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# Highly Active Catalysts of Bisphosphine Oxides for Asymmetric Heck Reaction

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Supporting Information: Procedures and characterization

Table of Contents

| | |
|---|---|
| I | General |
| II | Synthesis of chiral bisphosphine monoxides |
| III | Synthesis of aryl triflates |
| IV | Condition optimization of Heck reactions |
| V | Isolation of Heck products |
| VI | Mechanistic study |
| VII | Reference |

## I. General

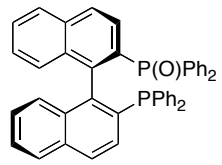
All NMR spectra were acquired on Bruker AVIII 400 MHz NMR spectrometers. $^{1}$H NMR (400 MHz) chemical shifts were recorded relative to $SiMe_4$ (δ 0.00) or residual protiated solvents ($CDCl_3$: δ 7.26; $CD_2Cl_2$: δ 5.32). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. $^{13}$C NMR chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.16; $CD_2Cl_2$: δ 53.84). $^{19}$F NMR (376 MHz) chemical shifts were recorded relative to an external standard ($BF_3 \cdot OEt_2$: δ 153.0). $^{31}$P NMR (126 MHz) chemical shifts were relative to an external standard (85% $H_3PO_4$: δ 0.00). Proof of purity of new compounds was demonstrated with copies of $^{1}$H, $^{13}$C, $^{31}$P and $^{19}$F NMR spectra.

Glassware was dried at 120 $^{o}$C for at least 3 h before use. Anhydrous 1,4-dioxane (Aldrich) was stored over activated 4 Å molecular sieve beads in an argon-filled glove box. Veratrole was distilled over $CaH_2$ under vacuum. Dry toluene, hexane, diethyl ether and dichloromethane were collected from a solvent purification system containing a column of activated alumina (1 m x 2) under argon. Dry THF was freshly distilled from sodium/benzophenone under argon. *N*-Ethyldiisopropylamine (Hünig's base) was distilled from $CaH_2$ under argon before use. All anhydrous solvents were stored in Schlenk tubes in the glove box.

Unless noted otherwise, commercially available chemicals were used as received without purification. The GC internal standard, *n*-$C_{14}H_{30}$ was degassed with argon and dried over activated 4 Å molecular sieve beads before use.

Flash chromatography was performed using Merck 40-63D 60 Å silica gel. Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 instrument with Agilent J & W GC column DB-5MS-UI. GC/MS analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Agilent J & W GC column DB-5MS-UI. ESI/MS analysis was conducted on a ThermoFinnigan LCQ Fleet MS spectrometer. Chiral HPLC analysis was performed on a Shimadzu LC-20AD instrument using Daicel Chiracel columns at 25°C and a mixture of HPLC-grade hexanes and isopropanol as eluent. Optical rotation was measured using a JASCO P-1030 Polarimeter equipped with a sodium vapor lamp at 589 nm and the concentration of samples was denoted as *c*. X-ray crystallography analysis was performed on a Bruker X8 APEX X-Ray diffractometer.

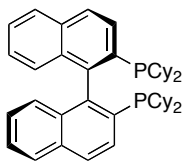
## II. Synthesis of chiral bisphosphine monoxides




**(*R*)-2-diphenylphosphino-2′-diphenylphosphinyl-1,1′-binaphthyl or (*R*)-BINAP(O) [152646-80-5].**[1] It was prepared from (*R*)-BINAP according to a modification of Grushin's method using $PdI_2$ catalyst and 1,2-dibromoethane as terminal oxidant.[1] Under argon, a dry 25-mL Schlenk tube was charged with $PdI_2$ (3.7 mg, 0.010 mmol), (*R*)-BINAP (250 mg, 0.40 mmol) and $CH_2Cl_2$ (2.5 mL). The mixture was stirred at 25 $^oC$ for 3 h until all $PdI_2$ was dissolved. A solution of NaOH (0.23 g, 5.75 mmol) in $H_2O$ (1.5 mL) was then added, followed by 1,2-dibromoethane (0.50 g, 2.66 mmol). The resulting mixture was stirred in a 50 $^oC$ bath for 14 h until (*R*)-BINAP was fully consumed (monitored by $^{31}P$ NMR spectroscopy). The pH of the reaction mixture was then adjusted to ~4 with 20% $H_3PO_4$ solution, followed by stirring with dppe (10 mg) for 5 min to remove Pd. The organic layer was separated, dried over $MgSO_4$, concentrated on a rotary evaporator, and purified by flash chromatography (10:1 $CH_2Cl_2$/EtOAc) in air, which afforded 0.216 g (84%) of the product as a white solid.

$^1H$ NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.62 - 7.57 (m, 3H), 7.41 (dd, *J* = 8.5, 2.9 Hz, 1H), 7.38-7.31 (m, 6H), 7.29-7.19 (m, 7H), 7.18-7.12 (m 1H), 7.10-7.01 (m, 4H), 6.98-6.93 (m, 2H), 6.90-6.86 (m, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.74-6.70 (m, 1H), 6.64 (d, *J* = 8.4 Hz, 1H).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ27.0 (s), -15.3 (s).

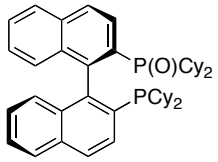



**(*R*)-2,2′-bis(dicyclohexylphosphino)-1,1′-binaphthyl or (*R*)-Cy-BINAP [139139-92-7].**[2] It was prepared according to a reported procedure (reported yield 34%).[2] In an argon-filled glove-box, $HPCy_2$ (0.23 g, 1.16 mmol), (dppe)$NiCl_2$ (0.106 g, 0.20 mmol) and dry DMF (4.0 mL) were charged into a 25-mL Schlenk tube. The mixture was heated with stirring in a 100 $^oC$ bath for 30 min. A solution of DABCO (0.90 g, 8.0 mmol) and (*R*)-1,1′-binaphthyl 2,2′-

bistriflate (1.10 g, 2.0 mmol) in dry DMF (6.0 mL) was added against flow of argon, followed by the addition of zinc dust (0.80 g, 12 mmol; activated by aqueous HCl and dried under vacuum). The mixture was stirred in a 115 $^{o}$C bath. Additional portions of $HPCy_2$ (0.23 g, 1.16 mmol each portion) were added after stirring at 115 $^{o}$C for 1 h, 3 h and 12 h, respectively. The mixture was further stirred at 115 $^{o}$C for 3 days and 125 $^{o}$C for 1 day. Upon cooling to r t, the product precipitated out, and it was collected by filtration together with zinc dust and washed with MeOH (3 mL x 3) under argon. It was redissolved in $CH_2Cl_2$ (5.0 mL) and passed through a pad of silica gel with $CH_2Cl_2$ washings to remove zinc dust. Removal of solvent under vacuum afforded 0.31 g (24%) of the product as a white powder, which was pure by $^{1}$H and $^{31}$P NMR spectroscopy.

$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, $J$ = 8.4 Hz, 2 H), 7.86 (d, $J$ = 8.1 Hz, 2 H), 7.72 (d, $J$ = 8.4 Hz, 2 H), 7.38 (ψt, $J$ = 7.4 Hz, 2H), 7.14 (ψt, $J$ = 7.5 Hz, 2H), 6.99 (d, $J$ = 8.5 Hz, 2 H), 2.15 (br s, 2H), 1.87 (d, $J$ = 11.1 Hz, 2H), 1.80-1.68 (m, 8 H), 1.51-1.16 (m, 22H), 1.00-0.71 (m, 10H).

$^{31}$P{$^{1}$H} NMR (162 MHz, $CDCl_3$): δ -9.6 (s).




**(*R*)-2-(Dicyclohexylphosphino)-2′-(dicyclohexylphosphinyl)-1,1′-binaphthyl or (*R*)-Cy-BINAP(O).** Grushin's procedure cannot be applied to other biphosphines due to low yield and poor *P*-monoxide selectivity. The titled compound was prepared according to our modification using a stoichiometric amount of $PdI_2$. Under argon, (*R*)-Cy-BINAP (41 mg, 0.063 mmol) and $PdI_2$ (33 mg, 0.091 mmol) were stirred in $CH_2Cl_2$ (5.0 mL) at RT for 6 h. Unreacted $PdI_2$ was then filtered off via a syringe filter. To the filtrate was added bis(*p*-methoxybenzylidene)-acetone (0.28 g, 0.95 mmol) and an aqueous NaOH solution (3.75 M, 2.5 mL). The resulting mixture was stirred at RT for 15 h. The organic layer was then separated and was stirred with dppe (56 mg, 0.14 mmol) at RT for 3 h to removed Pd. The resulting mixture was directly subjected to flash chromatography ($CH_2Cl_2$ and then 5:1 $CH_2Cl_2$/EtOAc) in the argon-filled glove box to give the product in 73% yield (31 mg) as white powder.

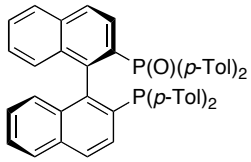
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, $J$ = 8.6, 1.9 Hz, 1H), 7.89 (ψd, $J$ = 8.6 Hz, 2H), 7.85 (d, $J$ = 8.1 Hz, 1H), 7.73-7.65 (m, 2H), 7.49-7.45 (m, 1H), 7.38-7.34 (m, 1H), 7.23-7.19 (m,

1H), 7.13-7.06 (m, 2H), 6.97 (d, $J$ = 8.4 Hz, 1H), 2.29-2.22 (m, 1H), 2.15-2.07 (m, 1H), 1.97-0.68 (m, 42H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ 145.0 (dd, $J$ = 7.1, 5.3 Hz), 144.1 (d, $J$ = 3.5 Hz), 143.8 (d, $J$ = 3.7 Hz), 135.8 (d, $J$ = 17.8 Hz), 134.5 (dd, $J$ =10.6, 2.1 Hz), 133.9 (3 peaks), 133.8, 133.3, 130.3 (d, $J$ = 2.5 Hz), 129.5 (d, $J$ = 2.4 Hz), 128.8, 128.7 (2 peaks), 128.1, 127.9, 127.8 (2 peaks), 127.3, 127.2, 127.1 (3 peaks), 126.9, 126.1, 125.7, 125.1, 38.7 (d, $J$ = 64.8 Hz), 37.0 (d, $J$ = 65.1 Hz), 35.7 (d, $J$ = 16.3 Hz), 33.0 (d, $J$ = 15.3 Hz), 32.2 (d, $J$ = 18.3 Hz), 31.7 (d, $J$ = 16.3 Hz), 30.2 (d, $J$ = 14.7 Hz), 29.0 (d, $J$ = 7.7 Hz), 27.9, 27.8 , 27.7, 27.6, 27.4 (d, $J$ = 9.4 Hz), 26.9 (3 peaks), 26.8 (2 peaks), 26.7, 26.6 (2 peaks), 26.5 (2 peaks), 26.4, 26.2, 26.1. (Not all $J$($^{13}$C-$^{31}$P) couplings were determined).

$^{31}$P{$^{1}$H} NMR (162 MHz, $CDCl_3$): δ 44.0 (s), -9.4 (s).

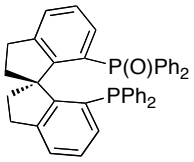
ESI-MS: Calcd for $C_{44}H_{56}OP_2$ $[M+H]^+$: 663.4, Found: 663.5.




**(*R*)-2-Di(*p*-tolyl)phosphino-2′-di(*p*-tolyl)phosphinyl-1,1′-binaphthyl or (*R*)-Tol-BINAP(O) [(*S*)-isomer 337529-05-2].**[3] It was prepared from (*R*)-Tol-BINAP similarly according to the procedure described for (*R*)-Cy-BINAP(O). The reaction was set up on 30 mg (0.044 mmol) scale and the product was isolated as a white powder in 70% yield (21 mg).

$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, $J$ = 8.6, 1.9 Hz, 1H), 7.81 (d, $J$ =8.1 Hz, 1H), 7.70-7.65 (m, 3H), 7.44-7.37 (m, 3H), 7.35-7.23 (m, 4H), 7.18-7.14 (m, 2H), 7.00 (d, $J$ = 7.1Hz, 2H), 6.96-6.92 (m, 3H), 6.88-6.86 (m, 3H), 6.82-6.79 (m, 4H), 6.75-6.71 (m, 1H), 6.61 (d, $J$ = 8.6 Hz, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 2.23 (s, 6H).

$^{31}$P{$^{1}$H} NMR (162 MHz, $CDCl_3$): δ 27.3 (s), -17.0 (s).

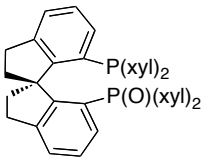



**(*R*)-7-diphenylphosphino-7′-diphenylphosphinyl-1,1′-spirobiindane or (*R*)-SDP(O) [(*S*)-isomer 528521-82-6].**[4] It was prepared from (*R*)-7,7′-diphenylphosphino-1,1′-spirobiindane or (*R*)-SDP using a stoichiometric amount of $PdI_2$ as oxidant. All the operations were conducted in an argon-filled glove box. (*R*)-SDP (50 mg, 0.085 mmol) was stirred with $PdI_2$

(43 mg, 0.12 mmol) in $CH_2Cl_2$ (8.0 mL) for 3 h until full conversion of the biphosphine (monitored by $^{31}P$ NMR spectroscopy). Unreacted $PdI_2$ was filtered off via a syringe filter. To the filtrate was added dibenzylideneacetone (200 mg, 0.85 mmol) and an aqueous NaOH solution (3.75 M, 4.0 mL). The mixture was stirred at RT for 12 h until full conversion of the Pd(II) complex as monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The organic phase was separated and was stirred with dppe (75 mg, 0.19 mmol) at RT for 3 h to removed Pd. The solution was then passed through a pad of silica gel, eluted with 10:1 $CH_2Cl_2$/EtOAc and concentrated under vacuum. Purification of the residue by flash chromatography (20:1 to 10:1 $CH_2Cl_2$/EtOAc) gave a white solid. Yield: 33 mg, 64%.

$^1H$ NMR (400 MHz, $CDCl_3$): δ 7.47-7.43 (m, 3H), 7.40-7.33 (m, 6H), 7.27-7.19 (m, 7H), 7.16-7.05 (m, 7H), 6.95 (dd, $J$ = 7.0, 5.2 Hz, 1H), 6.86-6.82 (m, 2H), 3.02-2.85 (m, 3H), 2.79-2.72 (m, 1H), 2.61 (dd, $J$ = 22.0, 9.9 Hz, 1H), 2.09-2.03 (m, 1H), 2.01-1.95 (m, 1H), 1.93-1.85 (m, 1H).

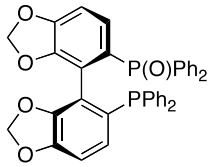
$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 29.4 (s), -18.3 (s).




**(*R*)-7-Bis(*m*-xylyl)phosphino-7′-bis(3,5-dimethylphenyl)phosphinyl-1,1′-spirobiindane or (*R*)-Xyl-SDP(O) [(*S*)-isomer 528521-85-9].**[4] All the operations were conducted in an argon-filled glove box. (*R*)-7,7′-bis(*m*-xylyl)phosphino-1,1′-spirobiindane ((*R*)-Xyl-SDP) (100 mg, 0.14 mmol) and $PdI_2$ (72 mg, 0.20 mmol) were stirred in $CH_2Cl_2$ (14 mL) at RT for 8 h, until the bisphosphine was fully converted to the $PdI_2$ complex (monitored by $^{31}P$ NMR spectroscopy: δ 27.4 for Pd complex). Unreacted $PdI_2$ was filtered off via a syringe filter. To the filtrate was added dba (334 mg, 1.43 mmol) and an aqueous NaOH solution (3.75 M, 7.0 mL). The mixture was stirred at RT for 15 h, until $^{31}P$ NMR spectroscopy showed full conversion of the $PdI_2$ complex. Then, the organic phase was separated and stirred with dppe (113 mg, 0.28 mmol) at RT for 3 h to removed Pd. The solution was then passed through a silica gel pad, eluted with 20:1 to 4:1 $CH_2Cl_2$/EtOAc. The fractions containing the desired product were concentrated under vacuum and purified as white solid by flash chromatography (20:1 to 4:1 $CH_2Cl_2$/EtOAc). Yield: 95 mg, 92%. This ligand was also prepared from (*R*)-7,7′-bis(trifluoromethanesulfonyloxy)-1,1′-spirobiindane according to a literature procedure[4] en route to (*S*)-Xyl-SDP (*vide infra*).

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.38-7.36 (m, 1H), 7.27-7.05 (m, 10H), 6.95 (s, 1H), 6.90 (s, 1H), 6.86 (s, 1H), 6.84 (s, 1H), 6.73 (s, 1H), 6.57 (s, 1H), 6.55 (s, 1H), 2.94-2.91 (m, 2H), 2.87-2.79 (m, 1H), 2.64-2.51 (m, 2H), 2.27 (s, 6H), 2.23 (s, 6H), 2.02 (s, 12H), 1.99-1.93 (m, 2H), 1.74-1.66 (m, 1H).

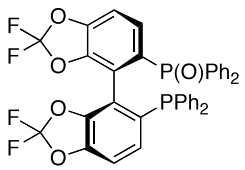
$^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$): δ 29.8 (s), -17.3 (s).




**(*R*)-5-Diphenylphosphino-5′-diphenylphosphinyl-4,4′-bi(1,3-benzodioxole) or (*R*)-Segphos(O) [(*S*)-isomer 950189-61-4].**[5] The titled compound was prepared according to our modification of Grushin procedure using a stoichiometric amount of $PdI_2$. Under argon, (*R*)-Segphos (50 mg, 0.082 mmol) and $PdI_2$ (42 mg, 0.12 mmol) were stirred in $CH_2Cl_2$ (8.0 mL) for 3 h at RT until full conversion of the bisphosphine, monitored by $^{31}$P NMR spectroscopy (Pd complex: δ 16.1). Unreacted $PdI_2$ was filtered off via a syringe filter and the filtrate was stirred with bis(*p*-methoxybenzylidene)acetone (266 mg, 0.90 mmol equiv) and an aqueous NaOH solution (3.75 M, 4.0 mL) at RT for 16 h, until all conversion of the Pd(II) complex, monitored by $^{31}$P NMR spectroscopy. The organic layer was separated and stirred with dppe (65 mg, 0.16 mmol) at RT for 3 h to remove Pd. The resulting solution was then passed through a pad of silica gel, washed with $CH_2Cl_2$, eluted by 2:1 $CH_2Cl_2$/EtOAc and concentrated under vacuum. The product was further purified as pale yellow solid by flash chromatography ($CH_2Cl_2$ to 1:2 $CH_2Cl_2$/EtOAc) in an argon-filled glove box. Yield: 50 mg, 97%.

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.71-7.66 (m, 2H), 7.64-7.59 (m, 2H), 7.46-7.42 (m, 2H), 7.38-7.31 (m, 4H), 7.28-7.22 (m, 10H), 6.98 (dd, $J$ = 14.1, 8.1 Hz, 1H), 6.75 (dd, $J$ = 8.1, 1.9 Hz, 1H), 6.62 (d, $J$ = 8.0 Hz, 1H), 6.55 (d, $J$ = 8.0, 3.4 Hz, 1H), 5.70 (d, $J$ = 1.6 Hz, 1H), 5.65 (d, $J$ = 1.4 Hz, 1H), 5.22 (d, $J$ = 1.6 Hz, 1H), 4.82 (d, $J$ = 1.4 Hz, 1H).

$^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$): δ 26.7 (s), -15.0 (s).




**(*R*)-5-Diphenylphosphino-5′-diphenylphosphinyl-2,2,2′,2′-tetrafluoro-4,4′-bi(1,3-**

**benzodioxole) or (*R*)-difluorphos(O).** The titled compound was prepared according to our modification of Grushin procedure using a stoichiometric amount of $PdI_2$. Under argon, (*R*)-Difluorphos (30 mg, 0.044 mmol) and $PdI_2$ (23 mg, 0.064 mmol) were stirred in $CH_2Cl_2$ (4.0 mL) at RT for 3 h until full conversion to the $PdI_2$ complex, monitored by $^{31}P$ NMR spectroscopy ($PdI_2$ complex: δ 15.4). Unreacted $PdI_2$ was filtered off via a syringe filter and the filtrate was stirred with dba (155 mg, 0.66 mmol) and an aqueous NaOH solution (3.75 M, 1.5 mL) at RT for 15 h. The organic layer was separated and stirred with dppe (53 mg, 0.13 mmol) at RT for 3 h to removed Pd. The resulting solution was then passed through a pad of silica gel, washed with $CH_2Cl_2$, eluted by 2:1 $CH_2Cl_2$/EtOAc. The fractions containing the product were concentrated under vacuum and further purified by flash chromatography ($CH_2Cl_2$ and then 1:1 $CH_2Cl_2$/EtOAc) in an argon-filled glove box, to afford white solid (29 mg, 71%).

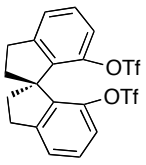
$^1H$ NMR (400 MHz, $CDCl_3$): δ 7.59-7.54 (m, 2H), 7.52-7.46 (m, 3H), 7.44-7.36 (m, 3H), 7.34-7.22 (m, 10H), 7.20-7.16 (m, 2H), 7.12 (dd, *J* = 13.1, 8.3 Hz, 1H), 7.06 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.87 (dd, *J* = 8.2, 3.1 Hz, 1H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ 145.6 (d, *J* = 2.3 Hz), 143.9, 143.6 (d, *J* = 16.1), 142.4 (d, *J* = 12.2 Hz), 137.1 (d, *J* = 12.3 Hz), 136.5 (d, *J* = 12.2), 134.6 (d, *J* = 15.0 Hz), 134.0 (2 peaks), 133.9 (d, *J* = 4.6 Hz), 133.8, 133.6, 133.4, 133.3, 133.0, 132.3, 132.2, 132.0, 131.9 (2 peaks), 131.8, 131.3 (d, *J* = 6.3 Hz), 130.5 (d, *J* = 13.0 Hz), 130.3 (d, *J* = 2.2 Hz), 129.0, 128.8 (d, *J* =8.7 Hz), 128.6, 128.5 (2 peaks), 128.4 (2 peaks), 128.3, 128.1, 127.0, 121.2-121.0 (m), 120.7 (d, *J* = 3.0 Hz), 120.3 (d, *J* = 3.2 Hz), 110.3, 109.2 (d, *J* = 14.8 Hz).

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -48.2 (d, *J* = 94.2 Hz), -49.2 (d, *J* = 90.0 Hz), -49.6 (d, *J* = 90.4 Hz), -50.1 (d, *J* = 94.1 Hz).

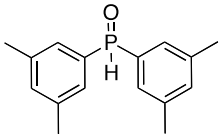
$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 27.7 (s), -15.0 (s).

ESI-MS: Calcd for $C_{38}H_{24}F_4O_5P_2$ $[M+H]^+$: 699.1, Found: 699.1.

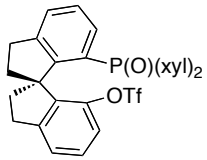



**(*R*)-7,7′-bis(trifluoromethanesulfonyloxy)-1,1′-spirobiindane [528521-72-4].**[4] (*R*)-1,1′-spirobiindane-7,7′-diol (1.00 g, 3.96 mmol), dry $CH_2Cl_2$ (16.0 mL) and analytical-grade pyridine (1.28 mL, 16.0 mmol) were charged into a 100-mL Schlenk flash under argon. The solution was cooled to 0 °C in an ice/water bath, followed by dropwise addition of triflic

anhydride (1.47 mL, 8.72 mmol) via a syringe. The mixture was allowed to warm up to RT and stirred overnight. The resulting mixture was directly subjected to flash chromatography (10:1 hexane/EtOAc), which afforded 1.99 g of the product (97%) as a white solid.
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.32-7.27 (m, 4H), 7.17-7.13 (m, 2H), 3.17-3.05 (m, 4H), 2.41-2.28 (m, 4H).
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$): δ -75.0 (s).



**Bis(*m*-xylyl)phosphine oxide [187344-92-9].** It was prepared according to a modified procedure.[6] Under argon, finely ground LiCl (1.59 g, 37.5 mmol) was dissolved in dry THF (75 mL) in a 250-mL Schlenk flask. Magnesium turnings (0.73 g, 30.0 mmol) were added to this solution, followed by addition of diisobutylaluminum hydride (0.30 mL, 1 M in cyclohexane). The mixture was stirred for 5 min at RT, followed by addition of 1-bromo-3,5-dimethylbenzene (5.55 g, 30.0 mmol). The stirring was continued for another 6 h at RT until all magnesium turnings were consumed. The resulting solution was cooled to -10 $^{o}$C in a salt/ice bath, followed by the addition of $HP(O)(OEt)_2$ (1.38 g, 10.0 mmol) in THF (2.0 mL). The mixture was allowed to warm up to RT and the stirring was continued for 18 h. The reaction was quenched by a saturated aqueous $NH_4Cl$ solution (100 mL), followed by extraction with EtOAc (100 mL x2). The organic extracts were combined and dried over $MgSO_4$, and concentrated on a rotary evaporator. The residue was purified by flash chromatography (hexane to 1:2 EtOAc/hexane), which afforded 2.35 g (90%) of the product as white powder.
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, $J$ = 478.9 Hz, 1H), 7.31 (d, $J$ = 14.2 Hz, 4H), 7.18 (s, 2H), 2.35 (s, 12H).
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 22.6 (s).



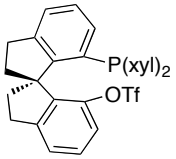

**(*R*)-7-Bis(3,5-dimethylphenyl)phosphinyl-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane [(*S*)-isomer: 528521-77-9].**[4] It was prepared according to the procedure for

the (*S*)-isomer.[4] Under argon, (*R*)-1,1′-spirobiindane 7,7′-bistriflate (0.516 g, 1.0 mmol), bis(3,5-dimethylphenyl)phosphine oxide (0.517 g, 2.0 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), 1,4-bis(diphenylphosphino)butane (21.3 mg, 0.05 mmol), *N*-ethyldiisopropylamine (0.68 mL, 4.0 mmol) and dry DMSO (3.3 mL) were charged into a dry 25-mL Schlenk tube and the mixture was stirred in a 100 °C bath for 21 h. After cooled to RT, the reaction was quenched by addition of 1 M HCl (30 mL), followed by extraction with $CH_2Cl_2$ (20 mL x 3). The combined organic extracts were washed with a saturated $NaHCO_3$ solution (10 mL), dried over $MgSO_4$, and concentrated on a rotary evaporator. The residue was purified by flash chromatography (3:1 hexane/EtOAc), which afforded 0.44 g (70%) of the product as white powder.

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.16 (dd, *J* = 7.5, 2.2 Hz, 1H), 7.09 (s, 1H), 7.06-6.98 (m, 5H), 6.86 (s, 1H), 6.83 (s, 1H), 6.26 (d, *J* = 8.2 Hz, 1H), 3.42-3.27 (m, 2H), 3.14-2.98 (m, 3 H), 2.35-2.30 (m, 2H), 2.25 (s, 6H, CH3), 2.23 (s, 6H, CH3), 2.20-2.17 (m, 1H).

$^{19}$F{$^1$H} NMR (376 MHz, $CDCl_3$): δ -75.2 (s).

$^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$): δ 30.3 (s).



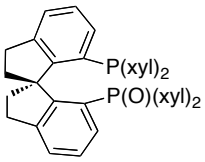

**(*R*)-7-Bis(3,5-dimethylphenyl)phosphino-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane [(*S*)-isomer: 528521-81-5].**[4] It was prepared based on a modification of a reported procedure for the (*S*)-isomer.[4] Under argon, (*R*)-7-bis(3,5-dimethylphenyl)phosphinyl-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane (465 mg, 0.74 mmol), *N*-ethyldiisopropylamine (5.1 mL, 30 mmol) and dry toluene (7.4 mL) were mixed in a dry 50-mL Schlenk tube. The solution was cooled to 0 °C and $HSiCl_3$ (1.2 mL, 12 mmol) was then added. The mixture was stirred rigorously in a 120 °C oil bath for 36 h and $^{31}$P NMR spectroscopy of the reaction mixture showed full conversion of phosphine oxide. The reaction was quenched by dilution with hexane (20 mL) and a saturated $Na_2CO_3$ solution (2.5 mL) under argon. The organic layer was passed through a pad of silica gel with $Et_2O$ washings. Removal of solvent under vacuum furnished 409 mg (90%) of the product as a white solid.

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.25-7.20 (m, 2H), 7.17-7.12 (m, 2H), 7.00 (dd, *J* = 7.3, 4.6

Hz, 1H), 6.90 (s, 1H), 6.84 (s, 1H), 6.69 (d, $J$ = 8.1 Hz, 1H), 6.65-6.61 (m, 4H), 3.10-3.03 (m, 4H), 2.59-2.51 (m, 1H), 2.37-2.22 (m, 3H), 2.19 (s, 6H), 2.17 (s, 6H).

$^{19}$F NMR (376 MHz, $CDCl_3$): δ -75.1 (s).

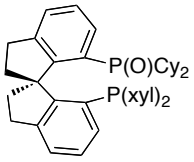
$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ -21.7 (s).




**(*R*)-7-Bis(3,5-dimethylphenyl)phosphino-7′-bis(*m*-xylyl)phosphinyl-1,1′-spirobiindane. CAS for (*S*)-isomer: 528521-85-9.**[4] It was prepared according to a reported procedure of the (*S*)-isomer.[4] Under argon, (*R*)-7-bis(3,5-dimethylphenyl)phosphino-7′-trifluoromethane-sulfonyloxy-1,1′-spirobiindane (367 mg, 0.60 mmol), bis(3,5-dimethylphenyl)phosphine oxide (312 mg, 1.21 mmol), $Pd(OAc)_2$ (6.8 mg, 0.030 mmol), 1,4-bis(diphenylphosphino)-butane (13 mg, 0.030 mmol), *N*-ethyldiisopropylamine (0.41 mL, 2.4 mmol) and dry DMSO (4.2 mL) were charged into a dry 25-mL Schlenk tube. The mixture was stirred in a 100 $^oC$ bath for 18 h, until $^{31}$P NMR spectroscopy of the reaction mixture showed full conversion of the triflate. The reaction was quenched by dilution with EtOAc (20 mL) and a saturated $Na_2CO_3$ solution (5 mL). The organic layer was separated and concentrated under vacuum. Purification by flash chromatography ($CH_2Cl_2$ to 20:1 $CH_2Cl_2$/EtOAc) under argon afforded 354 mg (82%) of the product as a white powder.

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.38-7.36 (m, 1H), 7.27-7.05 (m, 10H), 6.95 (s, 1H), 6.90 (s, 1H), 6.86 (s, 1H), 6.84 (s, 1H), 6.73 (s, 1H), 6.57 (s, 1H), 6.55 (s, 1H), 2.94-2.91 (m, 2H), 2.87-2.79 (m, 1H), 2.64-2.51 (m, 2H), 2.27 (s, 6H), 2.23 (s, 6H), 2.02 (s, 12H), 1.99-1.93 (m, 2H), 1.74-1.66 (m, 1H).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 29.8 (s), -17.3 (s).




**(*R*)-7-dicylcohexylphosphinyl-7′-bis(3,5-dimethylphenyl)phosphino-1,1′-spirobiindane.** It was prepared following a similar procedure of those symmetrically substituted analogs with $HP(O)Cy_2$. Under argon, (*R*)-7-bis(3,5-dimethylphenyl)phosphino-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane (140 mg, 0.23 mmol),

dicyclohexylphosphine oxide (100 mg, 0.47 mmol), $Pd(OAc)_2$ (10.3 mg, 0.046 mmol), 1,4-bis(diphenylphosphino)butane (19.6 mg, 0.046 mmol), *N*-ethyldiisopropylamine (0.16 mL, 0.92 mmol) and dry DMSO (1.6 mL) were charged into a dry 25-mL Schlenk tube. The mixture was stirred in a 100 $^oC$ bath for 40 h. The reaction was quenched by dilution with EtOAc (10 mL) and a saturated $Na_2CO_3$ solution (4 mL). The organic layer was separated and concentrated under vacuum. Purification by flash chromatography ($CH_2Cl_2$ to 20:1 $CH_2Cl_2$/EtOAc) under argon afforded 113 mg (73 %) of the product as a white powder.
$^1H$ NMR (400 MHz, $CDCl_3$): δ 7.33-7.29 (m, 2H), 7.26-7.18 (m, 2H), 7.14-7.11 (m, 1H), 7.08-7.05 (m, 1H), 6.84 (br s, 2H), 6.70 (d, $J$ = 7.6 Hz, 2H), 6.57 (d, $J$ = 7.3 Hz, 2H), 3.29-3.19 (m, 2H), 3.06-2.95 (m, 1H), 2.92-2.83 (m, 1H), 2.66-2.59 (m, 1H), 2.18 (s, 6H), 2.17 (s, 6H), 2.15-1.94 (m, 3H), 1.91-0.75 (m, 22H).
$^{13}C$ NMR (100 MHz, $CDCl_3$): δ 158.1 (d, $J$ = 251.4 Hz), 156.1 (m), 148.0 (d, $J$ = 3.9 Hz), 147.9 (d, $J$ = 4.0 Hz), 145.2 (d, $J$ = 7.7 Hz), 139.9 (d, $J$ = 12.8 Hz), 138.0 (d, $J$ = 15.5 Hz), 137.2, 137.1, 132.8, 132.6, 131.9, 131.7, 131.5, 130.8 (d, $J$ = 21.6 Hz), 130.3, 129.9 (d, $J$ = 3.3 Hz), 129.8, 129.4 (d, $J$ =12.3 Hz), 129.1 (d, $J$ = 3.2 Hz), 126.8 (d, $J$ = 2.8 Hz), 126.4, 126.0 (d, $J$ = 11.8 Hz), 125.2, 64.3, 42.4, 41.1 (d, $J$ = 4.8 Hz), 38.6 (d, $J$ = 66.1 Hz), 38.3 (d, $J$ = 64.6 Hz), 31.9, 31.4, 27.0, 26.9, 26.8, 26.7, 26.6, 26.5, 26.4, 26.3, 26.2 (d, $J$ = 2.6 Hz), 26.1, 26.0, 25.8 (d, $J$ = 3.0 Hz), 21.5, 21.4.
$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 44.0 (s), -9.4 (s).
ESI-MS: Calcd for $C_{45}H_{55}OP_2$ $[M+H]^+$: 673.4, Found: 673.4.

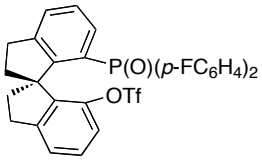
**Di(*p*-fluorophenyl)phosphine oxide [94940-35-9].**[7] It was prepared according to a modified procedure.[6] Under argon, finely ground LiCl (1.59 g, 37.5 mmol) was dissolved in dry THF (75 mL) in a 250-mL Schlenk flask. Magnesium turnings (0.73 g, 30.0 mmol) and a solution of diisobutylaluminium hydride solution in cyclohexane (0.30 mL, 1 M) were then added. The mixture was stirred for 10 min at RT, followed by addition of 3,5-dimethylbromobenzene (5.55 g, 30.0 mmol). The stirring was continued for another 2 h at RT until all magnesium turnings were consumed. The resulting solution was cooled to -10 $^oC$ in a salt/ice bath, followed by the addition of a solution of $HP(O)(OEt)_2$ (1.38 g, 10.0 mmol) in THF (2.0 mL). The mixture was allowed to warm up to RT and was stirred for 18 h. At the end of the reaction, it was quenched by 3 M HCl (50 mL) and extracted with EtOAc (100 mL x2). The organic extracts were combined and dried over $MgSO_4$, concentrated on a rotary evaporator. Purification of the residue by flash chromatography (10:1 hexane/EtOAc to

EtOAc) afforded 1.97 g (83 %) of the product as a pale yellow liquid.

$^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 484.8 Hz, 1H), 7.74-7.67 (m, 4H), 7.25-7.19 (m, 4H).

$^{19}F\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ -105.0

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 18.7 (s).




**(*R*)-7-Di(*p*-fluorophenyl)phosphinyl-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane.** Under argon, (*R*)-7,7′-bis(trifluoromethanesulfonyloxy)-1,1′-spirobiindane (516 mg, 1.00 mmol), di(*p*-fluorophenyl)phosphine oxide (520 mg, 2.18 mmol), $Pd(OAc)_2$ (45 mg, 0.20 mmol), 1,4-bis(diphenylphosphino)butane (85 mg, 0.20 mmol), *N*-ethyldiisopropylamine (0.68 mL, 4.0 mmol) and dry DMSO (3.3 mL) were charged sequentially into a dry 25-mL Schlenk tube. The mixture was capped tightly and stirred in a 100 $^{o}$C bath for 36 h. After cooled to RT, the solution was diluted with EtOAc (10 mL), washed sequentially with 1M HCl (5 mL) and a saturated $NaHCO_3$ solution (5 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator. Purification of the residue by flash chromatography (hexane to 1:2 hexane/EtOAc) afforded 454 mg (75%) of the product as pale yellow powder.

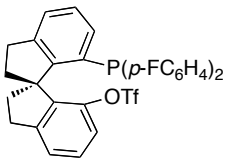
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* =7.5 Hz, 1H), 7.37-7.25 (m, 4H), 7.21-7.17 (m, 2H), 7.06-7.01(m, 5H), 6.93 (dd, *J* = 14.3, 7.6Hz, 1H), 6.33 (d, *J* = 8.2 H, 1H), 3.34 (dd, *J* = 15.4, 9.3 Hz, 1H), 3.22 (dd, *J* = 20.7, 9.5 Hz, 1H), 3.16-3.03 (m, 3H), 2.39-2.32 (m, 2H), 2.28-2.17 (m, 1H).

$^{13}$C NMR (100 MHz, $CDCl_3$)*:* δ 166.2 (dd, *J* = 34.1, 3.3 Hz), 163.7 (dd, *J* = 34.4, 3.2 Hz), 153.4 (d, *J* =7.1), 150.0, 146.6 (d, *J* = 10.1 Hz), 145.1, 141.0, 134.3 (d, *J* = 8.6 Hz), 134.2 (d, *J* = 8.6 Hz), 134.0 (d, *J* = 8.7 Hz), 133.8 (d, *J* = 8.9 Hz), 133.3 (d, *J* = 13.6 Hz), 132.0 (dd, *J* = 107.9, 3.4 Hz), 128.6 (m, 2C), 127.4 (dd, *J* = 105.0, 3.3 Hz), 126.9 (d, J = 102.2 Hz), 126.4 (d, *J* = 13.0 Hz), 124.0, 117.9 (q, *J* = 319.6), 117.5, 115.9-115.5 (m, 4C), 62.0 (d, *J* = 2.0 Hz), 40.2, 40.1, 32.0, 30.9.

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$): δ -75.1 (s), -107.5 (s), -107.6 (s).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 29.2 (s).

ESI-MS: Calcd for $C_{30}H_{22}F_5O_4PS$ $[M+H]^+$: 605.1, Found: 605.1.




**(*R*)-7-Di(*p*-fluorophenyl)phosphino-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane.** The entire operation including filtration was performed in an argon-filled glove box. (*R*)-7-Di(*p*-fluorophenyl)phosphinyl-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane (320 mg, 0.53 mmol), *N*-ethyldiisopropylamine (3.62 mL, 21 mmol) and dry toluene (5.3 mL) were charged into a dry 25-mL Schlenk tube. The solution was cooled to 0 $^{o}$C and then $HSiCl_3$ (0.86 mL, 8.5 mmol) was added. The resulting mixture was stirred rigorously in a 120 $^{o}$C bath for 42 h, until $^{31}$P NMR spectroscopy showed >95% conversion of the phosphine oxide. The reaction mixture was then diluted with hexane and saturated $NaHCO_3$ solution (~1.5 mL). The organic layer was directly loaded onto a silica gel pad and eluted with $Et_2O$. Removal of the solvent under vacuum afforded 280 mg (90%) of the pure product as a white powder.

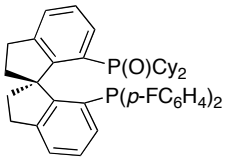
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 7.4 Hz, 1H), 7.22 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.16 (dd, *J* = 16.5, 7.6 Hz, 2H), 7.03-6.97 (m, 2H), 6.96-6.86 (m, 7H), 6.68 (d, *J* =8.1 Hz, 1H), 3.16-.301 (m, 4H), 2.54-2.46 (m, 1H), 2.38-2.23 (m, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ 164.6 (d, *J* = 37.1 Hz), 162.1 (d, *J* =36.9), 152.8 (d, *J* =25.6 Hz), 148.1 (d, *J* = 2.8 Hz), 145.7 (d, *J* = 2.4 Hz), 144.2 (d, *J* = 7.9 Hz), 142.0 (d, *J* = 3.7 Hz), 135.7 (d, *J* = 8.0 Hz), 135.5 (d, *J* = 8.1 Hz), 135.2 (d, *J* = 7.9 Hz), 135.0 (d, *J* = 7.8 Hz), 134.1-134.0 (m, 2C), 132.1 (d, *J* = 19.2 Hz), 131.5 (dd, *J* = 11.9, 3.4 Hz), 129.0, 127.8, 126.0, 124.3, 118.4, 118.0 (q, *J* = 319.7 Hz), 115.8 (d, *J* = 7.9 Hz), 115.6 (d, *J* = 7.6Hz), 115.5 (d, *J* = 6.8 Hz), 115.4 (d, *J* = 7.7 Hz), 61.7 (d, *J* = 3.3 Hz), 40.2 (d, *J* = 5.9 Hz), 39.2, 31.6, 30.9.

$^{19}$F{$^{1}$H} NMR (376 MHz, CDCl3): δ -75.1 (s), -112.8 (d, *J* = 4.3 Hz), -113.2 (d, *J* = 5.4 Hz).

$^{31}$P{$^{1}$H} NMR (162 MHz, $CDCl_3$): δ -23.8 (s).

ESI-MS: Calcd for $C_{30}H_{22}F_5O_3PS$ $[M+H]^+$: 589.1, Found: 589.1.




**(*R*)-7-Dicylcohexylphosphinyl-7′-di(*p*-fluorophenyl)phosphino-1,1′-spirobiindane or (*R*)-*p*-F-Ph-Cy-SDP(O).** The entire operation including flash chromatography was

performed in an argon-filled glove box. (*R*)-7-Di(4-fluorophenyl)phosphino-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane (430 mg, 0.73 mmol), dicyclohexylphosphine oxide (313 mg, 1.46 mmol), $Pd(OAc)_2$ (32 mg, 0.14 mmol), 1,4-bis(diphenylphosphino)butane (61 mg, 0.14 mmol), *N*-ethyldiisopropylamine (0.50 mL, 2.9 mmol) and dry DMSO (5.10 mL) were charged into a dry 25-mL Schlenk tube. The mixture was tightly capped and stirred vigorously in a 100 $^oC$ oil bath for 20 h. Upon cooling to RT, the solution was diluted with degassed EtOAc (20 mL), washed sequentially with 1 M HCl (5 mL) and a saturated $NaHCO_3$ solution (5 mL), and concentrated under vacuum. Purification of the residue by flash chromatography ($CH_2Cl_2$ to 10:1 $CH_2Cl_2$/EtOAc) furnished 414 mg (87%) of the pure product as white foam.

$^1H$ NMR (400 MHz, $CDCl_3$): δ 7.35-7.28 (m, 3H), 7.25-7.20 (m, 1H), 7.11-7.07 (m, 1H), 7.04-6.99 (m, 2H), 6.96-6.88 (m, 7H), 3.30-3.19 (m, 2H), 3.03-2.86 (m, 2H), 2.69-2.63 (m, 1H), 2.16-2.04 (m, 2H), 1.90-0.76 (m, 23H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ 164.4 (d, $J$ = 8.0 Hz), 161.9 (d, $J$ = 7.7 Hz), 158.1 (d, $J$ = 25.5 Hz), 155.9 (3 peaks), 147.7 (dd, $J$ = 9.0, 4.1 Hz), 145.9 (d, $J$ = 7.7 Hz), 136.7 (dd, $J$ = 22.8, 7.9 Hz), 135.44 (dd, $J$ =21.5, 7.8 Hz), 135.39 (d, $J$ = 13.7 Hz), 133.5 (dd, $J$ = 15.9, 3.3 Hz), 131.4 (d, $J$ = 1.4 Hz), 129.8, 129.7, 129.6 (2 peaks), 129.5, 128.9 (d, $J$ = 3.2 Hz), 126.8 (d, $J$ = 2.6 Hz), 126.7, 126.2 (d, $J$ = 11.7 Hz), 125.7, 115.5 (d, $J$ = 7.3 Hz), 115.4 (d, $J$ = 5.6 Hz), 115.3 (d, $J$ = 5.9 Hz), 115.2 (d, $J$ = 7.2 Hz), 64.2 (3 peaks), 42.3, 41.1 (d, $J$ = 4.4 Hz), 38.9 (d, $J$ = 21.5 Hz), 38.2 (d, $J$ = 20.0 Hz), 31.9, 31.3 (d, $J$ = 1.3 Hz), 27.0, 26.8 (2 peaks), 26.7, 26.6, 26.5 (2 peaks), 26.4, 26.2 (2 peaks), 26.0 (3 peaks), 25.9, 25.8 (2 peaks). Not all couplings were assigned.

$^{19}F\{^1H\}$ NMR (376 MHz, CDCl3): δ -113.1

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 45.7(s), -20.4(s).

ESI-MS: Calcd for $C_{41}H_{44}F_2OP_2$ $[M+H]^+$: 653.3, Found: 653.3.

$[\alpha]^{20}_D = +148^o$ ($c$ = 0.8, $CHCl_3$).

**III. Synthesis of aryl triflates**

**General Procedure.**[89] Under argon, a 100-mL Schlenk flask was charged successively with parent or substituted phenol (15 mmol, 1 equiv), dry DCM (30 mL) and analytical-grade pyridine (2.4 mL, 2 equiv). The solution was cooled to 0 $^{o}$C in an ice bath, then was treated with dropwise addition of triflic anhydride (3.0 mmol, 5.08 g, 1.2 equiv). The resulting mixture was allowed to warm up to RT and kept stirred for additional 5 hours. At the end of the reaction (monitored by TLC), the mixture was filtered. The filtrate was concentrated to ~5 mL on a rotary evaporator and the residue was subjected to flash chromatography (silica gel with hexane/EtOAc as eluent) to afford the desired aryl triflate.

**1-Naphthyl trifluoromethanesulfonate [99747-74-7].** Flash chromatography (hexane) yielded the target compound as colorless oil (93%).
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, $J$ = 8.3 Hz, 1H), 7.94-7.85 (m, 2H), 7.69-7.58 (m, 2H), 7.53-7.46 (m, 2H).

**2-Naphthyl trifluoromethanesulfonate [3857-83-8].** Flash chromatography (hexane) yielded the target compound as a white solid (96%).
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.94-7.87 (m, 3H), 7.76 (d, $J$ = 2.4 Hz, 1H), 7.61-7.55 (m, 2H), 7.38 (dd, $J$ = 9.0, 2.4 Hz, 1H).

**Phenyl trifluoromethanesulfonate [17763-67-6].** Flash chromatography (hexane) yielded the target compound as a colorless liquid (78%).
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.49-7.43 (m, 2H), 7.41-7.37 (m, 1H), 7.29-7.26 (m, 2H).

***o*-Anisyl trifluoromethanesulfonate [59099-58-0].** Flash chromatography (20:1 hexane/EtOAc) yielded the target compound as a colorless liquid (95%).
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.34-7.29 (m, 1H), 7.21 (dd, $J$ = 8.1, 1.4 Hz, 1H), 7.03 (dd, $J$ = 8.3, 1.3 Hz, 1H), 6.98 (ψtd, $J$ = 7.8, 1.4 Hz, 1H), 3.90 (s, 3H).

***o*-Tolyl trifluoromethanesulfonate [66107-34-4].** Flash chromatography (20:1 hexane/EtOAc) yielded the target compound as a colorless liquid (93%).
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.31-7.22 (m, 4H), 2.38 (s, 3H).

***p*-(Ethoxycarbonyl)phenyl trifluoromethanesulfonate [125261-30-5]**. Flash chromatography (10:1 hexane/EtOAc) yielded the target compound as a colorless liquid (94%).
$^1$H NMR (400 MHz, $CDCl_3$): δ 8.17-8.13 (m, 2H), 7.37-7.33 (m, 2H), 4.40 (q, $J$ = 7.1 Hz, 2H), 1.40 (t, $J$ = 7.1 Hz, 3H).

***p*-*tert*-Butylphenyl trifluoromethanesulfonate [154318-75-9]**. Flash chromatography (hexane) yielded the target compound as colorless oil (98%).
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.46-7.43 (m, 2 H), 7.20-7.17 (m, 2 H), 1.33 (s, 9 H).

***p*-Anisyl trifluoromethanesulfonate [66107-29-7]**. Flash chromatography (20:1 hexane/EtOAc) yielded the target compound as colorless oil (91%).
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.22-7.19 (m, 2 H), 6.94-6.92 (m, 2 H), 3.83 (s, 3 H).

***p*-(Trifluoromethyl)phenyl trifluoromethanesulfonate [146397-87-7]**. Flash chromatography (hexane) yielded the target compound as a colorless liquid (84%).
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, $J$ = 8.8 Hz, 2H), 7.42 (d, $J$ = 8.8 Hz, 2H).

***p*-Formylphenyl trifluoromethanesulfonate [17763-69-8].** Flash chromatography (4:1 hexane/EtOAc) afforded the target compound as a colorless liquid (74%).
$^1$H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 8.03-8.00 (m, 2H), 7.49-7.46 (m, 2H).

***p*-Chlorophenyl trifluoromethanesulfonate [29540-84-9].** Flash chromatography (hexane) afforded the target compound as a colorless liquid (96%).
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.45-7.41 (m, 2H), 7.25-7.21 (m, 2H).

***p*-Benzophenonyl trifluoromethanesulfonate [124643-34-1].** Flash chromatography (4:1 hexane/EtOAc) afforded the target compound as a colorless liquid (99%).
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.93-7.90 (m, 2H), 7.81-7.78 (m, 2H), 7.66-7.61 (m, 1H), 7.54-7.50 (m, 2H), 7.43-7.39 (m, 2H).

## IV. Catalyst discovery

In an argon-filled glove-box, $Pd(dba)_2$ (7.2 mg, 0.0125 mmol) and chiral ligand (0.015 mmol) were stirring in a solvent (2.0 mL) in a 25-mL reaction tube for 30 min, followed by addition of GC standard *n*-$C_{14}H_{30}$ (25 $\mu$L), 1-naphthyl triflate (138 mg, 0.5 mmol), cyclopentene (135 mg, 2.0 mmol, 4 equiv) and $Li_2CO_3$ (75 mg, 1.0 mmol). The mixture was stirred at 70 $^oC$ in an oil bath. The reaction was monitored by GC analysis of aliquots of the reaction mixture taken at time intervals. The ee of the Heck product was determined by chiral HPLC (Chiralcel OJ-H, 98:2 hexanes/isopropanol). The conversion of triflate, the olefinic selectivity and the ee of the major isomer were determined by GC and chiral HPLC.

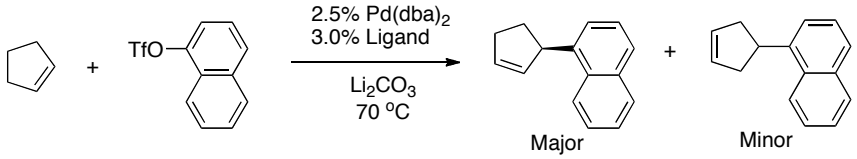
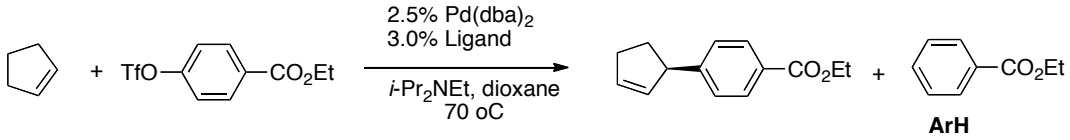



Table S1. Water as cosolvent in Heck reaction

| Ligand | Solvent | Time | Conv. (%) | Olefinic selectivity | Ee (%) |
|---|---|---|---|---|---|
| (*R*)-BINAP | Dry dioxane | 2 h | 4 | 4:1 | 6 |
| | | 5 h | 8 | 4:1 | 6 |
| | | 9 h | 15 | 4:1 | 6 |
| (*R*)-BINAP | 19:1 dioxane/$H_2O$ | 2 h | 4 | 4:1 | 21 |
| | | 5 h | 30 | 9:1 | 79 |
| | | 9 h | 100 | 19:1 | 91 |
| (*R*)-BINAP(O) | 19:1 dioxane/$H_2O$ | 0.5 h | 83 | 48:1 | 97 |
| | | 1 h | 100 | 48:1 | 97 |
| (*R*)-BINAP(O) | 19:1 dioxane/$H_2O$ ($50\ ^oC$) | 1 h | 32 | 60:1 | 98 |
| | | 4 h | 100 | 40:1 | 98 |




In an argon-filled glove-box, $Pd(dba)_2$ (1.4 mg, 2.5 mol%) and chiral ligand (3.0 mol%) were stirred in dioxane (0.10 mL) in a 4-mL reaction tube for 15 min, followed by addition of ArOTf (29.8 mg, 0.1 mmol), cyclopentene (27 mg, 0.4 mmol), $i$Pr$_2$NEt (26 mg, 0.2 mmol) and $n$-$C_{14}H_{30}$ (5 $\mu$L, GC internal standard). The tube was capped and the reaction was stirred in an oil bath at 70 $^{o}$C. Aliquotes were taken after stirring for 4 h and 16 h for GC and chiral HPLC analysis. The conversion of the triflate and yield of the Heck isomers were determined by GC. The ee of the major Heck product was determined by chiral HPLC (Daicel chiralcel OJ-H, 98:2 hexanes/isopropanol).

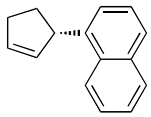
Table S2. Model reaction after 4 h and 16 h

| Entry | Ligands | Time | Conv. (%) | Prod. (%) | ArH (%) | Olefinic selectivity | Ee (%) |
|---|---|---|---|---|---|---|---|
| 1 | (*R*)-BINAP(O) | 4 h | 82 | 45 | 27 | 14:1 | 88 |
| | | 16 h | 100 | 57 | 35 | 15:1 | 88 |
| 2 | (*R*)-Tol-BINAP(O) | 4 h | 53 | 26 | 20 | 19:1 | 87 |
| | | 16 h | 94 | 42 | 34 | 22:1 | 86 |
| 3 | (*R*)-Cy-BINAP(O) | 4 h | 28 | 16 | 8 | 142:1 | 97 |
| | | 16 h | 47 | 26 | 16 | 82:1 | 96 |
| 4 | (*R*)-Segphos(O) | 4 h | 44 | 12 | 21 | 25:1 | 85 |
| | | 16 h | 85 | 23 | 43 | 22:1 | 80 |
| 5 | (*R*)-Difluorphos(O) | 4 h | 50 | 18 | 24 | 44:1 | 81 |
| | | 16 h | 100 | 33 | 50 | 47:1 | 78 |
| 6 | (*R*)-SDP(O) | 4 h | 99 | 60 | 26 | 14:1 | -88 |
| | | 16 h | 100 | 57 | 23 | 13:1 | -88 |
| 7 | (*R*)-Xyl-SDP(O) | 4 h | 100 | 83 | 15 | 26:1 | -98 |
| 8 | (*R*)-Xyl-Cy-SDP(O) | 4 h | 97 | 77 | 8 | 23:1 | -85 |
| | | 16 h | 100 | 77 | 8 | 17:1 | -84 |
| 9 | (*R*)-*p*FPh-Cy-SDP(O) | 4 h | 41 | 33 | 2 | 27:1 | -78 |
| | | 16 h | 68 | 54 | 5 | 21:1 | -76 |

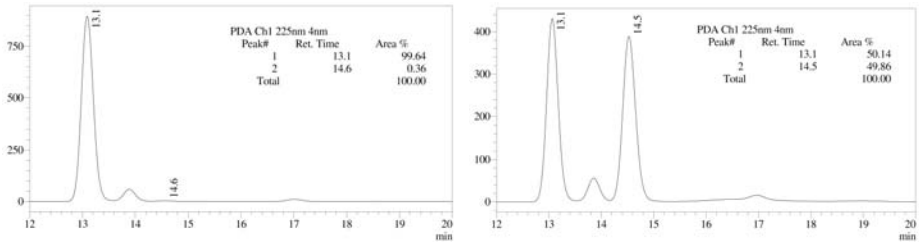
## V. Isolation of Heck products

In an argon-filled glove box, $Pd(dba)_2$ (7.2 mg, 0.013 mmol) and (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol) were stirred in dry 1,4-dioxane (0.50 mL) for 10-20 min in a 4-mL vial, followed by addition of *n*-$C_{14}H_{30}$ (25 μL, GC internal standard), aryl triflate (0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol, 2 equiv) and cyclic olefin (2.0 mmol, 4 equiv). The mixture was vigorously stirred in a preheated oil bath at a set temperature until the aryl triflate was fully consumed (monitored by GC). The reaction mixture was cooled to RT and subjected to flash chromatography (basic alumina, Brockmann grade I, pentane/$Et_2O$) to give the purified product. Silica gel may be also used for purification. The olefinic selectivity of Heck isomers in the crude mixture was determined by GC. The ee of the purified product was determined by chiral HPLC analysis with Daicel Chiralcel columns or by chiral GC analysis. Racemic products were prepared using the racemic ligand to facilitate determination of ee.

### Heck reaction of cyclopentene

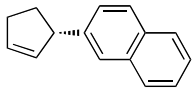


**(*S*)-3-(1-Naphthyl)cyclopentene [racemate: 90173-55-0].**[10] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), 1-naphthyl triflate (140 mg, 0.51 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and cyclopentene (180 μL, 2.0 mmol) were used. The reaction completed in 2.5 h at 50 °C. The product was isolated by flash chromatography (pentane) as colorless oil. Yield: 94 mg, 95%. Olefinic selectivity in the crude product: 17:1. $[\alpha]^{20}_D = +116^o$ (*c* = 1.5, $CHCl_3$).
Ee: 99%. Daicel Chiralcel OJ-H, 98:2 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 13.1 min (major) and 14.6 min (minor). The middle signal in the second trace was the olefin isomer.



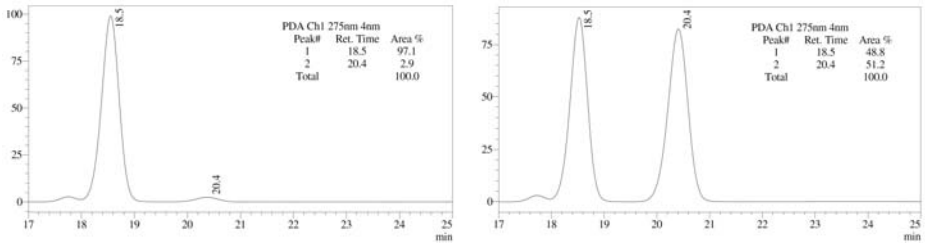

$^1$H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.3 Hz, 1H), 7.87-7.83 (m, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.54-7.46 (m, 2H), 7.42-7.38 (m, 1H), 7.31 (dd, *J* = 7.1, 1.0 Hz, 1H), 6.08-6.05 (m,

1H), 5.96-5.93 (m, 1H), 4.69-4.64 (m, 1H), 2.67-2.58 (m, 1H), 2.55-2.43 (m, 2H), 1.83-1.74 (m, 1H).

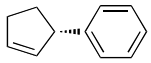


**(*S*)-3-(2-Naphthyl)cyclopentene [racemate 92425-28-0].**[11] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 $\mu$L), 2-naphthyl triflate (140 mg, 0.51 mmol), *N*-ethyldiisopropylamine (170 $\mu$L, 1.0 mmol) and cyclopentene (180 $\mu$L, 2.0 mmol) were used. The reaction completed in 1 h at 50 °C. The product was isolated by flash chromatography with pentane as colorless oil. Yield: 94 mg, 95%. Olefinic selectivity in the crude product: 11:1.

Ee: 94%. Daicel Chiralcel OJ-H, 98:2 hexanes/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 18.5 min (major) and 20.4 min (minor).



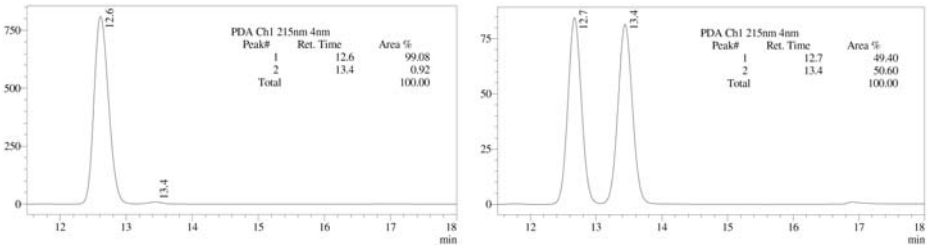

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.81-7.77 (m, 3H), 7.62 (s, 1H), 7.46-7.39 (m, 2H), 7.33 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.02-5.99 (m, 1H), 5.87-5.83 (m, 1H), 4.10-4.04 (m, 1H), 2.60-2.41 (m, 3H), 1.86-1.76 (m, 1H).



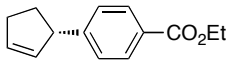
**(*S*)-3-Phenylcyclopentene [175274-02-9].**[12-14] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 $\mu$L), phenyl triflate (140 mg, 0.51 mmol), *N*-ethyldiisopropylamine (170 $\mu$L, 1.0 mmol) and cyclopentene (180$\mu$L, 2.0 mmol) were used. The reaction completed in 13 h at 50 °C. The product was isolated by flash chromatography (silica gel, pentane) as colorless oil. Yield: 53 mg, 73% (92% GC yield). Olefinic selectivity in the crude product: 38:1.

$[\alpha]^{20}_D$ = -210° (*c* = 1.3, $CHCl_3$). Lit. value: -212°.[1213]

Ee: 98%. Daicel Chiralcel OJ-H, 98:2 hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 12.6 min (major) and 13.4 min (minor).

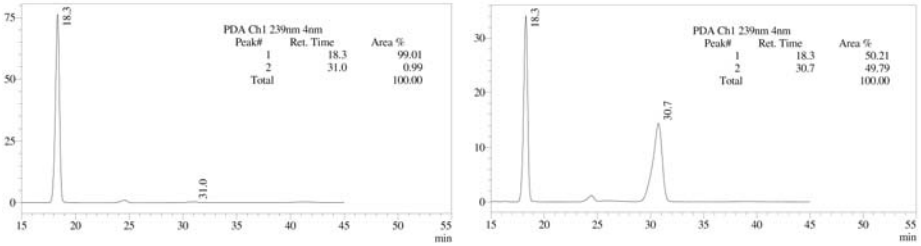



$^1$H NMR (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 2H), 7.20-7.17 (m, 3H), 5.95-5.93 (m, 1H), 5.79-5.77 (m, 1H), 3.90-3.88 (m, 1H), 2.53-2.36 (m, 3H), 1.77-1.69 (m, 1H).



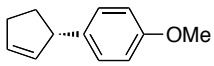

**(*S*)-3-[4-(Ethoxycarbonyl)phenyl]cyclopentene [racemate 115419-30-2].**[15] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *p*-(ethoxycarbonyl)phenyl triflate (150 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and cyclopentene (180 μL, 2.0 mmol) were used. The reaction was complete in 17 h at 50 °C. The product was isolated by flash chromatography with pentane/$Et_2O$ (10:1 to 5:1) as colorless oil. Yield: 99 mg, 91%. Olefinic selectivity in the crude product: 41:1.

Ee: 98%. Daicel Chiralcel OJ-H, 98:2 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 18.3 min (major) and 31.0 min (minor).




$^1$H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 5.99-5.97 (m, 1H), 5.78-5.75 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2 H), 3.97-3.92 (m, 1H), 2.55-2.38 (m, 3H), 1.75-1.68 (m, 1H), 1.38 (t, *J* = 7.1 Hz, 3H).

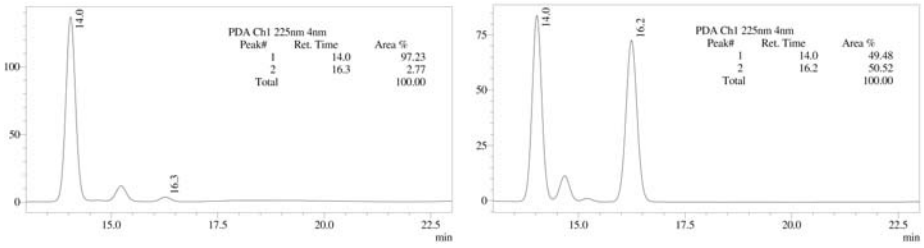
$^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.8, 152.0, 133.6, 132.8, 129.9, 128.5, 127.3, 60.9, 51.5, 33.8, 32.6, 14.5.



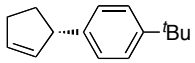

**(*S*)-3-(4-Methoxyphenyl)cyclopentene. [(-)-Isomer 38806-00-7].**[16] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *p*-anisyl triflate (128 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and

cyclopentene (180 $\mu$L, 2.0 mmol) were used. The reaction was complete in 21 h at 70 $^{o}$C. The product was isolated by flash chromatography with pentane/$Et_2O$ (10:0 to 10:1) as a colorless liquid. Yield: 73 mg, 84%. Olefinic selectivity in the crude product: 10:1.

Ee: 94%. Daicel Chiralcel OJ-H, 98:2 hexanes/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 14.0 min (major) and 16.3 min (minor). The middle signal in the second trace was the olefin isomer.




$^1$H NMR (400 MHz, $CDCl_3$): δ 7.13-7.09 (m, 2H), 6.85-6.82 (m, 2H), 5.93-5.90 (m, 1H), 5.77-5.74 (m, 1H), 3.88-3.81 (m, 1H), 3.79 (s, 3H), 2.49-2.35 (m, 3H), 1.71-1.65 (m, 1H).

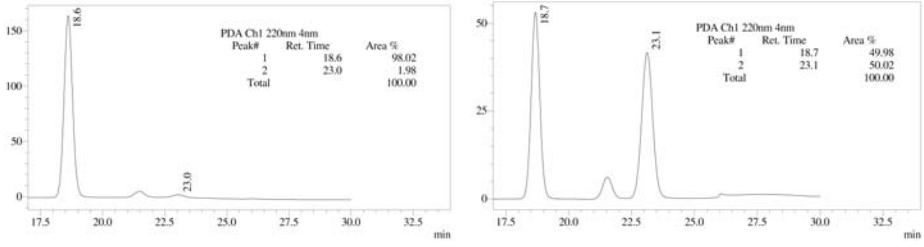



**(*S*)-3-(4-*tert*-Butylphenyl)cyclopentene.** $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 $\mu$L), *p-tert*-butylphenyl triflate (141 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 $\mu$L, 1.0 mmol) and cyclopentene (180 $\mu$L, 2.0 mmol) were used. The reaction was complete in 39 h at 70 $^{o}$C. The product was isolated by flash chromatography with pentane as colorless oil. Yield: 76 mg, 76%. Olefinic selectivity in the crude product: 31:1. A small amount of diarylated by product was also isolated .

GC-MS (EI): Calcd for $C_{15}H_{20}$ $M^+$: 200.2. Found: 200.1.

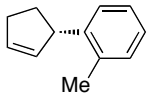
$[\alpha]^{20}_D$ = -20$^o$ (*c* = 1.2, $CHCl_3$).

Ee: 96%. Daicel Chiralcel OJ-H, *n*-hexane, flow rate = 0.33 mL/min. $T_R$ = 18.6 min (major) and 23.0 min (minor). The middle signal in the second trace was the olefin isomer.

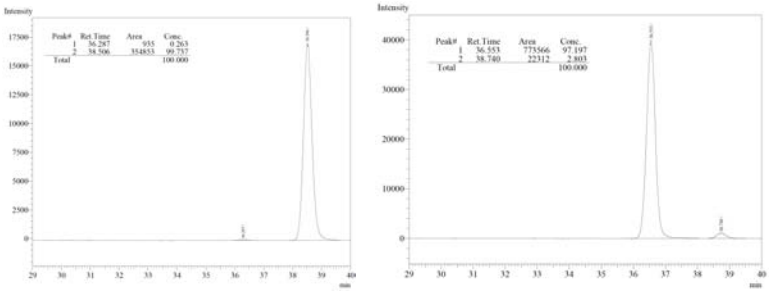



$^1$H NMR (400 MHz, $CDCl_3$): δ 7.33-7.30 (m, 2H), 7.14-7.11 (m, 2H), 5.94-5.91 (m, 1H), 5.79-5.76 (m, 1H), 3.90-3.84 (m, 1H), 2.53-2.34 (m, 3H), 1.77-1.69 (m, 1H), 1.31 (s, 9H).

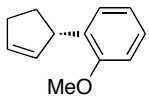
$^{13}$C NMR ($CDCl_3$, 100 MHz): δ 149.0, 143.7, 134.8, 131.9, 127.1, 125.5, 51.0, 34.6, 34.0, 32.8, 31.7.




**(*S*)-3-(o-Tolyl)cyclopentene [racemate 78135-01-0].**[17] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *o*-methylphenyl triflate (141 mg, 0.50 mmol), *N*-ethyldiisopropyl-amine (170 μL, 1.0 mmol) and cyclopentene (180 μL, 2.0 mmol) were used. The reaction was complete in 39 h at 50 °C. The product was isolated by flash chromatography with pentane as colorless oil. Yield: 59 mg, 75%. Olefinic selectivity in the crude product: 20:1. A small amount of diarylated product (1,3-di(2-methylphenyl)-cyclopentene) was also isolated from the reaction.
Ee: 99%. Chiral GC with Chiraldex B-PH column (30 m x 0.25 mm): carrier gas: He; flow rate: 0.91 mL/min; column temperature: 90 °C. $T_R$ = 36.3 min (minor) and 38.5 min (major).

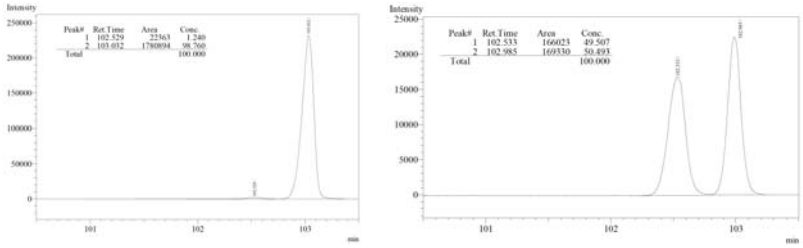


(The second trace showed the results using (*R*)-BINAP(O) ligand.)
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.17-7.07 (4H), 5.98-5.95 (m, 1H), 5.79-5.76 (m, 1H), 4.13-4.09 (m, 1H), 2.53-2.38 (m, 3H), 2.37 (s, 3H), 1.65-1.57 (m, 1H).

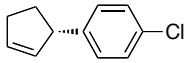



**(*S*)-3-(2-Methoxyphenyl)cyclopentene [racemate 31169-37-6].**[15] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *o*-anisyl triflate (128 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and cyclopentene (180 μL, 2.0 mmol) were used. The reaction completed in 21 h at 70 °C. The product was isolated by flash chromatography with pentane/$Et_2O$ (10:1) as colorless oil. Yield: 68 mg, 78%. Olefinic selectivity in the crude product: 19:1.
$[\alpha]^{20}_D$ = -79° (*c* = 1.2, $CHCl_3$).
Ee: 98%. Chiral GC with Chiraldex B-PH column (30 m x 0.25 mm): carrier gas: He; flow

rate: 0.91 mL/min; column temperature: 90 °C for 100 min then raised to 150 °C at the rate of 15 °C/min . $T_R$ = 102.5 min (minor) and 103.0 min (major).

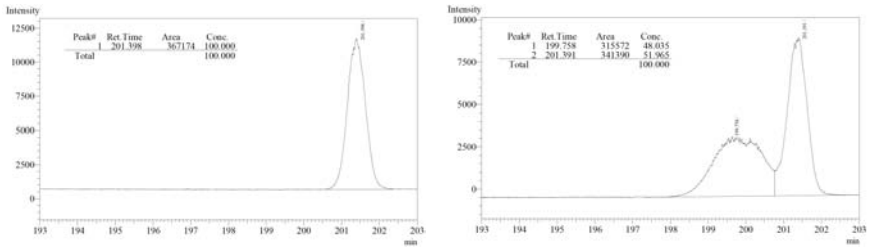


$^1$H NMR (400 MHz, $CDCl_3$): δ 7.17 (ψtd, *J* = 7.8, 1.8 Hz, 1H), 7.12 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.90 (ψtd, *J* = 7.4, 1.0 Hz, 1H), 6.86 (d, *J* =8.2 Hz, 1H), 5.95-5.92 (m, 1H), 5.78-5.75 (m, 1H), 4.29-4.25 (m, 1H), 3.84 (s, 3H), 2.47-2.37 (m, 3H), 1.67-1.61 (m, 1H).



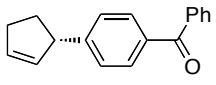

**(*S*)-3-(4-Chlorophenyl)cyclopentene [racemate: 2362-71-2].**[17] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *p*-chlorophenyl triflate (130 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and cyclopentene (180 μL, 2.0 mmol) were used. The reaction completed in 35 h at 50 °C. The product was isolated by flash chromatography with pentane as colorless oil. Yield: 62 mg, 70%. Olefinic selectivity in the crude product: 31:1.

Ee: >99%. Chiral GC with Chiraldex B-PH column (30 m x 0.25 mm): carrier gas: He; flow rate: 0.91 mL/min; column temperature: 80 °C for 200 min then raised at the rate of 15 °C/min to 150 °C.



$^1$H NMR (400 MHz, $CDCl_3$): δ 7.26-7.23 (m, 2H), 7.13-7.09 (m, 2H), 5.96-5.93 (m, 1H), 5.74-5.71 (m, 1H), 3.87-3.83 (m, 1H), 2.53-2.35 (m, 3H), 1.73-1.60 (m, 1H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ 145.1, 134.0, 132.6, 131.7, 128.7, 128.6, 50.8, 33.9, 32.6.



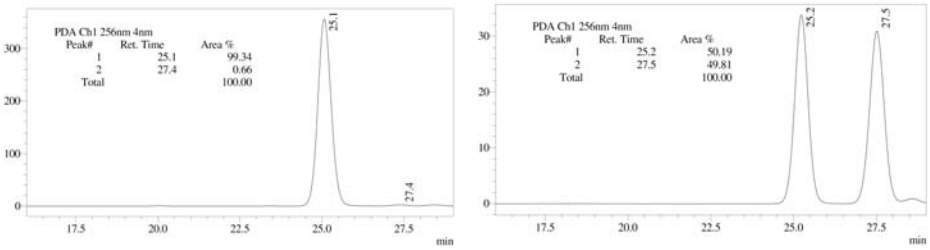

**(*S*)-3-(4-Benzophenonyl)cyclopentene.** $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O)

(10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *p*-benzophenonyl triflate (164 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and cyclopentene (180 μL, 2.0 mmol) were used. The reaction was complete in 5 h at 50 °C. The product was isolated by flash chromatography with pentane/$Et_2O$ (10:1 to 5:1) as colorless oil. Yield: 122 mg, 98%. Olefinic selectivity in the crude product: 70:1.

GC-MS (EI): Calcd for $C_{18}H_{16}O$ $M^+$: 248.1, Found: 248.1.

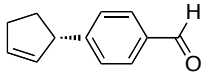
$[\alpha]^{20}_D$ = -170° (*c* = 1.3, $CHCl_3$).

Ee: 99%. Daicel Chiralcel OJ-H, 98:2 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 25.1 min (major) and 27.4 min (minor).




$^1H$ NMR (400 MHz, $CDCl_3$): δ 7.81-7.78 (m, 2H), 7.76-7.74 (m, 2H), 7.60-7.56 (m, 1H), 7.49-7.46 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.01-5.98 (m, 1H), 5.81-5.78 (m, 1H), 4.01-3.95 (m, 1H), 2.59-2.40 (m, 3H), 1.80-1.70 (m, 1H).

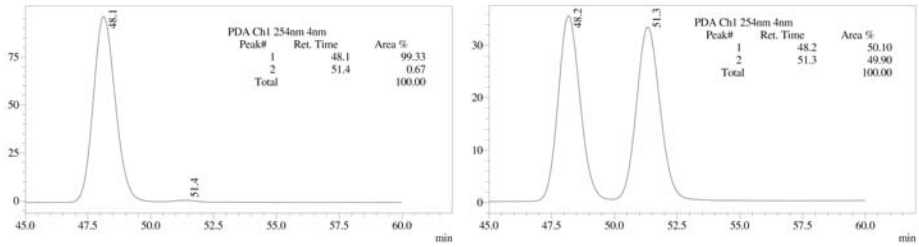
$^{13}C$ NMR (100 MHz, $CDCl_3$): δ 196.6, 151.8, 138.1, 135.6, 133.6, 132.9, 132.3, 130.6, 130.1, 128.4, 127.3, 51.5, 33.8, 32.7.




**(*S*)-3-(4-Formylphenyl)cyclopentene.** $Pd(dba)_2$ (14.4 mg, 0.025 mmol), (*R*)-Xyl-SDP(O) (21.6 mg, 0.030 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *p*-formylphenyl triflate (125 mg, 0.49 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and cyclopentene (180 μL, 2.0 mmol) were used. The reaction completed in 24 h at 50 °C. The product was isolated by flash chromatography with pentane/$Et_2O$ (10:1 to 5:1) as colorless oil. Yield: 80 mg, 94%. Olefinic selectivity in the crude product: 20:1.

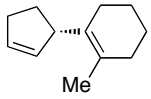
GC-MS (EI): Calcd for $C_{12}H_{12}O$ $M^+$: 172.1, Found: 172.1.

Ee: 99%. Daicel Chiralcel OJ-H, *n*-hexane, flow rate = 0.3 mL/min. $T_R$ = 48.1 min (major) and 51.4 min (minor).




$^1$H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.1 (d, $J$ = 8.2 Hz, 2H), 7.35 (d, $J$ = 8.1 Hz, 2H), 6.02-5.99 (m, 1H), 5.78-5.75 (m, 1H), 4.00-3.95 (m, 1H), 2.57-2.40 (m, 3H), 1.77-1.69 (m, 1H).

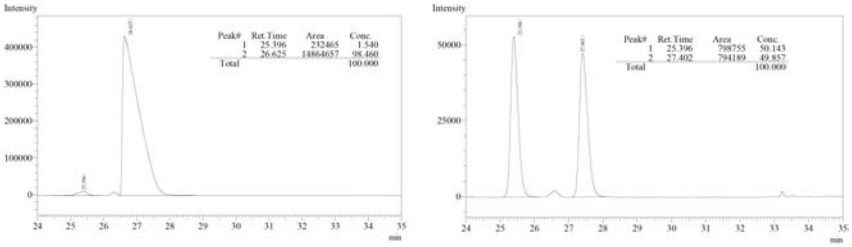
$^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.2, 154.1, 134.9, 133.3, 133.2, 130.2, 128.0, 51.7, 33.8, 32.7.




**(*S*)-3-(2-Methyl-1-cyclohexenyl)cyclopentene.** $Pd(dba)_2$ (7.2 mg, 0.025 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.030 mmol), 1,4-dioxane (0.75 mL), 2-methylcyclohexenyl triflate (122 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and cyclopentene (180 μL, 2.0 mmol) were used. The reaction completed in 4 h at 50 °C. The product was isolated by flash chromatography (silica gel, pentane) as colorless oil. Yield: 67 mg, 83%. Olefinic selectivity in the crude product: 92:1.

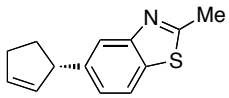
GC-MS (EI): Calcd for $C_{12}H_{18}$ $M^+$: 162.1, Found: 162.1.

Ee: 97%. Chiral GC with Chiraldex B-PH column (30 m x 0.25 mm): carrier gas: He with flow rate of 0.91 mL/min; isothermal at 90 °C. $T_R$ = 25.4 min (major) and 26.6 min (minor).




$^1$H NMR (400 MHz, $CDCl_3$): δ 5.79-5.75 (m, 1H), 5.55-5.52 (m, 1H), 3.87-3.81 (m, 1H), 2.40-2.28 (m, 2H), 2.07-1.98 (m, 1H), 1.96-1.93 (m, 2H), 1.86-1.79 (m, 2H), 1.66 (s, 3H), 1.59-1.47 (m, 5H).

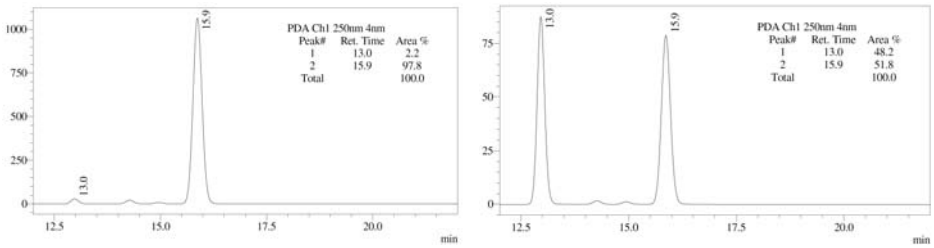
$^{13}$C NMR (100 MHz, $CDCl_3$): δ 134.3, 132.6, 131.1, 125.9, 47.6, 32.8, 32.5, 28.5, 25.0, 23.7, 23.5, 19.2.




**(*S*)-5-(Cyclopent-2-en-1-yl)-2-methylbenzothiazole.** $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (15 μL), 2-methylbenzo[*d*]thiazol-5-yl triflate (149 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and cyclopentene (180 μL, 2.0 mmol) were used. The reaction was complete in 24 h at 70 °C. The product was isolated by flash chromatography (silica gel, 10:1 hexane/EtOAc) as colorless oil. Yield: 106 mg, 98%. Olefinic selectivity in the crude product: 48:1.

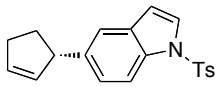
GC-MS (EI): Calcd for $C_{13}H_{13}NS$ $M^+$: 215.1, Found: 215.1.

Ee: 96%. Daicel Chiralcel IC, 95:5 hexanes/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 13.0 min (minor) and 15.9 min (major).




$^1$H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 1.5 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.20 (dd, *J* = 8.2, 1.5 Hz, 1H), 5.99-5.96 (m, 1H), 5.83-5.80 (m, 1H), 4.05-4.00 (m, 1H), 2.82 (s, 3H), 2.57-2.40 (m, 3H), 1.81-1.72 (m, 1H).

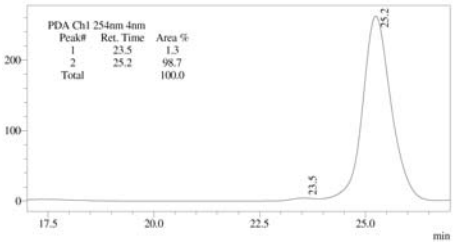
$^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.2, 154.0, 145.1, 134.2, 133.3, 132.4, 124.6, 121.2, 120.8, 51.3, 34.1, 32.6, 20.3.

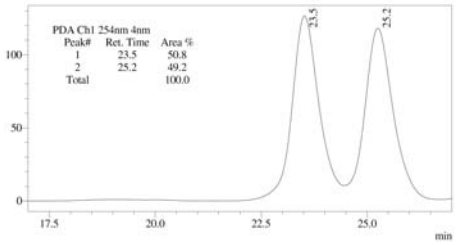



**(*S*)-*N*-Tosyl--5-(Cyclopent-2-en-1-yl)indole.** $Pd(dba)_2$ (5.4 mg, 0.009 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.011 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (15 μL), 1-tosyl-1*H*-indol-5-yl triflate (157 mg, 0.37 mmol), *N*-ethyldiisopropylamine (128 μL, 0.75 mmol) and cyclopentene (130 μL, 1.5 mmol) were used. The reaction was complete in 15 h at 70 °C. The product was purified by flash chromatography (silical gel, 10:1 hexane/EtOAc) as colorless oil in 91% yield (112 mg). Olefinic selectivity in the crude product: 18:1.

GC-MS (EI): Calcd for $C_{20}H_{19}NO_2S$ $M^+$: 337.1, Found: 337.1.

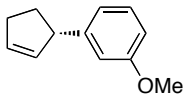
Ee: 97%. Daicel Chiralcel AD-H, 95:5 hexanes/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 23.5 min (minor) and 25.2 min (major).




$^1$H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, $J$ = 8.5 Hz, 1H), 7.76 (d, $J$ = 8.4 Hz, 2H), 7.52 (d, $J$ = 3.6 Hz, 1H), 7.32 (d, $J$ = 1.2 Hz, 1H), 7.21 (d, $J$ = 8.2 Hz, 2H), 7.14 (dd, $J$ = 8.5, 1.6 Hz, 1H), 6.58 (d, $J$ = 3.6 Hz, 1H), 5.95-5.92 (m, 1H), 5.77-5.75 (m, 1H), 3.97-3.92 (m, 1H), 2.53-2.35 (m, 3H), 2.33 (s, 3H), 1.74-1.66 (m, 1H).

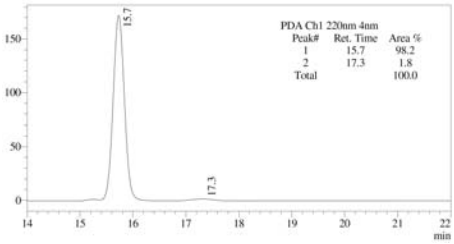
$^{13}$C NMR (100 MHz, $CDCl_3$): δ 144.9, 141.9, 135.6, 134.6, 133.6, 132.1, 131.1, 130.0, 127.0, 126.6, 124.5, 119.5, 113.5, 109.1, 51.3, 34.2, 32.6, 21.7.

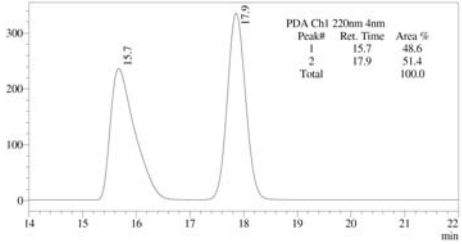



**(*S*)-3-(*m*-Anisyl)cyclopentene [racemate: 369650-02-2].**[18] $Pd(dba)_2$ (1.5 mg, 0.0026 mmol), (*R*)-Xyl-SDP(O) (2.2 mg, 0.0031 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (15 μL), *m*-anisyl triflate (128 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and cyclopentene (180 μL, 2.0 mmol) were used. The reaction was complete in 13 h at 50 °C. The product was purified by flash chromatography (silica gel, 20:1 pentane/$Et_2O$) as pale yellow oil in 98% yield (85 mg). Olefinic selectivity in the crude product: 128:1.

Procedure for 2 mmol scale: $Pd(dba)_2$ (1.5 mg, 0.0026 mmol, 0.13 mol%) ), (*R*)-Xyl-SDP(O) (2.3 mg, 0.0031 mol, 0.16 mol%), 1,4-dioxane (2 mL), *n*-$C_{14}H_{30}$ (60 μL), *m*-anisyl triflate (2.0 mmol, 512 mg), *N*-ethyldiisopropylamine (680 μL, 4 mmol) and cyclopentene (720 μL, 8 mmol) were used. The reaction completed in 6 days at 50 °C and afforded the product in 84% yield (292 mg) in 96% ee.

Ee: 96%. Daicel Chiralcel OJ-H, 99.8:0.2 hexanes/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 15.7 min (major) and 17.3 min (minor).

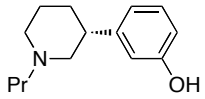


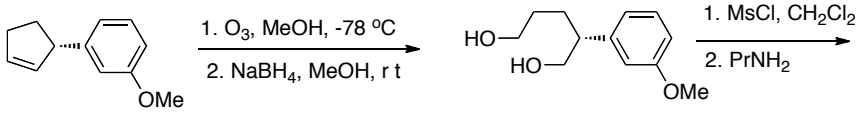

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.23-7.19 (m, 1H), 6.80-6.78 (m, 1H), 6.75-6.72 (m, 2H), 5.95-5.92 (m, 1H), 5.78-5.75 (m, 1H), 3.90-3.82 (m, 1H), 3.80 (s, 3H), 2.53-2.35 (m, 3H),

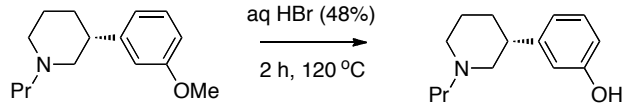
1.77-1.69 (m, 1H).

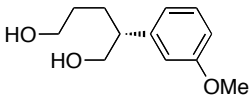
$^{13}$C NMR (100 MHz, $CDCl_3$): δ 159.9, 148.4, 134.3, 132.2, 129.5, 119.8, 113.1, 111.4, 55.3, 51.5, 33.8, 32.6.




**(+)-(*R*)-Preclamol [85976-54-1].**[18] It was prepared from (*S*)-3-(*m*-anisyl)cyclopentene. The ee determination by HPLC was facilitated by the use of racemic material.



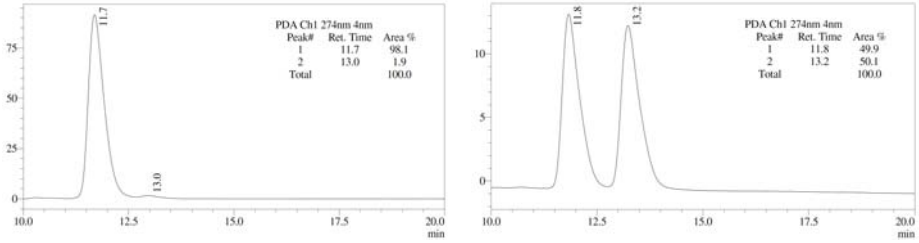




**(*R*)-2-(*m*-Anisyl)pentane-1,5-diol [racemate: 369650-35-1].**[18] A solution of (*S*)-3-(*m*-anisyl)cyclopentene (175 mg, 1.0 mmol, 96% ee) in MeOH (30 mL) was chilled to -78 °C in a dry ice/acetone bath. Ozone was gently bubbled through the solution until the solutuon turned in pale blue. Excess ozone was blown off by a gentle stream of nitrogen. At -78 °C, $NaBH_4$ (340 mg, 9 mmol) was added and the mixture was allowed to warm to RT. After stirring at RT for 1 h, the reaction was quenched by addition of saturated aqueous $NH_4Cl$ solution (40 mL). The product was extracted with EtOAc (40 mL x3). The combined organic portions were washed with brine, dried over $Na_2SO_4$ and concentrated to give the crude product. Purification by flash chromatography (silica gel, 10:1 $CH_2Cl_2$/MeOH) afforded the product as colorless oil in 79% yield (166 mg) in 96% ee. The material was used directly in the next step.

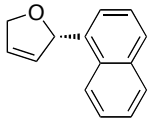
*Cyclization of the diol with propylamine.* Under argon, (*R*)-2-(*m*-anisyl)pentane-1,5-diol (152 mg, 0.7 mmol), dry $CH_2Cl_2$ (10 ml) and $NEt_3$ (0.40 g, 4 mmol) were charged into a 100-mL

Schlenk flask. The solution was chilled to 0 °C, followed by addition of MsCl (230 mg, 2.0 mmol). The resulting mixture was stirred at RT for 4 h, and it was then quenched by addition of saturated aqueous $NaHCO_3$ solution (20 mL). Extraction with $CH_2Cl_2$ (20 mL x3), drying over $Na_2SO_4$ and concentration on a rotavapor afforded the crude dimesylate. Dimesylate was directly mixed with *n*-$PrNH_2$ (0.65 g, 11 mmol) and stirred at RT for 1 d. The resulting mixture was diluted with $CH_2Cl_2$ (10 mL) and washed with saturated aqueous $Na_2CO_3$ solution. Purification by flash chromatography (silica gel, 20:1 to 10:1 $CH_2Cl_2$/MeOH) afforded *O*-methylpreclamol in 76% yield (130 mg) as white waxy solid in 96% ee.

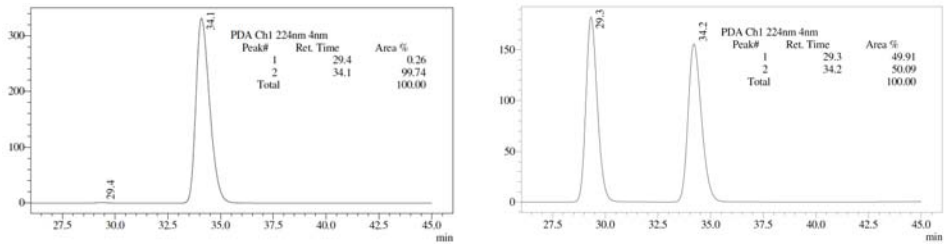
*O-Demethylation*. *O*-Methylpreclamol (117 mg, 0.5 mmol) was mixed with 48% HBr (2 mL) under argon in a 25-mL reaction tube. The mixture was stirred at 120 °C for 2 h. The resulting mixture was cooled to RT, diluted with $CH_2Cl_2$ (10 mL) and quenched with saturated $Na_2CO_3$ (5 mL). The organic layer was separated and the aqueous layer was extracted with $CH_2Cl_2$ (5 mL x 6). Combined organic portions were dried over $Na_2SO_4$ and concentrated to give the product as colorless oil in 95% yield (105 mg) in 96% ee. The product was NMR-pure and no further purification was performed.
$[\alpha]^{22}_D$ = +23.2° (*c* = 1.0, $CHCl_3$). Lit. value for its HCl salt: +7.4° in MeOH.[19]
Ee: 96%. Daicel Chiralcel AD-H, 90:10:0.1 hexanes/isopropanol/$NEt_3$, flow rate = 0.5 mL/min. $T_R$ = 11.7 min (major) and 13.0 min (minor).



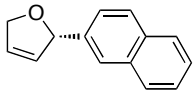

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.18 (ψt, *J* = 7.8 Hz, 1H), 6.81-6.80 (m, 1H), 6.76-6.70 (m, 2H), 3.23 (d, *J* = 11.9 Hz, 1H), 3.07 (d, *J* = 11.2 Hz, 1H), 2.98-2.90 (m, 1H), 2.45-2.29 (m, 2H), 2.04-1.95 (m, 3H), 1.86-1.71 (m, 2H), 1.62-1.45 (m, 3H), 0.87 (t, *J* = 7.4 Hz, 3H).
$^{13}$C NMR (100 MHz, $CDCl_3$): δ 156.9, 145.6, 130.0, 117.6, 114.8, 114.3, 61.6, 61.4, 54.2, 42.0, 30.0, 25.4, 19.4, 12.2.



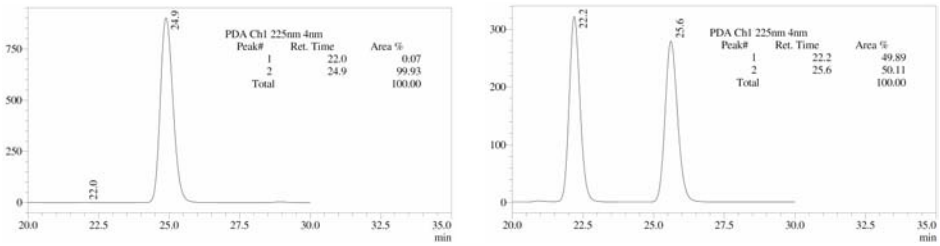
**(*S*)-2-(1-Naphthyl)-2,5-dihydrofuran [1072136-90-3].**[20] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 $\mu$L), 1-naphthyl triflate (140 mg, 0.51 mmol), *N*-ethyldiisopropylamine (170 $\mu$L, 1.0 mmol) and 2,3-dihydrofuran (150$\mu$L, 2.0 mmol) were used. The reaction was complete in 2.5 h at 50 $^{o}$C. The product was isolated by flash chromatography (10:1 to 3:1 pentane/$Et_2O$) as colorless oil.
Yield: 92 mg, 92%. Olefinic selectivity in the crude product: 262:1.
Ee: 99.5%. Daicel Chiralcel OD-H, 98:2 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 29.4 min (minor) and 34.1 min (major).



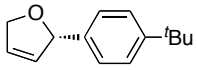

$^1$H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 9.3 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.56-7.44 (m, 4H), 6.58-6.55 (m, 1H), 6.16-6.13 (m, 1H), 6.10-6.07 (m, 1H), 4.97-4.85 (m, 2H).



**(*S*)-2-(2-Naphthyl)-2,5-dihydrofuran [131516-16-0].**[21] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 $\mu$L), 2-naphthyl triflate (140 mg, 0.51 mmol), *N*-ethyldiisopropylamine (170 $\mu$L, 1.0 mmol) and 2,3-dihydrofuran (150 $\mu$L, 2.0 mmol) were used. The reaction was complete in 1 h at 50 $^{o}$C. The product was isolated by flash chromatography (10:1 to 3:1 pentane/$Et_2O$) as colorless oil.
Yield: 93 mg, 93%. Olefinic selectivity in the crude product: 81:1.
Ee: >99.5%. Daicel Chiralcel OD-H, n-hexane/isopropanol 98/2, flow rate = 0.5 mL/min. $T_R$ = 22.0 min (minor) and 24.9 min (major).



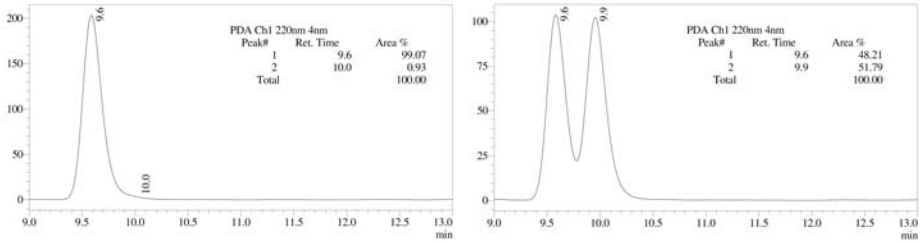

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.84-7.80 (m, 3H), 7.76 (s, 1H), 7.49-7.43 (m, 2H), 7.41 (dd, J = 8.5, 1.6 Hz, 1H), 6.09-6.06 (m, 1H), 5.97-5.93 (m, 1H), 4.98-4.93 (m, 1H), 4.85-4.80 (m, 1H).




**(*S*)-2-(4-*tert*-Butylphenyl)-2,5-dihydrofuran.** $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *p*-*tert*-butylphenyl triflate (142 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and 2,3-dihydrofuran (180 μL, 2.0 mmol) were used. The reaction completed in 13 h at 50 °C. The product was isolated by flash chromatography with pentane/$Et_2O$ (10:1 to 5:1) as colorless oil. Yield: 90 mg, 88%. Olefinic selectivity in the crude product: 141:1.

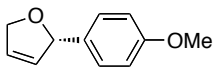
GC-MS (EI): Calcd for $C_{14}H_{18}O$ $M^+$: 202.1, Found: 202.2.

Ee: 98%. Daicel Chiralcel OD-H, 98:2 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 9.6 min (major) and 10.0 min (minor).




$^1$H NMR (400 MHz, $CDCl_3$): δ 7.39-7.36 (m, 2H), 7.25-7.23 (m, 2H), 6.05-6.03 (m, 1H), 5.91-5.88 (m, 1H), 5.79-5.76 (m, 1H), 4.89-4.83 (m, 1H), 4.78-4.73 (m, 1H), 1.31 (s, 9H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ 151.0, 139.1, 130.1, 126.8, 126.4, 125.6, 87.8, 75.8, 34.7, 31.5.

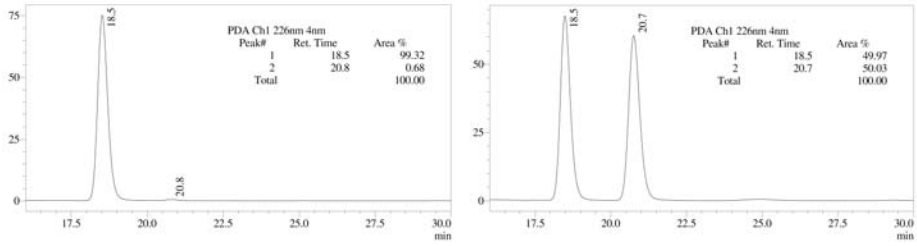



**(*S*)-2-(*p*-Anisyl)-2,5-dihydrofuran [131516-15-9].**[21] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *p*-anisyl triflate (128 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and 2,3-

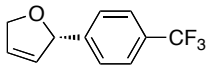
dihydrofuran (180 μL, 2.0 mmol) were used. The reaction was complete in 13 h at 50 °C. The product was isolated by flash chromatography (10:1 to 5:1 pentane/$Et_2O$) as colorless liquid. Yield: 80 mg, 91%. Olefinic selectivity in the crude product: 27:1.

$[\alpha]^{20}_D = -98^o$ ($c$ = 1.0, $CHCl_3$).

Ee: 99%. Daicel Chiralcel OD-H, 98:2 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 18.5 min (major) and 20.8 min (minor).

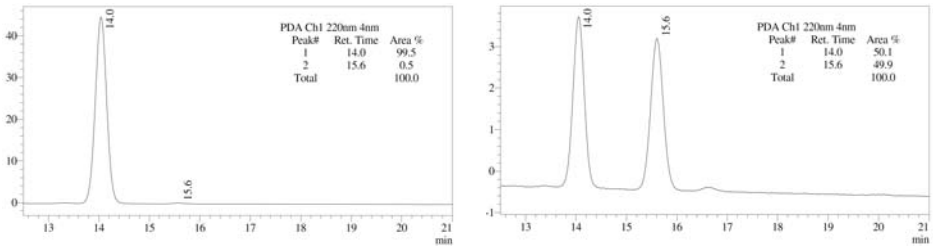



$^1$H NMR (400 MHz, $CDCl_3$): δ 7.25-7.21 (m, 2H), 6.90-6.86 (m, 2H), 6.05-6.03 (m, 1H), 5.88-5.85 (m, 1H), 5.77-5.73 (m, 1H), 4.87-4.82 (m, 1H), 4.76-4.71 (m, 1H), 3.80 (s, 3H).

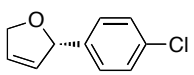



**(*S*)-2-[*p*-(Trifluoromethyl)phenyl]-2,5-dihydrofuran [331754-75-7].**[22] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *p*-(trifluoromethyl)phenyl triflate (148 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and 2,3-dihydrofuran (150 μL, 2.0 mmol) were used. The reaction was complete in 14 h at 50 °C. The product was isolated by flash chromatography (10:1 to 5:1 pentane/$Et_2O$) as a colorless liquid. Yield: 71 mg, 66% (77% GC yield). Olefinic selectivity in the crude product: 7:1.

Ee: 99%. Daicel Chiralcel OJ-H, 98:2 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 14.0 min (major) and 15.6 min (minor).



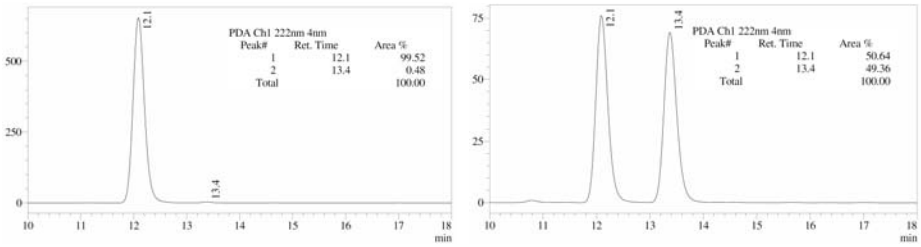

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, $J$ = 8.1 Hz, 2H), 7.42 (d, $J$ = 8.1 Hz, 2H), 6.08-6.05 (m, 1H), 5.90-5.83 (m, 2H), 4.93-4.87 (m, 1H), 4.83-4.78 (m, 1H).



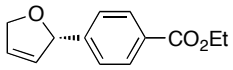
**(*S*)-2-(4-Chlorophenyl)-2,5-dihydrofuran [131516-11-5].**[21] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *p*-chlorophenyl triflate (130 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and 2,3-dihydrofuran (180 μL, 2.0 mmol) were used. The reaction was complete in 6 h at 50 °C. The product was isolated by flash chromatography (10:1 to 5:1 pentane/$Et_2O$) as colorless oil. Yield: 70 mg, 78%.

Olefinic selectivity in the crude product: 135:1.

Ee: 99%. Daicel Chiralcel OD-H, 98:2 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 12.1 min (major) and 13.4 min (minor).



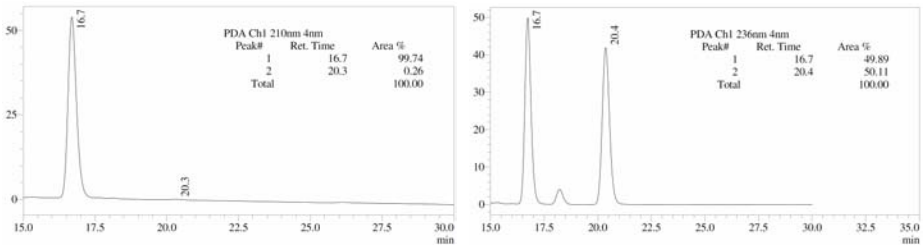

$^1H$ NMR (400 MHz, $CDCl_3$): δ 7.33-7.30 (m, 2H), 7.25-7.22 (m, 2H), 6.06-6.03 (m, 1H), 5.87-5.84 (m, 1H), 5.78-5.74 (m, 1H), 4.89-4.83 (m, 1H), 4.79-4.74 (m, 1H).




**(*S*)-2-[*p*-(Ethoxycarbonyl)phenyl]-2,5-dihydrofuran.** $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *p*-(ethoxycarbonyl)phenyl triflate (149 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and 2,3-dihydrofuran (150 μL, 2.0 mmol) were used. The reaction completed in 5 h at 50 °C. The product was isolated by flash chromatography (10:1 to 5:1 pentane/$Et_2O$) as colorless oil. Yield: 102 mg, 93%. Olefinic selectivity in the crude product: 64:1.

GC-MS (EI): Calcd for $C_{13}H_{14}O_3$ $M^+$: 218.1, Found: 218.1.

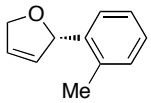
Ee: 99%. Daicel Chiralcel OD-H, 98:2 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 16.7 min (major) and 20.3 min (minor).




$^1H$ NMR (400 MHz, $CDCl_3$): δ 8.04-8.01 (m, 2H), 7.39-7.36 (m, 2H), 6.06-6.03 (m, 1H),

5.90-5.87 (m, 1H), 5.86-5.82 (m, 1H), 4.93-4.87 (m, 1H), 4.83-4.80 (m, 1H), 4.37 (q, $J$ = 7.1 Hz, 2H), 1.39 (t, $J$ = 7.1 Hz, 3H).

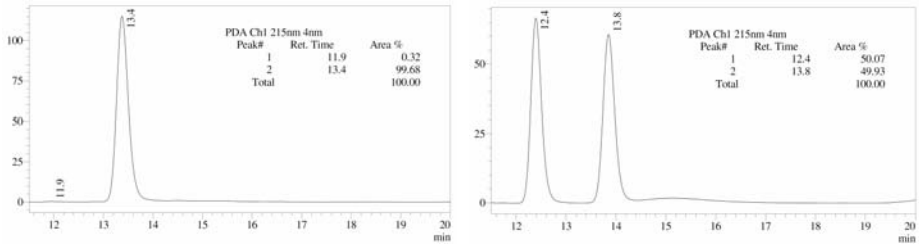
13C NMR (100 MHz, CDCl3): δ 166.6, 147.3, 130.0 (2 peaks), 129.7, 127.1, 126.2, 87.6, 76.2, 61.1, 14.5.




**(*S*)-2-(*o*-Tolyl)-2,5-dihydrofuran [1361252-01-8].**[23] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *o*-methylphenyl triflate (120 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and 2,3-dihydrofuran (150 μL, 2.0 mmol) were used. The reaction was complete in 14 h at 50 °C. The product was isolated by flash chromatography (10:1 to 5:1 pentane/$Et_2O$) as colorless oil. Yield: 67 mg, 81%. Olefinic selectivity in the crude product: 136:1

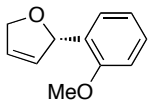
GC-MS (EI): Calcd for $C_{11}H_{12}O$ $M^+$: 160.1, Found: 160.1.

Ee: 99%. Daicel Chiralcel OD-H, 98:2 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 11.9 min (minor) and 13.4 min (major).




$^1$H NMR (400 MHz, $CDCl_3$): δ 7.33-7.29 (m, 1H), 7.22-7.13 (m, 3H), 6.05-6.02 (m, 2H), 5.94-5.90 (m, 1H), 4.91-4.85 (m, 1H), 4.81-4.76 (m, 1H), 2.40 (s, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ 140.1, 135.2, 130.6, 129.2, 127.7, 126.9, 126.4, 126.3, 85.2, 75.8, 19.1.

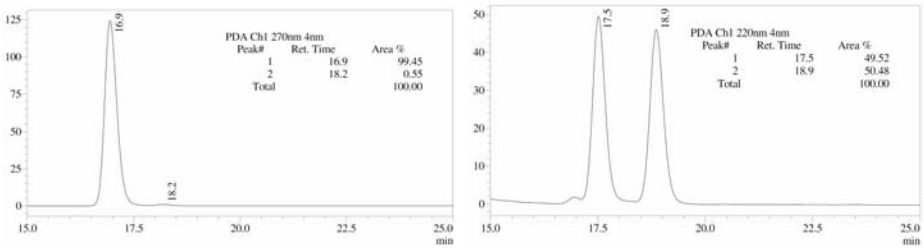



**(*S*)-2-(*o*-Anisyl)-2,5-dihydrofuran [racemate: 479682-88-7].**[24] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *o*-anisyl triflate (128 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and 2,3-dihydrofuran (180 μL, 2.0 mmol) were used. The reaction completed in 24 h at 50 °C. The product was isolated by flash chromatography (10:1 to 5:1 pentane/$Et_2O$) as colorless oil.

Yield: 78 mg, 89%.

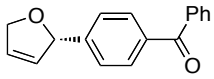
Olefinic selectivity in the crude product: >100:1

Ee: 99%. Daicel Chiralcel OJ-H, 98:2 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 16.9 min (major) and 18.2 min (minor).




$^1$H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.26-7.22 (m, 1H), 6.95 (ψt, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.15-6.12 (m, 1H), 6.00-5.93 (m, 2H), 4.89-4.83 (m, 1H), 4.81-4.76 (m, 1H), 3.85 (s, 3H).

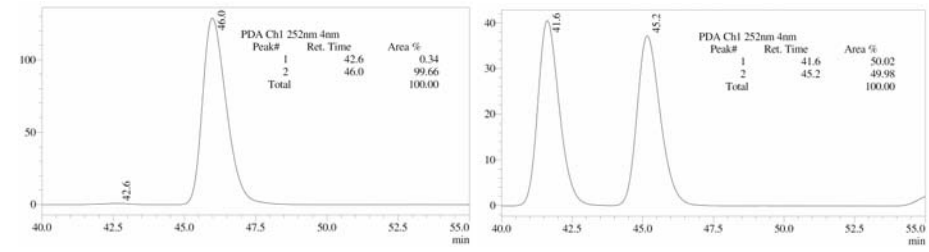
$^{13}$C NMR (100 MHz, $CDCl_3$): δ 156.3, 130.7, 129.6, 128.6, 126.6, 126.0, 120.8, 110.4, 82.6, 75.7, 55.5.




**(*S*)-2-(*p*-Benzophenonyl)-2,5-dihydrofuran [720688-72-2].**[25] $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *p*-benzophenonyl triflate (167 mg, 0.51 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and 2,3-dihydrofuran (180 μL, 2.0 mmol) were used. The reaction completed in 5 h at 50 °C. The product was isolated by flash chromatography with 10:1 to 5:1 pentane/$Et_2O$ as pale yellow liquid. Yield: 98 mg, 78%. Olefinic selectivity in the crude product: 18:1.

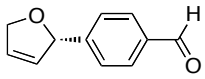
$[\alpha]^{20}_D$ = -91° (*c* = 1.5, $CHCl_3$).

Ee: 99%. Daicel Chiralcel OD-H, 99:1 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 42.6 min (minor) and 46.0 min (major). (It was reported that the (-)-isomer had longer retention time than the (+)-isomer when using Chiralcel OD connected with another OD-H).[25]

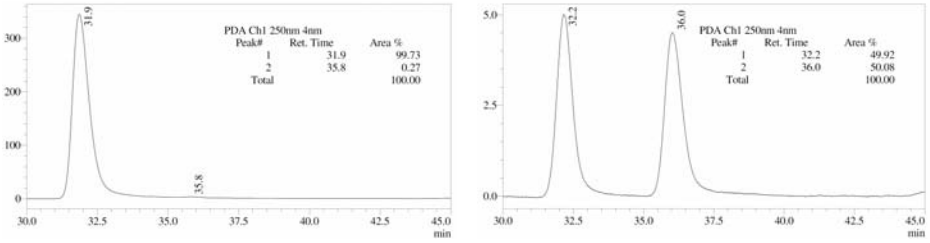



$^1$H NMR (400 MHz, $CDCl_3$): δ 7.81-7.78 (m, 4H), 7.61-7.56 (m, 1H), 7.50-7.41 (m, 4H),

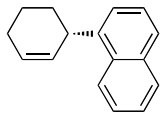
6.09-6.06 (m, 1H), 5.93-5.86 (m, 2H), 4.95-4.89 (m, 1H), 4.85-4.79 (m, 1H).
$^{13}$C NMR (100 MHz, $CDCl_3$): δ 196.6, 146.9, 137.8, 137.1, 132.5, 130.6, 130.2, 129.6, 128.4, 127.2, 126.2, 87.6, 76.3.



**(*S*)-2-(*p*-Formylphenyl)-2,5-dihydrofuran.** $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), *p*-formylphenyl triflate (128 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and 2,3-dihydrofuran (180 μL, 2.0 mmol) were used. The reaction was complete in 32 h at 50 °C. The product was isolated by flash chromatography (silica gel, 10:1 to 5:1 pentane/$Et_2O$) as pale yellow oil. Yield: 72 mg, 82%. Olefinic selectivity in the crude product: 73:1.
GC-MS (EI): Calcd for $C_{11}H_{10}O_2$ $M^+$: 174.1, Found: 174.1.
Ee: 99%. Daicel Chiralcel OD-H, 99:1 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 31.9 min (major) and 35.8 min (minor).



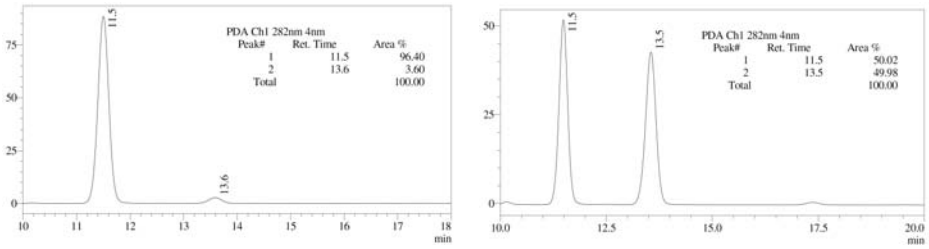

$^1$H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.88-7.86 (m, 2H), 7.49-7.47 (m, 2H), 6.09-6.06 (m, 1H), 5.91-5.85 (m, 2H), 4.95-4.89 (m, 1H), 4.85-4.79 (m, 1H).
$^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.1, 149.2, 136.0, 130.2, 129.4, 127.4, 126.8, 87.5, 76.3.



**(*S*)-3-(1-Naphthyl)cyclohex-1-ene [303030-27-5].**[13]
*Heck reaction using (R)-Xyl-SDP(O) as the ligand.* $Pd(dba)_2$ (14.4 mg, 0.025 mmol), (*R*)-Xyl-SDP(O) (21.6 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), 1-naphthyl triflate (138 mg, 0.50 mmol), and cyclohexene (203 μL, 2.0 mmol) were used. $Li_2CO_3$ (74 mg, 1.0 mmol) was used instead of *N*-ethyldiisopropylamine. The reaction was complete in 24 h at 70 °C. The product was purified by flash chromatography with pentane as colorless oil. Yield: 95 mg, 91%. Ee: 83%. Olefinic selectivity in the crude product: 26:1.$[\alpha]^{20}_D$ = +34°

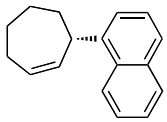
($c$ = 1.4, $CHCl_3$).

*Heck reaction using (R)-pFPh-Cy-SDP(O) as the ligand.* $Pd(dba)_2$ (14.4 mg, 0.025 mmol), (*R*)-*p*FPh-Cy-SDP(O) (19.6 mg, 0.030 mmol), *n*-$C_{14}H_{30}$ (25 $\mu$L), 1-naphthyl triflate (138 mg, 0.50 mmol), and cyclohexene (203 $\mu$L, 2.0 mmol) were used. $Li_2CO_3$ (113 mg, 1.5 mmol) was used instead of *N*-ethyldiisopropylamine. 1,2-Dimethoxybenzene (0.50 mL) was used as solvent and $Li_2CO_3$ (113 mg, 1.5 mmol) was used instead of *N*-ethyldiisopropylamine. The reaction was complete in 24 h at 80 $^oC$. The product was purified by flash chromatography with pentane as colorless oil. Yield: 91 mg, 86%. Olefinic selectivity in the crude product: 9:1. Ee: 93%. Daicel Chiralcel OJ-H, 98:2 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 11.5 min (major) and 13.6 min (minor).




$^1H$ NMR (400 MHz, $CDCl_3$): δ 8.13 (d, $J$ = 8.4 Hz, 1H), 7.87-7.85 (m, 1H), 7.71 (d, $J$ = 7.6 Hz, 1H), 7.53-7.34 (m, 4H), 6.03-6.00 (m, 1H), 5.85-5.82 (m, 1H), 4.24-4.22 (m, 1H), 2.18-2.14 (m, 3H), 1.76-1.68 (m, 3H).

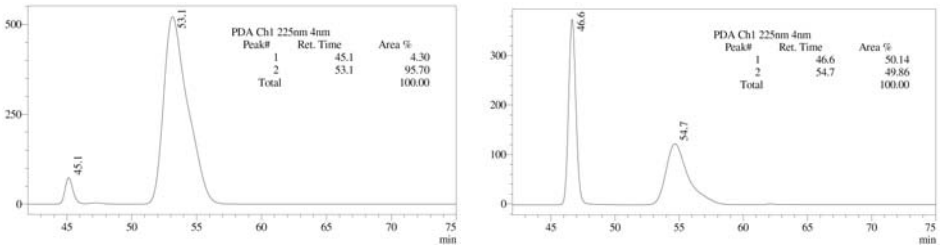
$^{13}C$ NMR (100 MHz, $CDCl_3$): δ 142.1, 134.3, 131.6, 130.4, 129.2, 129.0, 126.8, 125.9, 125.7, 125.5, 125.3, 123.6, 37.2, 31.1, 25.5, 21.1.



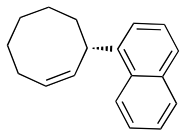
**(*S*)-3-(1-Naphthyl)cyclohept-1-ene.** $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 $\mu$L), 1-naphthyl triflate (141 mg, 0.51 mmol), *N*-ethyldiisopropylamine (170 $\mu$L, 1.0 mmol) and cycloheptene (192 mg, 2.0 mmol) were used. The reaction completed in 14 h at 50 $^oC$. The product was isolated by flash chromatography with pentane as a colorless liquid. Yield: 112 mg, 98%. GC-MS (EI): Calcd for $C_{17}H_{18}$ $M^+$: 222.1, Found: 222.1. Ee: 88%. $[\alpha]^{20}_D$ = +37$^o$ ($c$ = 1.9, $CHCl_3$).

When the reaction was carried out at 27 $^oC$, it completed in 5 days with 91% ee. Yield: 104 mg, 91%. Olefinic selectivity in the crude product: 14:1.

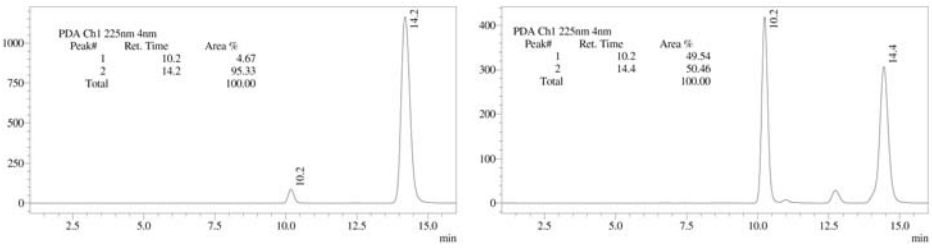
HPLC condition: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 99.9/0.1, flow rate = 0.25 mL/min. $T_R$ = 45.1 min (minor) and 53.1 min (major).




$^1$H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, $J$ = 8.2 Hz, 1H), 7.87-7.85 (m, 1H), 7.31-7.69 (m, 1H), 7.52-7.42 (m, 4H), 5.95-5.89 (m, 1H), 5.86-5.82 (1H), 4.29 (d, $J$ = 9.5 Hz, 1H), 2.40-2.32 (m, 2H), 2.08-1.93 (m, 3H), 1.91-1.71 (m, 2H), 1.58-1.48 (m, 1H).
$^{13}$C NMR (100 MHz, $CDCl_3$): 143.7, 137.6, 134.2, 131.6, 131.3, 129.0, 126.7, 125.8 (2C), 125.5, 124.2, 124.0, 42.9, 35.1, 31.0, 29.0, 27.3.



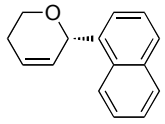
**(*S*)-3-(1-Naphthyl)cyclooctene.** $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), 1-naphthyl triflate (140 mg, 0.51 mmol), *N*-ethyldiisopropylamine (170 μL, 1.0 mmol) and cyclooctene (220 mg, 2.0 mmol) were used. The reaction completed in 16 h at 50 °C. The product was isolated by flash chromatography with pentane as colorless oil. Yield: 116 mg, 97%. Olefinic selectivity in the crude product: 10:1.
GC-MS (EI): Calcd for $C_{18}H_{20}O$ $M^+$: 236.2, Found: 236.1.
Ee: 88%.
The same reaction was carried out at 27 °C, and it completed in 60 h with slightly higher ee (91%). Yield: 118 mg, 97%. Olefinic selectivity in the crude product: 12:1. $[\alpha]^{20}_D$ = +197° (*c* = 1.5, $CHCl_3$).
HPLC condition: Daicel Chiralcel OJ-H, 99:1 *n*-hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 10.2 min (minor) and 14.2 min (major).




$^1$H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, $J$ = 8.3 Hz, 1H), 7.84 (d, $J$ = 8.2 Hz, 1H), 7.71 (d, $J$ =

7.7 Hz, 1H), 7.51-7.42 (m, 4H), 5.76-5.70 (m, 1H), 5.60-5.55 (m, 1H), 4.53-4.46 (m, 1H), 2.66-2.57 (m, 1H), 2.32-2.24 (m, 1H), 2.01-1.91 (m, 2H), 1.88-1.73 (m, 4H), 1.68-1.59 (m, 1H), 1.54-1.43 (m, 1H).

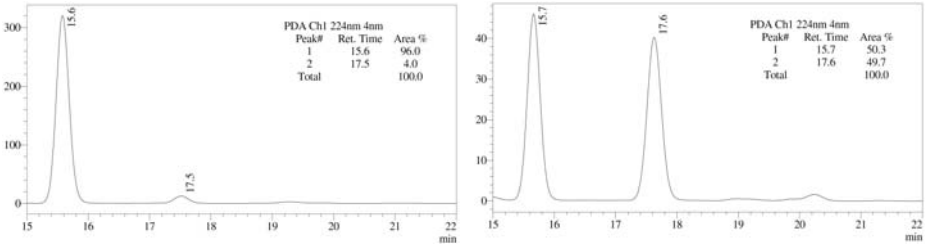
$^{13}$C NMR (100 MHz, $CDCl_3$): δ 142.4, 134.9, 134.1, 132.1, 128.9 (2 peaks), 126.7, 125.8 (2 peaks), 125.5, 123.8, 123.0, 37.7, 36.0, 29.9, 26.8, 26.7, 26.4.



**(*S*)-6-(1-Naphthyl)-3,6-dihydro-2*H*-pyran.** $Pd(dba)_2$ (14.4 mg, 0.025 mmol) and (*R*)-*p*FPh-Cy-SDP(O) (19.6 mg, 0.030 mmol), *n*-$C_{14}H_{30}$ (25 μL), 1-naphthyl triflate (138 mg, 0.50 mmol) and 3,4-dihydro-2*H*-pyran (168 mg, 2.0 mmol) were used. 1,2-Dimethoxybenzene (0.75 mL) was used as solvent and $Li_2CO_3$ (74 mg, 1.0 mmol) was used instead of *N*-ethyldiisopropylamine. The reaction was stirred at 70 °C for 2.5 d with 90% conversion of the triflate. The product was purified by flash chromatography (silica gel, 50:1 hexane/EtOAc) as a colorless liquid. Yield: 82 mg, 78%. Olefinic selectivity in the crude product: 5:1.

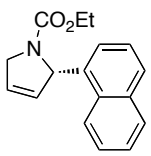
GC-MS (EI): Calcd for $C_{15}H_{14}O$ $M^+$: 210.1, Found: 210.1.

Ee: 92%. Daicel Chiralcel IC, hexane/isopropanol 98/2, flow rate = 0.5 mL/min. $T_R$ = 15.6 min (major) and 17.5 min (minor).




$^1$H NMR (400 MHz, $CDCl_3$): 8.26 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.57-7.42 (m, 4H), 6.13-6.08 (m, 1H), 6.00-5.96 (m, 1H), 5.88-5.87 (m, 1H), 4.04-3.98 (m, 1H), 3.91-3.85 (m, 1H), 2.44-2.35 (m, 1H), 2.25-2.16 (m, 1H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ 136.5, 134.2, 131.6, 129.4, 128.8 (2 peaks), 126.3, 125.9 (2 peaks), 125.7, 125.2, 124.2, 73.3, 63.0, 25.5.



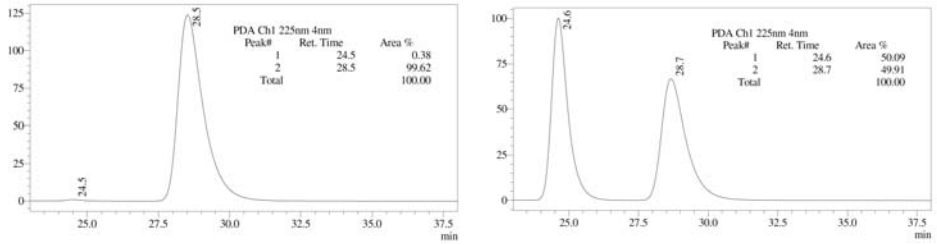
**(*S*)-*N*-Ethoxycarbonyl-2-(1-naphthyl)-2,5-dihydro-*1H*-pyrrole.** $Pd(dba)_2$ (7.2 mg, 0.013

mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 $\mu$L), 1-naphthyl triflate (140 mg, 0.51 mmol), *N*-ethyldiisopropylamine (170 $\mu$L, 1.0 mmol) and 2,3-dihydrofuran (180 $\mu$L, 2.0 mmol) were used. The reaction was complete in 44 h at 50 $^{o}$C. The product was isolated by flash chromatography (10:1 to 1:1 pentane/$Et_2O$) as colorless oil. Yield: 131 mg, 96%. Olefinic selectivity in the crude product: 54:1.

GC-MS (EI): Calcd for $C_{17}H_{17}NO_2$ $M^+$: 267.1, Found: 267.0.

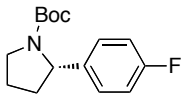
$[\alpha]^{20}_D$ = -263$^{o}$ (*c* = 1.2, $CHCl_3$).

Ee: 99%. Daicel Chiralcel AS-H, 98:2 hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 24.5 min (minor) and 28.5 min (major).

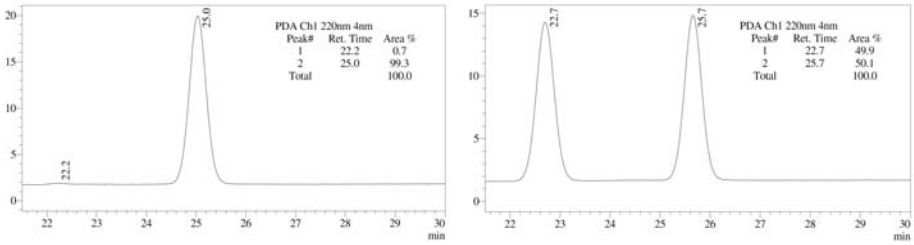



$^1$H NMR of 2 rotamers in 4:6 ratio (400 MHz, $CDCl_3$): δ 8.13 (dd, J = 8.4, 8.0 Hz, 1H), 7.89-7.84 (m, 1H), 7.76-7.74 (m, 1H), 7.56-7.41 (m, 3H), 7.37-7.33 (m, 1H), 6.39 (br s, 0.4H), 6.33 (br s, 0.6H), 5.96-5.84 (m, 2H), 4.51-4.43 (m, 2H), 4.22-4.08 (m, 1H), 3.96-3.91 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 1.2H), 0.81 (t, *J* = 7.0 Hz, 1.8H).

$^{13}$C NMR of 2 rotamers (100 MHz, $CDCl_3$): δ 155.3, 155.0, 137.9, 137.2, 134.1, 133.9, 131.1, 130.9, 130.6, 130.5, 129.0, 127.9, 127.8, 126.1, 125.9, 125.6, 124.7, 124.6, 123.2, 123.0, 122.9, 122.8, 65.4, 64.6, 61.3, 61.2, 60.9, 54.4, 54.0, 15.0, 14.5.



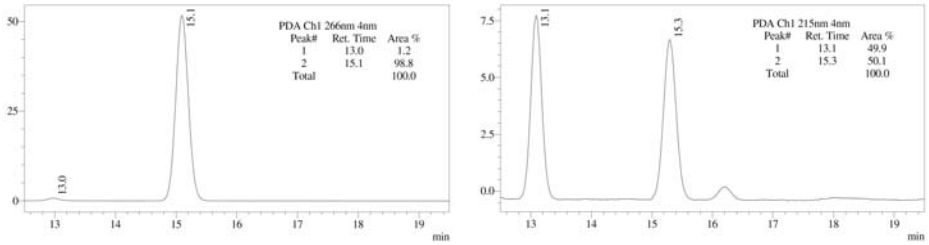

**(*S*)-*N*-Boc-2-(*p*-fluorophenyl)pyrrolidine [174310-77-1].**[26] It was prepared via asymmetric Heck reaction, followed by catalytic hydrogenation. Under argon, $Pd(dba)_2$ (7.2 mg, 0.013 mmol) and (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol) were stirred in 1,4-dioxane (0.50 mL) in a 10-mL reaction tube for 30 min, followed by addition of *n*-$C_{14}H_{30}$ (25 $\mu$L), 4-fluorophenyl triflate (122 mg, 0.50 mmol), *N*-ethyldiisopropylamine (170 $\mu$L, 1.0 mmol) and *N*-Boc-2,3-dihydro-1*H*-pyrrole (169 mg, 1.0 mmol). The mixture was stirred at 50 $^{o}$C in an oil bath. The reaction completed in 38 h. The reaction mixture was diluted with hexane (12 mL) and was filtered through cotton wool. The ee of this crude product was determined to be 98.6%. Daicel Chiralcel IC, 98:2 hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 22.2 min (minor) and 25.0 min (major).




The filtrate was used in catalytic hydrogenation directly. It was mixed with wet 5% wt/wt Pd/C (85 mg, 8 mol%) and was subjected to hydrogenation in a 125-mL Parr bomb with $H_2$ (80 psi) for 2 h at RT. The resulting mixture was subjected to flash chromatography (silica gel, 10:1 hexane/EtOAc). The product was isolated as pale yellow oil (96 mg, 73% yield over 2 steps) with 98% ee.

$[\alpha]^{22}_D = -64^o$ ($c$ = 1.5, $CHCl_3$).

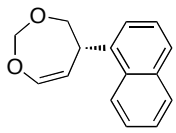
Daicel Chiralcel IC, 90:10 hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 13.0 min (minor) and 15.1 min (major).




$^1$H NMR for 2 rotamers with 35:65 ratio (400 MHz, $CDCl_3$): δ 7.14-7.12 (m, 2H), 7.01-6.95 (m, 2H), 4.92 (br s, 0.35H), 4.74 (br s, 0.65H), 3.61 (br, 1H), 2.31 (br, 1H), 1.94-1.75 (m, 3H), 1.46 (br, 3.1H), 1.19 (br, 5.9H).

$^{13}$C NMR of 2 rotamers with 35:65 ratio (100 MHz, $CDCl_3$): δ 161.7 (d, $J_{C\text{-}F}$ = 244.0 Hz), 154.7, 141.0, 127.1 (d, $J_{C\text{-}F}$ = 7.2 Hz), 115.0 (d, $J_{C\text{-}F}$ = 21.0 Hz), 79.5, 60.9, 60.3, 47.2, 36.2, 35.1, 28.7, 28.6, 28.3, 23.5, 23.3.

$^{19}$F{$^1$H} NMR (376 MHz, $CDCl_3$): δ -116.9 (s, 0.65F), -117.1 (s, 0.35F).



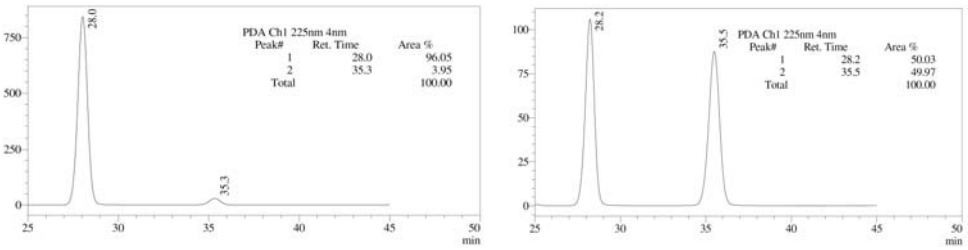
**(*S*)-5-(1-Naphthyl)-4,5-dihydro-1,3-dioxepine.** $Pd(dba)_2$ (7.2 mg, 0.013 mmol), (*R*)-Xyl-SDP(O) (10.8 mg, 0.015 mmol), 1,4-dioxane (0.50 mL), *n*-$C_{14}H_{30}$ (25 μL), 1-naphthyl triflate (140 mg, 0.51 mmol), and *cis*-4,7-dihydro-1,3-dioxepine (191 μL, 2.0 mmol) were used. $Li_2CO_3$ (74 mg, 1.0 mmol) was used instead of *N*-ethyldiisopropylamine. The reaction

completed in 44 h at 50 °C. The product was isolated by flash chromatography (4:1 pentane/$Et_2O$) as colorless oil. Yield: 112 mg, 98%. Olefinic selectivity in the crude product: 146:1.

GC-MS (EI): Calcd for $C_{15}H_{14}O_2$ $M^+$: 226.1, Found: 226.1.

$[\alpha]^{20}_D = +96^o$ ($c$ = 1.2, $CHCl_3$).

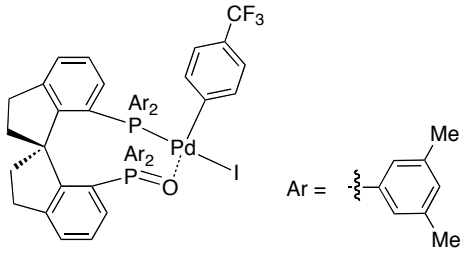
Ee: 92%. Daicel Chiralcel OJ-H, 98:2 hexane/isopropanol, flow rate = 0.5 mL/min. $T_R$ = 28.0 min (major) and 35.3 min (minor).




$^1H$ NMR (400 MHz, $CDCl_3$): δ 8.13 (d, $J$ = 8.4 Hz, 1H), 7.89-7.87 (m, 1H), 7.77 (d, $J$ = 7.9 Hz, 1H), 7.55-7.42 (m, 4H), 6.56 (dd, $J$ = 7.3, 2.5 Hz, 1H), 5.32 (d, $J$ = 7.0 Hz, 1H), 5.07 (ddd, $J$ = 7.3, 3.2, 0.6 Hz, 1H), 4.86 (d, $J$ = 7.0 Hz, 1H), 4.70-4.65 (m, 1H), 4.18 (dd, $J$ = 11.7, 4.6 Hz, 1H), 3.56 (dd, $J$ = 11.7, 9.2 Hz, 1H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ 146.4, 136.6, 134.2, 131.3, 129.3, 127.8, 126.4, 125.8 (2 peaks), 125.7, 123.1, 113.0, 98.4, 75.9, 44.1.

## VI. Mechanistic study




**Synthesis of Pd[(*R*)-Xyl-SDP(O)](*p*-$CF_3C_6H_4$)(I).** In an argon-filled glove box, $Pd_2(dba)_3$ (51 mg, 0.056 mmol) and (*R*)-Xyl-SDP(O) (80 mg, 0.11 mmol) were stirred in degassed MeOH (2.0 mL) in a 4-mL vial at RT for 10 min, followed by the addition of *p*-(trifluoromethyl)phenyl iodide (61 mg, 0.22 mmol, 4 equiv). The vial was covered in aluminum foil and the mixture was stirred rigorously at RT for 22 h. The resulting mixture was passed through a short plug of cotton wool to remove a small amount of Pd black precipitate. A large amount of yellowish brown crystals precipitated from the filtrate in a few minute on standing, due to cooling during solvent evaporation at RT. The crystals were filtrated and washed with a small amount of MeOH to give the pure product (63 mg, 52%). The crystals were suitable for X-ray diffractional analysis. Further cooling of the filtrate to -30 $^oC$ only resulted in the precipitation of dba. $^1H$ NMR spectroscopy in $CD_2Cl_2$ showed broad signals at RT and at -40 $^oC$, sharper signals were obtained. Further cooling of the filtrate at -30 $^oC$ only resulted the precipitation of dba. $^1H$ NMR spectroscopy in $CD_2Cl_2$ showed broad signals at RT and at -40 $^oC$, sharper signals were obtained.
ESI-MS: calcd for $[M-I]^+$ $C_{56}H_{54}F_3OP_2Pd$: 967.26. Found: 967.18.
$^1H$ NMR (400 MHz, $CD_2Cl_2$, 243 K): δ 7.78-7.59 (m, 4H), 7.46-7.43 (m, 2H), 7.26-7.21 (m, 1H), 7.17-7.04 (m, 5H), 6.98-6.90 (m, 3H), 6.81-6.79 (m, 2H), 6.70 (d, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 6.7 Hz, 1H), 6.42 (d, *J* = 12.5 Hz, 1H), 6.11-6.08 (m, 2H), 2.95-2.87 (m, 1H), 2.60-2.51 (m, 2H), 2.33 (s, 12H), 2.26 (s, 3H), 2.06-1.92 (m, 12H), 1.52-1.38 (m, 2H).

$^{13}C$ NMR (100 MHz, $CD_2Cl_2$, 243 K; most splitting was not identified): δ 153.2 (d, *J* = 8.4 Hz), 148.0 (d, *J* = 11.6 Hz), 147.1 (d, *J* = 9.1Hz), 145.4 (d, *J* = 10.1 Hz), 145.1, 138.7 (d, *J* = 11.8 Hz), 138.4 (d, *J* = 3.3 Hz), 138.0 (d, *J* = 10.9 Hz), 137.6, 137.5, 137.4, 137.3, 137.2 (2 peaks), 137.0, 133.4 (d, *J* = 1.5 Hz), 133.3, 133.2, 133.1 (2 peaks), 132.6 (d, *J* = 3.6 Hz), 132.2, 131.7 (d, *J* = 1.5Hz), 131.5, 130.5 (d, *J* = 2.1 Hz), 130.1, 129.6, 129.5, 129.3, 129.1, 129.0, 128.5, 121.2, 127.1, 126.9, 126.7, 126.6, 126.5, 126.4, 126.3 (3 peaks), 125.3, 123.9, 123.8 (q, *J* = 31.4 Hz),122.0, 121.5 (d, *J* = 3.0 Hz), 65.2, 39.4, 37.5, 30.4, 29.6, 21.6, 21.5, 21.3, 20.9.

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CD_2Cl_2$): δ -61.8 (s)

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CD_2Cl_2$): δ 38.1 (s), -15.6 (s).

**Stoichiometric olefin insertion into Pd[(*R*)-Xyl-SDP(O)](*p*-$CF_3$-phenyl)(I) in the presence of AgOTf.** In an argon-filled glove box, Pd[(*R*)-Xyl-SDP(O)](*p*-$CF_3$-phenyl) (29 mg, 0.026 mmol) was dissolved in 1,4-dioxane (0.50 mL) in a 4-mL vial. GC standard *n*-$C_{14}H_{30}$ (20 μL), *i*$Pr_2$NEt (47 μL, 0.26 mmol) and 2,3-dihydrofuran (19 mg, 0.26 mmol) were added, followed by AgOTf (11 mg, 0.043 mmol). The whole vial was covered with aluminum foil to shield the reaction from light. The mixture was stirred at RT with aliquots taken at intervals for GC analysis. GC yields of the product were determined to be 41% (15 min), 61% (1 h), 63% (3 h) and 65% (18 h). The olefinic selectivity of the Heck product in the crude mixture at the end was 85:1 and the ee was 98%.

## VII. References

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