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Supporting Information

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Diphenylphosphinosulfoximines as Ligands in Ir-catalyzed Asymmetric Imine Hydrogenations

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General Information: All experiments were carried out under argon atmosphere using standard Schlenk techniques. DMSO, DCM and toluene were dried and deoxygenated by standard procedures. Flash chromatography was carried out with Merck silica gel 60 (0.040-0.063 mm). Analytical thin layer chromatography was performed with Merck silica gel 60 F_{254} plates, and the products were visualized by UV detection (254 nm). Optical rotations: Perkin Elmer Model 241, measurements were carried out at RT, λ = 589 nm. ^{1}H- and ^{13}C NMR (300 or 400 and 75 or 100 MHz, respectively) spectra were recorded in $CDCl_3$ using TMS as internal standard. $CFCl_3$ and H_3PO_4 were used as external standards for ^{19}F NMR (282 MHz or 376 MHz) and ^{31}P NMR (121 MHz), respectively. Chemical shifts are given in ppm and spin-spin coupling constants, *J*, are given in Hz. IR spectra were recorded as KBr discs, capillaries or in $CHCl_3$. Elemental analyses were measured with a Heraeus Model CHN Rapid. Analytical HPLC were performed with Merck Hitachi (L-7000 UV, L-7000 pump, D-7000 integrator) and OD or OD-H columns from *Chiral Technologies* as stationary phases. All enantiomer ratios have been controlled by co-injections of the pure sample with the racemic substrates.

Diphenylphosphine was purchased from Acros. (*R*)-(3,5-Dimethyl)phenylmethylsulfoxide was prepared in analogy to a literature procedure.[1] Sulfoximines **5a-c,e**,[2] and aryl bromide **4**[3] were prepared by known procedures. Imines **7a-l** were synthesized in analogy to a literature procedure[4] or by the reaction of equimolar amounts of aniline and ketone in the presence of a catalytic amount of *p*-TsOH in toluene under refluxing conditions in a Dean-Stark apparatus. Racemic amines were prepared by reduction of the imines with sodium borohydride in ethanol.

(*S*)-*S*-Isobutyl-*S*-phenylsulfoximine (5d):

A mixture of **5a** (6.20 g, 40.0 mmol) and hexamethyldisilazane (HMDS; 8.90 mL, 42.0 mmol) was heated up to 140 °C for 1.5 h. After cooling to RT, the excess of HMDS was removed at reduced pressure and the remaining oil was dissolved in dry THF (60 mL) and cooled to −78 °C. Then *n*-butyllithium (25.6 mL, 41.0 mmol, 1.6 M in hexane) was added over a period of 30 min. The yellow solution was kept at −78 °C for 1 h, before it was warmed to RT and stirred for 1 h at RT. Then, it was cooled again to 0 °C and 2-iodopropane (4.40 mL, 44.0 mmol) was added via a syringe. The reaction was then stirred for 30 h at RT. After addition of a 1:1 mixture of sat. aq. NH_4Cl/MeOH (60 mL), the reaction was stirred for 3 h at RT. The aqueous phase was extracted three times with dichloromethane. The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated. The pure product was obtained as colorless oil after flash-chromatography using ethylacetate as eluent.

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3 a) O. Herd, A. Hessler, M. Hingst, M. Trepper, O. Stelzer, *J. Organomet. Chem.* **1996**, *522*, 69-76; b) D. J. Brauer, M. Hingst, K. W. Kottsieper, C. Liek, T. Nickel, M. Tepper, O. Stelzer, W. S. Sheldrick, *J. Organomet. Chem.* **2002**, *645*, 14-26.
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Yield: 3.60 g, 46%; $[\alpha]_D^{25}$ = 17.6 (*c* = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.9 Hz, 3 H; CH_3), 1.03 (d, *J* = 6.9 Hz, 3 H; CH_3), 2.22 (m_c, 1 H; CH), 2.35 (br, 1 H; NH), 3.00 (dd, *J* = 14.0, 6.6 Hz; 1 H, CH_2), 3.07 (dd, *J* = 14.0, 6.0 Hz, 1 H; CH_2), 7.47-7.69 (m, 3 H; Ar-H), 7.95-7.99 (m, 2 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.7, 22.9, 24.5, 65.2, 128.0, 129.0, 132.8, 143.0 ppm; IR (KBr): $\tilde{\nu}$ = 3274 (m), 2961 (s), 1227 (s), 1114 (m), 983 (s), 511 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 198.1 (7) [M^+], 155.0 (13), 141.1 (43), 132.1 (75), 125.0 (100); elemental analysis (%) calcd. for $C_{10}H_{15}NOS$: C 60.88, H 7.66, N 7.10; found: C 60.90, H 7.88, N 7.10.

(*R*)-*S*-Methyl-*S*-(3,5-dimethyl)phenylsulfoximine (5f):

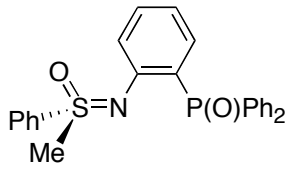
To a suspension (*R*)-(3,5-dimethyl)phenylmethylsulfoxide (2.00 g, 11.9 mmol), trifluoroacetamide (2.68 g, 23.7 mmol), MgO (1.91 g, 47.5 mmol), and $[Rh_2(OAc)_4]$ (131.3 mg, 0.297 mmol) in CH_2Cl_2 (60 mL) was added $PhI(OAc)_2$ (5.75 g, 17.8 mmol) at RT. The mixture was stirred for the period of 24 h. The resulting suspension was filtered through a pad of celite, and the filtrate was concentrated under reduced pressure (rotary evaporator). To the solution of the resulting residue in MeOH (30 mL) was added K_2CO_3 (8.21 g, 59.4 mmol) at RT, and the mixture was stirred for 2 h. Purification by column chromatography with ethylacetate as eluent afforded sulfoximine **5f** as colorless oil. Yield: 1.60 g, 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 6 H; CH_3), 3.10 (s, 3 H; CH_3), 7.25 (s, 1 H; Ar-H), 7.64 (s, 2 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 46.0, 124.8, 134.3, 138.9, 142.8 ppm.

General procedure for the *N*-arylation of sulfoximines 5a-f with aryl bromide 2:

In an oven-dried Schlenk tube was added NH-sulfoximine **5** (1.0 equiv.), aryl bromide **2** (1.1-1.5 equiv.), CsOAc (2.5 equiv.), CuI (1.1-1.5 equiv.) and DMSO (1.5 mL/mmol). The vessel was

closed and evacuated for 30 min. Then, the mixture was heated for 24-36 h at 90 °C (the consumption of **5** was monitored by TLC). After cooling the reaction to RT, an aqueous NH_3-solution was added. The product was extracted three times with DCM. The combined organic phases were dried ($MgSO_4$) and the solvent was evaporated. Sometimes it was necessary to dissolve the crude product in DCM again and to wash it twice with water in order to remove remaining DMSO. The pure product was obtained after column chromatography on silica gel.
In some cases the products still contains a yellow impurity after the column chromatography, which can be removed by filtration over a small plug of alox with ethylacetate/pentane (4:1) as eluent.

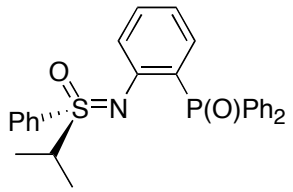
(*S*)-2-[(*S*-Phenyl-*S*-methylsulfoximinoyl)phenyl]diphenyl-phosphinoxide (6a):



Yield: 65%; m.p.: 206-208 °C; $[\alpha]_D^{25}$ −147.8 (*c* = 1.5, $CHCl_3$); R_f: 0.21 (ethylacetate, 254 nm); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.84 (s, 3 H; CH_3), 6.88 (m_c, 1 H; Ar-H), 7.05 (m_c, 1 H; Ar-H), 7.24 (m_c, 1 H; Ar-H), 7.33-7.53 (m, 10 H; Ar-H), 7.65-7.89 (m, 6 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.8, 120.8 (d, J_{C-P} = 12.5 Hz), 121.9 (d, J_{C-P} = 7.7 Hz), 125.0 (d, J_{C-P} = 106.5 Hz), 128.0 (d, J_{C-P} = 11.6 Hz), 128.1 (d, J_{C-P} = 11.6 Hz), 128.4, 129.1, 130.9 (d, J_{C-P} = 2.6 Hz), 131.2 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 9.7 Hz), 131.9 (d, J_{C-P} = 9.7 Hz), 133.1 (d, J_{C-P} = 105.5 Hz), 133.1, 133.2 (d, J_{C-P} = 2.0 Hz), 134.5 (d, J_{C-P} = 10.0 Hz), 134.8 (d, J_{C-P} = 105.8 Hz), 138.62, 148.5 (d, J_{C-P} = 4.5 Hz) ppm; ^{31}P NMR (121 MHz): δ = 28.8 ppm; IR (KBr): $\tilde{\nu}$ = 3428 (w), 3054 (w), 2988 (w), 2909 (w), 1582 (s), 1466 (s), 1439 (s), 1299 (s), 1260 (m), 1205 (s), 1184 (s), 1097 (m),

1015 (m), 777 (m), 745 (m), 710 (m), 610 (s), 542 (m); MS (EI): *m/z* (%) = 431 (21) [M^+], 416 (5), 369 (2), 340 (3), 306 (100), 291 (11), 272 (3), 214 (11), 201 (9), 183 (5), 167 (9), 125 (5), 91 (6), 77 (6); elemental analysis (%) calcd. for $C_{24}H_{22}NOPS$: C 69.59, H 5.14, N 3.25; found: C 69.38, H 5.43, N 3.10.

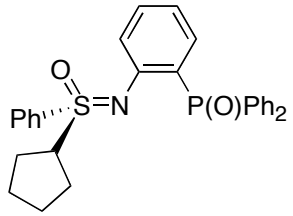
(*S*)-2-[(*S*-Phenyl-*S*-isopropylsulfoximinoyl)phenyl]diphenyl-phosphinoxide (6b):



Yield: 55%; m.p.: 220-222 °C; $[\alpha]_D^{25}$ −158.4 (*c* = 0.35, $CHCl_3$); R_f: 0.22 (DCM/acetone 4:1, 254 nm); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.6 Hz, 3 H; CH_3), 0.99 (d, *J* = 6.9 Hz, 3 H; CH_3), 2.91 (h, *J* = 6.6 Hz, 1 H; CH), 6.74 (m_c, 1 H; Ar-H), 6.97 (dd, *J* = 7.7, 5.0 Hz, 1H; Ar-H), 7.09-7.19 (m, 2 H; Ar-H), 7.36-7.55 (m, 8 H; Ar-H), 7.61-7.67 (m, 1 H; Ar-H), 7.74-7.83 (m, 6 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 15.1, 57.4, 119.9 (d, J_{C-P} = 12.7 Hz), 121.4 (d, J_{C-P} = 7.3 Hz), 123.4 (d, J_{C-P} = 107.3 Hz), 128.0 (d, J_{C-P} = 12.2 Hz), 128.1 (d, J_{C-P} = 11.9 Hz), 128.3 (d, J_{C-P} = 12.1 Hz), 129.0, 130.2, 130.6(d, J_{C-P} = 2.7 Hz), 131.0 (d, J_{C-P} = 2.6 Hz), 131.2 (d, J_{C-P} = 9.8 Hz), 131.7 (d, J_{C-P} = 2.6 Hz), 131.9 (d, J_{C-P} = 9.8 Hz), 132.1 (d, J_{C-P} = 9.3 Hz), 132.9, 133.0 (d, J_{C-P} = 1.6 Hz), 133.1 (d, J_{C-P} = 103.6 Hz), 133.3 (d, J_{C-P} = 10.7 Hz), 135.1, 135.2 (d, J_{C-P} = 106.8 Hz), 149.7 (d, J_{C-P} = 3.8 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$, TMS): δ = 29.15 ppm; IR (KBr): $\tilde{\nu}$ = 3454 m), 3047 (m), 1462 (s), 1437 (s), 1300 (s), 1247 (m), 1194 (s), 1174 (s); 1003 (m), 760 (s), 700 (s), 557 (s) cm^{-1}; MS (EI): *m/z* (%): 459.1 (17) [M^+], 416.0 (2), 340.0 (100), 292.0 (8), 214.0 (10), 198.0 (8), 167.0 (7); elemental analysis (%) calcd. for

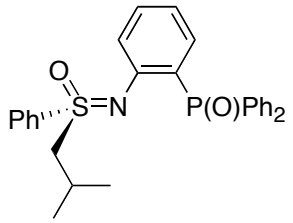
$C_{27}H_{26}NO_2PS$: C 70.57, H 5.70, N 3.05; found: C 70.61, H 5.70, N 2.94.

(*S*)-2-[(*S*-Phenyl-*S*-cyclopentylsulfoximinoyl)phenyl]diphenyl-phosphinoxide (6c):



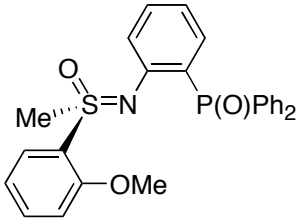
Yield: 83%; m.p.: 212-213 °C; $[\alpha]_D^{25}$ -213.5 (*c* = 0.5, $CHCl_3$); R_f: 0.41 (ethylacetate, 254 nm); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32-1.68 (m, 8 H; CH_2), 3.22 (quint, *J* = 8.0 Hz, 1H; CH), 6.79 (m_c, 1 H; Ar-H), 6.99 (dd, *J* = 8.0, 2.5 Hz, 1 H; Ar-H), 7.15 (m_c, 1 H; Ar-H), 7.27 (m_c, 1 H; Ar-H), 7.39-7.54 (m, 9 H; Ar-H), 7.77-7.86 (m, 6 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.3, 25.4, 26.6, 26.7, 66.2, 119.9 (d, J_{C-P} = 12.9 Hz), 121.4 (d, J_{C-P} = 7.6 Hz), 123.9 (d, J_{C-P} = 106.3 Hz), 128.0 (d, J_{C-P} = 12.0 Hz), 128.1 (d, J_{C-P} = 11.5 Hz), 129.1, 129.6, 130.6 (d, J_{C-P} = 2.2 Hz), 131.1 (d, J_{C-P} = 1.9 Hz), 131.3 (d, J_{C-P} = 9.9 Hz), 132.2 (d, J_{C-P} = 9.3 Hz), 132.85, 133.1, 133.6, 134.4 (d, J_{C-P} = 10.4 Hz), 135.5 (d, J_{C-P} = 107.1 Hz), 137.1, 149.5 (d, J_{C-P} = 3.8 Hz) ppm; ^{31}P NMR (121 MHz): δ = 29.0 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2962 (m), 2924 (m), 1466 (m), 1439 (m), 1304 (m), 756 (s) cm^{-1}; MS (EI): *m/z* (%): 485.3 (21) [M^+], 360.3 (7), 340.2 (100); HRMS($C_{29}H_{28}NO_2PS$): calc.: 485.15784; found: 485.15782.

(*S*)-2-[(*S*-Phenyl-*S*-isobutylsulfoximinoyl)phenyl]diphenyl-phosphinoxide (6d):



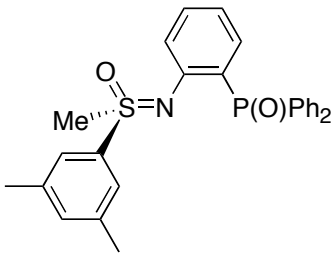
Yield: 56%; m.p.: 230-233 °C; $[\alpha]_D^{25}$ -166.9 (*c* = 0.61, $CHCl_3$); R_f: 0.14 (ethylacetate, 254 nm); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.66 (d, *J* = 6.9 Hz, 3 H; CH_3), 0.74 (d, *J* = 6.6 Hz, 3 H; CH_3), 1.74 (m, 1 H; CH), 2.55 (dd, *J* = 13.7, 8.0 Hz, 1 H; CH_2), 2.75 (dd, *J* = 13.7, 5.0 Hz, 1 H; CH_2), 6.72 (m_c, 1 H; Ar-H), 6.89 (m_c, 1 H; Ar-H), 7.03 (m_c, 1 H; Ar-H), 7.21-7.42 (m, 9H; Ar-H), 7.46-7.61 (m, 4 H; Ar-H), 7.64-7.78 (m, 3 H; Ar-H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.1, 22.7, 23.4, 65.0, 120.2 (d, J_{C-P} = 12.5 Hz), 121.3 (d, J_{C-P} = 7.3 Hz), 123.7 (d, J_{C-P} = 107.1 Hz), 127.8 (d, J_{C-P} = 12.1 Hz), 128.0 (d, J_{C-P} = 12.1 Hz), 128.3 (d, J_{C-P} = 12.1 Hz), 128.8, 129.1, 130.6 (d, J_{C-P} = 2.5 Hz), 131.1 (d, J_{C-P} = 2.6 Hz), 131.4 (d, J_{C-P} = 9.9 Hz), 132.1 (d, J_{C-P} = 9.8 Hz), 132.8, 133.1, 134.4 (d, J_{C-P} = 10.0 Hz), 134.9 (d, J_{C-P} = 106.2 Hz), 138.1, 148.9 (d, J_{C-P} = 4.2 Hz) ppm; ^{31}P NMR (121 MHz): δ = 28.8 ppm; IR (KBr): $\tilde{\nu}$ = 3407 (w), 3053 (m), 2959 (m), 2926 (m), 1581 (m), 1465 (s), 1437 (s), 1302 (s), 1186 (s), 1113 (m), 695 (s), 541 (s) cm^{-1} ; MS (EI): *m/z* (%): 473.1 (16) [M^+], 458.0 (5), 348.1 (12), 340.0 (100), 292.0 (9), 214 (8); elemental analysis (%) calcd. for $C_{28}H_{28}NO_2PS$: C 71.01, H 5.96, N 2.96; found: C 70.69, H 5.78, N 2.95.

(*R*)-2-[(*S*-(2-methoxy)phenyl-*S*-methylsulfoximinoyl)phenyl]-diphenylphosphinoxide (6e)



Yield: 66%; m.p.: 201°C; $[\alpha]_D^{25}$ = 32.6 (*c* = 1, $CHCl_3$); R_f: 0.23 (ethylacetate, 254 nm); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.82 (s, 3 H), 3.84 (s, 3 H), 6.83 (td, *J* = 7.7, 1.0 Hz, 1 H), 6.88–6.94 (m, 2 H), 7.10 (m_c, 1 H), 7.26 (m_c, 1 H), 7.33-7.56 (m, 9 H), 7.73-7.83 (m, 4 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 42.8, 56.2, 112.4, 120.6, 120.6 (d, J_{C-P} = 9.6 Hz), 121.3(d, J_{C-P} = 7.3 Hz), 124.6 (d, J_{C-P} = 107.0 Hz), 127.3, 127.9 (d, J_{C-P} = 12.2 Hz), 128.1 (d, J_{C-P} = 12.2 Hz), 130.8 (m, 2 C), 131.0 (d, J_{C-P} = 2.3 Hz), 131.8 (d, J_{C-P} = 9.8 Hz), 133.2, 133.8 (d, J_{C-P} = 105.3 Hz), 134.3 (d, J_{C-P} = 105.7 Hz), 134.7 (d, J_{C-P} = 9.7 Hz), 134.9, 148.6 (d, J_{C-P} = 4.4 Hz), 157.2 ppm; ^{31}P NMR (121 MHz): δ = 28.8 ppm; IR (KBr): $\tilde{\nu}$ = 3558 (m), 3350 (b), 3058 (m), 3027 (s), 2872 (m), 1596 (m), 1489 (s), 1405 (s), 1215 (m), 1185 (m), 1089 (s), 1013 (s), 968 (s), 829 (s), 797 (m), 753 (s), 695 (s), 544 (s) cm^{-1}; MS (EI): *m/z* (%) = 461 (30) [M^+], 446 (33), 399 (5), 306 (100), 292 (34), 214 (13), 201 (9), 167 (8).

(*R*)-2-[(*S*-(3,5-dimethyl)phenyl-*S*-methylsulfoximinoyl)phenyl]-diphenylphosphinoxide (6f)

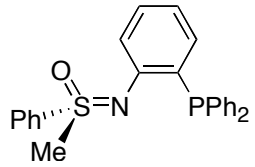


Yield: 74%; m.p.: 220-221°C; $[\alpha]_D^{25}$ –129.1 (*c* = 0.5, $CHCl_3$); R_f: 0.25 (ethylacetate/pentane 4:1, 254 nm, alox neutral); ^{1}H NMR: (300 MHz, $CDCl_3$): δ = 2.28 (s, 6 H; CH_3), 2.82 (s, 3 H; CH_3), 6.92 (td, *J* = 7.7, 1.5 Hz, 1 H; Ar-H), 7.05 (dd, *J* = 7.9, 5.0 Hz, 1 H; Ar-H), 7.12 (s, 1 H; Ar-H), 7.22-7.30 (m, 1 H; Ar-H), 7.30 (s, 2 H; Ar-H), 7.40-7.57 (m, 7 H; Ar-H), 7.72-7.80 (m, 2 H; Ar-H), 7.82-7.91 (m, 2 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1, 44.7, 120.9 (d, J_{C-P} = 12.5 Hz), 122.1 (d, J_{C-P}

= 7.2 Hz), 124.8 (d, J_{C-P} = 110.0 Hz), 125.6, 127.9 (d, J_{C-P} = 12.2 Hz), 128.1 (d, J_{C-P} = 12.4 Hz), 130.8 (d, J_{C-P} = 2.5 Hz), 131.1 (d, J_{C-P} = 2.5 Hz), 131.8 (d, J_{C-P} = 9.7 Hz), 131.9 (d, J_{C-P} = 9.8 Hz), 133.2, 133.3 (d, J_{C-P} = 105.0 Hz), 134.6 (d, J_{C-P} = 9.6 Hz), 134.9, 134.9 (d, J_{C-P} = 105.2 Hz), 138.3, 139.2, 148.5 (d, J_{C-P} = 4.1 Hz) ppm; ^{31}P NMR (121 MHz): δ = 28.9 ppm; IR (KBr): $\tilde{\nu}$ = 3057 (w), 1580 (m), 1463 (s), 1436 (s), 1296 (s), 1177 (s), 1115 (s), 755 (s), 695 (s), 546 (s) cm^{-1}; MS (EI): *m/z* (%): 459.0 (1) [M$^+$], 306.1 (4), 277.1 (100), 199.0 (11), 183.1 (8), 152.1 (5); elemental analysis (%) calcd. for $C_{27}H_{26}NO_2PS$: C 70.57, H 5.70, N 3.05; found: C 70.32, H 5.81, N 2.85.

General procedure for the reduction of the phosphineoxides:
In an oven-dried Schlenk-flask under an argon atmosphere were added phosphineoxide (1.0 equiv.) and dry toluene (3 mL/mmol). Then, the solution was cooled to 0 °C and degassed Et_3N (3.0-5.0 equiv.) and trichlorosilane (3.0-5.0 equiv.) were added. The heterogenous mixture was stirred for 12 h at 105 °C. Then, the reaction mixture was cooled to RT and degassed water (3 mL) was added. The solid was filtered off over a small plug of celite and thoroughly rinsed with ethylacetate. The organic phase was dried ($MgSO_4$) and evaporated to dryness. The pure product was obtained after flash chromatography on silica gel as colorless solid.

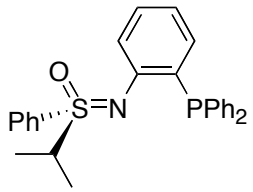
(*S*)-2-[(*S*-Phenyl-*S*-methylsulfoximinoyl)phenyl]diphenyl-phosphine (3a):



Yield: 70 %; m.p.: 147-148 °C; $[\alpha]_D^{25}$ = −119.5 (*c* = 1.1, $CDCl_3$); R_f: 0.69 (pentane/acetone 5:1, 254 nm); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.93 (s, 3H; CH_3), 6.65-6.70 (m, 1 H; Ar-H), 6.77-

6.81 (m, 1 H; Ar-H), 7.03-7.10 (m, 2 H; Ar-H), 7.30-7.42 (m, 12 H; Ar-H), 7.51 (tt, J = 5.4, 1.0 Hz, 1 H; Ar-H), 7.59-7.62 (m, 2 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.5, 120.7, 121.6, 128.1, 128.2, 128.3, 128.3, 128.5, 129.1, 129.4, 132.9 (d, J_{C-P} = 3.9 Hz), 133.8 (d, J_{C-P} = 19.7 Hz), 134.4 (d, J_{C-P} = 20.3 Hz), 137.4 (d, J_{C-P} = 11.0 Hz), 137.5 (d, J_{C-P} = 11.3 Hz), 139.3, 147.7 (d, J_{C-P} = 19.6 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -13.7 ppm; IR (KBr): $\tilde{\nu}$ = 3401 (b), 3049 (m), 2922 (m), 1574 (s), 1459 (s), 1432 (s), 1292 (s), 1257 (s), 1209 (s), 1092 (s), 1067 (m), 1017 (s), 743 (s), 695 (s), 527 (m), 501 (m); MS (CI, methane) m/z (%) = 444 (10) $[M^+ + C_2H_5]$, 432.0 (5) $[M^+ + CH_4]$, 416.0 (100) $[M^+ + H]$, 400.0 (70) $[M^+ - CH_3]$, 338.0 (6), 291.0 (9), 276.0 (6); MS (EI): m/z (%): 400.0 (100) $[M^+ - CH_3]$, 291.0 (8), 274.0 (11), 214.0 (7), 198.0 (6), 183.0 (6); elemental analysis (%) calcd. for $C_{25}H_{22}NOPS$: C 72.27, H 5.34, N 3.37; found: C 72.01, H 5.47, N 3.18.

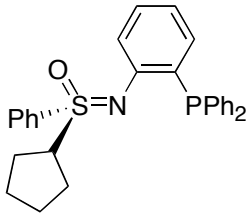
(*S*)-2-[(*S*-Phenyl-*S*-isopropylsulfoximinoyl)phenyl]diphenyl-phosphine (3b):



Yield: 73%; m.p.: 151-152 °C; R_f: 0.21 (pentane/acetone 15:4, 254 nm); $[\alpha]_D^{25}$ = -169.1 (c = 0.5, $CDCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (d, J = 6.9 Hz, 3 H; CH_3), 1.14 (d, J = 6.7 Hz, 3 H; CH_3), 3.15 (m_c, 1 H; CH), 6.63 (ddd, J = 7.7, 4.2, 1.7 Hz, 1 H; Ar-H), 6.71 (m_c, 1 H; Ar-H), 6.88-7.02 (ddd, J = 7.9, 4.7, 1.2 Hz, 1 H; Ar-H), 6.98 (m_c, 1 H; Ar-H), 7.30-7.56 (m, 13 H; Ar-H), 7.63-7.67 (m, 2 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.5, 15.6, 57.9, 120.1, 120.8, 128.1, 128.2, 128.4, 128.6, 129.1, 129.3, 130.0, 130.7 (d, J_{C-P} = 4.4 Hz), 132.9 (d, J_{C-P} = 4.0 Hz), 133.8 (d, J_{C-P} = 19.5 Hz), 134.7 (d, J_{C-P} = 20.4 Hz), 135.7, 137.5 (d, J_{C-P} = 15.3 Hz), 137.7 (d, J_{C-P}

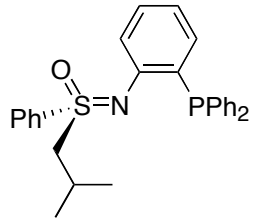
= 16.4 Hz), 148.2 (d, J_{C-P} = 18.8 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -12.9 ppm; IR (KBr): $\tilde{\nu}$ = 3436 (w), 3052 (m), 2982 (w), 2926 (w), 1576 (m), 1461 (s), 1435 (s), 1304 (s), 1260 (s), 1188 (s), 1094 (m), 753 (s), 694 (s); MS (EI): *m/z* (%): 400.1 (100) [M^+-C_3H_7], 323.1 (1), 292.1 (14), 274.0 (15), 214.0 (14), 198.0 (12), 183.0 (10), 167.0 (5); HRMS($C_{29}H_{28}NO_2PS$–C_3H_7): calc.: 400.09250; found: 400.09252.

(*S*)-2-[(*S*-Phenyl-*S*-cyclopentylsulfoximinoyl)phenyl]diphenyl-phosphine (3c):



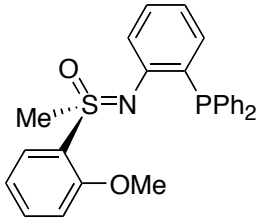
Yield: 51%; m.p.: 113-115 °C; R_f: 0.46 (pentane/acetone 3:1, 254 nm); $[\alpha]_D^{25}$ = -132.5 (*c* = 1.0, $CDCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37-1.71 (m, 6 H; CH_2), 1.80-2.04 (m, 2 H; CH_2), 3.37 (quint., *J* = 7.9 Hz, 1 H; CH), 6.59 (ddd, *J* = 7.4, 4.2, 1.5 Hz, 1 H; Ar-H), 6.71 (t, *J* = 7.7 Hz, 1 H; Ar-H), 6.91 (ddd, *J* = 7.9, 4.7, 1.2 Hz, 1 H; Ar-H), 6.96 (m_c, 1 H; Ar-H), 7.30-7.55 (m, 13 H; Ar-H), 7.67-7.72 (m, 2 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.5, 25.7, 26.8, 27.6, 66.8, 120.1, 120.8, 128.1 128.2, 128.2, 128.3, 128.6, 129.1, 129.2, 129.4, 130.8 (d, J_{C-P} = 5.6 Hz), 132.8 (d, J_{C-P} = 3.8 Hz), 133.7 (d, J_{C-P} = 19.3 Hz), 134.7 (d, J_{C-P} = 20.4 Hz), 138.0, 148.2 (d, J_{C-P} = 18.9 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -12.6 ppm; IR (KBr): $\tilde{\nu}$ = 3421 (w); 3051 (m), 2962 (m), 574 (m), 1458 (s), 1434 (s), 1299 (s), 1257 (s), 1189 (s), 1093 (m), 1013 (m), 751 (s), 726 (m), 694 (s); MS (EI): *m/z* (%): 400.1 (100) [M^+-C_4H_9], 324.0 (2), 292.0 (15), 274.0 (11), 214.0 (12), 198.0 (10) 183.0 (7); elemental analysis (%) calcd. for $C_{29}H_{28}NOPS$: C 74.18, H 6.01, N 2.98; found: C 73.88, H 6.16, N 2.69.

(*S*)-2-[(*S*-Phenyl-*S*-isobutylsulfoximinoyl)phenyl]diphenyl-phosphine (3d):



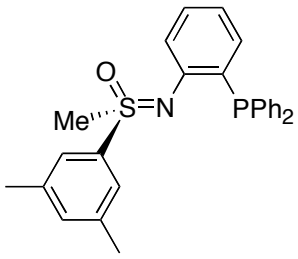
Yield: 81%; m.p.: 103-105 °C; R_f: 0.18 (pentane/acetone 5:1, 254 nm); $[\alpha]_D^{25}$ = -126.1 (*c* = 1.1, $CDCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.7 Hz, 3 H; CH_3), 0.88 (d, *J* = 6.7 Hz, 3 H; CH_3), 2.15 (hept, *J* = 6.7 Hz, 1 H; CH), 2.76 (dd, *J* = 13.7, 6.6 Hz, 1 H; CH_2), 3.09 (dd, *J* = 13.8, 5.7 Hz, 1 H; CH_2), 6.64-6.68 (m, 1 H; Ar-H), 6.73-6.77 (m, 1 H; Ar-H), 6.93-7.05 (m, 2 H; Ar-H), 7.33-7.54 (m, 13 H; Ar-H), 7.64-7.67 (m, 2 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.6, 22.8, 24.0, 65.4, 120.2, 121.0, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 129.1, 129.2, 131.0 (d, J_{C-P} = 6.2 Hz), 132.8 (d, J_{C-P} = 8.0 Hz), 133.6 (d, J_{C-P} = 19.6 Hz), 134.6 (d, J_{C-P} = 20.4 Hz), 137.5 (d, J_{C-P} = 10.4 Hz), 137.7 (d, J_{C-P} = 10.8 Hz), 138.9, 148.0 (d, J_{C-P} = 19.0 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -13.0 ppm; IR (KBr): $\tilde{\nu}$ = 3054 (m), 2961 (m), 1575 (m), 1462 (s), 1433 (s), 1290 (s), 1256 (s), 1192 (m), 1097 (m), 1011 (m), 743 (s), 696 (s) cm^{-1}; MS (EI): *m/z* (%): 457.9 (1) [M^+], 400.0 (100) [$M^+-C_4H_9$], 291.0 (9), 273.9 (9), 214.0 (6) 198.0 (5); elemental analysis (%) calcd. for $C_{28}H_{28}NOPS$: C 73.50, H 6.17, N 3.06; found: C 73.76, H 6.62, N 2.92.

(*R*)-2-{[*S*-(2-methoxy)phenyl-*S*-methyl-sulfoximinoyl]phenyl}-diphenylphosphine (3e)



Yield: 73 %; m.p.: 104-106 °C; R_f: 0.19 (pentane/acetone 10:1, 254 nm); $[\alpha]_D^{25}$ = +14.8 (c = 0.5, $CDCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.08 (s, 3 H; CH_3), 3.81 (s, 3 H; CH_3), 6.61-6.68 (m, 1 H; Ar-H), 6.74-6.81 (m, 1 H; Ar-H), 6.90-6.96 (m, 2 H; Ar-H), 7.05-7.14 (m, 2 H; Ar-H), 7.24-7.36 (m, 10 H; Ar-H), 7.47 (m_c, 1 H; Ar-H), 7.89 (m_c, 1 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.0, 56.0, 112.3, 120.4, 120.5, 121.3, 127.6, 128.1, 128.2, 128.3, 128.4, 129.3, 131.2, 131.4 (d, J_{C-P} = 6.4 Hz), 133.2, 134.0 (d, J_{C-P} = 20.0 Hz), 134.2 (d, J_{C-P} = 20.0 Hz), 134.8, 137.9 (d, J_{C-P} = 10.8 Hz), 148.2 (d, J_{C-P} = 19.6 Hz), 157.2 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -13.0 ppm; IR (KBr): $\tilde{\nu}$ = 3431 (b), 3048 (w), 2931 (w), 1578 (s), 1461 (s), 1433 (s), 1279 (s), 1260 (m), 1199 (m), 1079 (m), 1017 (s), 799 (w), 750 (s), 697 (m), 529 (w), 499 (w) cm^{-1}; MS (EI): m/z (%): 430.1 (100) [M^+-CH_3], 291.1 (11), 274.0 (14), 214.0 (7), 198.0 (10), 183.0 (9), 154.0 (5); elemental analysis (%) calcd. for $C_{26}H_{24}NOPS$: C 70.09, H 5.43, N 3.14; found: C 69.78, H 5.53, N 3.07.

(*R*)-2-[*S*-(3,5-dimethyl)phenyl-*S*-methylsulfoximinoyl)phenyl]-diphenylphosphine (3f)



Yield: 67 %; m.p.: 83-85 °C; R_f: 0.10 (pentane/acetone 9:1, 254 nm); $[\alpha]_D^{25}$ = + 116.8 (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 6 H; CH_3), 2.92 (s, 3 H; CH_3), 6.66-6.71 (m, 1 H; Ar-H), 6.80-6.85 (m, 1 H; Ar-H), 7.11-7.16 (m, 2 H; Ar-H), 7.31-7.42 (m, 13 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 44.2, 120.8, 121.6, 125.5, 128.2, 128.3, 128.4, 128.4, 128.5, 129.6, 133.1, 133.8, 134.0, 134.3, 134.8, 137.2 (d, J_{C-P}

= 9.3 Hz), 137.4 (d, J_{C-P} = 9.8 Hz), 139.2, 148.0 (d, J_{C-P} = 19.2 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ = -13.3 ppm; IR (KBr): $\tilde{\nu}$ = 3468 (m), 3051 (m), 2923 (m), 1461 (s), 1434 (s), 1290 (s), 1258 (s), 1203 (s), 1028 (s), 749 (s) cm^{-1}; MS (EI): *m/z* (%): 429.1 (30) [M^+-CH_3], 428.1 (100), 291.1 (6), 274.1 (8), 214.0 (4), 198.0 (6), 183.0 (6); HRMS($C_{27}H_{26}NOPS$–CH_3): calc.: 428.12380; found: 428.12383.

Analytical data for imines 7b-k, 9i, and 11

***N*-[(1-phenyl)propylidene]-4´-methoxyaniline (7b):**
Yellow needles; *E/Z* ratio: ≈7:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t_{major}, *J* = 7.7 Hz, 3 H; CH_3), 1.13 (t_{minor}, *J* = 7.4 Hz, 0.44 H; CH_3), 2.60 (q_{major}, *J* = 7.7 Hz, 2 H; CH_2), 2.71 (q_{minor}, *J* = 7.4 Hz, 0.40 H; CH_2), 3.61 (s_{minor}, 3 H; CH_3), 3.72 (s_{major}, 3 H; CH_3), 6.50 ($m_{c,\ minor}$, 0.44 H; Ar-H), 6.57 ($m_{c,\ minor}$, 0.18 H; Ar-H), 6.66 ($m_{c,\ major}$, 0.18 H; Ar-H), 6.82 ($m_{c,\ major}$, 2 H; Ar-H), 6.96-6.98 (m, 0.12 H; Ar-H), 7.12-7.14 (m, 0.14 H; Ar-H), 7.34 (m, 3 H; Ar-H), 7.80-7.85 (m, 2 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *major*-isomer: δ = 12.0, 23.3, 55.5, 114.2, 120.1, 127.4, 128.3, 130.1, 138.1, 144.7, 155.6, 171.1 ppm; *minor*-isomer: δ = 11.0, 34.5, 55.2, 113.6, 122.2, 127.7, 128.0, 138.1, 144.7, 155.6, 171.1 ppm; IR (KBr): $\tilde{\nu}$ = 2937 (w), 2930 (w), 1684 (m), 1507 (s), 1238 (s), 1029 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 239.1 (64) [M^+], 210.1 (100); elemental analysis (%) calcd. for $C_{16}H_{17}NO$: C 80.30, H 7.16, N 5.85; found: C 80.59, H 7.48, N 5.80.

***N*-[1-(2-Methyl)phenyl]-ethylidene-4´-methoxyaniline (7c):**
Orange oil; *E/Z* ratio = ≈1.3:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.04 (s, 2.2 H; CH_3), 2.17 (s, 3 H; CH_3), 2.45 (s, 2.17 H; CH_3), 2.48 (s, 3 H; CH_3), 6.61-6.75 (m, 3.3 H; Ar-H), 6.81 ($m_{c,major}$, 2 H; Ar-H), 6.91 ($m_{c,major}$, 2 H; Ar-H), 7.01-7.38 (m, 6.3 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *both isomers:* δ =

19.8, 20.2, 21.2, 29.4, 55.2, 55.5, 113.2, 114.2, 114.7, 116.3, 120.5, 122.2, 125.3, 125.7, 127.1, 127.1, 127.9, 128.4, 130.1, 131.0, 134.7, 139.2, 141.7, 141.7, 144.2, 155.78, 155.9, 170.0, 170.1 ppm; MS (EI): *m/z* (relative intensity) = 239.1 (100) [M^+], 224.1 (56); elemental analysis (%) calcd. for $C_{16}H_{17}NO$: C 80.30, H 7.16, N 5.85; found: C 80.42, H 7.32, N 6.03.

***N*-[1-(3-Methyl)phenyl]-ethylidene-4´-methoxyaniline (7d):**
Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3 H; CH_3), 2.43 (s, 3 H; CH_3), 3.82 (s, 3 H; CH_3), 6.77 (m_c, 2 H; Ar-H), 6.92 (m_c, 2 H; Ar-H), 7.27-7.36 (m, 2 H; Ar-H), 7.73 (m_c, 1 H; Ar-H), 7.84 (s, 1 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.4, 21.5, 55.4, 114.1, 120.6, 124.2, 127.5, 128.1, 130.9, 137.8, 139.6, 144.7, 155.7, 165.8 ppm; IR (KBr): $\tilde{\nu}$ = 2930 (m), 1624 (s), 1499 (s), 1291 (s), 1237 (s), 1028 (s), 841 (s), 795 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 239.1 (83) [M^+], 224.1 (100); elemental analysis (%) calcd. for $C_{16}H_{17}NO$: C 80.30, H 7.16, N 5.85; found C 80.28, H 7.25, N 5.78.

***N*-[1-(4-Methyl)phenyl]-ethylidene)-4´-methoxyaniline (7e):**
Yellow crystals; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3 H; CH_3), 2.42 (s, 3 H; CH_3), 3.82 (s, 3 H; CH_3), 6.76 (m_c, 2 H; Ar-H), 6.92 (m_c, 2 H; Ar-H), 7.25 (d, *J* = 8.2 Hz, 2 H; Ar-H), 7.88 (d, *J* = 8.2 Hz, 2 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.2, 21.3, 55.4, 114.1, 120.7, 127.0, 129.0, 137.0, 140.5, 144.9, 155.8, 165.5 ppm; IR (KBr): $\tilde{\nu}$ = 2945 (m), 1624 (s), 1505 (s), 1291 (s), 1237 (s), 1033 (s), 822 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 239.1 (85) [M^+], 224.1 (100); elemental analysis (%) calcd. for $C_{16}H_{17}NO$: C 80.30, H 7.16, N 5.85; found: C 80.41, H 7.17, N 5.80.

***N*-[1-(2-Methoxy)phenyl]ethylidene-4´-methoxyaniline (7f):**
Orange oil; *E/Z* ratio: ≈2:1; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.21 (s_{major}, 3 H; CH_3), 2.45 (s_{minor}, 1.5 H; CH_3), 3.67 (s_{minor}, 1.5 H;

CH_3), 3.72 (s_{minor}, 1.5 H; CH_3), 3.81 (s_{major}, 3 H; CH_3), 3.87 (s_{major}, 3 H; CH_3), 6.60 (m, 1.9 H; Ar-H), 6.76-7.02 (m, 7.5 H; Ar-H), 7.17 (m, 0.4 H; Ar-H), 7.36 (m_c, 0.8 H; Ar-H), 7.56 (m_c, 0.8 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): both isomers δ = 21.0, 28.6, 55.2, 55.2, 55.4, 110.5, 111.0, 113.3, 114.0, 120.2, 120.7, 120.7, 121.5, 127.9, 129.2, 129.3, 130.3, 131.4, 144.2, 155.7, 157.1, 168.1, 169.1 ppm; MS (EI): *m/z* (relative intensity) = 255.1 (86) [M^+], 240.1 (76), 225.1 (19), 133.1 (35), 123.1 (100.

***N*-[1-(3-Methoxy)phenyl]ethylidene-4´-methoxyaniline (7g):**
Yellow crystals; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 3 H; CH_3), 3.82 (s, 3 H; CH_3), 3.88 (s, 3 H; CH_3), 6.76 (m_c, 2 H; Ar-H), 6.91 (m_c, 2 H; Ar-H), 7.01 (m_c, 1 H; Ar-H), 7.35 (t, J = 8.0 Hz, 1 H; Ar-H), 7.50 (m_c, 1 H; Ar-H), 7.58 (m, 1 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.5, 55.4, 55.5, 111.7, 114.2, 116.6, 119.7, 120.6, 129.2, 141.1, 144.6, 155.8, 159.5, 165.4 ppm; IR (KBr): $\tilde{\nu}$ = 3004 (m), 2955 (m), 2933 (m), 1626 (s), 1592 (s), 1499 (s), 1458 (s), 1280 (m), 1233 (s), 1030 (s), 840 (s), 792 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 255.1 (87) [M^+], 240.1 (100), 148.1 (7); elemental analysis (%) calcd. for $C_{16}H_{17}NO_2$: C 75.27, H 6.71, N 5.49; found: C 75.42, H 6.93, N 5.47.

***N*-[1-(4-Methoxy)phenyl]ethylidene-4´-methoxyaniline (7h):**
Yellow crystals; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 3 H; CH_3), 3.81 (s, 3 H; CH_3), 3.86 (s, 3 H; CH_3), 6.74 (m_c, 2 H; Ar-H), 6.90 (m_c, 2 H; Ar-H), 6.94 (m_c, 2 H; Ar-H), 7.94 (m_c, 2 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2, 55.4, 55.5, 113.5, 114.1, 120.8, 128.6, 132.3, 144.8, 155.6, 161.3, 164.7 ppm; IR (KBr): $\tilde{\nu}$ = 2963 (m), 1625 (s), 1600 (s), 1502 (s), 1460 (m), 1239 (m), 1025 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 255.1 (79) [M^+], 240.1 (100); elemental analysis (%) calcd. for $C_{16}H_{17}NO_2$: C 75.27, H 6.71, N 5.49; found: C 74.94, H 7.01, N 5.45.

***N*-[1-(4-Chloro)phenyl]ethylidene-4´-methoxyaniline (7i):**
Yellow-green crystals; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 3 H; CH_3), 3.82 (s, 3 H; CH_3), 6.75 (m_c, 2 H; Ar-H), 6.91 (m_c, 2 H; Ar-H), 7.40 (m_c, 2 H; Ar-H), 7.90 (m_c, 2 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2, 55.5, 114.2, 120.7, 128.4, 136.3, 138.0, 144.2, 155.9, 164.3 ppm; IR (KBr): $\tilde{\nu}$ = 2962 (m), 1639 (s), 1497 (s), 1287 (s), 1236 (s), 1029 (s), 835 (s) cm^{-1}; MS (EI), *m/z* (relative intensity) = 259.0 (83) [M^+], 244.0 (100); elemental analysis (%) calcd. for $C_{15}H_{14}ClNO$: C 69.36, H 5.43, N 5.39; found: C 69.52, H 5.72, N 5.41.

***N*-[1-(1-naphthyl)-ethylidene]-4´-methoxyaniline (7j):**
Brown solid; *E/Z* ratio: ≈1.6:1; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s_{major}, 3 H; CH_3), 2.62 ($s_{minor,}$ 1.9 H; CH_3), 3.58 ($s_{minor,}$ 1.9 H; CH_3), 3.85 (s_{major}, 3 H; CH_3), 6.49 ($m_{c,major}$, 1 H; Ar-H), 6.62 ($m_{c,major}$, 1 H; Ar-H), 6.96 (m_c, 4 H; Ar-H), 7.15-7.90 (m, 10 H; Ar-H), 8.36 (d, *J* = 8.0 Hz, 0.5 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): both isomers δ = 22.0, 29.9, 55.1, 55.5, 113.4, 114.2, 114.2, 120.6, 120.7, 121.6, 124.5, 124.9, 125.0, 125.2, 125.9, 125.94, 126.4, 126.6, 128.1, 128.4, 129.0, 129.2, 130.1, 133.1, 133.9, 139.5, 144.2, 156.0, 169.3, 169.7 ppm; IR (KBr): $\tilde{\nu}$ = 2959 (m), 1605 (s), 1498 (s), 1461 (s), 1285 (s), 1239 (s), 1028 (s), 830 (s), 741 (s) cm^{-1}; MS (EI), *m/z* (relative intensity) = 275.1 (90) [M^+], 260.1 (100).

***N*-[1-(2-naphthyl)ethylidene]-4´-methoxyaniline (7k):**
Yellow crystals; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3 H; CH_3), 3.84 (s, 3 H; CH_3), 6.81 (m_c, 2 H; Ar-H), 6.94 (m_c, 2 H; Ar-H), 7.49-7.57 (m, 2 H; Ar-H), 7.86-7.95 (m, 3 H; Ar-H), 8.22 (dd, *J* = 8.7, 1.7 Hz, 1 H; Ar-H), 8.34 (s, 1 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.3, 55.5, 114.3, 120.8, 124.2, 126.3, 127.1, 127.5, 127.7, 128.0, 128.6, 128.9, 133.0, 134.4, 137.1, 156.0, 165.5 ppm; IR (KBr): $\tilde{\nu}$ = 3003 (m), 2961

(m), 1606 (s), 1500 (s), 1461 (s), 1285 (s), 1241 (s), 1028 (s), 830 (s), 742 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 275.1 (91) [M^+], 260.1 (100); elemental analysis (%) calcd. for $C_{19}H_{17}NO$: C 82.88, H 6.22, N 5.09; found: C 83.11, H 6.65, N 5.00.

***N*-[1-(4-Chloro)phenyl]ethylidene-2´-methoxyaniline (9i):**

Yellow crystals; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 3 H; CH_3), 3.79 (s, 3 H; CH_3), 6.77 (dd, *J* = 7.7, 1.6 Hz, 1 H; Ar-H), 6.93-6.99 (m, 2 H; Ar-H), 7.09 (m_c, 1 H; Ar-H), 7.41 (m_c, 2 H; Ar-H), 7.96 (m_c, 2 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.7, 55.6, 111.4, 120.4, 120.8, 124.2, 128.3, 128.6, 136.4, 137.6, 140.1, 148.7, 165.7 ppm; IR (KBr): $\tilde{\nu}$ = 3888 (m), 1630 (s), 1588 (s), 1490 (s), 1296 (s), 1111 (s), 1092 (s), 825 (s), 746 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 259.0 (78) [M^+], 244.0 (100), 229.0 (13); elemental analysis (%) calcd. for $C_{15}H_{14}ClNO$: C 69.36, H 5.43, N 5.39; found: C 69.28, H 5.51, N 5.38.

***(E)*-*N*-[1-(3,4-dihydronaphthyl)ethylidene]-4´-methoxyaniline (11):**

Brown solid; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.89-1.95 (m, 2 H; CH_2), 2.55-2.59 (m, 2 H; CH_2), 2-89-2.92 (m, 2 H; CH_2), 3.02 (s, 3 H; CH_3), 6.77 (m_c, 2 H; Ar-H), 6.91 (m_c, 2 H; Ar-H), 7.19-7.39 (m, 3 H; Ar-H), 8.33 (dd, *J* = 8.0, 1.1 Hz, 1 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.1, 29.9, 30.00, 55.5, 114.1, 120.8, 126.2 126.3, 128.6, 130.4, 133.9, 141.0, 144.49, 155.6, 165.7 ppm; IR (KBr): $\tilde{\nu}$ = 2945 (m), 1619 (s), 1594 (s), 1498 (s), 1452 (s), 1236 (s), 1206 (s), 1029 (s), 837 (s), 732 (m) cm^{-1}; MS (EI): *m/z* (relative intensity) = 251.1 (100) [M^+], 236.1 (56) [M^+-CH_3], 208.1 (11); elemental analysis (%) calcd. for $C_{17}H_{17}NO$: C 81.24, H 6.82, N 5.57; found: C 81.16, H 6.61, N 5.58.

General hydrogenation procedure:

General procedure for the asymmetric hydrogenation: Under an argon atmosphere, $[Ir(COD)Cl]_2$ (1.7 mg, 0.0025 mmol) and sulfoximine **3d** (2.5 mg, 0.0055 mmol) were placed in a 10 mL test tube equiped with a stirr bar. After the addition of dry toluene (0.5 mL), the yellow solution was stirred for 30 min. Then, iodine (2.5 mg, 0.010 mmol) was added and the solution turned red within another 30 min. To this catalyst solution was added the imine (0.5 mmol) and additional toluene (0.5 mL). The test tube was placed in an argon-filled steel autoclave, which was purged three times with hydrogen (5 bar) and finally pressurized to 20 bar. The reaction mixture was stirred for the indicated period of time. Then, the hydrogen gas was released and the reaction quenched by addition of pentane (3 mL). The product was filtered through a short plug of silica (3 cm) and eluted with pentane/acetone (20:1). The conversion was determined by ^{1}H NMR spectroscopy and the enantiomeric ratio analyzed with analytical HPLC using chiral columns.

***N*-(4-Methoxyphenyl)-1-phenylethylamine (8a):**[5]

Colorless oil; $[\alpha]_D^{25}$ = -3.0 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.38 (d, *J* = 6.7 Hz, 3 H; CH_3), 3.57 (s, 3 H; CH_3), 3.60 (br, 1 H; NH), 4.31 (q, *J* = 6.7 Hz, 1 H; CH), 6.37 (d, *J* = 9.2 Hz, 2 H; Ar-H), 6.59 (d, *J* = 9.2 Hz, 2 H; Ar-H), 7.09-7.14 (m, 1 H; Ar-H), 7.19-7.26 (m, 4 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0, 54.1, 55.6, 114.4, 114.7, 125.8, 126.7,

5 a) S. E. Denmark, N. Nakajima, O. J.-C. Nicaise, *J. Am. Chem. Soc.* **1994**, *116*, 8797-9798; b)Y. Chi, Y.-G. Zhou, X. Zhang, *J. Org. Chem.* **2003**, *68*, 4120-4122; c) A. Trifonova, J. S. Diesen, C. J. Chapman, P.G. Andersson, *Org. Lett.* **2004**, *6*, 3825-3827.

128.5, 141.5, 145.4, 151.8 ppm; IR (KBr): $\tilde{\nu}$ = 3377 (s), 2961 (m), 1515 (s), 1233 (s), 1031 (s), 816 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 227.3 (100) [M^+], 212.2 (66), 123.2 (34); elemental analysis (%): calcd. for $C_{15}H_{17}NO$: C 79.26, H 7.54, N 6.16; found: C 79.53, H 7.47, N 6.00.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 99/1, λ = 254 nm, 25 °C); t_r = 19.0 min [minor], t_r = 22.0 [major]; 96% *ee*.

_N_-(4-Methoxyphenyl)-1-phenylpropylamine (8b):[5b]

Light brown oil; $[\alpha]_D^{25}$ = −24.2 (*c* = 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.4 Hz, 3 H; CH_3), 1.63-1.79 (m, 2 H; CH_2), 3.58 (s, 3 H; CH_3), 3.71 (br, 1H; NH), 4.06 (t, *J* = 6.7 Hz, 1 H; CH), 6.38 (d, *J* = 9.2 Hz, 2 H; Ar-H), 6.59 (d, *J* = 8.9 Hz, 2 H; Ar-H), 7.11-7.29 (m, 5 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.8, 31.6, 55.7, 60.5, 114.4, 114.7, 126.5, 126.8, 128.4, 141.8, 144.1, 151.8 ppm; IR (KBr): $\tilde{\nu}$ = 3399 (m), 2963 (m), 2933 (m), 1513 (s), 1238 (s), 755 (m) cm^{-1}; MS (EI): *m/z* (relative intensity) = 241.1 (43) [M^+], 212.1 (100) [M^+-C_2H_5]; elemental analysis (%): calcd. for $C_{16}H_{19}NO$: C 79.63, H 7.94, N 5.80; found: C 79.47, H 8.21, N 5.88.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 99/1, λ = 254 nm, 25 °C); t_r = 19.3 min [minor], t_r = 21.5 [major]; 92% *ee*.

_N_-(4-Methoxyphenyl)-1-(2-methylphenyl)ethylamine (8c):[5b]

Colorless solid; $[\alpha]_D^{25}$ = +22.8 (c = 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.34 (d, *J*= 6.9 Hz, 2 H; CH_3), 2.33 (s, 3 H; CH_3), 3.57 (s, 3 H; CH_3), 3.58 (br, 1 H; NH), 4.51 (q, *J* = 6.6 Hz, 1 H; CH), 6.30 (d, *J* = 9.1 Hz, 2 H; Ar-H), 6.59 (d, *J* = 9.1 Hz, 2 H; Ar-H), 7.00-7.07 (m, 3 H; Ar-H), 7.29-7.34 (m, 2 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.0, 23.1, 50.4, 55.7, 114.1, 114.7, 124.5, 126.4, 130.4, 134.4, 141.4, 142.8,

151.6 ppm; IR (KBr): $\tilde{\nu}$ = 3400 (m), 2971 (m), 2930 (m), 1612 (s), 1241 (s), 1036 (m) cm^{-1}; MS (EI): *m/z* (relative intensity) = 241.1 (100) $[M^+]$, 226.1 (48) $[M^+-CH_3]$, 123.1 (47), 119.1 (54); elemental analysis (%): calcd. for $C_{16}H_{19}NO$: C 79.63, H 7.94, N 5.80; found: C 79.40, H 7.76, N 5.68.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 99/1, λ = 254 nm, 25 °C); t_r = 17.7 min [minor], t_r = 23.7 [major]; 94% *ee*.

***N*-(4-Methoxyphenyl)-1-(3-methylphenyl)ethylamine (8d):**[5b]

Colorless solid; $[\alpha]_D^{25}$ = -73.1 (*c* = 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.48 (d, *J* = 6.9 Hz, 3 H; CH_3), 2.33 (s, 3 H; CH_3), 3.69 (s, 3 H; CH_3), 3.71 (br, 1 H; NH), 4.38 (q, *J* = 6.9 Hz, 1 H; CH), 6.50 (d, *J* = 8.9 Hz, 2 H; Ar-H), 6.71 (d, *J* = 8.9 Hz, 2 H; Ar-H), 7.04-7.07 (m, 1 H; Ar-H), 7.18-7.23 (m, 3 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 25.0, 54.1, 55.5, 114.4, 114.6, 122.8, 126.5, 127.5, 128.4, 138.0, 141.6, 145.4, 151.7 ppm; IR (KBr): $\tilde{\nu}$ = 3400 (m), 2970 (m), 2931 (m), 1512 (s), 1456 (m), 1241 (s), 1035 (m), 819 (m), 756 (m) cm^{-1}; MS (EI): *m/z* (relative intensity) = 241.1 (100) $[M^+]$, 226.1 (48) $[M^+-CH_3]$, 123.1 (47), 119.1 (54); elemental analysis (%): calcd. for $C_{16}H_{19}NO$: C 79.63, H 7.94, N 5.80; found: C 79.69, H 7.94, N 6.07.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 99/1, λ = 254 nm, 25 °C); t_r = 19.7 min [minor], t_r = 23.0 [major]; 93% *ee*.

***N*-(4-Methoxyphenyl)-1-(4-methylphenyl)ethylamine (8e):**[5b]

Colorless solid; $[\alpha]_D^{25}$ = -22.1 (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.48 (d, *J* = 6.7 Hz, 3 H; CH_3), 2.33 (s, 3 H; CH_3), 3.70 (s, 3 H; CH_3), 3.73 (br, 1 H; NH), 4.39 (q, *J* = 6.6 Hz, 1 H; CH), 6.48 (m_c, 2 H; Ar-H), 6.70 (m_c, 2 H; Ar-H), 7.12 (d, *J* = 7.8 Hz, 2 H; Ar-H), 7.25 (d, *J* = 7.8 Hz, 2 H; Ar-H)

ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 25.2, 54.0, 55.8, 114.5, 114.7, 125.7, 129.2, 136.2, 141.5, 142.3, 151.7 ppm; ; IR (KBr): $\tilde{\nu}$ = 3400 (m), 2963 (m), 1512 (s), 1237 (s), 819 (s), 757 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 241.1 (100) [M^+], 226.1 (48) [M^+-CH_3], 123.1 (47), 119.1 (54); elemental analysis (%): calcd. for $C_{16}H_{19}NO$: C 79.63, H 7.94, N 5.80; found: C 79.84, H 7.85, N 5.69.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 99/1, λ = 254 nm, 25 °C); t_r = 20.3 min [minor], t_r = 23.0 [major]; 96% *ee*.

***N*-(4-Methoxyphenyl)-1-(2-methoxyphenyl)ethylamine (8f):**

Light yellow oil; $[\alpha]_D^{25}$ = +14.0 (*c* = 0.25, $CDCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.54 (d, *J* = 6.9 Hz, 3 H; CH_3), 3.75 (s, 3 H; CH_3), 3.94 (s, 3 H; CH_3), 3.97 (br, 1 H; NH), 4.87 (q, *J* = 6.9 Hz, 1 H; CH), 6.56 (d, *J* = 8.8 Hz, 2 H; Ar-H), 6.77 (d, *J* = 8.8 Hz, 2 H; Ar-H), 6.96 (m_c, 2 H; Ar-H), 7.26 (m_c, 1 H; Ar-H), 7.40 (dd, *J* = 7.4, 1.7 Hz, 1 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.8, 48.8, 55.2, 55.6, 110.3, 114.3, 114.5, 120.6, 126.3, 127.4, 132.7, 141.5, 151.5, 156.5 ppm; IR (KBr): $\tilde{\nu}$ = 3405 (m), 2961 (m), 1512 (s), 1237 (s), 755 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 257.1 (100) [M^+], 242.1 (58), 135.1 (86), 123.1 (29); elemental analysis (%): calcd. for $C_{16}H_{19}NO_2$: C 74.68, H 7.44, N 5.44; found: C, 74.86 H; 7.04 N 5.39.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 99/1, λ = 254 nm, 25 °C); t_r = 19.8 min [minor], t_r = 24.8 [major]; 90% *ee*.

***N*-(4-Methoxyphenyl)-1-(3-methoxyphenyl)ethylamine (8g):**

Colorless oil; $[\alpha]_D^{25}$ = −6.6 (*c* = 0.45, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.54 (d, *J* = 6.9 Hz, 3 H; CH_3), 3.75 (s, 3 H; CH_3), 3.83 (s, 3 H; CH_3), 3.84 (br, 1 H; NH), 4.44 (q, *J* = 6.9 Hz, 1 H; CH), 6.55 (d, *J* = 9.1 Hz, 2 H; Ar-H), 6.76 (d, *J* = 9.0 Hz,

2 H; Ar-H), 6.83 (ddd, *J* = 8.3, 2.8, 0.8, 1 H; Ar-H), 7.00-7.04 (m, 2 H; Ar-H), 7.30 (t, *J* = 7.8 Hz, 1 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.1, 54.2, 55.1, 55.6, 111.5, 111.8, 114.4, 114.6, 118.1, 129.4, 141.4, 147.3, 151.7, 159.7 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2960 (m), 1513 (s), 1241 (s), 1040 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 257.1 (100) [M$^+$], 242.1 (65), 135.1 (31), 123.1 (31); elemental analysis (%): calcd. for $C_{16}H_{19}NO_2$: C 74.68, H 7.44, N 5.44; found: C 74.83, H 7.55, N 5.58.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 99/1, λ = 254 nm, 25 °C); t_r = 33.8 min [minor], t_r = 39.3 [major]; 96% *ee*.

***N*-(4-Methoxyphenyl)-1-(4-methoxyphenyl)ethylamine (8h):**[5b,c]

Colorless oil; $[\alpha]_D^{25}$ = –17.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.51 (d, *J* = 6.7 Hz, 3 H; CH_3), 3.73 (s, 3 H; CH_3), 3.81 (s, 3 H; CH_3), 3.82 (br, 1 H; NH), 4.42 (q, *J* = 6.7 Hz, 1 H; CH), 6.53 (d, *J* = 8.9 Hz, 2 H; Ar-H), 6.75 (d, *J* = 8.9 Hz, 2 H; Ar-H), 6.90 (d, *J* = 9.2 Hz, 2 H; Ar-H), 7.33 (d, *J* = 9.1 Hz, 2 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0, 53.5, 55.1, 55.6, 113.9, 114.5, 114.6, 126.8, 137.4, 141.6, 151.7, 158.3 ppm; IR (KBr): $\tilde{\nu}$ = 2924 (s), 2856 (s), 1512 (s), 1241 (s), 758 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 257.1 (52) [M$^+$], 242.1 (5), 177.1 (5), 135.1 (100); elemental analysis (%): calcd. for $C_{16}H_{19}NO_2$: C 74.68, H 7.44, N 5.44; found: C 74.44, H 7.39, N 5.77.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 97/3, λ = 254 nm, 25 °C); t_r = 17.6 min [minor], t_r = 19.9 [major]; 94% *ee*.

***N*-(4-Methoxyphenyl)-1-(4-chlorophenyl)ethylamine (8i):**[5b,c]

Colorless solid; $[\alpha]_D^{25}$ = –16.1 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (d, *J* = 6.9 Hz, 3 H; CH_3), 3.70 (s, 3 H;

CH_3), 3.72 (br, 1 H; NH), 4.38 (q, *J* = 6.9 Hz, 1 H; CH), 6.46 (d, *J* = 8.9 Hz, 2 H; Ar-H), 6.72 (d, *J* = 8.9 Hz, 2 H; Ar-H), 7.26-7.31 (m, 4 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0, 53.6, 55.5, 114.4, 114.6, 127.2, 128.6, 132.1, 141.1, 144.0, 151.9 ppm; IR (KBr): $\tilde{\nu}$ = 3400 (m), 2928 (m), 1512 (s), 1238 (s), 758 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 261.1 (100) [M^+], 246.1 (50), 139.0 (38), 123.1 (48); elemental analysis (%): calcd. for $C_{15}H_{16}ClNO$: C 68.83, H 6.16, N 5.35; found: C 68.89, H 5.79, N 5.60.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 97/3, λ = 254 nm, 25 °C); t_r = 17.8 min [minor], t_r = 21.5 [major]; 95% *ee*.

_N_-(4-Methoxyphenyl)-1-(α-naphthyl}ethylamine (8j):[5a]

Colorless solid; $[\alpha]_D^{25}$ = +80.2 (*c* = 0.44, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.69 (d, *J* = 6.7 Hz, 3 H; CH_3), 3.71 (s, 3 H;CH_3), 3.91 (br, 1 H; NH), 5.27 (q, *J* = 6.7 Hz, 1 H; Ar-H), 6.49 (m_c, 2 H; Ar-H), .6.71 (m_c, 2 H; Ar-H), 7.46 (t, *J* = 7.9 Hz, 1 H; Ar-H), 7.53-7.64 (m, 2 H; Ar-H), 7.71 (d, *J* = 7.1 Hz, 1 H; Ar-H), 7.80 (d, *J* = 8.4 Hz, 1 H; Ar-H), 7.95 (m, 1 H; Ar-H), 8.23 (d, *J* = 8.4 Hz, 1 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.7, 50.0, 55.6, 114.2, 114.7, 122.3, 122.6, 125.3, 125.8, 126.0, 127.3, 129.1, 130.7, 134.0, 140.2, 141.4, 151.8 ppm; IR (KBr): $\tilde{\nu}$ = 3410 (m), 2940 (w), 1513 (s), 1236 (s), 1037 (m), 804 (m), 778 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 277.1 (100) [M^+], 262.1 (23) [M^+-CH_3], 155.1 (93), 123.1 (34); elemental analysis (%): calcd. for $C_{19}H_{19}NO$: C 82.28, H 6.90, N 5.05; found: C 81.95, H 6.92, N 4.91.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 99/1, λ = 254 nm, 25 °C); t_r = 34.5 min [minor], t_r = 47.3 [major]; 98% *ee*.

_N_-(4-Methoxyphenyl)-1-(β-naphthyl)ethylamine (8k):

Colorless solid; $[\alpha]_D^{25}$ = -21.1 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63 (d, *J* = 6.7 Hz, 3 H; CH_3), 3.73 (s, 3 H;CH_3), 3.90 (br, 1 H; NH), 4.64 (q, *J* = 6.7 Hz, 1 H; CH), 6.59 (m_c, 2 H; Ar-H), 6.76 (m_c, 2 H; Ar-H), 7.48-7.59 (m, 3 H; Ar-H), 7.85-7.91 (m, 4 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0, 54.4, 55.6, 114.6, 114.7, 124.2, 124.4, 125.4, 125.9, 127.6, 127.7, 128.4, 132.7, 133.5, 141.5, 143.0, 152.9 ppm; IR (KBr): $\tilde{\nu}$ = 3384 (m), 2964 (w), 1514 (s), 1230 (s), 1029 (s), 816 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 277.1 (100) [M^+], 262.1 (26) [M^+-CH_3], 155.1 (95), 123.1 (37); elemental analysis (%): calcd. for $C_{19}H_{19}NO$: C 82.28, H 6.90, N 5.05; found: C 81.89, H 6.68, N 4.93.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 99/1, λ = 254 nm, 25 °C); t_r = 36.5 min [minor], t_r = 43.0 [major]; 61% *ee*.

_N_-(2-Methoxyphenyl)-1-(4-chlorophenyl)ethylamine (12):

Colorless solid; $[\alpha]_D^{25}$ = +19.5 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (d, *J* = 6.9 Hz, 3 H; CH_3), 3.94 (s, 3 H; CH_3), 4.50 (q, *J* = 6.9 Hz, 1 H; CH), 4.69 (br, 1 H; NH), 6.36 (dd, *J* = 7.7, 1.7 Hz, 1 H; Ar-H), 6.70 (td, *J* = 7.7 1.7 Hz, 1 H; Ar-H), 6.78 (td, *J* = 7.7 1.7 Hz, 1 H; Ar-H), 6.84 (dd, *J* = 7.7, 1.7 Hz, 1 H; Ar-H), 7.33-7.38 (m, 4 H; Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.2, 52.8, 55.3, 109.2, 110.9, 116.5, 121.0, 127.1, 128.6, 132.1, 136.7, 143.9, 146.4 ppm; IR (KBr): $\tilde{\nu}$ = 3887 (s), 2837 (m), 1630 (s), 1588 (s), 1490 (s), 1242 (s), 1111 (s), 1092 (s), 825 (s), 746 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 261.1 (100) [M^+], 246.1 (50), 139.0 (38), 123.1 (48); elemental analysis (%): calcd. for $C_{15}H_{16}ClNO$: C 68.83, H 6.16, N 5.35; found: C 68.89, H 5.79, N 5.60.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 97/3, λ = 254 nm, 25 °C); t_r = 10.5 min [minor], t_r = 13.0 [major]; 79% *ee*.

***N*-(4-Methoxyphenyl)-1-(1,2,3,4-tetrahydro)naphthylamine (13):**
Light brown oil; $[\alpha]_D^{25}$ = -22.0 (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.64-1.86 (m, 4 H; CH_2), 2.60-2.76 (m, 2 H; CH_2), 3.49 (br, 1 H; NH), 3.64 (s, 3 H; CH_3), 4.43 (m_c, 1 H; CH), 6.52 (m_c, 2 H; Ar-H), 6.69 (m_c, 2 H; Ar-H), 6.99-7.10 (m, 3 H; Ar-H), 7.30-7.33 (m, 1 H; Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.4, 28.7, 29.4, 52.0, 55.8, 114.2, 114.9, 125.9, 126.9, 128.8, 129.1, 137.3, 138.3, 141.6, 151.7 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 3396 (m), 2933 (m), 1512 (s), 1239 (s) cm^{-1}; MS (EI): *m/z* (relative intensity) = 253.1 (100) [M^+], 131.1 (60), 123.1 (72).
The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptanes/*i*PrOH: 99/1, λ = 254 nm, 25 °C); t_r = 17.8 min [minor], t_r = 19.9 [major]; 91% *ee*.

Table A. Effect of the temperature[a]

Entry	Temperature [°C]	Conversion[%][b]	*ee* [%][c]
1	55	99	47
2	20	99	96
3	0	99	97

[a] Reaction conditions: imine **7a** (0.5 mmol), $[Ir(COD)Cl]_2$ (0.0025 mmol), **3d** (0.0055 mmol), iodine (0.01 mmol), 0.5 M toluene, RT, 20 bar. [b] According to ^1H NMR. [c] Determined by HPLC using a chiral column (Chiralcel OD-H).

Table B. Effect of the catalyst loading and hydrogen pressure[a]

Entry	Catalyst loading [mol-%]	Pressure [bar]	Conversion[%][b]	*ee* [%][c]

1	1.0	20	99	96
2	0.5	20	99	95
3	0.1	20	71	93
4	0.1	50	99	95

[a] Reaction conditions: imine **7a** (0.5 mmol), $[Ir(COD)Cl]_2$ (0.0025 mmol), **3d** (0.0055 mmol), iodine (0.01 mmol), 0.5 M toluene, RT. [b] According to ^1H NMR. [c] Determined by HPLC using a chiral column (Chiralcel OD-H).

Table C. Effect of the solvent[a]

Entry	Temperature [°C]	Conversion [%][b]	*ee* [%][c]
1	toluene	99	96
2	THF	99	81
3	DCM	99	93
4	MeOH	0	--

[a] Reaction conditions: imine **7a** (0.5 mmol), $[Ir(COD)Cl]_2$ (0.0025 mmol), **3d** (0.0055 mmol), iodine (0.01 mmol), 0.5 M, 20 bar, RT. [b] According to ^1H NMR. [c] Determined by HPLC using a chiral column (Chiralcel OD-H).