New P,N-Ferrocenyl Ligands for the Asymmetric Ir-Catalyzed Hydrogenation of Imines**

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Supporting Information :

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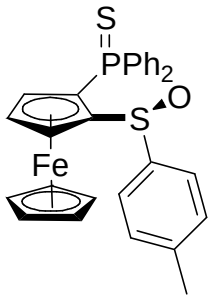
1. General

All reactions were carried out under nitrogen using standard Schlenk techniques. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 or AMX 600 or Varian VXR 400 S instrument. Chemical shifts are given as ppm relative to the residual solvent peak (chloroform-*d1*:7.24 ppm/77.0 ppm; benzene-*d6* 7.16 ppm/128.0 ppm). IR spectra were recorded on a Perkin Elmer 1420 Infrared Spectrometer. Mass spectra were recorded on a Finnigan Mat 95 Q spectrometer. Column chromatography purification was performed on Merck silica gel 60 (230-400 mesh ASTM). THF and toluene were dried with sodium/benzophenone and distilled. MeOH was treated with magnesium turnings (20 g/L), refluxed for 6 h and distilled off. Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by ^{1}H NMR. Elemental analysis was performed on an Elementar vario EL and with a Metrohm Titroprocessor 686. Yields referred to isolated yields of compounds estimated to be > 95% pure as determined by ^{1}H-NMR, capillary GC and combustion analysis (new compounds).

Sulfoxide (**1**) was prepared according to the literature procedure.[1] 3,5-Dimethyl-4-nitro anisole (91% yield) was prepared by slightly modified procedure[2] by using 2,6-Dimethylanisole instead of using 2,6-dimethyl-4-bromo anisole. $[Ir(COD)Cl]_2$ was purchased from STREM, NaBARF was prepared according to the literature procedure.[3]

(S_{Fc})-1-((*S*)-*p*-Tolylsulfinyl)-2-(diphenylphosphinothioyl) ferrocene (2):



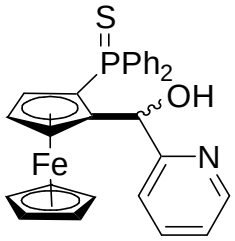
Preparation of LDA (Lithium Diisopropylamine): A 100 mL Schlenkflask was filled with diisopropyl amine (3.6 mL, 26.0 mmol, 1.30 equiv.) in THF (15 mL) under argon and cooled to −78 °C. Then slowly added *n*BuLi (1.51 M solution in *n*-pentane; 14.6 mL, 22.0 mmol, 1.10 equiv.) to the above solution at −78 °C. After addition was completed the solution was warmed to room temperature, stirred for 30 min and used as it is, in the below procedure.

A 500 mL Schlenkflask under an argon atmosphere was charged with sulfoxide **1**[1] (6.48 g, 20.0 mmol) in THF (200 mL) and cooled to −78 °C. Freshly prepared LDA (22.0 mmol) was added and the reaction mixture was stirred for 30 min at –78 °C. Chloro diphenylphosphine (5.30 g, 24.0 mmol, 1.20 equiv.) was added slowly at −78 °C. The reaction mixture was stirred at −78 °C for 1.5 h then warmed to room temperature and stirred for 1.5 h. A solution

of sulphur (1.92 g, 60.0 mmol, 3.0 equiv.) in butylamine (3 mL) was added to the reaction mixture at room temperature and stirred for 2-4 h (protection was monitored by ^{31}P-NMR). After quenching the reaction mixture with a saturated NH_4Cl solution, aqueous layer was extracted with CH_2Cl_2 (4 × 100 mL). The combined organic layers were washed with 2N HCl, water, brine, dried over $MgSO_4$ and evaporated under reduced pressure. Purification by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1) of the residue provided the desired compound (9.50 g, 17.60 mmol, 88 %) as a pale brown solid.

MP: 120.3-121.3 °C
$[\alpha]_D^{20}$ = −306 (c = 0.08, acetone).
^{1}H-NMR (300 MHz, C_6D_6): δ = 2.09 (s, 3H), 4.00-4.24 (m, 1H), 4.20 (s, 5H), 4.20-4.24 (m, 1H), 4.51-4.56 (m, 1H), 6.92 (d, *J* = 7.5 Hz, 2H), 7.15-7.24 (m, 6H), 7.94 (d, *J* = 7.8 Hz, 2H), 8.23-8.35 (m, 4H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 21.5, 71.9 (d, *J* = 10.0 Hz), 72.0 (d, *J* = 7.6 Hz), 72.5, 77.4 (d, *J* = 12.9 Hz), 80.0, 81.3, 126.5, 128.6 (d, *J* = 7.6 Hz), 128.8 (d, *J* = 1.8 Hz), 129.7, 131.8 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 3.5 Hz), 133.51 (d, *J* = 1.8 Hz), 133.52 (d, *J* = 24.1 Hz), 134.2 (d, *J* = 28.2), 135.4 (d, *J* = 28.8 Hz), 141.6, 143.0 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.45 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3436 (br, s), 1630 (br, w), 1436 (w), 1041 (m), 717 (m).
MS (70 eV, EI): *m/z* (%) = 540 (M^+, 26), 524 (22), 401 (100).
HRMS (EI): *m/z* calcd. for: [$C_{29}H_{25}P^{56}FeO^{32}S_2$] 540.0434, found: 540.0417

Preparation of ferrocenyl alcohol (3):



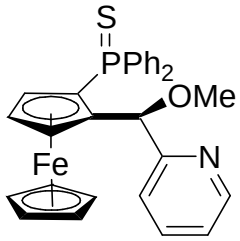
Preparation of PhLi: A 250 mL Schlenkflask was filled with iodobenzene (20.0 mmol, 1.36 ml, 2.0 equiv) in diethyl ether (100 mL) and cooled to 0 °C. Then tBuLi (1.5 M solution in pentane; 40.0 mmol, 26.70 mL) was added slowly dropwise at 0 °C. After addition was completed the reaction mixture was warmed to room temperature, stirred for 30 min and used as it is, in the below procedure.

A 500 mL Schlenkflask under an argon atmosphere was charged with ferrocenyl sulfoxide **2** (10.0 mmol, 5.40 g) in THF (10 mL) and cooled to −78 °C. A solution of freshly prepared PhLi in ether (0.20 M, 20.0 mmol, 100 mL) was slowly added and the reaction mixture was stirred at −78 °C for 10 min. 2-Pyridinecarboxaldehyde (2.30 mL, 24.0 mmol, 1.20 equiv) was added dropwise at −78 °C and reaction mixture was stirred for 1.5 h then at room temperature for 1.5 h. After quenching the reaction mixture with a saturated NH_4Cl solution, aqueous layer was extracted with diethyl ether (4 × 60 mL). The combined organic layers were washed with water, brine, dried over $MgSO_4$ and evaporated under reduced pressure. Purification of the residue by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1) afforded the two diastereomeric alcohols **3a** and **3b** (3.69 g, 7.20 mmol, 72 %) as an unseparable mixture **3** in 6:4 ratio (by ^{31}P-NMR).

^{1}H-NMR (200 MHz, C_6D_6): δ = 3.61-3.64 (m, 2H), 3.91-3.93 (m, 2H), 4.32 (s, 6H), 4.48 (s, 5H), 4.65 (s, 1H), 4.96 (d, *J* = 6.0 Hz, 1H), 5.32 (d, *J* = 9.0 Hz, 1H), 6.36-6.44 (m, 3H), 6.80-7.01 (m, 16H), 7.35-7.39 (m, 1H), 7.54-7.65 (m, 4H), 7.72-7.76 (m, 1H), 7.86-7.93 (m, 4H), 8.19-8.29 (m, 1H) ppm.
^{31}P-NMR (81 MHz, C_6D_6): +42.6 (minor, 40 %), +43.5 (major, 60%) ppm.

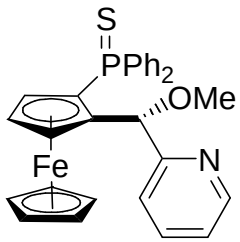
Preparation of ferrocenyl ethers 4a and 4b: A 50 mL Schlenkflask under an argon atmosphere, was charged with KH (104 mg, 2.60 mmol, 1.30 equiv.) in THF (4 mL) and cooled to 0 °C. A solution of alcohol **3** (dr 6:4, 1.01 g, 2.0 mmol) in THF (20 mL) was slowly added and the mixture was stirred at room temperature for 1 h. MeI (341 mg, 2.40 mmol, 1.20 equiv.) was then added dropwise at 0 °C and the reaction mixture was stirred at this temperature for 10 min then at room temperature for 30 min. After quenching the reaction mixture with a saturated NH_4Cl solution, aqueous layer was extracted with diethyl ether (4 × 20 mL). The combined organic layers were washed with water, brine, dried over $MgSO_4$ and evaporated under reduced pressure. Crude product was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1) to furnish the two methyl ethers **4a** (566 mg, 1.07 mmol, 54 %) and **4b** (367 mg, 0.70 mmol, 35 %) yellow solids.

(R_{Fc})-1-(Diphenylphosphinothioyl)-2-((*S*)-α-methoxypyridyl)methylferrocene (4a):



MP: 217.9-218.4 °C
$[\alpha]_D^{20}$ = −25.8 (c = 0.22, acetone).
^{1}H-NMR (300 MHz, C_6D_6): δ = 2.92 (s, 3H), 3.77 (dd, *J* = 2.2 Hz, 4.0 Hz, 1H), 3.94 (dd, *J* = 2.2 Hz, 4.0 Hz, 1H), 4.08-4.10 (m, 1H), 4.35 (s, 5H), 6.64 (s, 1H), 6.67-6.71 (m, 1 H), 7.03-7.13 (m, 7 H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.95-8.08 (m, 4H), 8.50-8.42 (m, 1H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 56.7, 69.1 (d, *J* = 10.5 Hz), 71.7, 72.9 (d, *J* = 8.8 Hz), 75.5 (d, *J* = 12.9 Hz), 75.8 (d, *J* = 94.5 Hz), 80.8, 92.6 (d, *J* = 11.8 Hz), 122.2, 122.3, 127.9, 128.2, 130.7 (d, *J* = 2.9 Hz), 130.93 (d, *J* = 2.9 Hz), 132.7 (d, *J* = 4.7 Hz), 132.8 (d, *J* = 4.7 Hz), 134.8 (d, *J* = 87.0 Hz), 135.7, 136.4 (d, *J* = 88.0 Hz), 149.1, 161.4 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.74 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3436 (br, s), 1630 (br, w), 1589 (s), 1436 (br, s), 3436 (m), 1099 (s), 819 (w), 715 (s), 502 (s).
MS (70 eV, EI): *m/z* (%) = 523 (M^+, 28), 458 (68), 428 (100), 288 (14).
HRMS (EI): *m/z* calcd. for: [$C_{29}H_{26}P^{56}FeNO^{32}S$] 523.0822, found: 523.0837

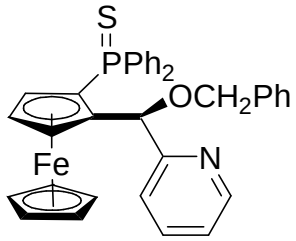
(R_{Fc})-1-(Diphenylphosphinothioyl)-2-((*R*)-α-methoxypyridyl)methylferrocene (4b):



MP: 199.3-200.8 °C
$[\alpha]_D^{20}$ = −21.7 (c = 0.18, acetone).
^{1}H-NMR (300 MHz, C_6D_6): δ = 3.30 (s, 3H), 3.57 (dd, *J* = 2.3 Hz, 4.0 Hz, 1H), 4.02 (dd, *J* = 2.3 Hz, 4.0 Hz, 1H), 4.50 (s, 5 H), 5.30 (dd, *J* = 1.8 Hz, 4.0 Hz, 1 H), 6.33-6.38 (m, 1H), 6.60 (s, 1 H), 6.63-6.73 (m, 3 H), 6.79-6.84 (m, 1H), 6.95-7.04 (m, 3H), 7.17-7.2 (m, 1H), 7.33-7.40 (m, 2H), 7.84-7.92 (m, 2H), 8.23-8.25 (m, 1H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 56.6, 69.5 (d, *J* = 10.2 Hz), 71.4, 72.4 (d, *J* = 9.5 Hz), 73.3 (d, *J* = 94.5 Hz), 74.4 (d, *J* = 12.3 Hz), 79.5, 95.5 (d, *J* = 11.8 Hz), 121.9, 124.1, 127.6, 127.8, 130.2 (d, *J* = 2.9 Hz), 131.0 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 10.6 Hz), 132.6 (d, *J* = 10.6 Hz), 134.5 (d, *J* = 60.0 Hz), 134.8, 135.6 (d, *J* = 60.0 Hz), 149.6, 160.0 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.59 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3436 (br, m), 1588 (w), 1436 (s), 1158 (s), 1099 (s), 819 (m), 615 (s).
MS (70 eV, EI): *m/z* (%) = 523 (M^+, 25), 458 (60), 428 (100), 426(32).
HRMS (EI): *m/z* calcd. for: [$C_{29}H_{26}P^{56}FeNO^{32}S$] 523.0822, found: 523.0845

Preparation of ferrocenyl ethers 5a and 5b: A 50 mL Schlenktube under an argon atmosphere, was charged with KH (104 mg, 2.60 mmol, 1.30 equiv.) in THF (4 mL) and cooled to 0 °C. A solution of alcohol **3** (dr 6:4, 1.01 g, 2.0 mmol) in THF (20 mL) was slowly added and the reaction mixture was stirred at room temperature for 1 h. Benzyl bromide (411 mg, 2.40 mmol, 1.20 equiv) was then added dropwise at 0 °C and the reaction mixture was stirred at this temperature for 10 min and then at room temperature for 30 min. After quenching the reaction mixture with a saturated NH_4Cl solution, aqueous layer was extracted with diethyl ether (4 × 20 mL). The combined organic layers were washed with water, brine, dried over $MgSO_4$ and solvents were evaporated under reduced pressure. Purification of the residue by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1) provided the two benzyl ethers **5a** (649 mg, 1.08 mmol, 54 %) and **5b** (433 mg, 0.72 mmol, 36 %) as yellow solids.

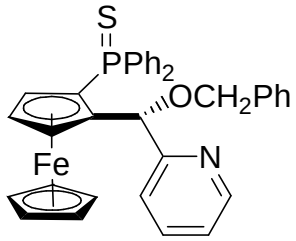
(R_{Fc})-1-(Diphenylphosphinothioyl)-2-(((*S*)-α-benzyloxy)pyridyl))methylferrocene (5a):



MP: 173.1-175.0 °C
$[\alpha]_D^{20}$ = −62.6 (c = 0.3, CH_2Cl_2).
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.60 (s, 1H), 4.33 (s, 5 H), 4.34 (s, 1H), 4.50 (dd, *J* = 11.6 Hz, 22.0 Hz, 2H), 5.20 (s, 1H), 6.50 (s, 1H), 6.74-6.82 (m, 1 H), 6.96-7.06 (m, 3H), 7.12-7.20 (m, 4H), 7.26-7.47 (m, 8 H), 7.67-7.74 (m, 2 H), 8.27-8.36 (m, 1 H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 69.4 (d, *J* = 10.6 Hz), 70.9, 71.0, 71.4 (d, *J* = 9.4 Hz), 72.6 (d, *J* = 94.6 Hz), 74.4 (d, *J* = 12.8 Hz), 76.8, 94.2 (d, *J* = 11.9 Hz), 122.3, 124.1, 127.5, 127.6, 127.8, 127.9, 128.0, 128.2, 130.4 (d, *J* = 2.8 Hz), 131.1 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 11.0 Hz), 132.0 (d, *J* = 11.0 Hz), 133.1 (d, *J* = 49.2 Hz), 134.3 (d, *J* = 49.6 Hz), 135.7, 138.4, 158.9 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.98 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3436 (br, s), 3056 (br, w), 1589 (m), 1436 (s), 1102 (s), 1052 (s), 819 (w), 750 (m), 715 (s), 695 (s)..
MS (70 eV, EI): *m/z* (%) = 599 (M^+, 36), 534 (38), 429 (100), 288 (41), 154 (40).

HRMS (EI): *m/z* calcd. for: [$C_{35}H_{30}P^{56}FeNO^{32}S$] 599.1135, found: 599.1120

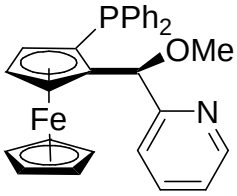
(R_{Fc})-1-(Diphenylphosphinothioyl)-2-(((*R*)-α-benzyloxy)pyridyl))methylferrocene (5b):



MP: 129.7-130.8 °C
$[\alpha]_D^{20}$ = −48.0 (c = 0.3, CH_2Cl_2).
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.63 (s, 1H), 4.36 (s, 5H), 4.37-4.40 (m, 1H), 4.53 (q, *J* = 11.7 Hz, 2H), 5.23 (s, 1H), 6.53 (s, 1H), 6.82 (s, 1H), 7.04-7.10 (m, 3H), 7.13-7.21 (m, 4H), 7.29-7.53 (m, 8H), 7.68-7.79 (m, 2H), 8.34 (s, 1H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 69.7 (d, *J* = 10.5 Hz), 71.3, 71.6 (d, *J* = 9.4 Hz), 72.9 (d, *J* = 94.5 Hz), 74.7 (d, *J* = 12.2 Hz), 77.1, 94.5 (d, *J* = 11.7 Hz), 122.5, 124.4, 127.8, 127.9, 128.1, 128.3, 128.5, 130.7 (d, *J* = 3.3 Hz), 131.4 (d, *J* = 2.8 Hz), 131.9 (d, *J* = 10.5 Hz), 132.3 (d, *J* = 10.5 Hz), 133.4 (d, *J* = 49.8 Hz), 134.5 (d, *J* = 49.8 Hz), 136.0, 138.7, 149.1, 159.2 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.96 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3435 (b, s), 1629 (b, w), 1436 (s), 1101 (s), 821 (m), 714 (s), 694 (s).
MS (70 eV, EI): *m/z* (%) = 599 (M^+, 10), 534 (8), 429 (27), 428 (100), 427 (25)
HRMS (EI): *m/z* calcd. for: [$C_{35}H_{30}P^{56}FeNO^{32}S$] 599.1122, found: 599.1148

Typical procedure 1 for the desulfurization of the compounds 4a-5b. An argon flushed 50 mL Schlenkflask was loaded about 1.5 g of Raney Ni slurry (Raney Ni in water). Raney Ni was washed with MeOH (4 × 15 mL). To this flask was then transferred a solution of the protected ligand (**4a-5b)** (0.80 mmol) in THF (3 mL), then added 20 mL MeOH and stirred at room temperature under argon atmosphere for 12 h. The reaction mixture was filtered under argon. The Raney Ni residue was washed with THF (4 × 10 mL). The combined filtrate was concentrated under reduced pressure to afford the pure product as a yellow solid and stored under argon.

(R_{Fc})-1-(Diphenylphosphino)-2-(((*S*)-α-methoxy)pyridyl))methylferrocene (6a):

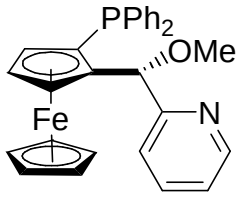


Prepared according to **TP1** from **4a** (420 mg, 0.80 mmol) and obtained as a yellow solid (331 mg, 0.67 mmol, 84 %).

MP: 120.3-122.4 °C
$[\alpha]_D^{20}$ = +234 (c = 0.1, CH_2Cl_2)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.93 (s, 3H), 3.36 (s, 1H), 3.81 (s, 5H), 4.03 (s, 1H), 4.20-4.23 (m, 1H), 5.49 (d, *J* = 3.3 Hz, 1H), 7.22-7.30 (m, 5H), 7.38-7.39 (m, 2H), 7.51-7.63 (m, 4H), 7.69.7.75 (m, 2H), 8.68-8.69 (m, 1H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 68.7, 69.71, 69.74, 70.0 (d, *J* = 3.9 Hz), 71.7 (d, *J* = 4.5 Hz), 76.0 (d, *J* = 9.2 Hz), 82.2 (d, *J* = 10.9 Hz), 92.8 (d, *J* = 24.9 Hz), 121.8, 122.6, 127.4, 127.63 (d, *J* = 6.5 Hz), 128.0 (d, *J* = 8.0 Hz), 128.7, 129.0, 130.8, 132.3, 132.4 (d, *J* = 18.3 Hz), 135.2 (d, *J* = 21.5 Hz), 148.7, 160.6 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = -21.17 ppm.
IR(neat): υ_{max} (cm^{-1}) = 2920 (w), 1728 (w), 1586 (m), 1428 (m), 1126 (m), 1080 (s), 1105 (s), 810 (s), 748 (s), 698 (s).
MS (70 eV, EI): *m/z* (%) = 491 (M^+, 39), 427 (28), 426 (100), 396 (32), 262 (30), 154 (37).
HRMS (EI): *m/z* calcd. for: [$C_{29}H_{26}P^{56}FeNO$] 491.1101, found: 491.1108

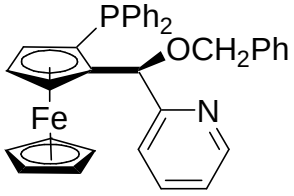
(R_{Fc})-1-(Diphenylphosphino)-2-(((*R*)-α-methoxy)pyridyl))methylferrocene (6b):



Prepared according to **TP1** from **4b** (420 mg, 0.80 mmol) and obtained as a yellow solid (325 mg, 0.66 mmol, 82 %).

MP: 140.2-144.0 °C
$[\alpha]_D^{20}$ = +214 (c = 0.1, CH_2Cl_2)
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.34 (s, 3H), 3.65 (s, 1H), 4.10 (s, 5H), 4.26-4.31 (m, 1H), 4.66 (s, 1H), 5.39 (s, 1H), 6.76-6.79 (m, 3H), 6.94-7.12 (m, 4H), 7.28-7.33 (m, 3H), 7.49 (br s, 2H), 7.70-7.71 (m, 1H), 8.07 (m, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 68.1, 68.7, 69.7, 70.0 (d, *J* = 3.4 Hz), 71.7 (d, *J* = 4.2 Hz), 76.5 (d, *J* = 9.6 Hz), 82.8 (d, *J* = 9.8 Hz), 92.9 (d, *J* = 24.7 Hz), 121.7, 122.0, 127.0, 127.5 (d, *J* = 6.4 Hz), 127.9 (d, *J* = 8.0 Hz), 128.9, 131.9 (d, *J* = 18.5 Hz), 135.0 (d, *J* = 21.3 Hz), 135.8, 137.5 (d, *J* = 9.2 Hz), 139.1 (d, *J* = 9.2 Hz), 148.5, 160.3 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = -21.25 ppm.
IR(neat): υ_{max} (cm^{-1}) = 2928 (w), 1725 (w), 1586 (m), 1430 (m), 1162 (m), 1087 (s), 1104 (s), 816 (s), 744 (s), 698 (s).
MS (70 eV, EI): *m/z* (%) = 491 (M^+, 47), 427 (28), 426 (100), 396 (37), 262 (38), 154 (50).
HRMS (EI): *m/z* calcd. for: [$C_{29}H_{26}P^{56}FeNO$] 491.1101, found: 491.1110.

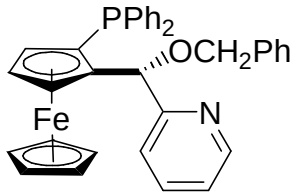
(R_{Fc})-1-(Diphenylphosphino)-2-(((*S*)-α-benzyloxy)pyridyl))methylferrocene (7a):



Prepared according to **TP1** from **5a** (480 mg, 0.80 mmol) and obtained as a yellow solid (402 mg, 0.71 mmol, 88 %).

MP: 49.8-53.5 °C
$[\alpha]_D^{20}$ = +230 (c = 0.1, CH_2Cl_2)
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.83 (s, 5H), 3.90 (s, 1H), 4.13 (d, *J* = 10.9 Hz, 1H), 4.22 (s, 1H), 4.26 (t, *J* = 2.6 Hz, 1H), 4.31 (d, *J* = 10.9 Hz, 1H), 5.88 (s, 1H), 6.73-6.74 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 7.16-7.24 (m, 5H), 7.28-7.30 (m, 1H), 7.38-7.39 (m, 3H), 7.61-7.65 (m, 3H), 7.74-7.77 (m, 1H), 8.70-8.71 (m, 1H) ppm.
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 69.8, 70.0, 70.49 (d, *J* = 3.4 Hz), 70.5, 71.7, 71.9 (d, *J* = 4.5 Hz), 76.5 (d, *J* = 10.6 Hz), 95.1 (d, *J* = 26 Hz), 122.3, 122.8, 127.4, 127.4, 127.8 (d, *J* = 1.7 Hz), 127.9, 128.0, 128.1 (d, *J* = 1.7 Hz), 128.4, 129.1, 132.4 (d, *J* = 18.0 Hz), 135.4 (d, *J* = 22.0 Hz), 137.6, 137.9 (d, *J* = 10.2 Hz), 140.5 (d, *J* = 10.0 Hz), 160.7 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = -21.58 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3054 (br, w), 2858 (br, w), 1587 (m), 1432 (m), 1047 (s), 817 (m), 739 (s), 690 (s).
MS (70 eV, EI): *m/z* (%) = 567 (M^+, 38), 502 (87), 461 (57), 396 (100), 276 (33), 154 (34).
HRMS (EI): *m/z* calcd. for: [$C_{35}H_{30}P^{56}FeNO$] 567.1414, found: 567.1389

(R_{Fc})-1-(Diphenylphosphino)-2-(((*R*)-α-benzyloxy)pyridyl))methylferrocene (7b):



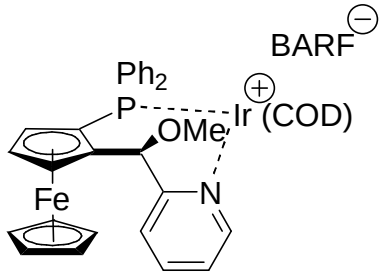
Prepared according to **TP1** from **5b** (482 mg, 0.80 mmol) and obtained as a yellow solid (390 mg, 0.69 mmol, 86 %).

MP: 58.0-60.2 °C
$[\alpha]_D^{20}$ = +134 (c = 0.1, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.69-3.70 (m, 1H), 4.05 (s, 5H), 4.28 (t, *J* = 2.3 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 4.79-4.80 (m, 1H), 5.71 (d, *J* = 2.1 Hz, 1H), 6.71-6.79 (m, 3H), 6.91-6.95 (m, 2H), 7.01-7.04 (m, 1H), 7.18-7.20 (m, 1H) 7.27-7.39 (m, 7H), 7.42-7.51 (m, 4H), 8.03-8.05 (m, 1H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 69.0 (d, *J* = 4.5 Hz), 69.1, 69.9, 70.8, 71.3 (d, *J* = 4.8 Hz), 73.8 (d, *J* = 10.5 Hz), 80.7 (d, *J* = 7.3 Hz), 95.9 (d, *J* = 24.3 Hz), 121.8 (d, *J* = 1.5 Hz), 122.1, 127.0, 127.4 (d, *J* = 2.2 Hz), 127.5, 127.6, 127.9 (d, *J* = 7.8 Hz), 128.3, 128.9 (d, *J* = 0.8 Hz), 131.9 (d, *J* = 18.2 Hz), 135.2 (d, *J* = 21.3 Hz), 135.9, 137.6 (d, *J* = 9.6 Hz), 138.6, 139.3 (d, *J* = 9.2 Hz), 148.4, 160.7 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = -22.49 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3050 (w), 2860 (w), 1586 (m), 1432 (m), 1066 (m), 1026 (m), 815 (m), 740 (s), 692 (s), 614 (m).
MS (70 eV, EI): *m/z* (%) = 568 ($[M+H]^+$, 38), 567 (M^+, 100), 502 (58), 461 (47), 385 (83), 276 (41), 212 (72).
HRMS (EI): *m/z* calcd. for: [$C_{35}H_{30}P^{56}FeNO$] 567.1414, found: 567.1436

Typical procedure 2 for the preparation of iridium complexes 8a-9b. A 25 mL Schlenk-flask under an argon atmosphere, was charged with P,N-ligand (**6a-7b**) (0.50 mmol) , $[Ir(COD)Cl]_2$ (0.25 mmol) in CH_2Cl_2 (5 mL) and stirred at room temperature for 1 h. NaBARF (0.75 mmol, 1.50 equiv.) was added followed by water (5 mL) and the resulting

two-phase reaction mixture was stirred vigorously for 30 min. The separated aqueous layer was extracted with CH_2Cl_2 (4 × 15 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$. The residue was purified by column chromatography yielding the Ir-complex as a bright orange solid.

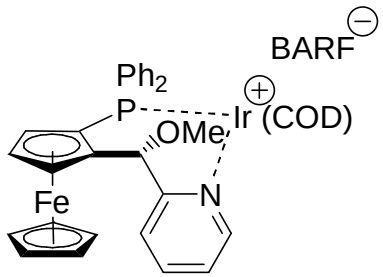
Iridium complex (8a):



Prepared according to **TP2** from P,N-ligand **6a** (246 mg, 0.50 mmol), $[Ir(COD)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol). Purification by flash chromatography (silica gel, CH_2Cl_2) afforded the iridium complex **8a** (746 mg, 90 %) as a bright orange solid.

MP: 184.3-185.4 °C
$[\alpha]_D^{20}$ = +69 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.27-1.68 (m, 4H), 1.80-2.16 (m, 3H), 2.29-2.66 (m, 5H), 3.13 (s. 4H), 3.70 (s, 2H), 3.68-3.79 (m, 1H), 4.08-4.15 (m, 3H), 4.48 (t, *J* = 2.6 Hz, 1H), 4.91-4.96 (m, 1H), 6.82-6.95 (m, 3H), 7.30-7.33 (m, 3H), 7.45-7.64 (m, 7H), 7.69-7.74 (m, 7H), 7.84-7.94 (m, 3H), 8.06-8.17 (m, 2H), 8.77-8.78 (m, 1H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 26.6 (d, *J* = 2.2 Hz), 28.5 (d, *J* = 1.8 Hz), 32.9 (d, *J* = 1.9 Hz), 36.2 (d, *J* = 4.1 Hz), 58.4, 65.1, 67.4, 69.9 (d, *J* = 8.5 Hz), 70.1 (d, *J* = 6.3 Hz), 70.4, 71.5 (d, *J* = 55.4 Hz), 73.3 (d, *J* = 2.3 Hz), 81.9 (d, *J* = 1.9 Hz), 93.6-94.0 (m), 117.5 (q, *J* = 4.0 Hz), 120.5, 123.2, 123.6, 125.9, 126.2, 128.4 (q, *J* = 2.7 Hz), 128.6, 128.7 (q, *J* = 2.9 Hz), 129.1 (q, *J* = 2.7 Hz), 129.2 (d, *J* = 11.2 Hz), 129.9 (d, *J* = 58.8 Hz), 130.8 (d, *J* = 2.8 Hz), 132.7 (d, *J* = 2.9 Hz), 134.8 , 135.6 (d, *J* = 14.4 Hz), 137.1 (q, *J* = 291.2 Hz), 149.8, 161.7 (q, *J* = 53.7 Hz), 164.9 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +9.7 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2930 (w), 1272 (w), 1354 (s), 1273 (s), 1111 (s), 1096 (s), 887 (m), 716 (m), 668 (s).
MS (FAB): 793 ($[M+H]^+$, 41), 792 (M^+, 100), 791 (63), 650 (21).
HRMS (EI): *m/z* calcd. for: [$C_{37}H_{38}PNO^{193}Ir^{56}Fe$]: 792.1660, found 792.1658

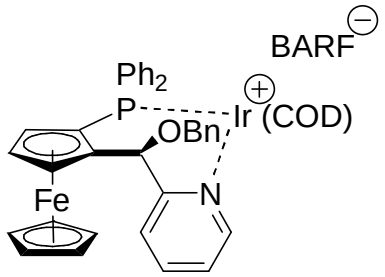
Iridium complex (8b):



Prepared according to **TP2** from P,N-ligand **6b** (246 mg, 0.50 mmol), $[Ir(COD)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol). Purification by flash chromatography (silica gel, CH_2Cl_2) afforded the iridium complex **8b** (736 mg, 89 %) as a bright orange solid.

MP: 189.3-190.9 °C
$[\alpha]_D^{20}$ = +50 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 1H), 1.55 (s, 1H), 1.74-1.84 (m, 2H), 2.13-2.18 (m, 1H), 2.40-2.62 (m, 5H), 3.56 (s, 3H), 3.66-3.67 (m, 1H), 4.14-4.24 (m, 2H), 4.38 (s, 4H), 4.47-4.56 (m, 2H), 4.63-4.66 (m, 1H), 5.03-5.04 (m, 1H), 6.61-6.64 (m, 1H), 6.73-6.77 (m, 2H), 6.81 (s, 1H), 7.07-7.12 (m, 2H), 7.20-7.25 (m, 1H), 7.33-7.56 (m, 12H), 7.70-7.71 (m, 7H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 27.4 (d, *J* = 1.9 Hz), 31.0 (d, *J* = 2.3 Hz), 32.3 (d, *J* = 2.2 Hz), 35.1 (d, *J* = 4.0 Hz), 58.0, 60.6, 66.9, 67.4, 69.4 (d, *J* = 6.7 Hz), 71.2, 71.8 (d, *J* = 6.1 Hz), 73.2 (d, *J* = 1.9 Hz), 85.5 (d, *J* = 1.7 Hz), 88.6 (d, *J* = 11.6 Hz), 91.7 (d, *J* = 16.2 Hz), 92.8 (d, *J* = 13.3 Hz), 117.4, 120.5, 121.8, 123.2, 124.5, 125.0, 125.7 (d, *J* = 32.0 Hz), 128.6, 128.7-128.0 (m), 128.8 (d, *J* = 6.5 Hz), 129.0 (q, *J* = 2.9 Hz), 129.4 (d, *J* = 2.7 Hz), 130.7 (d, *J* = 2.4 Hz), 130.9, 131.3 (d, *J* = 11.3 Hz), 131.4, 131.9 (d, *J* = 2.6 Hz), 132.8 (d, *J* = 10.0 Hz), 134.5, 138.8, 149.2, 161.7 (q, *J* = 50.1 Hz), 161.8 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +9.6 ppm
IR (neat): υ_{max} (cm^{-1}) = 2925 (w), 1609 (w), 1353 (m), 1273 (s), 1156 (s), 1122 (s), 1095 (s), 887 (m), 838 (m), 715 (m), 668 (m).
MS (ESI): 793 ($[M+H]^+$, 41), 792 (M^+, 100), 790 (65), 452 (11).
HRMS (ESI): *m/z* calcd. for: [$C_{37}H_{38}P^{56}FeNO^{193}Ir$] 792.1670, found: 792.1639

Iridium complex (9a):

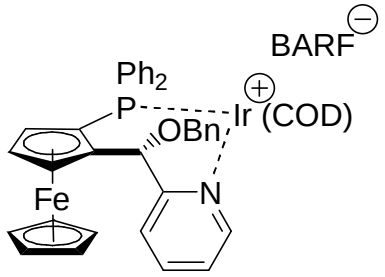


Prepared according to **TP2** from P,N-ligand **7a** (284 mg, 0.50 mmol), $[Ir(COD)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol). Purification by flash chromatography (silica gel, CH_2Cl_2) provided the iridium complex **9a** (780 mg, 90 %) as a bright orange solid.

MP: 178.1-180.7 °C
$[\alpha]_D^{20}$ = +54 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.23 (m, 2H), 1.52-1.57 (m, 3H), 1.75-1.79 (m, 1H), 2.00-2.09 (m, 2H), 2.29-2.35 (m, 1H), 2.48-2.52 (m, 2H), 3.13 (s, 4H), 3.64-3.65 (m, 1H), 3.97-3.98 (m, 1H), 4.07 (t, *J* = 2.6 Hz, 1H), 4.19-4.22 (m, 1H), 4.51 (t, *J* = 2.6 Hz, 1H), 4.86-4.87 (m, 2H), 5.04-5.05 (m, 1H), 6.87-6.95 (m, 3H), 7.34-7.41 (m, 8H), 7.44-7.48 (m, 1H), 7.52 (br, s, 3H), 7.60-7.61 (m, 3H), 7.72-7.78 (m, 8H), 7.92-7.96 (m, 1H), 8.02-8.03 (m, 1H), 8.09-8.13 (m, 2H), 8.75-8.77 (m, 1H). ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 26.9 (d, *J* = 2.3 Hz), 28.7 (d, *J* = 2.1 Hz), 32.2 (d, *J* = 1.9 Hz), 35.7 (d, *J* = 4.5 Hz), 65.5, 67.0, 70.2 (q, *J* = 8.2 Hz), 70.4, 71.7 (d, *J* = 55.0 Hz), 72.3, 73.3 (d, *J* = 2.2 Hz), 78.6 (d, *J* = 1.8 Hz), 93.9, 94.0 (d, *J* = 6.8 Hz), 94.6 (d, *J* = 14.2 Hz), 117.4-117.5 (m), 120.5, 123.2, 123.8, 125.9, 126.1, 127.2, 128.6, 128.7 (q, *J* = 2.8 Hz), 128.9,

129.1 (q, *J* = 2.9 Hz), 129.2 (d, *J* = 11.0 Hz), 130.0 (d, *J* = 58.7 Hz), 130.8 (d, *J* = 2.6 Hz), 132.7 (d, *J* = 2.2 Hz), 133.4 (q, *J* = 360.1 Hz), 134.7-134.8 (m), 135.5 (d, *J* = 14.0 Hz), 136.4, 149.7, 161.7 (q, *J* = 50.1 Hz), 165.1 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +9.6 ppm
IR (neat): υ_{max} (cm^{-1}) = 2927 (w), 1608 (w), 1353 (m), 1272 (s), 1117 (s), 1000 (w), 886 (m), 838 (m), 712 (m), 668 (m), 681 (m).
MS (ESI): 869 ($[M+H]^+$, 44), 868 (M^+, 100), 866 (49), 584 (10), 391 (5).
HRMS (ESI): *m/z* calcd. for: [$C_{43}H_{42}P^{56}FeNO^{193}Ir$] 868.1938, found: 868.1964

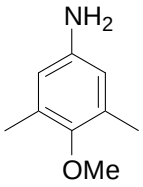
Iridium complex (9b):



Prepared according to **TP2** from P,N-ligand **7b** (284 mg, 0.5 mmol), $[Ir(COD)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol) Flash chromatographical purification (silica gel, CH_2Cl_2) provided the iridium complex **9b** (763 mg, 88 %) as a bright orange solid.

MP: 71.5-75.7 °C
$[\alpha]_D^{20}$ = +27 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.77-1.92 (m, 3H), 2.13-2.54 (m, 7H), 3.69-3.71 (m, 1H), 4.15-4.20 (m, 1H), 4.23-4.29 (m, 1H), 4.34 (s, 4H), 4.48-4.53 (m, 1H), 4.57-4.66 (m, 3H), 4.77-4.80 (m, 1H), 5.17-5.18 (m, 1H), 6.60-6.64 (m, 1H), 6.73-6.78 (m, 2H), 6.96 (s, 1H), 7.08-7.12 (m, 2H), 7.20-7.24 (m, 1H), 7.40-7.57 (m, 16H), 7.71-7.72 (m, 8H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 27.9 (d, *J* = 2.2 Hz), 31.6 (d, *J* = 2.3 Hz), 31.7 (d, *J* = 2.3 Hz), 34.5 (d, *J* = 3.5 Hz), 61.2, 66.7 (d, *J* = 57.0 Hz), 67.3, 69.8 (d, *J* = 7.2 Hz), 71.2, 71.7 (d, *J* = 6.3 Hz), 72.3, 73.2 (d, *J* = 1.4 Hz), 82.9, 88.7 (d, *J* = 12.1 Hz), 91.9 (d, *J* = 15.7 Hz), 93.4 (d, *J* = 13.0 Hz), 117.4-117.5 (m), 122.2, 123.2, 125.6, 125.9, 126.8 (q, *J* = 365.0 Hz), 127.5, 128.4-128.5 (m), 128.7-128.9 (m), 129.0, 129.1 (t, *J* = 3.0 Hz), 129.3-129.4 (m), 130.8 (d, *J* = 2.5 Hz), 131.26 (d, *J* = 54.0 Hz), 131.27 (d, *J* = 11.3 Hz), 131.9 (d, *J* = 2.5 Hz), 132.8 (d, *J* = 9.8 Hz), 134.8 (br, s), 136.4, 138.9, 149.3, 161.7 (q, *J* = 50.0 Hz), 161.8 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +5.71 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2928 (w), 1609 (m), 1353 (m), 1273 (s), 1117 (s), 1001 (m), 839 (m), 669 (m), 682 (m).
MS (ESI): 869 ($[M+H]^+$, 44), 868 (M^+, 100), 866 (46), 584 (18).
HRMS (ESI): *m/z* calcd. for: [$C_{43}H_{42}P^{56}FeNO^{193}Ir$] 868.1938, found: 868.1948

Preparation of 2,6-Dimethyl-4-amino anisole[2]. A 1.0 L flask was charged with 2,6-dimethyl-4-nitro anisole (180 mmol, 32.6 g), active charcoal (20%, 36.0 mmol, 434 mg), $FeCl_3.6H_2O$ (10%, 18.0 mmol, 4.90 g), MeOH (500 mL) and refluxed. While the reaction mixture was refluxing, $NH_2NH_2{\cdot}H_2O$ (1.8 mol, 57.5 g, 55.8 mL) was added slowly and continued stirring for overnight. Reaction mixture was cooled to room temperature, filtered and washed with MeOH (3 × 100 mL). Evaporated the filtrate under reduced pressure, filtered the residue through a short pad of silica gel and washed with ether to afford the amine in 96 % yield as a pale yellow crystalline solid.

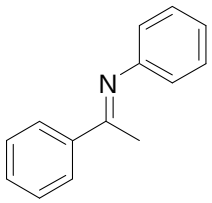


MP: 62-64 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.21-2.25 (m, 6H), 3.68 (s, 3H), 4.02 (br, 2H, NH), 6.42-6.45 (m, 2H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.3, 60.2, 116.1, 131.8, 140.9, 150.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3400 (s), 2955 (m), 1623 (w), 1472 (m), 1212 (m), 1013 (s), 796 (m).
MS (70 eV, EI): *m/z* (%) = 151 (M^+, 88), 137 (26), 136 (100), 108 (47), 93 (28).
HRMS (EI): *m/z* calcd. for: [$C_9H_{13}NO$] 151.0997, found 151.0999.

Typical procedure 3 for the preparation of imines. A 250 mL round-bottomed flask was filled with a ketone (10.0 mmol), an amine (12.0 mmol) and molecular sieves (4 Å, 8 g) in toluene (60 mL). The reaction mixture was refluxed until full conversion was reached (conversion was monitored by GC). The reaction mixture was filtered through celite, solvent was evaporated and the crude product was further purified as specified for each substrate.

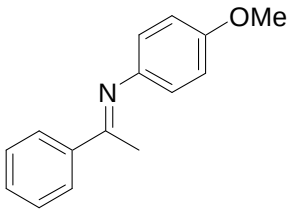
Racemic amines were prepared by reduction of the imines with sodium borohydride in ethanol or Methanol.

***N*-phenyl-1-phenylethylideneamine (10a)[4]:** Prepared according to **TP3** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and aniline (12.0 mmol, 1.12 g, 1.1 mL, 1.20 equiv.). Recrystallisation from *n*-pentane, afforded the desired imine (1.42 g, 7.30 mmol, 73 %) as a yellow crystalline solid.



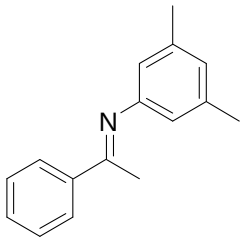
MP: 38-39 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 3H), 6.79 (d, *J* = 7.3 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.40-7.44 (m, 3H), 7.98 (dd, *J* = 7.5 Hz, 2.1 Hz, 2H) ppm.

***N*-(4-methoxy)phenyl-1-phenylethylideneamine (10b)[5]:** Prepared according to **TP3** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 4-methoxy aniline (12.0 mmol, 1.48 g, 1.20 equiv.). Recrystallisation from *n*-pentane:EtOAc, afforded the desired imine (1.42 g, 6.29 mmol 63 %) as a yellow crystalline solid.



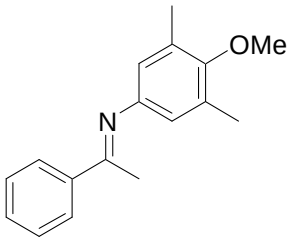
MP: 87.3-87.9 °C.
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 3.80 (s, 3H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 7.43-7.45 (m, 3H), 7.95-7.98 (m, 2H) ppm.

***N*-(3,5-Dimethyl)phenyl-1-phenylethylideneamine (10c):** Prepared according to **TP3** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,5.dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL, 1.20 equiv.). Purification by vacuum distillation (120 °C, 0.1 mbar) afforded the desired imine (1.72 g, 7.79 mmol, 78 %) as a yellow oil.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3H), 2.32 (s, 6H), 6.43 (s, 2H), 6.73 (s, 1H), 7.43-7.49 (m, 3H), 7.95-7.98 (m, 2H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.4, 21.3, 117.0, 124.9, 127.1, 128.3, 130.3, 133.1, 138.5, 151.5, 165.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2915 (w), 1682 (w), 1633 (s), 1589 (s), 1450 (m), 1367 (m), 1274 (s), 1150 (m), 1029 (m), 845 (s), 763 (s), 672 (s).
MS (70 eV, EI): *m/z* (%) = 223 (M^+, 84), 208 (100), 105 (15), 103 (6), 77 (11).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{17}N$] 223.1361, found: 223.1364.

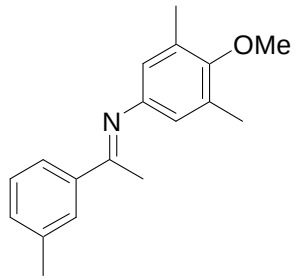
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenylethylideneamine (12a):** Prepared according to **TP3** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by vacuum distillation (140 °C, 0.1 mbar) afforded the desired imine (1.90 g, 7.50 mmol, 75 %) as a yellow solid.



MP: 65.5-66.7 °C.
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 3H), 2.28 (s, 6H), 3.70 (s, 3H), 6.48 (s, 2H), 7.43-7.46 (m, 3H), 7.95-7.98 (m, 2H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.2, 17.5, 59.9, 119.8, 127.3, 128.4, 128.5, 130.6, 133.1, 140.4, 150.2, 164.6 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2945 (m), 2822 (w), 1686 (w), 1629 (s), 1471 (m), 1448 (s), 1278 (s), 1213 (s), 1007 (s), 874 (m), 766 (s), 692 (s).
MS (70 eV, EI): *m/z* (%) = 253 (M^+, 32), 238 (100), 223 (2), 194 (2), 91 (10).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{19}NO$] 253.1467, found: 253.1462.

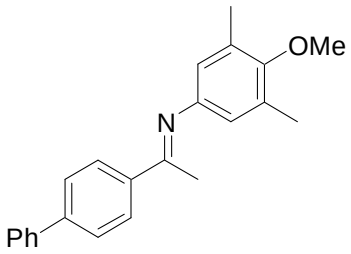
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-methyl)phenylethylideneamine (12b):** Prepared according to **TP3** from 3-methyl acetophenone (10.0 mmol, 1.34 g, 1.33 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash

chromatography (silica gel; *n*-pentane:diethyl ether 40:1 (2% Et_3N)) afforded the desired imine (1.95 g, 7.29 mmol, 73 %) as a yellow oil.



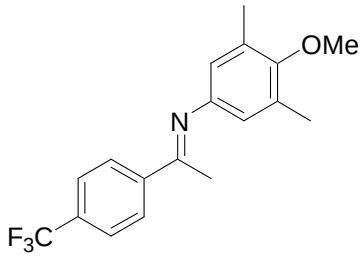
^{1}H-NMR (300 MHz, C_6D_6): δ = 1.97 (s, 3H), 2.17 (s, 3H), 2.24 (s, 6H), 3.43 (s, 3H), 6.52 (s, 2H), 7.04-7.07 (m, 1H), 7.16-7.18 (m, 1H), 7.81-7.84 (m, 1H), 7.99 (s, 1H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 16.3, 16.9, 21.4, 59.4, 119.9, 124.9, 128.2, 128.3, 131.2, 131.3, 137.8, 140.2, 148.3, 153.5, 164.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2922 (w), 1631 (m), 1477 (m), 1282 (m), 1217 (s), 1010 (m), 875 (m), 694 (s).
MS (70 eV, EI): *m/z* (%) = 267 (M^+, 42), 252 (100), 133 (2), 118 (4).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{21}NO$] 267.1623, found: 267.1628.

***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-phenyl)phenylethylideneamine (12c):** Prepared according to **TP3** from 4-phenyl acetophenone (10.0 mmol, 1.96 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Recrystallisation from *n*-pentane, afforded the desired imine (2.47 g, 7.50 mmol, 75 %) as a yellow solid.



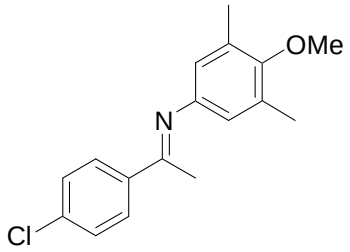
MP: 96.3-97.3 °C
^{1}H-NMR (400 MHz, C_6D_6): δ = 2.00 (s, 3H), 2.26 (s, 6H), 3.45 (s, 3H), 6.55 (s, 2H), 7.18-7.25 (m, 3H), 7.48-7.51 (m, 2H), 7.53-7.55 (m, 2H), 8.09-8.12 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 16.4, 16.8, 59.4, 120.0, 127.2, 127.5, 127.8, 128.1, 129.1, 131.4, 139.0, 140.9, 143.3, 148.2, 153.6, 163.9 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2929 (w), 1623 (m), 1595 (m), 1214 (s), 1066 (s), 870 (s), 765 (s), 693 (s).
MS (70 eV, EI): *m/z* (%) = 329 (M^+, 52), 314 (100), 207 (6), 157 (5).
HRMS (EI): *m/z* calcd. for: [$C_{23}H_{23}NO$] 329.1780, found: 329.1765.

***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-trifluoromethyl)phenylethylideneamine (12d):** Prepared according to **TP3** from 4-trifluoromethyl acetophenone (10.0 mmol, 1.88 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by vacuum distillation (160 °C, 0.1 mbar) afforded the desired imine (2.70 g, 8.40 mmol, 84 %) as a yellow oil.



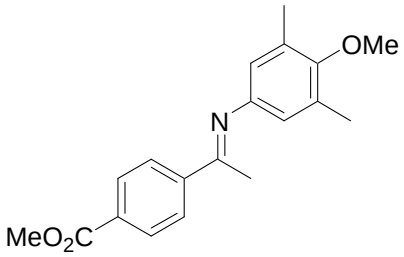
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 3H), 2.28 (s, 6H), 3.70 (s, 3H), 6.48 (s, 2H), 7.43-7.46 (m, 2H), 7.95-7.98 (m, 2H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.2, 17.4, 59.9, 119.3, 125.2 (q, *J* = 3.6 Hz), 127.4, 127.5 (q, *J* = 283.3 Hz), 128.6, 131.3, 132.0 (q, *J* = 16.8 Hz), 146.7, 152.3, 164.0 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2935 (br, w), 1633.2 (m), 1478 (m), 1326 (s), 1220 (s), 1124 (s), 1111 (s), 1011 (s), 843 (s), 605 (m).
MS (70 eV, EI): *m/z* (%) = 321 (M^+, 48), 306 (100), 302 (2), 171 (2), 91 (5).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{18}NF_3O$] 321.1340, found: 321.1329.

***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-chloro)phenylethylideneamine (12e):** Prepared according to **TP3** from 4-chloro acetophenone (10.0 mmol, 1.54 g, 1.29 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 40:1 (2% Et_3N)) afforded the desired imine (2.16 g, 7.51 mmol, 75 %) as a yellow oil.



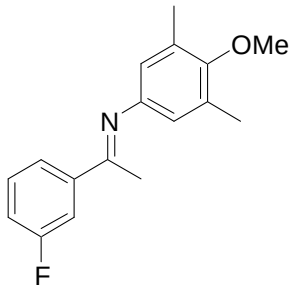
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3H), 2.27 (s, 6H), 3.70 (s, 3H), 6.40 (s, 2H), 7.37-7.44 (m, 2H), 7.87-7.90 (m, 2H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.1, 17.2, 59.8, 119.4, 128.4, 131.2, 136.4, 138.0, 146.9, 153.1, 164.0 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2936 (br, w), 1631 (m), 1589 (m), 1477 (m), 1398 (w), 1272 (w), 1219 (s), 1091 (s), 1011 (s), 830 (s), 756 (m).
MS (70 eV, EI): *m/z* (%) = 287 (M^+, 38), 274 (30), 272 (100), 91 (5).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{18}N^{35}ClO$] 287.1077, found: 287.1078.

***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-carbomethoxy)phenylethylideneamine (12f):** Prepared according to **TP3** from methyl 4-acetyl-benzoate (10.0 mmol, 1.78 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 40:1 (2% Et_3N)) provided the desired imine (2.33 g, 7.50 mmol, 75 %) as a bright yellow solid.



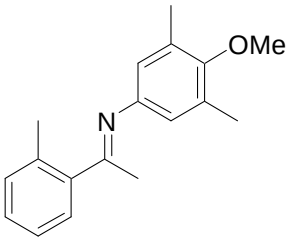
MP: 90.0-92.4 °C.
^{1}H-NMR (300 MHz, C_6D_6): δ = 1.84 (s, 3H), 2.20 (s, 6H), 3.43 (s, 3H), 3.52 (s, 3H), 6.46 (s, 2H), 7.95-7.97 (m, 2H), 8.19-8.21 (m, 2H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 16.3, 16.8, 51.7, 59.4, 119.8, 127.5, 129.8, 131.4, 132.1, 143.8, 147.7, 153.8, 163.6, 166.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2955 (w), 1718 (s), 1627 (m), 1437 (m), 1272 (s), 1112 (s), 1007 (s), 768 (s), 696 (s) ppm.
MS (70 eV, EI): *m/z* (%) = 311 (M^+, 56), 296 (100), 132 (11).
HRMS (EI): *m/z* calcd. for: [$C_{19}H_{21}NO_3$] 311.1521, found: 311.1515.

***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl propylidene amine (12g):** Prepared according to **TP3** from 3-fluoro acetophenone (10.0 mmol, 1.38 g, 1.23 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 40:1 (2% Et_3N)) provided the desired imine (2.06 g, 7.59 mmol, 76 %) as a yellow oil.



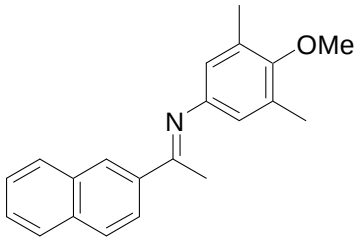
^{1}H-NMR (300 MHz, C_6D_6): δ = 1.81 (s, 3H), 2.22 (s, 6H), 3.43 (s, 3H), 6.44 (s, 2H), 6.84-7.00 (m, 2H), 7.62-7.65 (m, 1H), 7.79-7.84 (m, 1H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 16.3, 16.7, 59.4, 114.4 (d, *J* = 23.0 Hz), 117.1 (d, *J* = 22.0 Hz), 119.8, 123.1 (d, *J* = 2.8 Hz), 129.9 (d, *J* = 7.7 Hz), 131.4, 142.5 (d, *J* = 7.5 Hz), 147.6, 153.7, 163.0 (d, *J* = 3.0 Hz), 163.4 (d, *J* = 245.0 Hz) ppm.
IR (neat): υ_{max} (cm^{-1}) = 2937 (br, w), 1691 (w), 1633 (m), 1585 (m), 1481 (m), 1440 (s), 1266 (s), 1217 (s), 1010 (m), 867 (s), 784 (s), 686 (s).
MS (70 eV, EI): *m/z* (%) = 271 (M^+, 44), 256 (100), 120 (5).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{18}NFO$] 271.1372, found:271.1363.

***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(2-methylphenyl) ethylidene amine (12h):**
Prepared according to **TP3** from 2-methyl acetophenone (10.0 mmol, 1.34 g, 1.30 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 40:1 (2% Et_3N)) afforded the desired imine (1.98 g, 7.40 mmol, 74 %) as a yellow oil.



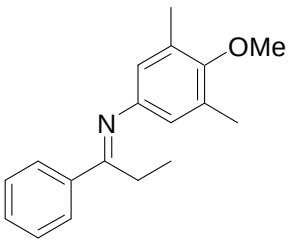
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.92 (s, 3H), 2.06 (s, 3H), 2.24 (s, 6H), 3.44 (s, 3H), 6.55 (s, 2H), 6.86-6.87 (m, 1H), 7.10-7.12 (m, 2H), 7.30-7.33 (m, 1H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.3, 20.5, 29.2, 59.4, 119.5, 125.8, 127.8, 128.6, 129.6, 131.5, 135.9, 140.1, 148.0, 153.7, 168.1 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2925 (w), 1641 (m), 1479 (s), 1217 (s), 1009 (s), 871 (m), 744 (s).
MS (70 eV, EI): *m/z* (%) = 268 ($[M+H]^+$, 12), 267 (M^+, 88), 252 (100), 135 (15), 130 (31), 91 (56).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{21}NO$] 267.1623, found: 267.1614.

***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(2-naphthyl) ethylidene amine (12i):** Prepared according to **TP3** from 2-acetyl naphthalene (10.0 mmol, 1.70 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 80:1 (2% Et_3N)) afforded the desired imine (1.94 g, 6.39 mmol, 64 %) as a yellow oil.



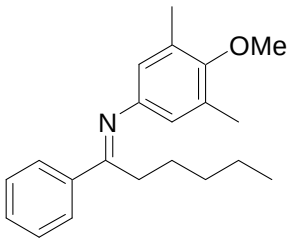
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.05 (s, 3H), 2.26 (s, 6H), 3.45 (s, 3H), 6.56 (s, 2H), 7.27-7.30 (m, 2H), 7.62-7.74 (m, 3H), 8.22-8.23 (m, 1H), 8.56 (dd, *J* = 1.8 Hz, 8.8 Hz, 1H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.4, 16.7, 59.4, 119.9, 124.9, 126.4, 127.2, 128.0, 128.1, 128.2, 129.1, 131.4, 133.5, 134.9, 137.6, 148.3, 153.6, 164.1 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2912 (w), 1641 (m), 1489 (s), 1207 (s), 1109 (s), 789 (m), 690 (s).
MS (70 eV, EI): *m/z* (%) = 304 ($[M+H]^+$, 11), 303 (M^+, 48), 288 (100), 151 (6).
HRMS (EI): *m/z* calcd. for: [$C_{21}H_{21}NO$] 303.1623, found: 303.1622.

***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl propylidene amine (12j):** Prepared according to **TP3** from propiophenone (10.0 mmol, 1.34 g, 1.34 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 80:1 (2% Et_3N)) afforded the desired imine in (2.09 g, 7.81 mmol, 78 %) as a yellow oil.



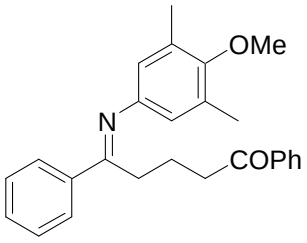
^{1}H-NMR (400 MHz, C_6D_6): δ = 0.89 (t, *J* = 7.7 Hz, 3H)), 2.23 (s, 6H), 2.52 (q, *J* = 7.7 Hz, 2H), 3.43 (s, 3H), 6.53 (s, 2H), 7.19-7.24 (m, 3H), 8.00-8.02 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 13.1, 16.4, 23.0, 59.4, 119.4, 128.0, 128.6, 130.2, 131.4, 138.6, 148.2, 153.4, 169.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2980 (w), 1705 (m), 1600 (s), 1220 (m), 1110 (m), 795 (m), 699 (m).
MS (70 eV, EI): *m/z* (%) = 267 (M^+, 75), 252 (100), 238 (99), 111 (20), 91 (29).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{21}NO$] 267.1623, found: 267.1629.

***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl hexylidene amine (12k):** Prepared according to **TP3** from n-hexanophenone (10.0 mmol, 1.76 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 100:1 (2% Et_3N)), afforded the desired imine (2.23 g, 7.21 mmol, 72 %) as a yellow oil.



^{1}H-NMR (400 MHz, C_6D_6): δ = 0.85 (t, *J* = 7.7 Hz, 3H), 1.17-1.20 (m, 4H), 1.57-1.59 (m, 2H), 2.17 (s, 6H), 2.38-2.42 (m, 2H), 3.37 (s, 3H), 6.66 (s, 2H), 7.03-7.07 (m, 1H), 7.15-7.19 (m, 2H), 7.25-7.27 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 15.3, 16.7, 22.9, 28.6, 32.1, 39.3, 59.5, 116.2, 126.7, 127.2, 128.7, 131.1, 144.0, 149.5, 153.6, 169.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2990 (w), 1745 (m), 1600 (s), 1225 (m), 1010 (m), 699 (m).
MS (70 eV, EI): *m/z* (%) = 309 (M^+, 40), 294 (18), 253 (99), 238 (100), 151 (30).
HRMS (EI): *m/z* calcd. for: [$C_{21}H_{27}NO$] 309.2093, found: 309.2094.

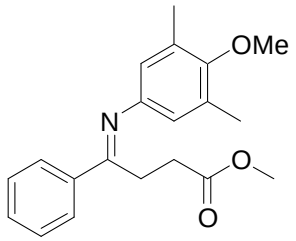
5-[(*N*-(3,5-Dimethyl-4-methoxy)phenyl)imino]-1,5-diphenylpentan-1-one (12l): Prepared according to **TP3** from 1,5-diphenyl-1,5-pentanedione (10.0 mmol, 2.52 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 4:1 (2% Et_3N)), provided the desired imine (2.70 g, 7.0 mmol, 70 %) as a dark brown oil.



^{1}H-NMR (400 MHz, C_6D_6): δ = 1.53-1. 60 (m, 2H), 1.75-1.82 (m, 2H), 2.11 (s, 6H), 3.04-3.09 (m, 2H), 3.32 (s, 3H), 6.82 (s, 2H), 6.99-7.22 (m, 8H), 7.74-7.76 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 16.5, 23.8, 34.6, 38.6, 59.5, 114.0, 127.0, 128.2, 128.8, 130.7, 131.1, 132.7, 134.4, 137.5, 144.0, 149.5, 153.8, 161.7, 198.7 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3360 (m), 2949 (w), 1700 (s), 1680 (s), 1635 (m), 1189 (s), 1100 (s), 760 (s), 685 (s).

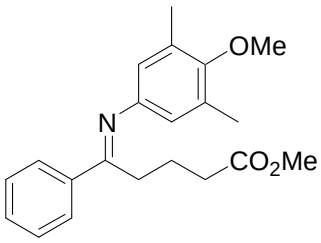
MS (70 eV, EI): *m/z* (%) = 385 (M^+, 42), 280 (45), 266 (80), 253 (88), 238 (100).
HRMS (EI): *m/z* calcd. for: [$C_{26}H_{27}NO_2$] 385.2042, found: 385.2038.

Methyl 4-[(*N*-(3,5-dimethyl-4-methoxyphenyl))imino]-4-phenylbutanoate (12m): Prepared according to **TP3** from methyl 3-benzoylpropionate (10.0 mmol, 1.92 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 5:1 (2% Et_3N)), provided the desired imine (2.24 g, 6.89 mmol, 69 %) as a dark brown oil.



^{1}H-NMR (400 MHz, C_6D_6): δ = 2.20 (s, 6H), 2.29-2.31 (m, 2H), 2.52 (t, *J* = 6.4 Hz, 2H), 3.34 (s, 3H), 3.39 (s, 3H), 6.50 (s, 2H), 7.00-7.10 (m, 3H), 7.17-7.19 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 16.3, 32.3, 33.4, 51.2, 59.4, 119.3, 127.9, 128.2, 128.7, 130.4, 138.3, 147.7, 153.6, 166.8, 172.8 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2950 (w), 1735 (s), 1686 (s), 1219 (s), 1165 (s), 1009 (m), 758 (s), 690 (s).
MS (70 eV, EI): *m/z* (%) = 325 (M^+, 99), 310 (43), 266 (28), 250 (45), 238 (100).
HRMS (EI): *m/z* calcd. for: [$C_{20}H_{23}NO$] 325.1678, found: 325.1662.

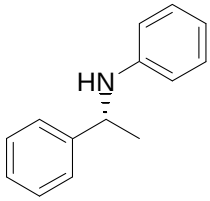
Methyl 5-[(*N*-(3,5-dimethyl-4-methoxyphenyl))imino]-5-phenylpentanoate (12n): Prepared according to **TP3** from methyl 4-benzoylbutanoate[6] (10.0 mmol, 2.06 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 5:1 (2% Et_3N)), provided the desired imine (2.37 g, 6.99 mmol, 70 %) as a dark brown oil.



^{1}H-NMR (400 MHz, C_6D_6): δ = 1.94-2.00 (m, 2H), 2.13-2.17 (m, 2H), 2.23 (s, 6H), 2.55 (t, *J* = 6.4 Hz, 2H), 3.28 (s, 3H), 3.32 (s, 3H), 6.90 (s, 2H), 7.03-7.13 (m, 3H), 7.77-7.80 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 18.6, 19.5, 33.0, 33.4, 50.9, 59.7, 120.2, 127.8, 128.5, 130.0, 132.7, 137.4, 145.9, 153.0, 167.0, 173.1 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2945 (w), 1700 (s), 1686 (s), 1189 (s), 1165 (s), 798 (s), 650 (s).
MS (70 eV, EI): *m/z* (%) = 339 (M^+, 60), 324 (25), 308 (27), 266 (65), 253 (55), 238 (100).
HRMS (EI): *m/z* calcd. for: [$C_{21}H_{25}NO_3$] 339.1834, found: 339.1845.

Typical procedure for Ir-catalyzed hydrogenation of the imines: A 25 mL Schlenkflask under an argon atmosphere was loaded with Ir-complex (0.005 mmol) and imine (0.5 mmol) in toluene:MeOH (4:1). The mixture was stirred at room temperature for 10-15 min. Then the solution was transferred under argon to an autoclave which was equipped with a glass tube and a stirring bar. The autoclave was then purged three times with hydrogen (5 bar) and finally pressurized to 10 bar. The reaction mixture was stirred for the indicated period of time until full conversion was achieved. Then the hydrogen gas was released, evaporated the solvents and filtered through a short pad of silica gel
Conversion was checked by ^{1}H-NMR/GC and enantioselectivity was determined using either Chiral GC or Chiral HPLC.

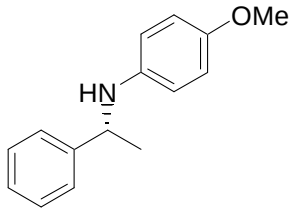
(*R*)-*N*-phenyl-1-phenyl ethyl amine (11a)[4, 7]: obtained as a yellow oil.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.50 (d, *J* = 7.1 HZ, 3H), 3.95 (br, NH), 4.48 (q, *J* = 6.9 Hz, 1H), 6.50 (d, *J* = 7.9 Hz, 2H), 6.65 (t, *J* = 7.4 HZ, 1H), 7.06 (dd, *J* = 8.9 Hz, 7.4 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 2H) ppm.
The enantiomer ratio was determined by Chiral GC DEX-CB Column (100 °C (5 min), 5 °C/min 160 °C (50 min));
With catalyst **8a:** t_r = 20.9 min [minor], t_r = 21.1 min [major]; 84% *ee*.
$[\alpha]_D^{20}$ = −3.9 (c = 1.0, $CHCl_3$)

With catalyst **9a:** t_r = 20.9 min [minor], t_r = 21.1 min [major]; 84% *ee*.
$[\alpha]_D^{20}$ = −3.9 (c = 1.0, $CHCl_3$)

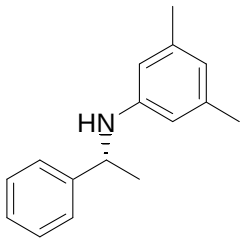
(*R*)-*N*-(4-methoxy)phenyl-1-phenyl ethylidene amine (11b)[7]: obtained as a yellow oil.



^{1}H-NMR (300 MHz, C_6D_6): δ = 1.13 (d, *J* = 6.85 Hz, 3H), 3.31 (br, 1H, -NH), 3.54 (s, 3H), 4.17 (q, *J* = 6.6 Hz, 1H), 6.32-6.73 (m, 2H), 6.64-6.69 (m, 2H), 7.00-7.05 (m, 1H), 7.10-7.21 (m, 4H) ppm.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 ml/min, heptane/iPrOH: 90/10, λ = 215 nm, 25 °C);
With catalyst **8a:** t_r = 14.9 min [major], t_r = 16.2 min [minor]; 88% *ee*.
$[\alpha]_D^{20}$ = +1.3 (c = 1.0, $CHCl_3$)

With catalyst **9a:** t_r = 14.9 min [major], t_r = 16.2 min [minor]; 88% *ee*.
$[\alpha]_D^{20}$ = +1.3 (c = 1.0, $CHCl_3$)

(*R*)-*N*-(3,5,-Dimethyl)phenyl-1-phenyl ethyl amine (11c)[8]: Obtained as a pale yellow oil;

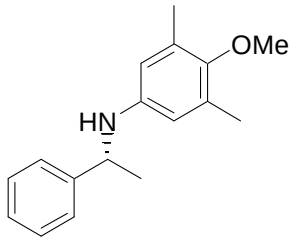


^{1}H-NMR (300 MHz, C_6D_6): δ = 1.21 (d, *J* = 7.1 Hz, 3H), 2.13 (s, 6H), 3.71 (br, 1H, NH), 4.32 (q, *J* = 7.0 Hz, 1H), 6.16 (s, 2H), 6.37 (s, 1H), 7.06-7.08 (m, 1H), 7.13-7.18 (m, 2H), 7.23-7.25 (m, 2H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 21.6, 24.8, 53.5, 112.0, 120.0, 126.1, 127.0, 128.8, 138.5, 145.8, 147.6 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3406 (br, w), 2914 (w), 1597 (s), 1512 (m), 1452 (m), 1336 (m), 1184 (m), 822 (m), 696 (m).
MS (70 eV, EI): *m/z* (%) = 225 (M^+, 39), 210 (100), 121 (34), 120 (10), 105 (42).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{19}N$] 225.1517, found: 225.1511.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 9.7 min [minor], t_r = 11.0 min [major]; 94% *ee*.
$[\alpha]_D^{20}$ = −12.8 (c = 0.5, CH_2Cl_2)

With catalyst **9a:** t_r = 9.5 min [minor], t_r = 10.7 min [major]; 93% *ee*.
$[\alpha]_D^{20}$ = −11.3 (c = 0.5, CH_2Cl_2)

(*R*)-(–)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl ethyl amine (13a): Obtained as a pale yellow solid;

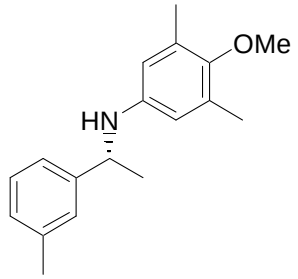


MP: 86.3 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.49 (d, *J* = 6.7 Hz, 3H), 2.15 (s, 6H), 3.62 (s, 3H), 4.41 (q, *J* = 6.7 Hz, 1H), 6.21 (s, 2H), 7.22-7.25 (m, 1H), 7.29-7.39 (m, 4H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.2, 24.7, 54.1, 59.9, 113.6, 125.9, 126.8, 128.6, 131.2, 143.0, 145.2, 149.0 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3381 (m), 2924 (br, m), 1609 (m), 1487 (s), 1190 (s), 1006 (s), 830 (m), 701 (m).
MS (70 eV, EI): *m/z* (%) = 255 (M^+, 100), 240 (87), 136 (77), 105 (98).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{21}NO$] 255.1623, found: 255.1627.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 1.0 mL/min, heptane/iPrOH: 80/20, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 6.4 min [minor], t_r = 7.6 min [major]; 94% *ee*.
$[\alpha]_D^{20}$ = −6.3 (c = 0.6, CH_2Cl_2)

With catalyst **9a:** t_r = 10.1 min [minor], t_r = 11.7 min [major]; 92% *ee*.
$[\alpha]_D^{20}$ = −5.7 (c = 0.6, CH_2Cl_2)

(*R*)–(+)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-methyl)phenyl ethyl amine (13b): Obtained as a viscous yellow oil;

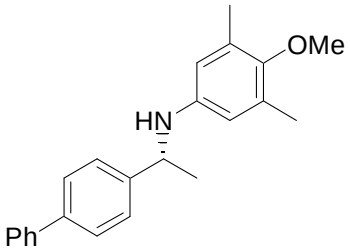


^{1}H-NMR (400 MHz, C_6D_6): δ = 1.23 (d, *J* = 6.9 Hz, 3H), 2.11 (s, 3H), 2.17 (s, 6H), 3.37 (s, 3H), 3.42 (br, 1H, NH), 4.29 (q, *J* = 6.9 Hz, 1H), 6.18 (s, 2H), 6.88-6.90 (m, 1H), 7.10-7.12 (m, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 16.5, 21.5, 25.1, 53.9, 59.5, 114.0, 123.3, 126.7, 127.8, 128.8, 131.1, 138.2, 143.8, 146.2, 149.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3396 (br, w), 2923 (w), 1607 (s), 1486 (s), 1222 (s), 1189 (m), 1009 (m), 835 (m), 784 (m).
MS (70 eV, EI): *m/z* (%) = 271 ($[M+2H]^+$, 9), 270 ($[M+H]^+$, 100), 213 (5).
HRMS (EI): *m/z* calcd. for: $[C_{18}H_{24}NO]$; $[M+H]^+$: 270.1858, found: 270.1846
The enantiomer ratio was determined by HPLC using Chiralcel AD column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 10.2 min [major], t_r = 11.8 min [minor]; 93% *ee*.
$[\alpha]_D^{20}$ = +4 (c = 0.6, CH_2Cl_2)

With catalyst **9a:** t_r = 10.4 min [major], t_r = 11.9 min [minor]; 92% *ee*.
$[\alpha]_D^{20}$ = +2.7 (c = 0.6, CH_2Cl_2)

(*R*)–(+)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-phenyl)phenyl ethyl amine (13c): Obtained as a yellow powder.



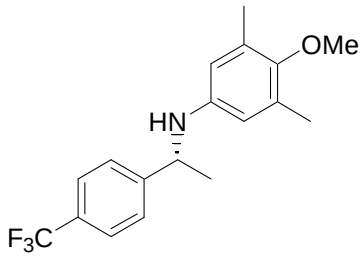
MP: 156.2-157.9 °C
^{1}H-NMR (400 MHz, C_6D_6): δ = 1.24 (d, *J* = 6.7 Hz, 3H), 2.19 (s, 6H), 3.38 (s, 3H), 3.43 (br, 1H, NH), 4.34 (q, *J* = 6.7 Hz, 1H), 6.20 (s, 2H), 7.09-7.13 (m, 1H), 7.17-7.21 (m, 2H), 7.27-7.31 (m, 2H), 7.43-7.47 (m, 4H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 16.5, 25.0, 53.5, 59.5, 114.0, 126.6, 127.3, 127.4, 127.7, 129.0, 131.2, 140.2, 141.5, 143.7, 145.2, 149.6 ppm.

IR (neat): υ_{max} (cm^{-1}) = 3354 (w), 2924 (w), 1604 (m), 1484 (s), 1217 (s), 998 (s), 827 (s), 767 (s), 699 (s).
MS (70 eV, EI): *m/z* (%) = 331 (M^+, 41), 316 (24), 181 (100), 165 (19), 151 (26), 136 (32).
HRMS (EI): *m/z* calcd. for: [$C_{23}H_{25}NO$] 331.1936, found: 331.1930.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 17.5 min [minor], t_r = 23.1 min [major]; 92% *ee*.
$[\alpha]_D^{20}$ = +48.7 (c = 0.6, CH_2Cl_2)

With catalyst **9a:** t_r = 17.7 min [minor], t_r = 23.5 min [major]; 90% *ee*.
$[\alpha]_D^{20}$ = +47.3 (c = 0.6, CH_2Cl_2)

(*R*)–(+)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-trifluoromethyl)phenyl ethyl amine (13d): Obtained as a yellow oil;



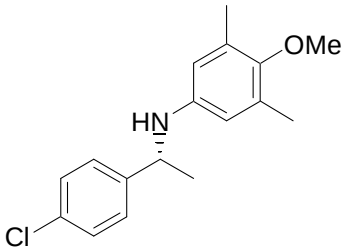
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.50 (d, *J* = 6.7 Hz, 3H), 2.14 (s, 6H), 3.60 (s, 3H), 4.45 (q, *J* = 6.7 Hz, 1H), 6.20 (s, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.2, 24.7, 54.1, 59.9, 113.8, 124.2 (q, *J* = 271.0 Hz), 125.6 (q, *J* = 3.8 Hz), 126.3, 129.6 (q, *J* = 32.3 Hz), 131.4, 142.3, 149.3, 149.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3349 (m), 2966 (w), 1605 (m), 1488 (m), 1323 (s), 1222 (s), 1155 (s), 1062 (s), 1005 (s), 835 (s), 607 (m).
MS (70 eV, EI): *m/z* (%) = 323 (M^+, 100), 308 (77), 293 (11), 173 (33), 150 (21), 136 (4).
HRMS (EI): *m/z* calcd.for: [$C_{18}H_{20}F_3NO$] 323.1497, found: 323.1481.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C);

With catalyst **9a:** t_r = 14.4 min [minor], t_r = 18.5 min [major]; 89% *ee*.
$[\alpha]_D^{20}$ = +10.2 (c = 0.5, CH_2Cl_2)

With catalyst **8a:** t_r = 14.3 min [minor], t_r = 18.5 min [major]; 88% *ee*.
$[\alpha]_D^{20}$ = +9.9 (c = 0.5, CH_2Cl_2)

(*R*)–(+)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-chloro)phenyl ethyl amine (13e): Obtained as a yellow oil;

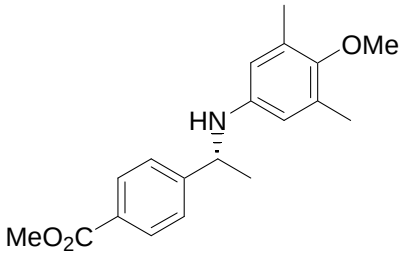


^{1}H-NMR (400 MHz, C_6D_6): δ = 1.06 (d, *J* = 7.1 Hz, 3H), 2.17 (s, 6H), 3.27 (br, 1H, NH), 3.38 (s, 3H), 4.10 (q, *J* = 6.6 Hz, 1H), 6.07 (s, 2H), 6.91-6.95 (m, 2H), 7.08-7.13 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 16.5, 24.8, 53.1, 59.5, 114.0, 127.5, 128.9, 131.2, 132.6, 143.4, 144.5, 149.7 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2926 (w), 1608 (m), 1487 (s), 1337 (w), 1222 (s), 1090 (m), 1010 (s), 825 (s), 730 (m), 695 (m).
MS (70 eV, EI): *m/z* (%) = 289 (M^+, 87), 276 (20), 274 (69), 150 (28), 139 (100), 136 (83).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{20}N^{35}ClO$] 289.1233, found: 289.1227.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 13.7 min [minor], t_r = 17.1 min [major]; 92% *ee*.
$[\alpha]_D^{20}$ = +8.3 (c = 0.6, CH_2Cl_2)

With catalyst **9a:** t_r = 13.9 min [minor], t_r = 17.5 min [major]; 92% *ee*.
$[\alpha]_D^{20}$ = +8.3 (c = 0.6, CH_2Cl_2)

(*R*)-(+)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-carbomethoxy)phenyl ethyl amine (13f): Obtained as a yellow solid;



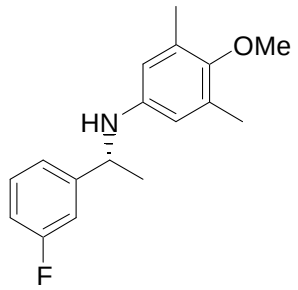
MP: 113.7-115.2 °C
^{1}H-NMR (400 MHz, C_6D_6): δ = 1.08 (d, *J* = 6.8 Hz, 3H), 2.16 (s, 6H), 3.34 (br, 1H, NH), 3.36 (s, 3H), 3.47 (s, 3H), 4.18 (q, *J* = 6.8 Hz, 1H), 6.08 (s, 2H), 7.14-7.15 (m, 2H), 8.07-8.09 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 16.5, 24.6, 51.4, 53.6, 59.5, 114.0, 126.1, 129.5, 130.3, 131.2, 143.4, 149.7, 151.4, 166.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3350 (m), 2994 (w), 1713 (s), 1605 (m), 1431 (m), 1279 (s), 1220 (s), 1114 (s), 1009 (s), 831 (s), 764 (s), 712 (s).
MS (70 eV, EI): *m/z* (%) = 313 (M^+, 94), 298 (90), 163 (100), 136 (80), 150 (41).
HRMS (EI): *m/z* calcd. for: [$C_{19}H_{23}NO_3$] 313.1678, found: 313.1679.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 25.2 min [minor], t_r = 28.9 min [major]; 94% *ee*.
$[\alpha]_D^{20}$ = +23.3 (c = 0.6, CH_2Cl_2)

With catalyst **9a:** t_r = 24.2 min [major], t_r = 28.0 min [minor]; 92% *ee*.
$[\alpha]_D^{20}$ = +22.0 (c = 0.6, CH_2Cl_2)

(*R*)–(–)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-fluoro)phenyl ethyl amine (13g): Obtained as a yellow oil;

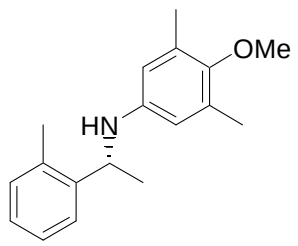


^{1}H-NMR (400 MHz, C_6D_6): δ = 1.07 (d, *J* = 6.8 Hz, 3H), 2.16 (s, 6H), 3.28 (br, 1H, NH), 3.37 (s, 3H), 4.14 (q, *J* = 6.8 Hz, 1H), 6.08 (s, 2H), 6.67-6.72 (m, 1H), 6.88-6.91 (m, 2H), 7.00-7.03 (m, 1H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 16.5, 24.7, 53.4 (d, *J* = 1.8 Hz), 59.5, 113.0 (d, *J* = 21.6 Hz), 113.8 (d, *J* = 21.3 Hz), 113.9, 121.7 (d, *J* = 2.6 Hz), 130.3 (d, *J* = 7.9 Hz), 131.2, 143.4, 149.6 (d, *J* = 6.1 Hz), 149.7, 163.7 (d, *J* = 245.5 Hz) ppm.
IR (neat): υ_{max} (cm^{-1}) = 3389 (br, w), 2927 (w), 1608 (m), 1485 (s), 1222 (s), 1009 (s), 835 (m), 784 (s), 696 (s).
MS (70 eV, EI): *m/z* (%) = 275 ($[M+2H]^+$, 7), 274 ($[M+H]^+$, 100), 193 (5).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{21}NFO$]; $[M+H]^+$: 274.1607, found: 274.1595
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 14.6 min [minor], t_r = 18.0 min [major]; 93% *ee*.
$[\alpha]_D^{20}$ = −12 (c = 0.6, CH_2Cl_2)

With catalyst **9a:** t_r = 14.8 min [minor], t_r = 18.3 min [major]; 91% *ee*.
$[\alpha]_D^{20}$ = −10.7 (c = 0.6, CH_2Cl_2)

(*R*)–(+)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(2-methyl)phenyl ethyl amine (13h): Obtained as a viscous yellow oil;



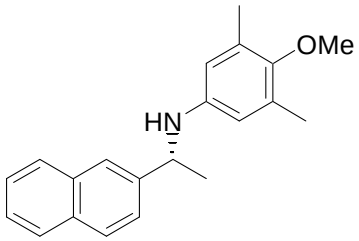
^{1}H-NMR (300 MHz, C_6D_6): δ = 1.18 (d, *J* = 6.7 Hz, 3H), 2.16 (s, 6H), 2.22 (s, 3H), 3.37 (brs, 4H), 4.50 (q, *J* = 6.7 Hz, 1H), 6.09 (s, 2H), 7.01-7.03 (m, 2H), 7.05-7.10 (m, 1H), 7.39-7.41 (m, 1H) ppm.

^{13}C-NMR (75 MHz, C_6D_6): δ = 16.5, 18.9, 22.7, 50.1, 59.5, 113.7, 125.1, 126.8, 126.9, 130.8, 131.1, 134.8, 143.5, 143.7, 149.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3406 (br, w), 2964 (m), 2920 (m), 1617 (s), 1500 (s), 1447 (m), 1317 (m), 801 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 269 (M^+, 100), 254 (72), 151 (35), 136 (51), 119 (68), 91 (13).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{23}NO$] 269.1780, found: 269.1774.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 13.9 min [major], t_r = 15.7 min [minor]; 94% *ee*.
$[\alpha]_D^{20}$ = +1.8 (c = 0.6, CH_2Cl_2)

With catalyst **9a:** t_r = 13.9 min [major], t_r = 15.7 min [minor]; 93% *ee*.
$[\alpha]_D^{20}$ = +1.7 (c = 0.6, CH_2Cl_2)

(*R*)–(–)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(2-naphthyl) ethyl amine (13i): Obtained as a viscous yellow oil;

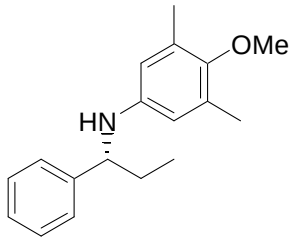


^{1}H-NMR (600 MHz, C_6D_6): δ = 1.27 (d, *J* = 6.7 Hz, 3H), 2.14 (s, 6H), 3.35 (s, 3H), 3,53 (br, NH, 1H), 4.43 (q, *J* = 6.7 Hz, 1H), 6.20 (s, 2H), 7.21-7.24 (m, 2H), 7.35 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.60-7.63 (m, 3H), 7,73 (s, 1H) ppm.
^{13}C-NMR (150 MHz, C_6D_6): δ = 16.5, 24.9, 54.0, 59.5, 114.0, 124.6, 124.8, 125.6, 126.2, 127.9, 128.1, 128.7, 131.2, 133.3, 134.2, 143.6, 143.8, 149.6 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3405 (br, w), 2864 (m), 2910 (m), 1687 (s), 1510 (s), 1477 (m), 1297 (m), 891 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 305 (M^+, 56), 290 (30), 155 (100), 136 (35).
HRMS (EI): *m/z* calcd. for: [$C_{21}H_{23}NO$] 305.1780, found: 305.1785.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 9.1 min [minor], t_r = 10.2 min [major]; 92% *ee*.
$[\alpha]_D^{20}$ = −22.4 (c = 0.6, CH_2Cl_2)

With catalyst **9a:** t_r = 9.1 min [minor], t_r = 10.2 min [major]; 92% *ee*.
$[\alpha]_D^{20}$ = −22.3 (c = 0.6, CH_2Cl_2)

(*R*)–(+)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl propyl amine (13j): Obtained as a yellow oil;

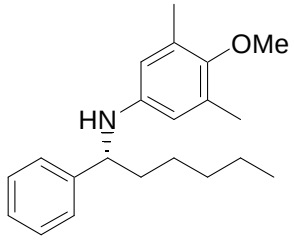


^{1}H-NMR (400 MHz, C_6D_6): δ = 0.75 (t, *J* = 7.4 Hz, 3H), 1.48-1.55 (m, 2H), 2.10 (s, 6H), 3.30 (s, 3H), 3.43 (br, 1H, NH), 4.04 (t, *J* = 6.6 Hz, 1H), 6.10 (s, 2H), 6.98-7.02 (m, 1H), 7.09-7.13 (m, 3H), 7.17-7.18 (m, 1H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 10.9, 16.5, 31.9, 59.5, 60.1, 114.0, 126.7, 127.0, 128.7, 131.1, 144.0, 144.8, 149.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3394 (br, w), 2930 (m), 1608 (m), 1487 (s), 1220 (s), 1009 (s), 835 (m), 750 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 269 (M^+, 21), 240 (100), 136 (9), 91 (15).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{23}NO$] 269.1780, found: 269.1791.
The enantiomer ratio was determined by HPLC using Chiralcel AD column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 10.4 min [major], t_r = 12.4 min [minor]; 94% *ee*.
$[\alpha]_D^{20}$ = +2.0 (c = 0.6, CH_2Cl_2)

With catalyst **9a:** t_r = 10.3 min [major], t_r = 12.3 min [minor]; 92% *ee*.
$[\alpha]_D^{20}$ = +1.9 (c = 0.6, CH_2Cl_2)

(*R*)-(+)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl-hexylamine (13k):obtained as a pale yellow oil.

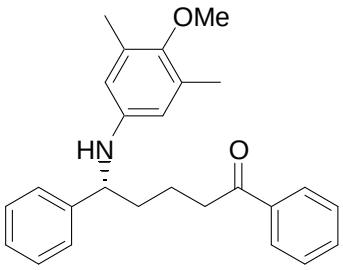


^{1}H-NMR (400 MHz, C_6D_6): δ = 0.82 (t, *J* = 7.0 Hz, 3H), 1.15-1.32 (m, 6H), 1.52-1.58 (m, 2H), 2.14 (s, 6H). 3.34 (s, 3H), 3.52 (br, NH), 4.18 (t, *J* = 7.1 Hz, 1H), 6.18 (s, 2H), 7.00-7.04 (m, 1H), 7.12-7.14 (m, 2H), 7.22-7.24 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 14.2, 16.5, 22.9, 26.4, 32.1, 39.3, 58.8, 59.5, 114.0, 126.7, 127.0, 128.7, 131.1, 144.0, 145.3, 149.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2928 (m), 1608 (m), 1488 (m), 1222 (s), 1011 (m), 832 (m), 755 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 327 (M^+, 37), 241 (100), 226 (8), 117 (17).
HRMS (EI): *m/z* calcd. for: [$C_{21}H_{29}NO$] 311.2249, found: 311.2248.
The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 11.0 min [minor], t_r = 12.3 min [major]; 95% *ee*.
$[\alpha]_D^{20}$ = +2.4 (c = 0.5, CH_2Cl_2)

With catalyst **9a:** t_r = 11.7 min [minor], t_r = 12.9 min [major]; 94% *ee*.
$[\alpha]_D^{20}$ = +2.1 (c = 0.5, CH_2Cl_2)

(*R*) –(–)-5-[(*N*-(3,5-Dimethyl-4-methoxy)phenyl)amino]-1,5-diphenylpentan-1-one (13l): obtained as a dark brown oil.

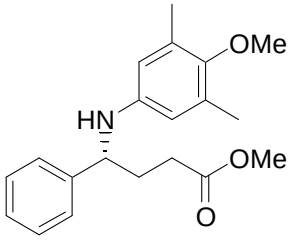


^{1}H-NMR (400 MHz, C_6D_6): δ = 1.59-1.68 (m, 3H), 1.81-1.87 (m, 1H), 2.17 (s, 6H), 2.46-2.48 (m, 2H), 3.37 (s, 3H), 3.83 (br, NH), 4.25 (t, *J* = 6.7 Hz, 1H), 6.24 (s, 2H), 7.02-7.09 (m, 3H), 7.11-7.14 (m, 2H), 7.17-7.18 (m, 1H), 7.26-7.28 (m, 2H), 7.80-7.82 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 16.5, 21.0, 37.8, 38.6, 58.7, 59.5, 114.0, 126.7, 127.0, 128.2, 128.6, 128.8, 131.1, 132.7, 137.5, 144.0, 145.1, 149.5, 198.7 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3010 (w), 1788 (m), 1685 (s), 1129 (m), 1155 (s), 1009 (m), 795 (m).
MS (70 eV, EI): *m/z* (%) = 389 ($[M+2H]^+$, 22), 388 ($[M+H]^+$, 100), 237 (15).
HRMS (EI): *m/z* calcd. for: [$C_{26}H_{30}NO_2$] 388.2270, found: 388.2277.
The enantiomer ratio was determined by HPLC using a Chiralcel AD column (flow rate 0.2 mL/min, heptane/iPrOH: 80/20, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 57.0 min [major], t_r = 64.5 min [minor]; 99% *ee*.
$[\alpha]_D^{20}$ = −11 (c = 0.4, CH_2Cl_2)

With catalyst **9a:** t_r = 57.2 min [major], t_r = 64.7 min [minor]; 98% *ee*.
$[\alpha]_D^{20}$ = −9 (c = 0.4, CH_2Cl_2)

(*R*)-(+)-Methyl 4-[(*N*-(3,5-dimethyl-4-methoxy)phenyl)amino]-4-phenyl butanoate (13m): obtained as a dark brown oil.



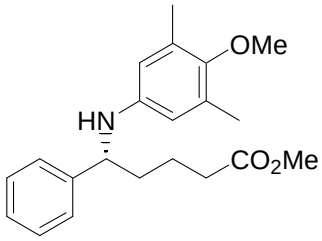
^{1}H-NMR (400 MHz, C_6D_6): δ = 2.15 (s, 6H), 2.16-2.21 (m, 2H), 2.53 (t, *J* = 6.4 Hz, 1H), 2.80 (t, *J* = 6.8 Hz, 1H), 3.30 (s, 3H), 3.35 (s, 3H), 3.72 (br, NH), 4.24 (t, *J* = 6.8 Hz, 1H), 6.19 (s, 2H), 7.00-7.04 (m, 2H), 7.09-7.13 (m, 2H), 7.17 (s, 1H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 16.5, 31.1, 33.6, 51.1, 58.1, 59.4, 114.0, 126.6, 128.5, 128.8, 131.1, 132.8, 143.7, 149.6, 173.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3393 (br, w), 2949 (w), 1732 (s), 1488 (s), 1220 (s), 1162 (s), 1009 (s), 837 (m), 750 (s), 700 (s).
MS (70 eV, EI): *m/z* (%) = 327 (M^+, 37), 241 (100), 226 (8), 117 (17).

HRMS (EI): *m/z* calcd. for: [$C_{20}H_{25}NO_3$] 327.1834, found: 327.1825.
The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 80/20, λ= 215 nm, 25 °C);

With catalyst **8a:** t_r = 19.5 min [major], t_r = 25.3 min [minor]; 92% *ee*.
[α]$_D^{20}$ = +21 (c = 0.6, CH_2Cl_2)

With catalyst **9a:** t_r = 19.6 min [major], t_r = 25.4 min [minor]; 90% *ee*.
[α]$_D^{20}$ = +15.7 (c = 0.6, CH_2Cl_2)

(*R*)-(+)-Methyl 5-[(*N*-(3,5-dimethyl-4-methoxy)phenyl)amino]-4-phenyl pentanoate (13n): obtained as a yellow oil.

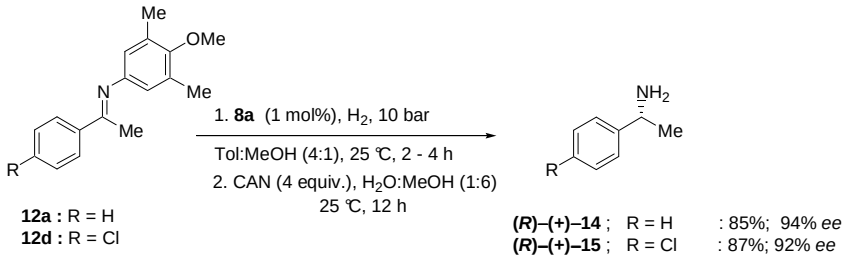


^{1}H-NMR (400 MHz, C_6D_6): δ = 1.51-1.53 (m, 3H), 1.64-1.68 (m, 1H), 2.01-2.04 (m, 2H), 2.17 (s, 6H), 3.30 (s, 3H), 3.37 (s, 3H), 3.62 (br, NH), 4.17 (t, *J* = 6.2 Hz, 1H) 6.19 (s, 2H), 7.03-7.05 (m, 1H), 7.12-7.16 (m, 2H), 7.19-7.21 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 16.5, 22.0, 33.6, 38.4, 50.9, 58.4, 59.5, 113.9, 126.6, 127.1, 128.7, 131.1, 143.8, 144.8, 149.5, 173.1 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2949 (w), 1732 (s), 1684 (m), 1488 (m), 1222 (s), 1152 (m), 1010 (m), 753 (m), 700 (s).
MS (70 eV, EI): *m/z* (%) = 341 (M^+, 100), 310 (13), 241 (45), 240 (46), 225 (18).
HRMS (EI): *m/z* calcd. for: [$C_{21}H_{27}NO_3$] 341.1991, found: 341.1979.
The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 80/20, λ= 215 nm, 25 °C);

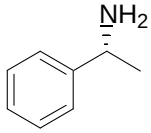
With catalyst **8a:** t_r = 16.1 min [minor], t_r = 17.3 min [major]; 98% *ee*.
[α]$_D^{20}$ = +8 (c = 0.6, CH_2Cl_2)

With catalyst **9a:** t_r = 16.1 min [minor], t_r = 17.3 min [major]; 98% *ee*.
[α]$_D^{20}$ = +8.1 (c = 0.6, CH_2Cl_2)

General procedure for the preparation of primary amines: To a 50 mL round-bottomed flask was added amine of type **13** (0.40 mmol) in MeOH:H_2O (28 mL; 6:1). CAN (660 mg, 3.0 equiv.) was added at 0 °C and warmed to room temperature and stirred for overnight. Washed the mixture with CH_2Cl_2 (5 mL) and the aqueous layer was made alkaline by adding 2N NaOH. Extracted the aqueous layer with ethyl acetate (4 × 20 mL) and washed the combined organic layers with brine, dried over $MgSO_4$ and isolated the primary amine by column chromatography (silica gel, *n*-pentane:ethyl acetate (1:1; 2% Et_3N)).

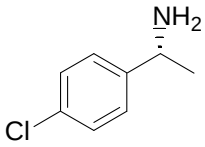


(*R*)–(+)-α-methyl benzylamine (14)[9]: Purified by flash chromatography (silica gel; *n*-pentane:ethyl acetate 1:1 (2% Et_3N)) to afford the desired compound (49 mg, 85 %) as a yellow oil.



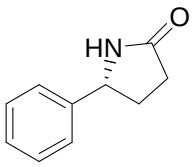
$[\alpha]_D^{20}$ = +28.9 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.58 (d, *J* = 6.8 Hz, 3H), 1.68 (br, 2H), 4.25 (q, *J* = 6.8 Hz, 1H), 7.30-7.43 (m, 5H) ppm.

(*R*)–(+)-α-methyl benzylamine (15)[10]: Purified by flash chromatography (silica gel; *n*-pentane:ethyl acetate 1:1 (2% Et_3N)) to afford the desired compound (51 mg, 82 %) as a yellow oil.



$[\alpha]_D^{20}$ = +18.9 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.48 (d, *J* = 7.0 Hz, 3H), 1.62 (br, 2H), 4.21 (q, *J* = 6.9 Hz, 1H), 7.15-7.17 (m, 2H), 7.87-7.99 (m, 2H) ppm.

(*R*)-(+)-5-Phenylpyrrolidin-2-one (16)[11]: Purified by flash chromatography (silica gel; *n*-pentane:ethylacetate 1:1 (2% Et_3N)) to afford the title compound (46 mg, 72 %) as a pale oil.

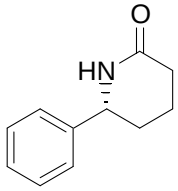


^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.97-2.11 (m, 1H), 2.40-2.72 (m, 3H), 4.82 (t, *J* = 7.0 Hz, 1H), 6.70 (brs, NH), 7.34-7.48 (m, 5H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 30.9, 31.4, 58.2, 125.8, 127.8, 128.9, 143.0, 178.9 ppm.
MS (70 eV, EI): *m/z* (%) = 161 (M^+, 67), 117 (100), 104 (8), 77 (17).
HRMS (EI): *m/z* calcd. for: [$C_{10}H_{11}NO$] 161.0841, found: 161.0843.
The enantiomer ratio was determined by Chiral GC using a Chiral DEX-CB column (100 °C (5), 5 °C/min to 160 °C (60))

With catalyst **8a:** t_r = 36.7 min [major], t_r = 41.0 min [minor]; 92% *ee*.
$[\alpha]_D^{20}$ = +41.0 (c = 0.4, CH_2Cl_2)

With catalyst **9a:** t_r = 36.7 min [major], t_r = 41.0 min [minor]; 90% *ee*.
$[\alpha]_D^{20}$ = +37.5 (c = 0.4, CH_2Cl_2)

(*R*)-(+)-6-Phenylpiperidin-2-one (17)[12]: purified by flash chromatography (silica gel; *n*-pentane:ethyl acetate 1:1 (2% Et_3N)) to furnish the title compound (55 mg. 78 %) as a pale yellow solid.



MP: 118-119 °C
^{1}H-NMR (400 MHz, C_6D_6): δ = 1.19-1.27 (m, 2H), 1.42-1.48 (m, 2H), 2.04-2.11 (m, 1H), 2.15-2.22 (m, 1H), 3.94-3.97 (m, 1H), 6.80 (br, s, NH), 6.98-7.06 (m, 3H), 7.09-7.13 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 19.6, 31.2, 32.1, 57.3, 126.4, 127.5, 128.7, 143.7, 171.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3266 (br, w), 2955 (w), 1655 (s), 1623 (s), 1478 (s), 1355 (s), 1175 (m), 737 (s), 695 (s).
MS (70 eV, EI): *m/z* (%) = 176 ($[M+H]^+$, 12), 175 (M^+, 100), 119 (26), 106 (34), 98 (10), 77 (11).
HRMS (EI): *m/z* calcd. for: [$C_{11}H_{13}NO$] 175.0997 found 175.0989
The enantiomer ratio was determined by Chiral GC using a Chiral DEX-CB column (100 °C (5), 5 °C/min to 160 °C (60))

t_r = 38.7 min [minor], t_r = 40.8 min [major]; 97% *ee*.
$[\alpha]_D^{20}$ = +40.0 (c = 2.0, $CHCl_3$)

References:

[1]. Guillaneux, D.; Kagan, H. B. *J. Org. Chem.* **1995,** *60*, 2502.
[2]. Bruice, T. C.; Kharasch, N.; Winzler, R. J. *J. Org. Chem.* **1953,** *18*, 83.
[3]. Reger, D. L.; Wright, T. D.; Little, C. A.; Lamba, J. J. S.; Smith, M. D. *Inorg. Chem.* **2001**, *40*, 3810
[4]. Schnider, P.; Koch, G.; Prétôt, R.; Wang, G.; Bohnen, F. M.; Krüger, C.; Pfaltz, A *Chem. Eur. J.* **1997,** *3*, 887.
[5]. Barluenga, J. ; Fernández, A. M. ; Aznar, F. ; Valdés, C. *Chem. Eur. J.* **2004,** *10*, 494.
[6]. Scheiper, B.; Bonnekessel, M.; Krause, H.; Fuerstner, A. *J. Org. Chem.* **2004**, *69*, 3943.
[7]. Iwadate, N.; Yoshida, K.; Imamoto, T. *Org. Lett.* **2006,** *8*, 2289;
[8]. Kwong, F. Y.; Buchwald, S. L. *Org. Lett,* **2003,** *5*, 793.
[9]. Chi, Y.; Zhou, Y.; Zhang, X. *J. Org. Chem.* **2003,** *10*, 4120.
[10]. Mereyala, H. B.; Pola, P. *Tetrahedron: Asymmetry* **2003,** *14*, 2683.
[11]. Ramachandran, P. V.; Burghardt, T. E. *Chem. Eur. J.* **2005,** *11*, 4387.
[12]. Davis, F. A.; Chao, B.; Fang, T.; Szewczyk, J. M. *Org. Lett.* **2000**, *2*, 1041.