, 1H), 7.82-7.83 (m, 3H), 7.89-7.92 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 26.5, 47.5, 58.5, 118.3, 122.7, 122.8, 124.4, 124.6, 125.8, 126.6, 126.7, 126.8, 126.9, 126.9, 127.0, 130.0, 130.0, 130.4, 130.5, 130.7, 131.5, 132.2, 132.5, 133.0, 133.5, 134.0, 142.6; ^{31}P NMR ($CDCl_3$) δ 19.80; IR (KBr) 3137, 2868, 1591, 1435, 1196, 993, 722, 692 cm^{-1}; ESI-MS *m/z* 434 ($M+Na^+$); HRMS [FAB(+)] Calcd for $C_{27}H_{27}NOP^+$ ($M+H^+$) 412.1825. Found 412.1819.

***N*-(1-Methyl-1-(1-indanyl)-but-3-enyl)-diphenylphosphinamide (6e) (entry 5)**



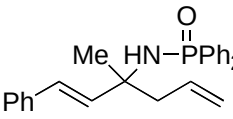
white powder; ^{1}H NMR ($CDCl_3$) δ 2.24-2.26 (m, 1H), 2.36-2.42 (m, 1H), 2.75-2.78 (m, 2H), 2.81-2.85 (m, 2H), 3.35-3.37 (d, *J* = 6.1 Hz, 1H), 5.06-5.08 (d, *J* = 10.1 Hz, 1H), 5.13-5.16 (d, *J* = 17.1 Hz, 1H), 7.05-7.09 (m, 3H), 7.30-7.35 (m, 5H), 7.38-7.41 (m, 2H), 7.69-7.76 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 28.4, 37.9, 37.9, 44.9, 66.1, 117.7, 122.5, 123.0, 124.6, 126.3, 126.6, 126.7, 126.7, 129.7, 129.8, 130.0, 130.0, 130.1, 130.1, 132.3, 141.8, 144.3, 144.3; ^{31}P NMR ($CDCl_3$) δ 19.60; IR (KBr) 3172, 2941, 2850, 1638, 1478, 1435, 1186, 720, 694 cm^{-1}; ESI-MS *m/z* 396 ($M+Na^+$); HRMS [FAB(+)] Calcd for $C_{24}H_{25}NOP^+$ ($M+H^+$) 374.1668. Found 374.1667.

***N*-(1-Methyl-1-(3-thienyl)-but-3-enyl)-diphenylphosphinamide (6f) (Table 1, entry 6)**



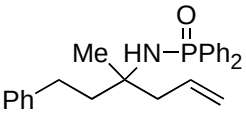
white powder; ^{1}H NMR ($CDCl_3$) δ 1.66 (s, 3H), 2.81-2.82 (d, *J* = 7.0Hz, 2H), 3.52-3.53 (d, *J* = 4.9Hz, 1H), 5.09-5.11 (d, *J* = 12.2Hz, 1H), 5.19-5.22 (d, *J* = 17.1Hz), 5.58-5.66 (m,1H), 6.89-6.91 (dd, *J* = 3.7, 4.9Hz), 6.93-6.94 (dd, *J* = 0.9, 3.7 Hz, 1H), 7.16-7.17 (dd, *J* = 1.0, 5.2 Hz, 1H), 7.39-7.47 (m, 6H), 7.87-7.94 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 27.9, 48.7, 57.4, 118.7, 121.9, 122.3, 125.4, 126.9, 127.0, 127.1, 130.0, 130.0, 130.1, 130.1, 130.1, 132.5, 132.8, 133.5, 133.8, 151.7, 151.8; ^{31}P NMR ($CDCl_3$) δ 19.41; IR (KBr) 3917, 3074, 2925, 1638, 1591, 1438, 1200, 723, 697 cm^{-1}; ESI-MS *m/z* 390 ($M+Na^+$); HRMS [FAB(+)] Calcd for $C_{21}H_{23}NOPS^+$ ($M+H^+$) 368.1232. Found 368.1233.

***N*-(1-Methyl-1-(3-phenylallylidene)-but-3-enyl)-diphenylphosphinamide (6g) (entry 7)**



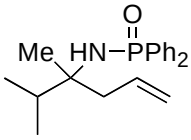
pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.21-1.26 (m, 3H), 2.56-2.60 (d, *J* = 3.7 Hz, 2H), 3.18-3.19 (d, *J* = 5.2 Hz, 1H), 5.17-5.25 (dd, *J* = 13.3, 25.8 Hz, 2H), 5.81-5.90 (m, 1H), 6.24-6.27 (d, *J* = 16.2 Hz, 1H), 6.45-6.48 (d, *J* = 16.2 Hz, 1H), 7.18-7.28 (m, 5H), 7.41-7.54 (m, 6H), 7.87-7.94 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 23.06, 23.34, 23.81, 25.18, 46.94, 56.34, 118.1, 124.9, 125.9, 126.8, 126.9, 129.9, 129.9, 130.0, 130.1, 130.4, 130.5, 132.1, 132.1, 132.6, 132.8, 133.6, 133.8, 134.5, 135.2; ^{31}P NMR ($CDCl_3$) δ 19.74; IR (neat) 3202, 2975, 2926, 1736, 1638, 1592, 1474, 1178, 698 ESI-MS *m/z* 410 ($M+Na^+$); HRMS [FAB(+)] Calcd for $C_{25}H_{27}NOP^+$ ($M+H^+$) 388.1825. Found 388.1820.

***N*-(1-Methyl-1-phenethyl-but-3-enyl)-diphenylphosphinamide (6h) (entry 8)**



pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 3H), 1.85-1.88 (m, 2H), 2.42-2.46 (m, 2H), 2.67-2.76 (m, 2H), 2.87-2.88 (d, *J* = 6.1 Hz, 1H), 5.15-5.20 (m, 2H), 5.82-5.91 (m, 1H), 7.15-7.17 (m, 3H), 7.24-7.27 (m, 2H), 7.40-7.48 (m, 6H), 7.84-7.90 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 24.7, 29.5, 43.2, 46.0, 56.6, 118.2, 124.8, 127.3, 127.3 127.4, 127.4, 130.4, 130.4, 130.6, 130.6, 130.6, 130.7, 130.7, 130.8, 132.7, 132.8, 133.6, 134.6, 141.1, 141.1; ^{31}P NMR ($CDCl_3$) δ 19.60; IR (neat) 3218, 2926, 1637, 1438, 1194, 720, 697 cm^{-1}; ESI-MS m/z 412 ($M+Na^+$); HRMS [FAB(+)] Calcd for $C_{25}H_{29}NOP^+$ ($M+H^+$) 390.1981. Found 390.1991.

***N*-(1-methyl-(1-methyl-ethyl)-but-3-enyl)-diphenylphosphinamide (6i) (entry 9)**

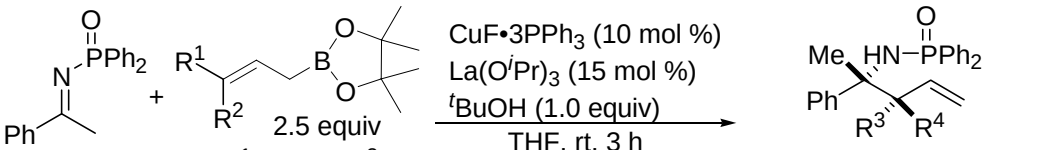


white powder; ^{1}H NMR ($CDCl_3$) δ 0.93-0.94 (d, J = 6.7 Hz, 3H), 0.99-1.01 (d, J = 6.7 Hz, 3H), 1.08 (s, 3H), 1.77 (m, 1H), 2.36-2.40 (dd, J = 6.7, 13.7 Hz, 1H), 2.47-2.51 (dd, J = 7.9, 13.7 Hz, 1H), 2.76-2.77(d, J = 5.5 Hz, 1H), 5.12-5.20 (m, 2H), 5.84-5.89 (m, 1H), 7.41-7.48 (m, 6H), 7.85-7.92 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 15.8, 20.1, 35.0, 43.5, 58.9, 117.2, 126.7, 126.8, 126.8, 126.9, 129.8, 129.9, 130.0, 130.2, 130.3, 132.5, 133.3, 133.3, 134.3, 134.4; ^{31}P NMR ($CDCl_3$) δ 19.12; IR (KBr) 3207,2956, 1638, 1436, 1187, 1122, 748, 696, 532 cm^{-1}; ESI-MS *m/z* 350 ($M+Na^+$); HRMS [FAB(+)] Calcd for $C_{20}H_{27}NOP^+$ ($M+H^+$) 328.1825. Found 328.1814.

6. Catalytic Crotylation of 2a

Catalytic crotylation of **2a** proceeded in excellent yield. Although α/γ selectivity is moderate when *N*-benzyl ketoimine is used as a substrate, a catalytic crotylation of **2a** produced only γ-addition products (*syn* and *anti* isomers were inseparable.). Relative configuration of the major isomer was the same regardless of the geometry (*E* or *Z*) of allylboronate.

Scheme S-3. Catalytic Crotylation of **2a**



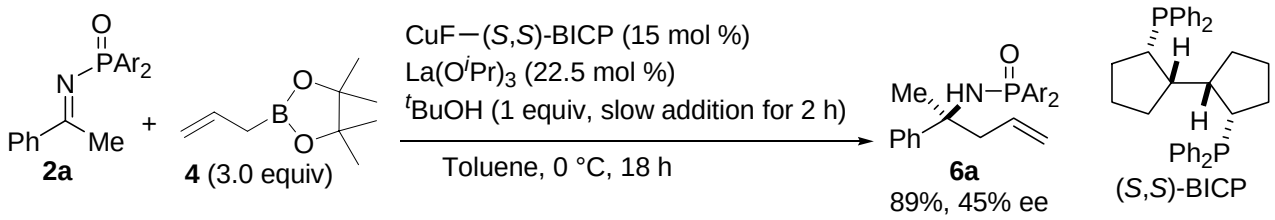
16a: dr (**17j**/**17k**) = 63/37 (total yield: 91%)
16b: dr (**17j**/**17k**) = 60/40 (total yield: 100%)

Following the typical procedure for catalytic allylation of ketoimines afforded inseparable mixture of **17j** and **17k**. The stereochemistries were temporarily assigned based on the analogy of ^{1}H NMR pattern (chemical shifts of 3-Me and 3-C–H) to the crotylated products from acetophenone.[9] **Presumed *syn* product:** ^{1}H NMR ($CDCl_3$) δ 0.85 (d, *J* = 6.7 Hz, 3H), 1.54 (s, 3H), 2.58 (quintet, *J* = 6.7 Hz, 1H), 3.62 (d, *J* = 6.1 Hz, 1H), 4.99-5.11 (m, 2H), 5.55-5.67 (m, 1H), 7.08-7.84 (m, 15H) **Presumed *anti* product:** ^{1}H NMR ($CDCl_3$) δ 0.91 (d, *J* = 6.7 Hz, 3H), 1.74 (s, 3H) 2.64 (quintet, *J* = 6.7 Hz, 1H), 3.48 (d, *J* = 5.5 Hz, 1H), 4.99-5.11 (m, 2H), 5.55-5.67 (m, 1H), 7.08-7.84 (m, 15H)

7. Catalytic Enantioselective Allylation of 2a

Catalytic Enantioselective Allylation of Dpp Ketoimine **2a** gave unsatisfactory results. (*S*,*S*)-BICP proved to be the best chiral ligand after screening of various chiral ligands. The best enantiomeric excess was 45% ee (Scheme S-4).

Scheme S-4. Catalytic Enantioselective Allylation of **2a**

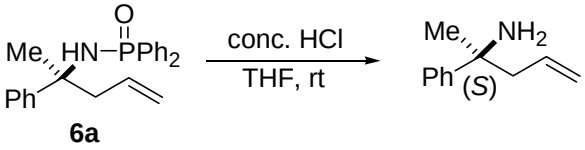


A typical procedure for catalytic enantioselective allylation of ketoimines: CuF_2•$2H_2O$ (2.1 mg, 0.015 mmol) and (*S*,*S*)–BICP (15.2 mg, 0.03 mmol) were refluxed in MeOH (1.0 mL) for 2 h. The solvent was evaporated, and the resulting amorphous was coevaporated with toluene (0.1 mL) twice. Then LiO^iPr (0.113 mg, 0.0225 mmol) was added, and the solvent was evaporated under vacuum. The resulting white solid was dissolved in toluene (0.1 mL), and the mixture was cooled to 0 °C. Allylboronate **4** (47 μL, 0.25 mmol) and substrate ketoimine **2a** (32 mg, 0.1 mmol) were added, followed by the slow addition of ^{t}BuOH (5.3 M in toluene, 0.1 mmol, 18.8 μL) over 2 h. After 18 h, H_2O was added to quench the reaction. The product was extracted with AcOEt, and the combined organic layer was washed with satd. NaCl aq. After drying over Na_2SO_4, filtration, evaporation, and purification through silica gel column chromatography gave the allylated product **6a**.

***N*-(1-methyl-1-phenyl-but-3-enyl)-diphenylphosphinamide (6a)** HPLC: DAICEL CHIRALCEL OD-H, hexane/2-propanol 20/1, 1.0 mL/min, t_R 8.5 min (minor), 11.5 min (major). $[\alpha]^{20}_D$ –21.5 (*c* = 1.42, $CHCl_3$) (45% ee).

Determination of absolute configuration: The absolute configuration was determined through the conversion to the known compound as follows.

Scheme S-5. Removal of Dpp Group



6a (19.0 mg, 33% ee) was treated with 0.4 mL conc. HCl in THF (1/1 v/v) at ambient temperature for 2 h. After evaporation of the solvent, H_2O was added and water layer was washed with AcOEt. 1 N NaOH was added to alkalify the water layer. The product was extracted with AcOEt, and the combined organic layer was washed with satd. NaCl aq. After drying over Na_2SO_4, filtration, evaporation, and purification with preparative TLC gave the free amine (2.1 mg, 25%). $[\alpha]^{22}_D$ –5.3 (c = 0.3, CH_2Cl_2). By comparison to the reported optical rotations ($[\alpha]_D$ +45.8 (c = 0.86, CH_2Cl_2 for optically pure amine;[5] $[\alpha]_D$ +38.1 (c = 1.06, CH_2Cl_2 for 90% ee)[6], the absolute configuration was determined to be (*S*).

8. Mechanistic Studies

8.1. Effect of LiO^{i}Pr on the Generation of Allylcopper from Allylboronate

(Figure 1 (a) in the text): To an NMR tube equipped with an inner tube containing CD_3OD were added CuF•3PPh$_3$ (26.1 mg, 0.03 mmol) and 500 μL THF. Allylboronate **4** (17.1 μL, 0.09 mmol) was added and NMR spectrum was measured. Three peaks were observed at 14.8 ppm, 4.2 ppm, and –13.4 ppm. By comparison to the chemical shift of the authentic sample **13b**, which was synthesized with a procedure analogous to that of a literature method,[10] the peak at 4.2 ppm was assigned to be **13b**. The peak at –13.4 ppm was assigned to **12b**, on the basis of our previous NMR studies.[9]

(Figure 1 (b) in the text): To an NMR tube equipped with an inner tube containing CD_3OD, CuF•3PPh$_3$ (26.1 mg, 0.03 mmol) and 275 μL THF were added. LiO^{i}Pr (0.2 M in THF, 225 μL, 0.045 mmol) and allylboronate **4** (17.1 μL, 0.09 mmol) were added successively and NMR spectrum was measured. Commercially available **13a** (purchased from Aldrich) in THF showed a peak at 4.2 ppm. Therefore, the peak at 4.2 ppm should represent the mixture of **13a** and **13b**.

The peak intensity of **13b** (and **13a**) should correlate with the concentration of active species **14**.[9] Therefore, the peak intensity ratio indicates that the concentration of **14** increases significantly in the presence of LiO^{i}Pr.

8.2. Possible Origin of LiO^{i}Pr Effect: Support for the Existence of Cation Exchange between 12a and 12b

(Figure 1 (c) in the text): To an NMR tube equipped with an inner tube containing CD_3OD, LiO^{i}Pr (0.2 M in THF, 250 μL, 0.05 mmol) and 250 μL THF were added. Allylboronate **4** (9.4 μL, 0.05 mmol) was added and NMR spectrum was measured. Two peaks corresponding to **4** and **12a** (–10.1 ppm) were observed.

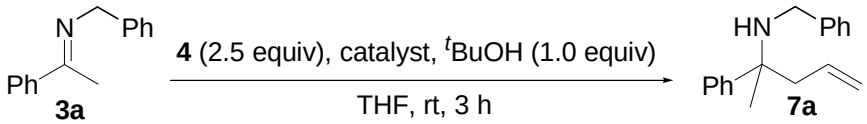
(Figure 1 (d) in the text): Solutions of **12a** and **12b** (250 μL each) were mixed and NMR spectrum was measured. Although the peaks of **4** and **12a** disappeared, **12b** remained. **13a** (and partially **13b** might overlap on this peak) appeared.

The formation of **13a** (and **13b**) in Figure 1 (d) in the text suggests the formation of allylcopper **14**. **14** should be generated from copper trialkoxyborate **12c** after cation exchange between **12a** and **12b**.

8.3. Catalytic Allylation Using CuO^{t}Bu

To confirm the feasibility that CuO^{t}Bu is involved in the catalytic cycle, CuO^{t}Bu was prepared[11] and used in the reaction with **3a** (Table S-3). Allylation of **3a** proceeded with CuO^{t}Bu alone (entry 1). Because CuO^{t}Bu itself can promote the reaction efficiently, we propose the catalytic cycle shown in Scheme 2 in the text, which involves CuO^{t}Bu as a precursor to regenerate allylcopper **14**. Addition of 15 mol % of LiO^{i}Pr (Table S-3, entry 2) or 2 mol % of CuF•3PPh$_3$ (Table S-3, entry 3) improved the yield, suggesting that both LiO^{i}Pr and fluoroboronbate **13b**[12] are involved in accelerating the catalyst regeneration step from CuO^{t}Bu. The highest reaction rate was observed when both **13b** and LiO^{i}Pr are present in the reaction media (entry 4), even though the final chemical yield of **7a** did not change significantly. Therefore, both LiO^{i}Pr and **13b** can accelerate the catalyst turnover.

Table S-3. CuO^{t}Bu-Catalyzed Allylation of **3a**



entry	catalyst	yield (%)[a]
1	CuO^{t}Bu (10 mol %)	76
2	CuO^{t}Bu (10 mol %), LiO^{i}Pr (15 mol %)	86
3	CuO^{t}Bu (8 mol %), CuF•3PPh$_3$ (2 mol %)	92
4[b]	CuF•3PPh$_3$ (10 mol %), LiO^{i}Pr (15 mol %)	90

[a] Isolated yield. [c] Reaction time was 2 h.

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[12] **13b** prepared according to ref. 10 was not isolable. Therefore, we prepared **13b** *in situ* from CuF•3PPh$_3$ and allylboronate **4**.