Supporting Information

for

Synthesis of axially chiral gold complexes and their applications in asymmetric catalyses

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**General remarks.** Dichloromethane was freshly distilled from calcium hydride; THF and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR and $^{31}$P NMR spectra were recorded on a Bruker AM-400 spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm$^{-1}$. Flash column chromatography was performed using 300–400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF$_{254}$) were used. Elementary analysis was taken on a Carlo-Erba 1106 analyzer. Mass spectra were recorded by ESI, and HRMS were measured on a HP-5989 instrument.

**Synthesis of NHC–Au(I) complexes**

**Synthesis of (S)-2'-(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalen]-2-ol (6)**

![Synthesis of (S)-2'-(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalen]-2-ol (6)]

Tf$_2$O (1.18 mL, 10 mmol) was added dropwise into a solution of (S)-binaphthol (2.86 g, 10 mmol) and iPr$_2$NEt (1.74 mL, 10 mmol) in CH$_2$Cl$_2$ (50 mL) at 0 °C under argon. The reaction mixture was stirred for 1 h at this temperature and then quenched with saturated NaHCO$_3$. Extractive workup was performed with CH$_2$Cl$_2$, and the combined extracts were washed with brine and dried over anhydrous Na$_2$SO$_4$. The solvents was evaporation, then dried under vacuum, the crude product and NiCl$_2$(dppe) (530 mg, 1 mmol) was dissolved into THF (40 mL) under argon. To this solution was added dropwise a 1 M THF solution of 3,5-bis(trifluoromethyl)phenyl magnesium bromide (60 mL, 60 mmol) at 0 °C, and stirring was continued under reflux for overnight. The reaction was quenched with saturated NH$_4$Cl carefully and extractive workup was conducted with EA. The organic extracts were washed with brine and dried over anhydrous Na$_2$SO$_4$. Removal of solvents and purification of the residual oil by column
chromatography on silica gel afforded (S)-6 (1.59 g, 3.3 mmol, 33% yield) as yellow powder. This is a known compound. \(^1\) \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS): \(\delta\) 8.10 (d, \(J = 8.4\) Hz, 1H, ArH), 8.01 (d, \(J = 8.0\) Hz, 1H, ArH), 7.77 (t, \(J = 9.2\) Hz, 2H, ArH), 7.66 (d, \(J = 8.4\) Hz, 1H, ArH), 7.59-7.53 (m, 4H, ArH), 7.45-7.37 (m, 2H, ArH), 7.28-7.19 (m, 2H, ArH), 7.12 (d, \(J = 9.2\) Hz, 1H, ArH), 6.98 (d, \(J = 8.4\) Hz, 1H, ArH), 4.81 (br, 1H, OH); \(^1\)\(^9\)F NMR (376 MHz, CDCl\(_3\), CFCl\(_3\)): \(\delta\) -63.107.

\[\text{Diagram of compound (S)-6}\]
Synthesis of (S)-2’-(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalen]-2-yl trifluoromethanesulfonate (7)

2-hydroxy-1,1’-binaphthyl derivative 6 (1.45 g, 3.0 mmol) was dissolved into dry CH₂Cl₂ (12 mL) at 0 °C. Then pyridine (0.7 mL, 9.0 mmol) was added, followed by slow syringe addition of triflic anhydride (1.27 g, 4.5 mmol). The reaction mixture was returned to room temperature slowly. After complete consumption of starting material as monitored by TLC, the solution volume was doubled with CH₂Cl₂. The mixture was washed with 1.0 N HCl, followed by water and saturated NaHCO₃. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was evaporated and dried under vacuum to yield the solid triflate 7 (1.83 g, 99% yield). This is a known compound.¹ ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.16 (d, J = 8.4 Hz, 1H, ArH), 8.02 (d, J = 8.0 Hz, 1H, ArH), 7.97-7.94 (m, 2H, ArH), 7.67 (d, J = 8.8 Hz, 1H, ArH), 7.60-7.55 (m, 3H, ArH), 7.48-7.44 (m, 3H, ArH), 7.42-7.36 (m, 2H, ArH), 7.30-7.26 (m, 2H, ArH); ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -63.325, -75.020.
Synthesis of (S)-N-benzyl-2'-(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalen]-2-amine (8)

Pd(OAc)$_2$ (34 mg, 0.15 mmol) and xantphos [4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; 174 mg, 0.3 mmol], freshly prepared triflate (S)-7 (1.83 g, 3 mmol) and Cs$_2$CO$_3$ (1.97 g, 6 mmol), were added to freshly distilled dry toluene (9 mL) in a sealable reaction vessel under argon, and the reaction mixture was stirred at rt. After 5 min, benzylamine (0.4 mL, 3.6 mmol) was added under argon. The mixture was stirred for 3 d at 80 °C. The reaction mixture was then cooled to room temperature, diluted with EA, and filtered through celite. The organic extracts were washed with brine and dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated to obtain crude product. The pure product (S)-8 (976 mg, 57% yield) was purified by flash chromatography on silica gel using CH$_2$Cl$_2$/hexanes as the eluent. This is a known compound.\(^1\)\(^1\)H NMR (400 MHz, CDCl$_3$, TMS): \(\delta\) 8.09 (d, \(J = 8.4\) Hz, 1H, ArH), 8.00 (d, \(J = 8.4\) Hz, 1H, ArH).
8.4 Hz, 1H, ArH), 7.71-7.65 (m, 5H, ArH), 7.58-7.54 (m, 2H, ArH), 7.47 (d, $J = 8.0$ Hz, 1H, ArH), 7.40-7.35 (m, 1H, ArH), 7.24-7.10 (m, 5H, ArH), 7.03-7.00 (m, 2H, ArH), 6.95 (d, $J = 9.2$ Hz, 1H, ArH), 6.85-6.82 (m, 1H, ArH), 4.28 (s, 2H, CH$_2$), 3.87 (br, 1H, NH); $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$): $\delta$ -63.020; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.7, 143.1, 139.3, 137.6, 134.0, 133.9, 132.8, 132.7, 130.5 (d, $^2J(C,F) = 33$ Hz), 129.8, 129.3, 129.03, 129.02, 128.5, 128.3, 128.1, 127.4, 127.3, 127.1, 127.03, 127.02, 126.8, 126.62, 126.58, 123.4, 123.1 (d, $^1J(C,F) = 271$ Hz), 121.9, 120.3 (septet, $^3J(C,F) = 3.7$ Hz), 114.1, 113.5, 47.8.
Synthesis of (S)-2'-(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalen]-2-amine (9)

A solution of 2-benzylamino-1,1'-binaphthyl derivative (S)-8 (856 mg, 1.5 mmol) was dissolved in MeOH (12 mL) in an oven-dried two-neck flask equipped with a argon supply. Under argon, 5% Pd/C (86 mg) was added. The argon atmosphere was then removed under vacuum, and the apparatus was placed under 1 atm of H₂ (hydrogen balloon). The mixture was stirred for overnight under reflux, until complete consumption of starting material was indicated by TLC. The hydrogen atmosphere was then removed under vacuum, and the reaction mixture was flushed generously with nitrogen. The suspended Pd/C was removed by filtration through celite, and the solvent was evaporated to obtain the solid product (S)-9 (685 mg, 95% yield). They are indefinitely stable if stored in a argon atmosphere. This is a known compound.¹

¹¹H NMR (400 MHz, CDCl₃, TMS): δ 8.09 (d, J = 8.8 Hz, 1H, ArH), 8.00 (d, J = 8.0 Hz, 1H, ArH), 7.70-7.65 (m, 5H, ArH), 7.55 (t, J = 8.0 Hz, 1H, ArH), 7.52 (s, 1H, ArH), 7.47 (d, J =
8.4 Hz, 1H, ArH), 7.39-7.35 (m, 1H, ArH), 7.15-7.10 (m, 2H, ArH), 6.94 (d, J = 8.8 Hz, 1H, ArH), 6.84-6.82 (m, 1H, ArH), 3.58 (br, 2H, NH); $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$): $\delta$ -63.470; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.1, 142.4, 137.5, 133.83, 133.77, 132.7, 132.5, 130.4 (d, $^2$J(C,F) = 33 Hz), 129.6, 129.1, 129.0, 128.3, 128.0, 127.7, 127.4, 127.3, 126.9, 126.7, 126.4, 123.5, 123.1 (d, $^1$J(C,F) = 271 Hz), 122.2, 120.3, 117.4, 114.4.
Synthesis of (S)-2'-(3,5-bis(trifluoromethyl)phenyl)-N-(2-nitrophenyl)-[1,1'-binaphthalen]-2-amine (10)

A mixture of 2-amino-1,1'-binaphthyl derivative (S)-9 (673 mg, 1.4 mmol), 1-bromo-2-nitrobenzene (563 mg, 2.8 mmol), Pd\(_2\)(dba)\(_3\) (64 mg, 0.07 mmol), DPE-phos (77 mg, 0.14 mmol) and Cs\(_2\)CO\(_3\) (913 mg, 2.8 mmol) was dissolved into toluene (6.0 mL) under argon. The mixture was stirred at 80 °C for 3 d. The reaction mixture was then cooled to room temperature, diluted with EA, and filtered through celite. The organic extracts were washed with brine and dried over anhydrous Na\(_2\)SO\(_4\). The solvent was evaporated to obtain crude product. The pure product (S)-10 (792 mg, 94% yield) was purified by flash chromatography on silica gel using PE/EA as the eluent. This is a new compound. [\(\alpha\)]\(_{20}\)^D 26.7 (c 0.25, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS): \(\delta\) 8.83 (s, 1H, NH), 8.11 (d, \(J = 8.8\) Hz, 1H, ArH), 8.02 (d,
$J = 8.0 \text{ Hz, 1H, ArH}, 7.98 (\text{dd}, J_1 = 8.8 \text{ Hz}, J_2 = 1.6 \text{ Hz, 1H, ArH}), 7.89-7.87 (\text{m, 2H, ArH}), 7.65 (\text{d, } J = 8.4 \text{ Hz, 1H, ArH}), 7.58-7.54 (\text{m, 1H, ArH}), 7.51 (\text{s, 1H, ArH}), 7.49 (\text{d, } J = 9.2 \text{ Hz, 1H, ArH}), 7.46-7.42 (\text{m, 3H, ArH}), 7.39-7.34 (\text{m, 3H, ArH}), 7.29 (\text{d, } J = 8.4 \text{ Hz, 1H, ArH}), 7.19-7.15 (\text{m, 1H, ArH}), 6.76 (\text{d, } J = 8.8 \text{ Hz, 1H, ArH}), 6.70-6.66 (\text{m, 1H, ArH}); ^{19}\text{F NMR (376 MHz, CDCl}_3, \text{CFCl}_3): } \delta -63.480; ^{13}\text{C NMR (100 MHz, CDCl}_3): \delta 142.9, 140.8, 136.6, 135.3, 135.0, 134.6, 133.6, 133.5, 132.5, 131.8, 130.7, 130.6 (\text{d, } ^2J(C,F) = 33 \text{ Hz}), 129.7, 129.3, 129.1, 128.6, 128.3, 127.6, 127.5, 127.10, 127.06, 127.0, 126.5, 126.0, 125.6, 125.4, 122.8 (\text{d, } ^1J(C,F) = 271 \text{ Hz}), 121.3, 120.3 (\text{septet, } ^3J(C,F) = 3.7 \text{ Hz}), 118.2, 115.0; \text{IR (CH}_2\text{Cl}_2): } v 2962, 1612, 1496, 1277, 1259, 1128, 1090, 1015, 797, 737, 707, 680 \text{ cm}^{-1}; \text{MS (m/z): HRMS (ESI) Calcd. for C}_{34}\text{H}_{21}\text{F}_6\text{N}_2\text{O}_2 ([M+H]^+); 603.1502. Found: 603.1489.
Synthesis of \((S)-N^1-(2'-(3,5\text{-bis(trifluoromethyl)}phenyl)-[1,1'\text{-binaphthalen}]-2\text{-y})\text{yl}benzene-1,2-diamine (11)\)

\[
\begin{align*}
\text{10} & \xrightarrow{\text{H}_2 (1 \text{ atm})} \text{Pd/C, MeOH} \rightarrow \text{11 (95% yield)}
\end{align*}
\]

A mixture of 1,1’-binaphthyl derivative \((S)-10\) (782 mg, 1.3 mol) and 10\% Pd/C (78 mg) was dissolved into MeOH (6 mL) under argon. The argon atmosphere was then removed under vacuum, and the apparatus was placed under 1 atm of H\(_2\) (hydrogen balloon). The mixture was stirred for overnight under reflux, until complete consumption of starting material was indicated by TLC. The hydrogen atmosphere was then removed under vacuum. The suspended Pd/C was removed by filtration through celite. The solvent was evaporated to obtain crude product \((S)-11\) (706 mg, 95\% yield). This is a new compound. \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS): \(\delta\) 8.11 (d, \(J = 8.0\) Hz, 1H, ArH), 8.01 (d, \(J = 8.0\) Hz, 1H, ArH), 7.73-7.66 (m, 5H, ArH), 7.59-7.54 (m, 3H, ArH), 7.42-7.38 (m, 1H, ArH), 7.22-7.18 (m, 2H, ArH), 7.01-6.97 (m, 1H, ArH), 6.96-6.91 (m, 1H, ArH), 6.89 (d, \(J = 9.2\) Hz, 1H, ArH), 6.65-6.58 (m, 3H, ArH), 4.71 (s, 1H, NH), 3.42 (br, 2H, NH\(_2\)); \(^{19}\)F NMR (376 MHz, CDCl\(_3\), CFCl\(_3\)): \(\delta -63.382;\) \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 143.1, 142.7, 141.7, 137.6, 134.3, 133.9, 132.8, 132.4, 130.6 (d, \(^2\)J(C,F) = 33 Hz), 129.6, 129.5, 129.1, 128.5, 128.2, 128.0, 127.5, 127.4, 127.3, 127.1, 127.0, 126.5, 126.2, 126.1, 123.8, 123.0 (d, \(^1\)J(C,F) = 271 Hz), 122.6, 121.7, 120.4 (septet, \(^3\)J(C,F) = 3.6 Hz), 118.9, 115.73, 115.71, 115.69. IR (CH\(_2\)Cl\(_2\)): \(\nu\) 3482, 3381, 3057, 2927, 1620, 1385, 1277, 1178, 1129, 813, 739, 708, 681 cm\(^{-1}\). MS (m/z): HRMS (ESI) Calcd. for C\(_{34}\)H\(_{22}\)F\(_6\)N\(_2\) ([M+H]\(^+\)); 572.1687. Found: 572.1690.
Synthesis of (S)-1-(2’-(3,5-bis(trifluoromethyl)phenyl)-[1,1’-binaphthalen]-2-yl)-1H-benzo[d]imidazole (12)

To a solution of 1,1’-binaphthyl derivative (S)-11 (686 mg, 1.2 mmol) in HC(OEt)$_3$ (11 mL) under argon a catalytic amount of TsOH was added. The mixture was stirred for overnight at 100 °C. Until complete consumption of starting material was indicated by TLC, the solvent was evaporated to obtain crude product. The (S)-12 (621 mg, 89% yield) was purified by flash chromatography on silica gel using PE/EA as the eluent. This is a new compound. [$\alpha$]$^{\text{D}}_20$ -42.8 (c 0.05, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ 8.10 (t, $J$ = 8.4 Hz, 2H, ArH), 8.02 (d, $J$ = 8.4 Hz, 2H, ArH), 7.67-7.59 (m, 3H, ArH), 7.53-7.44 (m, 6H, ArH), 7.38 (d, $J$ = 8.4 Hz, 1H, ArH), 7.19-7.15 (m, 1H, ArH), 6.97-6.93 (m, 2H, ArH), 6.80 (s, 2H, ArH), 6.32 (d, $J$ = 8.0 Hz, 1H, ArH); $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$): $\delta$ -63.128;
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 142.5, 142.0, 141.9, 135.8, 135.0, 133.9, 133.2, 133.1, 132.4, 132.3, 131.2, 130.76, 130.71 (d, $^2J(C,F) = 33$ Hz), 130.3, 130.0, 128.8, 128.7, 128.4, 128.3, 128.0, 127.3, 127.1, 127.0, 126.8, 126.5, 123.7, 123.6, 122.65, 122.62 (d, $^1J(C,F) = 271$ Hz), 120.4, 120.0, 108.6. IR (CH$_2$Cl$_2$): v 2917, 2849, 1490, 1455, 1386, 1278, 1264, 1183, 1135, 820, 799, 737, 707 cm$^{-1}$; MS (m/z): HRMS (ESI) Calcd. for C$_{35}$H$_{21}$F$_6$N$_2$ ([M+H]$^+$); 583.1603. Found: 583.1600.
The compound (S)-12 (291 mg, 0.5 mmol) and CH$_3$I (0.1 mL, 2.0 mmol) in CH$_3$CN (2.0 mL) were stirred under reflux for 5 h. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid compound (S)-13 (362 mg, quantitative yield) was used for the next reaction without further purification.
Synthesis of compound (S)-14

The compound (S)-12 (291 mg, 0.5 mmol) and BnBr (0.1 mL, 1.0 mmol) in dioxane (2.0 mL) were stirred under reflux for 5 h. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid compound (S)-14 (376 mg, quantitative yield) was used for the next reaction without further purification.

Synthesis of gold-complexes (S)-15a and (S)-15b

The compound (S)-13 (145 mg, 0.2 mmol) and AuCl·S(Me)₂ (59 mg, 0.2 mmol), NaOAc (33 mg, 0.4 mmol) were refluxed in CH₃CN (2 mL) for overnight. The volatiles were then removed under reduced pressure and the residue was purified by a silica gel flash column chromatography to afford (S)-15a (84 mg, 46% yield) and (S)-15b (68 mg, 37% yield). A single crystal grown from gold-complex (S)-15a or (S)-15b in a saturated solution of CH₂Cl₂/pentane was suitable for X-ray crystal analysis. (S)-15a: white
solid; [α]D20 -64.7 (c 0.10, CH2Cl2); 1H NMR (400 MHz, CDCl3, TMS): δ 8.17-8.13 (m, 2H, ArH), 7.94 (d, J = 8.8 Hz, 1H, ArH), 7.90-7.88 (m, 1H, ArH), 7.74-7.70 (m, 1H, ArH), 7.66-7.59 (m, 3H, ArH), 7.56-7.50 (m, 2H, ArH), 7.42 (d, J = 8.4 Hz, 1H, ArH), 7.34-7.28 (m, 4H, ArH), 7.06 (s, 2H, ArH), 6.86-6.82 (m, 1H, ArH), 5.60 (d, J = 8.4 Hz, 1H, ArH), 3.78 (s, 3H, CH3); 19F NMR (376 MHz, CDCl3, CFCl3): δ -63.096; 13C NMR (100 MHz, CDCl3): δ 141.5, 140.8, 134.9, 134.5, 133.4, 132.9, 132.6, 131.3, 131.0, 130.9, 130.7, 129.9, 129.2, 129.1, 129.0, 128.5, 128.41, 128.37, 127.9, 127.6, 127.3, 126.9, 126.8, 126.4, 123.7, 123.4, 121.0, 120.6, 113.2, 111.4, 34.8. IR (CH2Cl2): ν 3059, 2926, 1594, 1385, 1346, 1277, 1182, 1133, 897, 820, 745, 713 cm⁻¹; MS (m/z): HRMS (ESI) Calcd. for C36H26AuF6IN3 ([M+NH4]+); 938.0736. Found: 938.0728.

Ar = 3.5-2CF3C6H3
(S)-15b: white solid; $[\alpha]_D^{20} -66.1$ (c 1.45, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ 8.17 (d, $J = 8.4$ Hz, 1H, ArH), 8.13 (d, $J = 8.0$ Hz, 1H, ArH), 7.85 (d, $J = 8.0$ Hz, 1H, ArH), 7.79-7.69 (m, 4H, ArH), 7.63 (d, $J = 8.0$ Hz, 1H, ArH), 7.59-7.54 (m, 3H, ArH), 7.50-7.46 (m, 1H, ArH), 7.23 (d, $J = 8.8$ Hz, 2H, ArH), 7.17 (s, 2H, ArH), 7.08-7.04 (m, 1H, ArH), 6.47-6.42 (m, 2H, ArH), 3.94 (s, 3H, CH$_3$);

$^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$): $\delta$ -62.451; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 134.6, 134.5, 134.1, 134.6.
134.0, 133.6, 131.4, 131.34, 131.27, 129.1, 129.0, 128.8, 128.66, 128.58, 128.5, 128.3, 128.2, 127.8, 126.9, 126.5, 124.1, 123.4, 118.6, 31.9. IR (CH₂Cl₂): ν 2923, 2851, 1726, 1465, 1387, 1277, 1181, 1131, 894, 823, 743, 712, 681 cm⁻¹; MS (m/z): HRMS (ESI) Calcd. for C₃₆H₂₆AuF₆IN₃ ([M +NH₄]⁺); 938.0736. Found: 938.0725.

![Chemical structure](image1)

\[ Ar = 3.5-2 \text{CF}_3\text{C}_6\text{H}_3 \]

![Chemical structure](image2)

\[ Ar = 3.5-2 \text{CF}_3\text{C}_6\text{H}_3 \]
Synthesis of gold complex (S)-16

The compound (S)-14 (152 mg, 0.2 mmol) and AuCl·S(Me)₂ (59 mg, 0.2 mmol), NaOAc (33 mg, 0.4 mmol) were refluxed in CH₃CN (2 mL) for overnight. The volatiles were then removed under reduced pressure and the residue was purified by a silica gel flash column chromatography. Gold complex (S)-16 (142 mg, 75% total yield) was obtained as mixture: white solid; [α]₂₀° -82.2 (c 0.75, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.21-8.11 (m, 5H, ArH), 8.02 (d, J = 8.8 Hz, 2H, ArH), 7.95 (d, J = 8.4 Hz, 2H, ArH), 7.85-7.42 (m, 29H, ArH), 7.35-7.26 (m, 15H, ArH), 7.20-7.18 (m, 2H, ArH), 7.14-7.13 (m, 4H, ArH), 7.06 (d, J = 8.0 Hz, 1H, ArH), 6.95-6.92 (m, 5H, ArH), 6.80-6.75 (m, 6H, ArH), 6.52 (d, J = 8.0 Hz, 1H, ArH), 6.47-6.43 (m, 1H, ArH), 5.84 (d, J = 15.6 Hz, 1H, CH₂), 5.75-5.72 (m, 4H, ArH and CH₂), 5.36 (d, J = 15.6 Hz, 1H, CH₂), 5.14 (d, J = 15.2 Hz, 2H, CH₂); ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -62.571, -63.093; ¹³C NMR (100 MHz, CDCl₃): δ 142.4, 135.3, 134.45, 134.38, 133.3, 132.8, 132.5, 130.70, 130.66, 130.59, 130.0, 129.8, 129.2, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 127.9, 127.8, 127.68, 127.56, 127.4, 127.2, 127.14, 127.05, 126.9, 126.8, 126.6, 125.4, 124.53, 124.46, 124.2, 123.0, 120.5, 111.5, 110.8, 52.6. IR (CH₂Cl₂): ν 3061, 2924, 1594, 1478, 1406, 1278, 1182, 1133, 897,
820, 745, 706 cm\(^{-1}\); MS (m/z): HRMS (ESI) Calcd. for C\(_{42}\)H\(_{30}\)AuBr\(_6\)N\(_3\) ([M +NH\(_4^+\)]\(^+\)); 966.1187. Found: 966.1185.
The synthesis of P–Au(I) complexes

(S)-2′-(diphenylphosphino)-1,1′-binaphthyl-2-ol (17) was prepared according to published literature procedures.2

Synthesis of gold-complex (S)-18

The compound (S)-17 (454 mg, 1.0 mmol) and AuCl·S(Me)2 (294 mg, 1.0 mmol) were stirred in CH3CN (10 mL) for overnight. The volatiles were then removed under reduced pressure and the residue was purified by a silica gel flash column chromatography to afford pure product (S)-18 (603 mg, 88% yield). A single crystal grown from gold complex (S)-18 in a saturated solution of CH2Cl2/pentane was
suitable for X-ray crystal analysis. white solid; $[\alpha]^{20}_D$ -35.4 (c 0.20, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ 7.99-7.93 (m, 3H, ArH), 7.80 (d, $J = 8.4$ Hz, 1H, ArH), 7.60-7.56 (m, 1H, ArH), 7.50-7.45 (m, 3H, ArH), 7.42-7.17 (m, 12H, ArH), 6.86-6.82 (m, 1H, ArH), 6.45 (d, $J = 8.4$ Hz, 1H, ArH), 5.17 (br, 1H, OH); $^{31}$P NMR (162 MHz, CDCl$_3$, 85% H$_3$PO$_4$): $\delta$ 26.116; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 141.8, 136.5, 134.4, 133.7, 133.24, 133.22, 133.1, 132.39, 132.35, 130.5, 130.2, 129.8, 129.0, 128.9, 128.6, 128.4, 127.6, 127.3, 127.2, 127.1, 127.0, 126.6, 124.2, 123.7, 123.0, 112.6, 110.4. IR (CH$_2$Cl$_2$): $\nu$ 3359, 3055, 2924, 1623, 1513, 1435, 1269, 1098, 972, 937, 814, 743, 692 cm$^{-1}$; MS (m/z): HRMS (ESI) Calcd. for C$_{32}$H$_{27}$AuClNOP ($[\text{M+NH}_4]^+$); 704.1179. Found: 704.1170.
(S)-2'-(diphenylphosphoryl)-1,1'-binaphthyl-2-yl trifluoromethanesulfonate 19 was prepared according to the previous literature procedures.²

Synthesis of (S)-diphenyl(2'-phenyl-[1,1'-binaphthalen]-2-yl)phosphine oxide (20)

(S)-2'-(diphenylphosphoryl)-1,1'-binaphthyl-2-yl trifluoromethanesulfonate 19 (3.01 g, 5 mmol) and NiCl₂(dppe) (285 mg, 0.5 mmol) was dissolved into toluene (40 mL) under argon. To this solution was added dropwise a 1 M THF solution of phenylmagnesium bromide (30 mL, 30 mmol) at 0 °C, and stirring was continued under reflux for overnight. The reaction was quenched with saturated NH₄Cl carefully and extractive workup was conducted with EA. The organic extracts were washed with brine and dried over anhydrous Na₂SO₄. Removal of solvents and purification of the residual oil by column chromatography on silica gel afforded compound (S)-20 (556 mg, 21% yield) as yellow powder. This is a new compound. white solid; [α]²⁰D -168.3 (c 0.80, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.88 (d, J = 8.4 Hz, 1H, ArH), 7.85-7.82 (m, 2H, ArH), 7.78 (d, J = 8.0 Hz, 1H, ArH), 7.56-7.47 (m, 3H, ArH), 7.35-7.28 (m, 5H, ArH), 7.17-7.00 (m, 12H, ArH), 6.94 (t, J = 8.0 Hz, 2H, ArH), 6.87 (d, J = 8.8 Hz, 1H, ArH). ³¹P NMR (162 MHz, CDCl₃, 85% H₃PO₄): δ 33.064; ¹³C NMR (100 MHz, CDCl₃): δ 143.7, 143.6, 141.2, 139.1, 134.7, 134.6, 133.85, 133.82, 133.2, 132.7, 132.34, 132.29, 132.14, 132.09, 131.7, 131.49, 131.47, 131.39, 131.38, 131.30, 131.28, 131.17, 131.14, 131.09, 129.4, 128.8, 128.7, 128.6, 128.3, 128.1, 128.04, 128.02, 127.9, 127.8, 127.7, 127.64, 127.62, 127.47, 127.44, 127.3, 127.27,
127.1, 126.8, 126.3, 126.0, 125.3; IR (CH₂Cl₂): ν 3054, 1591, 1495, 1436, 1200, 1115, 1028, 873, 819, 762, 722, 694 cm⁻¹; MS (m/z): HRMS (ESI) Calcd. for C₃₈H₂₈OP ([M+H]+); 531.1872. Found: 531.1865.
Synthesis of (S)-diphenyl(2'-phenyl-[1,1'-binaphthalen]-2-yl)phosphine (21)

Et$_3$N (0.3 mL, 2 mmol) was added dropwise to a solution of compound (S)-20 in toluene (530 mg, 1.0 mmol) under argon. This solution was added SiHCl$_3$ (0.2 mL, 2.0 mmol) under an ice-water bath, and stirring was continued at 120 °C for overnight. The reaction was quenched with saturated NH$_4$Cl carefully and extractive workup was conducted with EA. The organic extracts were washed with brine and dried over anhydrous Na$_2$SO$_4$. Removal of solvents and purification of the residual oil by column
chromatography on silica gel afforded compound (S)-21 (416 mg, 81% yield) as yellow powder. This is a known compound. white solid; $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ 8.04 (d, $J$ = 8.4 Hz, 1H, ArH), 7.89 (d, $J$ = 8.0 Hz, 1H, ArH), 7.83 (d, $J$ = 8.0 Hz, 1H, ArH), 7.72 (d, $J$ = 8.4 Hz, 1H, ArH), 7.65 (d, $J$ = 8.4 Hz, 1H, ArH), 7.46 (t, $J$ = 8.0 Hz, 1H, ArH), 7.42 (d, $J$ = 8.8 Hz, 1H, ArH), 7.35-7.28 (m, 2H, ArH), 7.23-7.20 (m, 1H, ArH), 7.14 (d, $J$ = 7.2 Hz, 1H, ArH), 7.10-7.01 (m, 8H, ArH), 6.97-6.88 (m, 5H, ArH), 6.77 (d, $J$ = 8.8 Hz, 1H, ArH), 6.60 (t, $J$ = 7.2 Hz, 2H, ArH). $^{31}$P NMR (162 MHz, CDCl$_3$, 85% H$_3$PO$_4$): $\delta$ -13.790; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.8, 144.5, 141.8, 139.55, 139.52, 138.2, 138.0, 137.5, 137.4, 135.2, 135.1, 134.9, 134.8, 134.5, 134.4, 133.9, 133.7, 133.36, 133.35, 133.02, 133.01, 132.38, 132.37, 132.2, 130.7, 129.4, 128.4, 128.3, 128.2, 128.0, 127.98, 127.94, 127.90, 127.89, 127.86, 127.7, 127.60, 127.57, 127.4, 127.2, 126.6, 126.3, 125.9, 125.4; IR (CH$_2$Cl$_2$): v 3053, 1585, 1494, 1434, 1264, 1206, 1115, 1027, 894, 818, 739, 697, 675 cm$^{-1}$; MS (m/z): HRMS (ESI) Calcd. for C$_{38}$H$_{28}$P ([M+H]$^+$); 515.1923. Found: 515.1921.
Synthesis of gold complex (S)-22

The compound (S)-21 (257 mg, 0.5 mmol) and AuCl·S(Me)₂ (147 mg, 0.5 mmol) were stirred in CH₃CN (5 mL) for overnight. The volatiles were then removed under reduced pressure and the residue was purified by a silica gel flash column chromatography to afford (S)-22 (339 mg, 91% yield). A single crystal grown from gold complex 22 in a solution of CH₂Cl₂/pentane was suitable for X-ray crystal
analysis. white solid; $\alpha^{20}_D$ -80.7 (c 0.95, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ 8.27 (d, $J = 8.8$ Hz, 1H, ArH), 8.05 (d, $J = 8.4$ Hz, 1H, ArH), 7.90 (d, $J = 8.0$ Hz, 1H, ArH), 7.84 (d, $J = 8.4$ Hz, 1H, ArH), 7.67 (d, $J = 8.4$ Hz, 1H, ArH), 7.62-7.57 (m, 1H, ArH), 7.47 (t, $J = 7.6$ Hz, 1H, ArH), 7.40-7.35 (m, 4H, ArH), 7.28-7.24 (m, 2H, ArH), 7.22-7.12 (m, 6H, ArH), 6.97 (d, $J = 7.6$ Hz, 2H, ArH), 6.92 (t, $J = 7.2$ Hz, 2H, ArH), 6.88 (d, $J = 7.6$ Hz, 1H, ArH), 6.84 (d, $J = 8.8$ Hz, 1H, ArH), 6.77 (t, $J = 7.6$ Hz, 2H, ArH); $^{31}$P NMR (162 MHz, CDCl$_3$, 85% H$_3$PO$_4$): $\delta$ 22.898, 22.825, 22.751, 22.697; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 151.4, 134.6, 134.4, 134.1, 133.9, 133.7, 133.5, 133.2, 133.1, 131.5, 131.44, 131.37, 131.35, 131.25, 129.9, 129.3, 129.04, 128.98, 128.92, 128.89, 128.87, 128.85, 128.84, 128.7, 128.64, 128.59, 128.51, 128.4, 128.3, 128.2, 127.8, 127.5, 126.81, 126.80, 126.6, 126.5, 126.47, 126.1, 126.0, 124.1, 123.4. IR (CH$_2$Cl$_2$): $\nu$ 3054, 1589, 1494, 1480, 1436, 1306, 1265, 1098, 1027, 819, 763, 744, 698 cm$^{-1}$; MS (m/z): HRMS (ESI) Calcd. for C$_{38}$H$_{31}$AuClNP ([M+NH$_4$]+); 764.1543. Found: 764.1532.
Typical procedure for intramolecular hydroamination reaction

A mixture of Au catalyst (5 mol %) and AgX (5 mol %) in solvent (0.5 mL) was stirred at room temperature for 5 min under argon, then a solution of compound 24 (76.6 mg, 0.20 mmol) in solvent (0.5 mL) was added into the resulting solution. The resulting suspension was stirred at 85 °C for 36 h. Column chromatography of the reaction mixture gave the desired product. The enantiomeric purity of the product was determined by chiral HPLC analysis.

Compound 24 was prepared according to the previously reported method.

2-methyl-4,4-diphenyl-1-tosylpyrrolidine (25): ¹H NMR (400MHz, CDCl₃, TMS): δ 7.61 (d, J = 8.0 Hz, 2H, ArH), 7.27-7.09 (m, 12H, ArH), 4.17 (d, J = 10.4 Hz, 1H, CH₂), 3.94 (dd, J₁ = 10.4 Hz, J₂ = 0.4 Hz, 1H, CH₂), 3.82-3.74 (m, 1H, CH), 2.78 (ddd, J₁ = 12.4 Hz, J₂ = 7.2 Hz, J₃ = 0.4 Hz, 1H, CH₂), 2.38 (s, 3H, CH₃), 2.26 (dd, J₁ = 12.4 Hz, J₂ = 7.2 Hz, 1H, CH₂), 1.25 (d, J = 6.4 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 145.6, 144.8, 142.9, 135.3, 129.5, 128.43, 128.42, 128.4, 127.1, 126.6, 126.42, 126.39, 126.2, 58.3, 55.4, 52.2, 45.9, 22.1, 21.4; [α]D²⁰ 20.1 (c 1.2, CH₂Cl₂), for 29% ee; Chiralcel PA-2, hexane/i-PrOH = 60/40, 0.5 mL/min, 214 nm, t_major = 45.07 min, t_minor = 27.49 min.
### Translation

| Peak No. | Peak name | Retention time | Peak height   | Peak area    | Content |
|----------|-----------|----------------|---------------|--------------|---------|
| 1        |           | 27.353         | 1223504.375   | 52971004.000 | 49.0193 |
| 2        |           | 45.495         | 507170.813    | 55090580.000 | 50.9807 |
| Total    |           |                | 1730675.188   | 108061584.000| 100.0000 |
### Translation

| Peak No. | Peak name | Retention time | Peak height | Peak area    | Content    |
|----------|-----------|----------------|-------------|--------------|------------|
| 1        |           | 27.495         | 1498459.875 | 73299120.000 | 34.8481    |
| 2        |           | 45.075         | 1066793.250 | 137039824.000 | 65.1519    |
| Total    |           |                | 2565253.125 | 210338944.000 | 100.0000   |
Figure SI-1. The crystal data of compound 23 have been deposited in CCDC with number 920618. Empirical Formula: C_{26}H_{16}; Formula Weight: 328.39; Crystal Color, colorless; Crystal Dimensions: 0.212 x 0.156 x 0.113 mm; Crystal System: Monoclinic; Lattice Parameters: a = 5.8492(16)Å, b = 13.351(4)Å, c = 21.102(6)Å; α = 90°, β = 91.971(5)°, γ = 90°; V = 1646.9(8)Å³; Space group: P2(1)/n; Z = 4; D_{calc} = 1.324 g/cm³; F_{000} = 688; Final R indices [I>2sigma(I)]: R1 = 0.0678; wR2 = 0.1630.
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