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Supporting Information

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New, Readily Available Biaryl P,N-Ligands for Asymmetric Catalysis**

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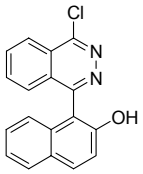
General:
All reactions were performed in oven dried glass ware under argon. For the reactions, solvents were purified by distillation and dried by passage over activated alumina under an argon atmosphere (H_2O content < 30 ppm, *Karl-Fischer* titration). DMF was not distilled but dried over molecular sieves (4Å). Dichloroethane was used as received by Fluka. For hydroboration reactions: Solvents were degassed by bubbling through argon for 1 h. Catecholborane was distilled under vacuum just before use. For cycloadditions: Tetrahydrofuran (THF) was degassed by bubbling through argon for 1 h. *N*,*N*-diisopropylethylamine was distilled under nitrogen from calcium hydride. For alkyne/imine additions: Alkynes and aldehydes were freshly distilled prior to use. For flash chromatography and extractions technical grade solvents were used, which were distilled prior to use. All chemicals were purchased from ACROS, Aldrich, Fluka, Lancaster or STREM and used as received unless noted otherwise.
Chromatographic purification was performed as flash chromatography using Merck silica gel 60 with 0.1-0.4 bar pressure of N_2.
TLC was performed on Merck silica gel 60 F_{254} TLC glass plates and visualized with UV light and/or permanganate stain.
^{1}H-NMR spectra were recorded on a VARIAN Mercury 300 MHz or a Bruker AMX-400 400 MHz spectrometer in chloroform-*d* or DMSO-d_6. All signals are reported in ppm relative to TMS. The data is reported as (s=singlet, d=doublet, t=triplet, q=quartet, quint=quintet, m=multiplet or unsolved signal, br=broad, coupling constant(s) in Hz, integration).
^{13}C-NMR spectra were recorded with ^{1}H-decoupling on VARIAN Mercury 75 MHz or Bruker AMX-400 100 MHz spectrometer in chloroform-*d*, all signals are reported in ppm relative to TMS, multipilcity was assigned by recording DEPT spectra. For the P-containing compounds: P-C couplings in ^{13}C-NMR were not assigned. For diastereomeric mixtures: multiplicity in ^{13}C-NMR was not assigned.
^{31}P-NMR spectra were recorded with ^{1}H-decoupling on VARIAN Mercury 120 MHz spectrometer in chloroform-*d*, all signals are reported in ppm relative to 85% H_3PO_4 in water.
Infrared spectra were recorded on a Perkin-Elmer spectrum RX-I FT-IR spectrometer as thin films. The data is being reported as absorption maxima (ν, cm^{-1}) with corresponding characteristic intensity (w=weak, m=medium, s=strong, br=broad).

Melting points were measured on a Buechi 510 melting point apparatus using open glass capillaries and are uncorrected. Mass spectrometric measurements were performed by the mass spectrometry service of the LOC at the ETHZ.
Combustion analyses were performed by the Mikroelementarische Laboratorium of the LOC at the ETHZ.
Enantiomeric excesses were determined by chiral HPLC analysis with Merck-Hitachi D-7000 system. Solvent mixtures, conditions, retention times and Chiracel columns used are given in parentheses.
Optical rotation $[\alpha]_D$ were measured by Jasco DID-1000 Polarimeter, 10 cm, 1 ml cell. Concentration (c, g/100 ml), solvent of the each sample are given in parentheses.
1,4-Dichloro-phthalazine[1] (commercially available form Aldrich), $[Rh(cod)_2]BF_4$,[2] and α-iminoesters[3] were prepared according to literature procedure.



1-(4-Chlorophthalazin-1-yl)-naphthalen-2-ol (**1**).
Improved procedure according to.[4] A solution of 9.96 g (50 mmol) 1,4-dichloro-phthalazine in 180 ml dichloroethane was treated with 7.24 g (50 mmol) 2-naphthol and 7.38 g (55 mmol) $AlCl_3$ and stirred at 80 °C for 17 h. The dark red solution was poured in ice water (600 ml), the resulting brown suspension was stirred vigorously for 1 h. The solid was filtered and washed with diethylether. The solid was dried to give 11.8 g (77%) of the title compound (**1**) as a beige solid.
^{1}H-NMR (300 MHz, DMSO-d_6): 6.99 (d, J = 8.0, 1H), 7.24-7.35 (m, 2H), 7.37 (d, J = 8.9, 1H), 7.49 (d, J = 8.3, 1H), 7.91-8.01 (m, 2H), 8.04 (d, J = 9.0, 1H), 8.13-8.19 (m, 1H), 8.41 (d, J = 8.4, 1H), 9.94 (s, 1H).

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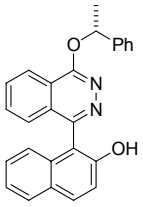
1 Amberg, W.; Bennani, Y. L.; Chadha, R. K.; Crispino, G. A.; Davis, W. D.; Hartung, J.; Jeong, K. S.; Ogino, Y.; Shibata, T.; Sharpless, B. K. *J. Org. Chem*. **1993**, *58*, 844-849.
[2] Schenk, T. G.; Downes, J. M.; Milne, C. R. C.; Mackenzie, P. B.; Boucher, H.; Whelan J.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2334-2337.
[3] Longmire, J. M.; Wang, B.; Zhang, X. *J. Am. Chem. Soc.,* **2002**, *124*, 4236-4238.

Physicochemical data were in agreement with literature[4]



(*R*)-1-[4-(1-Phenylethoxy)-phthalazin-1-yl]-naphthalen-2-ol. To a suspension of 1.21 g (50.4 mmol) NaH in 100 ml THF at 23 °C was added cautiously over 10 min a solution of 3.11 g (25.5 mmol) (*R*)-phenylethanol in 5 ml THF. The mixture was stirred for 15 min, then 7.66 g (25.0 mmol) 1-(4-chlorophthalazin-1-yl)-naphthalen-2-ol (**1**) were added portionwise. The resulting red suspension was stirred for 26 h at 23 °C, then the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and poured into brine. The organic phase was separated and the water phase was extracted two more time with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by FC (hexane/EtOAc 5:1 to 2:1) to give 8.07 g (82%) of the title compound as a 1:1 mixture of diastereomers, as a white foam.

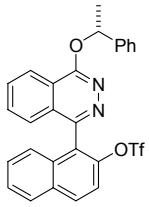
^{1}H-NMR (400 MHz, $CDCl_3$) 1.80 (d, *J* = 6.5, 3H), 1.82 (d, *J* = 6.5, 3H), 6.63-6.70 (m, 2H), 7.05-7.38 (m, 15H), 7.49-7.57 (m, 7H), 7.66-7.80 (m, 5H), 8.30-8.37 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$) 22.6, 22.7, 74.6, 74.7, 114.5, 114.6, 119.4, 119.6, 120.6, 120.7, 123.0, 123.1, 123.1, 124.6, 124.6, 126.2, 126.2, 126.3, 126.9, 127.0, 127.8, 127.8, 128.0, 128.1, 128.5, 128.5, 128.6, 128.6, 129.3, 129.3, 130.9, 132.0, 132.1, 132.1, 132.2, 133.3, 133.3, 142.2, 142.3, 153.8, 153.8, 154.2, 154.2, 159.5, 159.5.

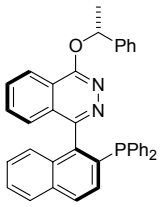
HRMS (MALDI) calcd. for $C_{26}H_{21}N_2O_2$ $[M+H]^+$ 393.1598 found 393.1603.

Anal. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; N, 7.14. Found: C, 79.42; H, 5.25; N, 7.21.

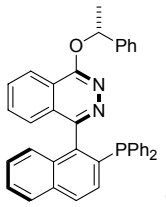
[4] Pal, M.; Batchu, V. R.; Parasuraman, K.; Yeleswarapu, K. *J. Org. Chem.* **2003**, *68*, 6806-6809.



(*R*)-Trifluoromethanesulfonic acid 1-[4-(1-phenylethoxy)-phthalazin-1-yl]-naphthalen-2-yl ester (**2**).
A solution of 0.91 g (2.3 mmol) 1-[4-(1-phenylethoxy)-phthalazin-1-yl]-naphthalen-2-ol in 0.56 ml (6.9 mmol) pyridine and 10 ml dichloromethane at 0 °C was treated dropwise with 0.41 ml (2.4 mmol) triflic anhydride. The resulting solution was stirred at 0 °C for 2 h, quenched with sat. aq. NH_4Cl. The organic layer was separateted and the water phase was washed twice with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by FC (toluene/hexane 20:1) to yield 1.1 g (91%) of the title compound (**2**) as a white foam.
^{1}H-NMR (400 MHz, $CDCl_3$) 1.89 (d, J = 6.5, 3H), 1.91 (d, J = 6.5, 3H), 6.87 (sextet, J = 6.5, 2H), 7.27-7.47 (m, 12H), 7.53-7.64 (m, 6H), 7.65-7.71 (m, 4H), 7.85-7.90 (m, 2H), 7.97-8.01 (m, 2H), 8.09-8.13 (m, 2H), 8.43-8.46 (m, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$) 22.4, 22.5, 74.8, 74.9, 118.0 (q, J_{CF} = 320), 118.2 (q, J_{CF} = 320), 119.5, 119.6, 120.0, 123.4, 123.4, 125.4, 125.4, 125.9, 126.1, 126.3, 126.4, 126.4, 126.5, 126.5, 126.7, 127.2, 127.4, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4, 128.5, 129.1, 129.1, 131.6, 131.7, 132.1, 132.1, 132.3, 132.4, 132.4, 132.4, 133.3, 133.3, 133.5, 142.2, 142.4, 145.3, 145.4, 150.5, 150.6, 159.7, 159.7.
HRMS (MALDI) calcd. for $C_{27}H_{20}F_3N_2O_4S$ $[M+H]^+$ 525.1090 found 525.1085.



(**3a**)



(**3b**)

(*R,M*)-1-(2-Diphenylphosphanylnaphthalen-1-yl)-4-(1-phenylethoxy)-phthalazine (**3a**) and (*R,P*)1-(2-Diphenylphosphanylnaphthalen-1-yl)-4-(1-phenylethoxy)-phthalazine (**3b**).
A solution of 94 mg (0.18 mmol) Ni(dppe)Cl_2 in 5 ml DMF at 23 °C was treated with 0.62 ml (3.56 mmol)

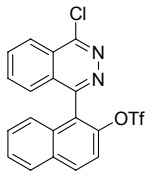
diphenylphosphine. The resulting dark red solution was stirred at 100 °C for 30 min. Then a solution of 1.0 g (1.8 mmol) trifluormethanesulfonic acid 1-[4-(1-phenylethylamino)-phthalazin-1-yl]-naphthalen-2-yl ester (**2**) and 0.80 g (7.1 mmol) DABCO[5] in 5 ml DMF was added via syringe, the flask was washed with 1 ml DMF. The resulting dark green solution was stirred at 100 °C for 14 h. The mixture was concentrated under reduced pressure (20 mbar, 60 °C bath temperature). The residue was purified by FC (toluene → toluene/EtOAc 10:1) to give 750 mg (70%) of the the title compounds (**3a** and **3b**) as an off white solid as a 1:1 mixture of diastereomers.
Pure **3a** can be obtained by slowly crystallizing a 1:1 mixture form CH_2Cl_2/hexane: The CH_2Cl_2 is slowly evaporated under a stream of argon, colorless crystals form which is pure **3a**.
The diastereomers can also be separated by FC (toluene/EtOAc 200:3).

3a: (top spot)
mp: 179-180 °C.
$[\alpha]_D^{27}$ = -160.4 (c= 0.53, $CHCl_3$).
^{1}H-NMR (400 MHz, $CDCl_3$) 1.84 (d, *J* = 6.5, 3H), 6.84 (q, *J* = 6.5, 1H), 7.06 (d, *J* = 8.2, 1H), 7.11-7.32 (m, 13H), 7.35-7.48 (m, 5H), 7.61-7.65 (m, 1H), 7.71-7.76 (m, 1H), 7.85 (d, *J* = 8.2, 1H), 7.88 (d, *J* = 8.3, 1H), 8.35 (d, *J* = 8.2, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) 22.6 (CH_3), 74.4 (CH), 119.8 (C), 123.1 (CH), 126.0 (CH), 126.5 (CH), 126.6 (CH), 126.6 (CH), 126.7 (CH), 126.9 (CH), 127.6 (CH),127.9 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 128.3 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 129.1 (CH), 129.9 (C), 129.9 (C), 130.1 (CH), 131.4 (CH), 131.6 (CH), 133.0 (C), 133.0 (C), 133.1 (CH), 133.3 (CH), 133.5 (C), 133.7 (CH), 133.9 (CH), 135.8 (C), 135.9 (C), 137.1 (C), 137.2 (C), 137.3 (C), 137.5 (C), 141.0 (C), 141.4 (C), 142.7 (C), 156.2 (C), 156.3 (C), 159.2 (C).
^{31}P-NMR (121 MHz, $CDCl_3$) -13.2.
FTIR (KBr, cm^{-1}): 1581 (m), 1537 (m), 1493 (m), 1479 (m), 1378 (s), 1358 (s), 1310 (s), 1056 (m), 884 (m), 819 (m) 741 (s), 692 (s)
HRMS (MALDI) calcd. for $C_{39}H_{29}N_2OP$ $[M+H]^+$ 561.2090 found 561.2089.
Anal. Calcd for $C_{38}H_{29}N_2OP$: C, 81.41; H, 5.21; N, 5.00. Found: C, 81.14; H, 5.32; N, 4.84.

[5] 1,4-Diazabicyclo[2.2.2]octane

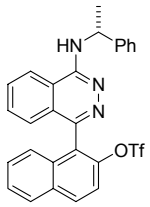
A X-ray grade sample (colorless plate) was obtained after recrystallization from CH_2Cl_2-hexane. X-ray crystallography proved its configuration about axial chirality as *M*.

3b: (bottom spot)
mp: 64-65 °C.
$[\alpha]_D^{25}$ = 78.5 (c= 0.25, $CHCl_3$).
^{1}H-NMR (400 MHz, $CDCl_3$) 1.88 (d, *J* = 6.5, 3H), 6.83 (q, *J* = 6.5, 1H), 7.07-7.76 (m, 14H), 7.39-7.52 (m, 5H), 7.63-7.67 (m, 2H), 7.72-7.78 (m, 1H), 7.87-7.92 (m, 2H), 8.33-8.37 (m, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) 22.5 (CH_3), 74.4 (CH), 119.8 (C), 123.1 (CH), 126.0 (CH), 126.5 (CH), 126.5 (CH), 126.5 (CH), 126.7 (CH), 126.9 (CH), 127.7 (CH), 128.0 (CH), 128.2 (CH), 128.2 (CH), 128.2 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.4 (CH), 129.0 (CH), 129.9 (C), 129.9 (C), 130.0 (CH), 131.4 (CH), 131.7 (CH), 133.0 (C), 133.0 (C), 133.1 (C), 133.3 (CH), 133.5 (CH), 133.6 (CH), 133.8 (CH), 136.2 (C), 136.3 (C), 136.8 (C), 136.9 (C), 137.3 (C), 137.4 (C), 140.7 (C), 141.0 (C), 142.6 (C), 156.2 (C), 156.2 (C), 159.3 (C).
^{31}P-NMR (121 MHz, $CDCl_3$) -12.3
FTIR (KBr, cm^{-1}): 1582 (m), 1537 (m), 1491 (m), 1433 (m), 1410 (m), 1378 (s), 1307 (s), 1164 (w), 1111 (w) 1068 (m), 817 (w), 742 (s), 693 (s)
HRMS (MALDI) calcd. for $C_{39}H_{29}N_2OP$ $[M+H]^+$ 561.2090 found 561.2085.
Anal. Calcd for $C_{38}H_{29}N_2OP$: C, 81.41; H, 5.21; N, 5.00. Found: C, 81.34; H, 5.49; N, 4.86.



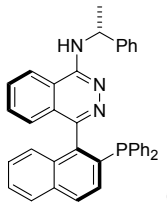
Trifluoromethanesulfonic acid 1-(4-chlorophthalazin-1-yl)-naphthalen-2-yl ester.
A suspension of 1.0 g (3.3 mmol) 1-(4-chlorophthalazin-1-yl)-naphthalen-2-ol (**1**) and 0.80 ml (9.8 mmol) pyridine in 10 ml CH_2Cl_2 at 0 °C was treated dropwise with 0.58 ml (3.4 mmol) triflic anhydride, stirred at 0 °C for 2h, the resulting solution was quenched with sat. aq. NH_4Cl soln. The organic phase was separated and the water phase was extracted twice with CH_2Cl_2. The combined organic layers

where dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by FC (hexane:EtOAc 3:1) to yield 1.3 g (93%) of the title compound as a light brown foam.
mp: 54-55 °C (foam).
^{1}H-NMR (300 MHz, $CDCl_3$) 7.27 (d, J = 6.9, 1H), 7.41-7.47 (m, 2H), 7.57-7.66 (m, 2H), 7.80-7.87 (m, 1H), 8.00-8.07 (m, 2H), 8.17 (d, J = 9.3, 1H), 8.46 (d, J = 8.4, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$)118.0 (C, q, J_{CF} = 312), 119.3 (CH), 125.1 (C), 125.5 (CH), 125.7 (C), 125.8 (CH), 126.2 (CH), 127.4 (CH), 128.3 (CH), 128.4 (CH), 132.3 (C),132.3 (CH), 132.8 (C), 133.8 (CH), 134.0 (CH), 145.1 (C), 155.0 (C), 155.6 (C).
FTIR (thin film, cm^{-1}): 3073 (w), 1583(w), 1569 (w) 1528 (w), 1512 (m) 1423 (s), 1376 (m), 1290 (s) 1217 (s), 1138 (s), 1072 (m), 950 (s), 833 (s), 770 (m), 639 (m), 622 (m).
HRMS (MALDI) calcd. for $C_{19}H_{11}ClF_3N_2O_3S$ $[M+H]^+$ 439.0126 found 439.0131.
Anal. Calcd for $C_{19}H_{10}ClF_3N_2O_3S$: C, 52.01; H, 2.30; N, 6.38. Found: C, 52.27; H, 2.56; N, 6.31.

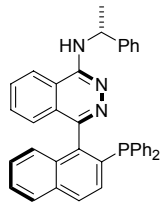


Trifluoromethanesulfonic acid 1-[4-(1-phenylethylamino)-phthalazin-1-yl]-naphthalen-
2-yl ester (**4**).
A solution of 4.9 g (11 mmol) trifluoromethanesulfonic acid 1-(4-chlorophthalazin-1-yl)-naphthalen-2-yl ester in 7.2 ml (56 mmol) (*R*)-1-phenylethylamine was stirred for 4 h at 120 °C, then cooled to 23 °C. The resulting viscous mixture was purified by FC (toluene/ EtOAc 7:1) to yield 5.4 g (93%) of the title compound (**4**) as a 1:1 mixture of diastereomers as a light brown solid.
^{1}H-NMR (300 MHz, $CDCl_3$) 1.79 (t, J = 6.7, 6H), 5.49 (d, J = 7.0, 2H), 5.88 (quint, J = 6.8, 2H), 7.13-7.65 (m, 22H), 7.73-7.82 (m, 2H), 7.85-7.90 (m, 2H), 7.94-8.00 (m, 2H), 8.08 (d, J = 9.1, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$) 21.9, 22.0, 50.7, 50.7, 117.8, 117.8, 118.0 (q, J_{CF} = 320), 118.7 (q, J_{CF} = 320), 119.4, 119.5, 120.8, 126.1, 126.1, 126.4, 126.5, 126.7, 126.7, 127.1, 127.2, 127.2, 127.4, 127.5, 127.5, 127.7, 128.1, 128.2, 128.5, 128.6, 131.3, 131.3, 131.4, 131.4, 131.4,

131.5, 132.5, 132.5, 133.6, 133.6, 144.0. 144.3. 145.5, 145.6, 146.5, 146.5, 152.7, 152.8.
HRMS (MALDI) calcd. for $C_{27}H_{21}F_3N_3O_3S$ $[M+H]^+$ 524.1250 found 524.1258.
Anal. Calcd for $C_{27}H_{20}F_3N_3O_3S$: C, 61.94; H, 3.85; N, 8.03. Found: C, 62.15; H, 3.99; N, 7.79.



(**5a**)



(**5b**)

(*R,M*)-[4-(2-Diphenylphosphanylnaphthalen-1-yl)-phthalazin-1-yl]-(1-phenylethyl)-amine (**5a**) and (*R,P*)-[4-(2-Diphenylphosphanyl-naphthalen-1-yl)-phthalazin-1-yl]-(1-phenyl-ethyl)-amine (**5b**).
A solution of 80 mg (0.15 mmol) Ni(dppe)Cl_2 in 4 ml DMF at 23 °C was treated with 0.53 ml (3.0 mmol) diphenylphosphine. The resulting dark red solution was stirred at 130 °C for 30 min. Then a solution of 840 mg (1.5 mmol) trifluoromethanesulfonic acid 1-[4-(1-phenylethylamino)-phthalazin-1-yl]-naphthalen-2-yl ester (**4**) and 680 mg (6.0 mmol) DABCO in 4 ml DMF was added via syringe, the flask was washed with 1 ml DMF. The resulting dark green solution was stirred at 130 °C for 14 h. The mixture was concentrated under reduced pressure (20 mbar, 60 °C bath temperature). The residue was purified by FC (toluene → toluene/EtOAc 5:1) to give 730 mg (80%) of the the title compounds as an off white solid as a 1:1.2 (**5a:5b**) mixture of diastereomers.
Pure **5a** can be obtained crystallizing a mixture form toluene/CH_2Cl_2/hexane. The solid is dissolved in toluene and minimal amount of CH_2Cl_2, upon addition of hexane a precipitate forms which is pure **5a**.
The diastereomers can also be separated by FC (toluene/EtOAc 10:1).

5a (top spot)
mp: >210°C.
$[\alpha]_D^{29}$ = -162.0 (c= 0.54, $CHCl_3$).
^{1}H-NMR (400 MHz, $CDCl_3$) 1.68 (d, *J* = 6.8, 3H), 5.34 (d, *J* = 7.2, 1H), 5.81 (quint, *J* = 6.9, 1H), 7.01 (d, *J* = 8.1, 1H), 7.11-7.18 (m, 5H), 7.18-7.24 (m, 8H), 7.28-7.33 (m, 3H),

7.36-7.43 (m, 2H), 7.50-7.53 (m, 2H), 7.55-7.59 (m, 1H), 7.70 (d, *J* = 8.3, 1H), 7.79-7.84 (m, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$) 22.2 (CH_3), 50.4 (CH), 117.7 (C), 120.3 (CH), 126.5 (CH), 126.7 (CH), 126.8 (CH), 126.8 (CH), 126.9 (CH), 126.9 (CH), 127.2 (CH), 127.8 (CH), 128.0 (CH), 128.2 (CH), 128.2 (CH), 128.2 (CH), 128.3 (CH), 128.3 (C), 128.3 (C), 128.4 (CH), 128.6 (CH), 128.8 (CH), 130.1 (CH), 130.7 (CH), 130.8 (CH), 133.1 (CH), 133.2 (C), 133.3 (CH), 133.3 (C), 133.6 (C), 133.7 (CH), 133.9 (CH), 135.8 (C), 136.0 (C), 137.3 (C), 137.4 (C), 137.7 (C), 137.8 (C), 141.8 (C), 142.1 (C), 144.6 (C), 152.2 (C), 152.5 (C), 152.6 (C).
^{31}P-NMR (121 MHz, $CDCl_3$) -13.18.
FTIR (thin film, cm^{-1}): 3351 (br, s), 1654 (w), 1559 (w), 1508 (s), 1420 (w), 1361 (w), 1217 (w), 820 (w), 772 (s), 698 (m).
HRMS (MALDI) calcd. for $C_{38}H_{31}N_3P^+$ $[M+H]^+$ 560.2250 found 560.2257.
Anal. Calcd for $C_{17}H_{21}NO_3$: C, 81.55; H, 5.40; N, 7.51; P, 5.53. Found: C, 81.44; H, 5.52; N, 7.39; P, 5.67.
A X-ray grade sample (colorless plate) was obtained after recrystallization from toluene-hexane. X-ray crystallography proved its configuration about axial chirality as *M*.

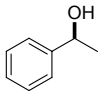
5b (bottom spot)
mp: 185-188 °C.
$[\alpha]_D^{26}$ = 127.3 (c= 0.39, $CHCl_3$).
^{1}H-NMR (300 MHz, $CDCl_3$) 1.78 (d, *J* = 6.7, 3H), 5.41 (d, *J* = 6.9, 1H), 5.85 (quint., *J* = 6.7, 1H), 7.09 (d, *J* = 8.1, 1H), 7.13-7.52 (m, 18H), 7.56-7.67 (m, 3H), 7.80 (d, *J* = 8.3, 1H), 7.86-7.91 (m, 2H).
^{13}C-NMR (75 MHz, $CDCl_3$) 21.9 (CH_3), 50.6 (CH), 117.5 (C), 120.2 (CH), 126.3 (CH), 126.5 (CH), 126.6 (CH), 127.1 (CH), 127.7 (CH), 127.9 (CH), 128.0 (CH), 128.0 (CH), 128.0 (CH), 128.1 (CH), 128.5 (CH), 128.6 (CH), 129.9 (CH), 130.6 (CH), 130.6 (CH), 133.1 (CH), 133.1 (C), 133.3 (CH), 133.4 (CH), 133.4 (C), 133.7 (CH), 135.9 (C), 136.1 (C), 136.9 (C), 137.0 (C), 137.4 (C), 137.6 (C), 141.3 (C), 141.7 (C), 144.2 (C), 152.1 (C), 152.3 (C), 152.3 (C).
^{31}P-NMR (121 MHz) -12.77.
FTIR (thin film, cm^{-1}): 3347 (br, s), 3056(m), 1615 (w), 1558 (w), 1508 (s), 1434 (w), 1366 (w), 1215 (w), 817 (w), 744 (s), 696 (s).
HRMS (MALDI) calcd. for $C_{38}H_{31}N_3P^+$ $[M+H]^+$ 560.2250 found 560.2249.

Anal. Calcd for $C_{17}H_{21}NO_3$: C, 81.55; H, 5.40; N, 7.51; P, 5.53. Found: C, 81.44; H, 5.41; N, 7.44.

Hydroboration reactions:

Preparation of the Rh-complex:
According to the literature:[6] In a 10 ml schlenk flask degassed CH_2Cl_2 (5 ml) was added to $[Rh(cod)_2]BF_4$ (41 mg, 0.1 mmol) and (*R,M*)-1-(2-diphenylphosphanyl-naphthalen-1-yl)-4-(1-phenyl-ethoxy)-phthalazine (**3a**) (59 mg, 0.105 mmol). The mixture was stirred for 20 min, the solvent was then removed in vacuo. The yellow-orange residue was scratched from the wall of the flask with a spatula and triturated with degassed diethyl ether (5 ml). The ether was removed via cannula and the yellow-orange residue dried in vacuo. The complex is not air stable and was stored in a glove box with exclusion of oxygen and moisture at 25 °C.

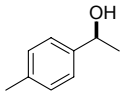
Catalytic hydroboration with catecholborane:
According to the literature:[6] A solution of rhodium complex (3.4 mg, 4 µmol) in degassed CH_2Cl_2 was transferred with a syringe to the reaction vessel. The CH_2Cl_2 was evaporated in vacuo, then dry, degassed toluene (1 ml), olefin (0.4 mmol) and 56 µl (0.45 mmol) freshly distilled (important!) catecholborane were added. The solution was stirred at room temperature until the olefin has been completely consumed (typically 2 h), cooled with ice bath, and quenched with EtOH (1ml). NaOH (1 ml, 2M in H_2O) and H_2O_2 (1 ml, 30% in H_2O) were added, the mixture was allowed to warm up to RT over 30 min and was then stirred for 2 h at this temperature. Et_2O (10 ml) was added to the mixture, and the organic layer was then washed with 1M aq. NaOH solution and then dried over Na_2SO_4. After evaporation of the solvent, the product was purified by chromatography on silica (pentane/diethylether 2:1).



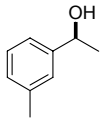
(*S*)-1-Phenylethanol.
Prepared according to the general procedure using styrene (41.7 mg, 0.40 mmol). Purification by flash column chromatography on silica gel afforded 35.7 mg (73%). Ratio

[6] Doucet, H.; Fernandez, E.; Layzell, T. P.; Brown, J. M. *Chem. Eur. J.* **1999**, 5, 1320-1330.

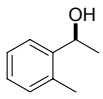
1-phenylethanol/2-phenylethanol was >99:1 as judged by ^{1}H NMR. The enantioselectivity was 92% ee (Daicel Chiralcel OD-H column 250 x 4.6 mm i.d with hexane : 2-propanol = 99 : 1, flow rate 0.9 ml/min, UV fluorescence 254 nm; $t_{r(minor)}$ = 24.5 min, $t_{r(major)}$ = 32.5 min). $[\alpha]^{29}_D$ -49.5 (c=0.525, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[6]



(*S*)-1-(4-Methylphenyl)ethanol.
Prepared according to the general procedure using 4-methylstyrene (47.3 mg, 0.40 mmol). Purification by flash column chromatography on silica gel afforded 51.2 mg (94%). Ratio 1-(4-methylphenyl)ethanol/2-(4-methylphenyl)ethanol was 98:2 as judged by ^{1}H NMR. The enantioselectivity was 92% ee (Daicel Chiralcel OD-H column 250 x 4.6 mm i.d with hexane : 2-propanol = 99.5 : 0.5, flow rate 0.9 ml/min, UV fluorescence 254 nm; $t_{r(minor)}$ = 39.8 min, $t_{r(major)}$ = 42.6 min). $[\alpha]^{27}_D$ -53.0 (c=0.55, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[6]

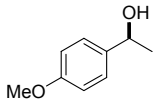


(*S*)-1-(3-Methylphenyl)ethanol.
Prepared according to the general procedure using 3-methylstyrene (47.3 mg, 0.40 mmol). Purification by flash column chromatography on silica gel afforded 46.4 mg (85%). Ratio 1-(3-methylphenyl)ethanol/2-(3-methylphenyl)ethanol was 92:8 as judged by ^{1}H NMR. The enantioselectivity was 84% ee (Daicel Chiralcel OD-H column 250 x 4.6 mm i.d with hexane : 2-propanol = 99 : 1, flow rate 0.8 ml/min, UV fluorescence 254 nm; $t_{r(minor)}$ = 20.1 min, $t_{r(major)}$ = 28.6 min). $[\alpha]^{26}_D$ -42.6 (c=0.62, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[6]

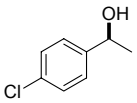


(*S*)-1-(2-Methylphenyl)ethanol.

Prepared according to the general procedure using 2-methylstyrene (47.3 mg, 0.40 mmol). Purification by flash column chromatography on silica gel afforded 44.2 mg (81%). Ratio 1-(2-methylphenyl)ethanol/2-(2-methylphenyl)ethanol was 91:9 as judged by ^{1}H NMR. The enantioselectivity was 91% ee (Daicel Chiralcel OB-H column 250 x 4.6 mm i.d with hexane : 2-propanol = 90 : 10, flow rate 0.5 ml/min, UV fluorescence 254 nm; $t_{r(major)}$ = 10.0 min, $t_{r(minor)}$ = 13.7 min$[\alpha]^{29}_D$ -72.1 (c=0.535, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[6]



(*S*)-1-(4-Methoxyphenyl)ethanol.
Prepared according to the general procedure using 4-methoxystyrene (53.7 mg, 0.40 mmol). Purification by flash column chromatography on silica gel afforded 48.5 mg (80%). Ratio 1-(4-methoxyphenyl)ethanol/2-(4-methoxyphenyl)ethanol was 95:5 as judged by ^{1}H NMR. The enantioselectivity was 90% ee (Daicel Chiralcel OD-H column 250 x 4.6 mm i.d with hexane : 2-propanol = 99 : 1, flow rate 0.9 ml/min, UV fluorescence 254 nm; $t_{r(minor)}$ = 40.0 min, $t_{r(major)}$ = 45.6 min). $[\alpha]^{28}_D$ -45.5 (c=0.545, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[6]

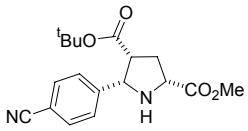


(*S*)-1-(4-Chlorophenyl)ethanol.
Prepared according to the general procedure using 4-chlorostyrene (55.4 mg, 0.40 mmol). Purification by flash column chromatography on silica gel afforded 54.2 mg (87%). Ratio 1-(4-chlorophenyl)ethanol/2-(4-chlorophenyl)ethanol was 98:2 as judged by ^{1}H NMR. The enantioselectivity was 87% ee (Daicel Chiralcel OD-H column 250 x 4.6 mm i.d with hexane : 2-propanol = 99 : 1, flow rate 0.9 ml/min, UV fluorescence 254 nm; $t_{r(major)}$ = 24.8 min, $t_{r(minor)}$ = 27.6 min). $[\alpha]^{27}_D$ -42.4 (c=0.495, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[6]

General procedure for the [3+2] cycloaddition reactions:

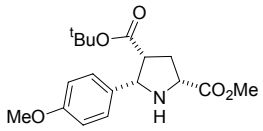
To a solution of α-iminoester (250 µmol, azeotroped with toluene) in THF (0.5 ml) at −40 °C was added the 0.01 M silver / ligand catalyst (750 µl, 7.5 µmol), freshly distilled *tert*-butyl acrylate (55 µl, 375 µmol), and *N*,*N*-diisopropylethylamine (4.4 µl, 25 µmol) sequentially. The solution was stirred at −40 °C for 36 h under argon atmosphere. The reaction was quenched with a solution of acetic acid (16.5 µ, 275 µmol) in THF. After evaporation of the solvent, the product was purified by flash chromatography on silica gel (ethyl acetate : hexane containing1 % triethylamine).

Preparation of the 0.01 M silver / ligand catalysts:
According to the literature:[7] In a 10 ml schlenk flask degassed THF (6.7 ml) was added to silver (I) acetate (11.2 mg, 0.67 mmol) and (*R*,S_a)- 1-(2-diphenylphosphanyl-naphthalen-1-yl)-4-(1-phenyl-ethoxy)-phthalazine (**3a**) (45.1 mg, 0.08 mmol). The mixture was stirred for 1 h to make a solution of 0.01M silver / ligand catalyst. This solution could be stored at −20 °C for at least one month.



tert-Butyl (2*R*,4*R*,5*S*)-2-methoxycarbonyl-5-(4-cyanophenyl)pyridin-4-carboxylate.
Prepared according to the general procedure using 50.6 mg (250 µmol) of *N*-(4-cyanobenzyliden-glycin methylester and 3 mol % silver / ligand **3a** catalyst. Purification by flash column chromatography on silica gel (ethyl acetate : hexane = 2 : 3 containing 1 % triethylamine) afforded 77.8 mg (94%) as white powder. The enantioselectivity was 95% ee (Daicel Chiralpak AS column 250 x 4.6 mm i.d with hexane : 2-propanol = 90 : 10, flow rate 1.0 ml/min, UV fluorescence 205 nm; $t_{r(minor)}$ = 20.0 min, $t_{r(major)}$ = 23.0 min). $[\alpha]^{28}_{D}$ −28.6 (c = 1.05, CH_2Cl_2). All other spectroscopic data was in agreement with the literature.[7]

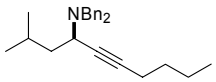
[7] Chen, C.; Li, X..; Schreiber, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 10174-10175.



tert-Butyl (2*R*,4*R*,5*S*)-2-methoxycarbonyl-5-(4-methoxyphenyl)pyrrolidin-4-carboxylate.
Prepared according to the general procedure using 51.8 mg (250 µmol) of *N*-(4-methoxybenzyliden-glycin methylester and 3 mol % silver / ligand **3a** catalyst. Purification by flash column chromatography on silica gel (ethyl acetate : hexane = 3 : 7 in 1 % triethylamine) afforded 72.3 mg (88%) as white powder. The enantioselectivity was 92% ee (Daicel Chiralpak AS column 250 x 4.6 mm i.d with hexane : 2-propanol = 90 : 10, flow rate 1.0 ml/min, UV fluorescence 205 nm; $t_{r(minor)}$ = 8.1 min, $t_{r(major)}$ = 11.8 min). $[\alpha]^{29}_{D}$ –29.1 (c = 0.99, CH_2Cl_2). All other spectroscopic data was in agreement with the literature.[7]

General Procedure for Alkyne/Imine Additions.

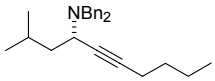
According to:[8] A 10 ml schlenk tube equipped with a magnetic stirrer and a septum was charged with CuBr (5.0 mol%), **5a** or **5b** (5.5 mol%) and powdered 4Å molecular sieves. The schlenk was flushed with argon for 5 minutes and then 1 ml toluene was added. The resulting suspension was stirred for 1 hour at 23 °C. To the reaction mixture was subsequently added alkyne (1.0 equiv.), aldehyde (1.0 equiv.), dibenzylamine (1.0 equiv.) and 1 ml toluene. Upon full conversion, the reaction mixture was directly subjected to flash column chromatography on silica gel.



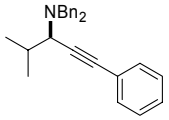
(*R*)-*N*,*N*-Dibenzyl-2-methyl-5-decyn-4-amine.
Prepared according to the general procedure from 1-hexyne (41 mg, 0.50 mmol, 1.0 equiv.), 3-methylbutanal (43 mg, 0.50 mmol, 1.0 equiv.), dibenzylamine (99 mg, 0.50 mmol, 1.0 equiv.) CuBr (3.6 mg, 0.025 mmol, 0.050 equiv.), **5a** (15.4 mg, 0.028 mmol, 0.055 equiv.) and 4Å molecular sieves (0.30 g) in 2 ml toluene at 23 °C for 5 days. Purification by flash column chromatography on silica gel afforded 128

[8] N. Gommermann, C. Koradin, K. Polborn, P. Knochel, *Angew. Chem.Int. Ed.* **2003**, *42*, 5763-5766

mg (74%) of a colorless oil. The enantioselectivity was 91% ee (Daicel Chiralcel OD-H column 250 x 4.6 mm i.d and Daicel Chiralpak OD-H column 150 x 4.6 mm i.d with hexane : 2-propanol = 99.7 : 0.3, flow rate 0.2 ml/min, UV fluorescence 254 nm; $t_{r(minor)}$ = 45.3 min, $t_{r(major)}$ = 50.3 min). $[\alpha]^{D}_{32}$ = +167 (c = 1.09, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[8]

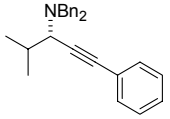


(*S*)-*N*,*N*-Dibenzyl-2-methyl-5-decyn-4-amine.
Prepared according to the general procedure from 1-hexyne (41 mg, 0.50 mmol, 1.0 equiv.), 3-methylbutanal (43 mg, 0.50 mmol, 1.0 equiv.), dibenzylamine (99 mg, 0.50 mmol, 1.0 equiv.) CuBr (3.6 mg, 0.025 mmol, 0.050 equiv.), **5b** (15.4 mg, 0.028 mmol, 0.055 equiv.) and 4Å molecular sieves (0.30 g) in 2 ml toluene at 23 °C for 5 days. Purification by flash column chromatography on silica gel afforded 125 mg (72%) of a colorless oil. The enantioselectivity was 94% ee (Daicel Chiralcel OD-H column 250 x 4.6 mm i.d and Daicel Chiralpak OD-H column 150 x 4.6 mm i.d with hexane : 2-propanol = 99.7 : 0.3, flow rate 0.2 ml/min, UV fluorescence 254 nm; $t_{r(major)}$ = 45.2 min, $t_{r(minor)}$ = 53.4 min). $[\alpha]^{D}_{30}$ = -173 (c = 0.87, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[8]

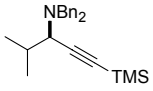


(*R*)-*N*,*N*-Dibenzyl-4-methyl-1-phenyl-1-pentyn-3-amine.
Prepared according to the general procedure from phenylacetylene (51 mg, 0.50 mmol, 1.0 equiv.), 2-methylpropanal (36 mg, 0.50 mmol, 1.0 equiv.), dibenzylamine (99 mg, 0.50 mmol, 1.0 equiv.) CuBr (3.6 mg, 0.025 mmol, 0.050 equiv.), **5a** (15.4 mg, 0.028 mmol, 0.055 equiv.) and 4Å molecular sieves (0.30 g) in 2 ml toluene at 23 °C for 4 days. Purification by flash column chromatography on silica gel afforded 156 mg (88%) of a colorless oil. The enantioselectivity was 90% ee (Daicel Chiralpak OD-H column 250 x 4.6 mm i.d and Daicel Chiralcel OD-H column 150 x 4.6 mm i.d with hexane : 2-propanol = 99.5 : 0.5, flow rate 0.2 ml/min, UV fluorescence 254 nm; $t_{r(minor)}$ = 40.2 min, $t_{r(major)}$ = 45.2 min). $[\alpha]^{D}_{30}$ = +299 (c =

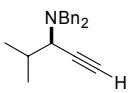
1.08, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[8]



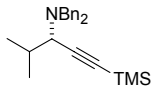
(*S*)-*N*,*N*-Dibenzyl-4-methyl-1-phenyl-1-pentyn-3-amine.
Prepared according to the general procedure from phenylacetylene (51 mg, 0.50 mmol, 1.0 equiv.), 2-methylpropanal (36 mg, 0.50 mmol, 1.0 equiv.), dibenzylamine (99 mg, 0.50 mmol, 1.0 equiv.) CuBr (3.6 mg, 0.025 mmol, 0.050 equiv.), **5b** (15.4 mg, 0.028 mmol, 0.055 equiv.) and 4Å molecular sieves (0.30 g) in 2 ml toluene at 23 °C for 4 days. Purification by flash column chromatography on silica gel afforded 145 mg (82%) of a colorless oil. The enantioselectivity was 95% ee (Daicel Chiralcel OD-H column 250 x 4.6 mm i.d and Daicel Chiralpak OD-H column 150 x 4.6 mm i.d with hexane : 2-propanol = 99.5 : 0.5, flow rate 0.2 ml/min, UV fluorescence 254 nm; $t_{r(major)}$ = 37.3 min, $t_{r(minor)}$ = 42.1 min). $[\alpha]^{D}_{28}$ = -312 (c = 0.95, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[8]



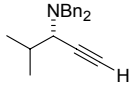
(*R*)-*N*,*N*-Dibenzyl-4-methyl-1-(trimethylsilyl)-1-pentyn-3-amine.
Prepared according to the general procedure from triemthylsilylacetylene (74 mg, 0.75 mmol, 1.5 equiv.), 2-methylpropanal (36 mg, 0.50 mmol, 1.0 equiv.), dibenzylamine (99 mg, 0.50 mmol, 1.0 equiv.) CuBr (3.6 mg, 0.025 mmol, 0.050 equiv.), **5a** (15.4 mg, 0.028 mmol, 0.055 equiv.) and 4Å molecular sieves (0.30 g) in 2 ml toluene at 23 °C for 3 days. Purification by flash column chromatography on silica gel afforded 147 mg (84%) of a colorless oil.
$[\alpha]^{D}_{33}$ = +237 (c = 0.99, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[8]



(*R*)-*N*,*N*-Dibenzyl-4-methyl-1-pentyn-3-amine.
N,*N*-Dibenzyl-4-methyl-1-(trimethylsilyl)-1-pentyn-3-amine (105 mg, 0.300 mmol, 1.0 equiv.) was dissolved in 2 ml THF (reagent quality) and cooled to -78 °C. To the solution was added Bu_4NF (0.330 ml, 0.330 mmol, 1.1 equiv.) dropwise and the reaction was then allowed to warm to 23 °C. After 30 minutes, thin layer chromatography revealed full conversion. The reaction was quenched with water and extracted with ether. Purification by flash column chromatography on silica gel afforded 77.4 mg (93%) of a colorless oil. The enantioselectivity was 98% ee (Daicel Chiralcel OD-H column 250 x 4.6 mm i.d and Daicel Chiralpak OD-H column 150 x 4.6 mm i.d with hexane : 2-propanol = 99,9 : 0.1, flow rate 0.2 ml/min, UV fluorescence 254 nm; $t_{r(minor)}$ = 44.9 min, $t_{r(major)}$ = 48.5 min). $[\alpha]^{D}_{35}$ = +205 (c = 1.07, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[8]



(*S*)-*N*,*N*-Dibenzyl-4-methyl-1-(trimethylsilyl)-1-pentyn-3-amine.
Prepared according to the general procedure from triemthylsilylacetylene (74 mg, 0.75 mmol, 1.5 equiv.), 2-methylpropanal (36 mg, 0.50 mmol, 1.0 equiv.), dibenzylamine (99 mg, 0.50 mmol, 1.0 equiv.) CuBr (3.6 mg, 0.025 mmol, 0.050 equiv.), **5b** (15.4 mg, 0.028 mmol, 0.055 equiv.) and 4Å molecular sieves (0.30 g) in 2 ml toluene at 23 °C for 3 days. Purification by flash column chromatography on silica gel afforded 143 mg (82%) of a colorless oil.
$[\alpha]^{D}_{31}$ = -237 (c = 1.1, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[8]



(*S*)-*N*,*N*-Dibenzyl-4-methyl-1-pentyn-3-amine.
N,*N*-Dibenzyl-4-methyl-1-(trimethylsilyl)-1-pentyn-3-amine (105 mg, 0.300 mmol, 1.0 equiv.) was dissolved in 2 ml THF (reagent quality) and cooled to -78 °C. To the solution was added Bu_4NF (0.330 ml, 0.330 mmol, 1.1 equiv.) dropwise and the reaction was then allowed to warm to 23 °C. After 30 minutes, thin layer chromatography revealed full conversion. The reaction was quenched with water and

extracted with ether. Purification by flash column chromatography on silica gel afforded 74.1 mg (89%) of a colorless oil. The enantioselectivity was 99% ee (Daicel Chiralcel OD-H column 250 x 4.6 mm i.d and Daicel Chiralpak OD-H column 150 x 4.6 mm i.d with hexane : 2-propanol = 99,9 : 0.1, flow rate 0.2 ml/min, UV fluorescence 254 nm; $t_{r(major)}$ = 41.9 min, $t_{r(minor)}$ = 50.0 min). $[\alpha]^{D}_{24}$ = -206 (c = 1.51, $CHCl_3$). All other spectroscopic data was in agreement with the literature.[8]