SUPPORTING INFORMATION

Asymmetric, Catalytic Synthesis of α -Chiral Amines Using a Novel Bis(phosphine) Monoxide Chiral Ligand

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General experimental procedures. Characterization data for new compounds. ^1H and ^{13}C NMR spectra. HPLC traces and conditions for the separation of 1:1 mixture and enantioenriched compounds.

General: All non-aqueous reactions were run under an inert atmosphere (nitrogen or argon) with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds.¹ All glassware was stored in the oven and/or was flame-dried prior to use under an inert atmosphere of gas. Anhydrous solvents were obtained either by filtration through drying columns (THF, ether, CH_2Cl_2 , benzene, DMF, CH_3CN , toluene, hexane, methanol) on a GlassContour system (Irvine, CA), by distillation over calcium hydride (Et_3N , $\text{ClCH}_2\text{CH}_2\text{Cl}$, pyridine, diisopropylamine, isopropanol) or by distillation over sodium/benzophenone (DME, toluene). Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel (Merck 60 F₂₅₄). Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, iodine, or aqueous potassium permanganate. Flash column chromatography was performed using 230-400 mesh silica (EM Science or Silicycle) of the indicated solvent system according to standard technique.² Melting points were obtained on a Buchi melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin Elmer Spectrum One FTIR and are reported in reciprocal centimeters (cm^{-1}). Nuclear magnetic resonance spectra (^1H , ^{13}C) were recorded either on a Bruker AV 300, AMX 300, AV 400, ARX 400 spectrometer. Chemical shifts for ^1H NMR spectra are recorded in parts per million with the solvent resonance as the internal standard (chloroform, δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sept = septuplet, m = multiplet and br = broad), coupling constant in Hz, integration, and assignment. Chemical shifts for ^{13}C NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuteriochloroform (77.00 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. Optical rotations were determined with a Perkin-Elmer 341 polarimeter at 589 or 546 nm. Data are reported as follows: $[\alpha]_D^{\text{temp}}$, Concentration (c in g/100 mL), and solvent. High resolution mass spectra were performed by the Centre régional de spectroscopie de masse de l'Université de Montréal. Combustion analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal.

Analytical High Performance Liquid Chromatography was performed either on HP 1100 Analytical Instrument equipped with a diode array UV detector. Data are reported as follows: (column type, eluent, flow rate: retention time (t_r)).

Reagents: Me-DuPHOS, Me_2Zn and $\text{Cu}(\text{OTf})_2$ were purchased from Strem chemicals. $(\text{CuOTf})_2 \cdot \text{toluene}$ and all other starting materials were purchased from Aldrich. Unless otherwise stated, commercial reagents were used without purification. Diethylzinc was purchased neat from AkzoNobel and used without purification.

The *N*-diphenylphosphinoylimines **5**³⁻²¹, **11**^{8,10-12,14,15,18-20}, **12**^{11,18}, **13**^{5-7,10,12,14,18}, **14**^{4,5,9,14,18}, **15**^{6-7,9-11,14,18}, **16**^{11,18}, **17**^{5-7,10,13-17,19}, **18**^{4-9,15,17,19-21}, **19**^{9,10,12,14,17} were prepared according to a known literature procedures. The resulting *N*-diphenylphosphinic amides **6**^{8,13,16}, **24**^{8,11,13-21}, **25**^{8,11,14,15,18-20}, **26**^{11,18}, **27**^{13,14,18}, **28**^{14,18}, **29**^{11,14,18}, **30**^{11,18}, **31**^{13-17,19}, **32**^{8,15,17,19-21}, **33**^{14,17}, **39**²³, **40**⁸, **41**^{19,24} were compared to authentic samples. Racemic samples for HPLC comparison were prepared by addition of EtMgCl, MeMgBr, RLi or RCuCN in THF to *N*-diphenylphosphinoylimines. Dibutylzinc was prepared according to Noller's procedure and diisopropylzinc according to Knochel's procedure.²⁵ Ligand **45** was prepared according to a known literature procedure.²⁷ Ligand **44** was prepared according literature procedure.²⁷ Ligand **45** was obtained in quantitative yield by oxidation of **44** with hydrogen peroxide.

General procedure for diethylzinc addition to diphenylphosphinoylimine.

In the same flask, ligand **10** (8 mg, 0.025 mmol, 0.03 equiv) and Cu(OTf)₂ (17 mg, 0.048 mmol, 0.06 equiv) were dissolved in toluene (3 mL). The resulting dark green heterogeneous solution was stirred for 1 h at room temperature the neat diethylzinc (171 μ L, 1.64 mmol, 2.00 equiv) was added at room temperature and the resulting dark red suspension was stirred for 20 min at room temperature and an additional 10 min at 0 °C. A cold (0 °C) suspension of diphenylphosphinoylimine **5** (245 mg, 0.80 mmol, 1.00 equiv) in toluene (4 mL + 1 mL to rinse) was transferred (Teflon cannula) to the catalyst solution. After stirring for 20 h at 0 °C, the reaction was quenched with saturated NH₄Cl and the aqueous layer was extracted rapidly with CH₂Cl₂ (3x). The combined organic layers were dried over Na₂SO₄. Concentration and purification by silica gel column chromatography (100% EtOAc) afforded *N*-[(1*S*)-1-phenylpropyl]-*P,P*-diphenyl-phosphinic amide (**24**) (258 mg, 96 %yield) as a white solid.

General procedure for dimethylzinc addition to diphenylphosphinoylimine.

In the same flask, ligand **10** (10.8 mg, 0.033 mmol, 0.05 equiv) and (CuOTf)₂•toluene (17 mg, 0.033 mmol, 0.05 equiv) were dissolved in toluene (1.5 mL). The resulting dark yellow heterogeneous solution was stirred for 1h at room temperature Neat dimethylzinc (0.140 mL, 2 mmol, 3 equiv) was added at room temperature and the resulting yellow suspension was stirred for an additional 30 min before a fine suspension of diphenylphosphinoylimine **5** (200 mg, 0.66 mmol, 1 equiv) in toluene (3 mL + 1.5 mL) was transferred (Teflon cannula) to the catalyst solution. After stirring for 48h at room temperature, the reaction was quenched with saturated NH₄Cl and the aqueous layer was extracted rapidly with CH₂Cl₂ (3x). The combined organic layers were dried over Na₂SO₄. Concentration and purification by silica gel column chromatography (100% EtOAc) afforded *N*-[(1*S*)-1-phenylethyl]-*P,P*-diphenyl-phosphinic amide (**6**) (185 mg, 87 %) as a white solid.

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(2*R*,5*R*)-1-{2[(2*R*,5*R*)-2,5-Dimethylphospholan-1-yl]phenyl}-2,5-dimethylphospholane 1-oxide (BozPHOS) (10). To a solution of (*R,R*)-Me-DUPHOS (500 mg, 1.63 mmol, 1.00 equiv) in THF (16 mL, 0.1 M) was added BH₃•DMS (10 M, 180 μ L, 1.80 mmol, 1.10 equiv) at 0 °C. The mixture was stirred 45 min at this temperature and treated with H₂O₂ (30% (v/v) 2.0 mL, 19.60 mmol, 12.00 equiv). After 45 min of additional stirring at room temperature, the reaction was quenched with saturated Na₂SO₃ at 0 °C. Aqueous layers were extracted with AcOEt (3x), dried over Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was immediately dissolved in benzene (16 mL, 0.1 M) and treated with Dabco™ (275 mg, 2.45 mmol, 1.50 equiv) at 50 °C. The reaction mixture was further stirred for 5 h at 50 °C, evaporated under reduced pressure and directly purified on silica gel (95:5 AcOEt:MeOH) affording a white air-stable solid (477 mg, 90%): mp 123-125 °C; *R_f* 0.20 (100% AcOEt); $[\alpha]_D^{20}$ -250.5 (*c* 0.65, benzene); ¹H NMR (400 MHz, C₆D₆) δ 7.46-7.42 (m, 1H, *ArH*), 7.30-7.24 (m, 1H, *ArH*), 7.09 (tt, *J* = 7.6, 1.5 Hz, 1H, *ArH*), 7.01 (tddd, *J* = 7.6, 2.5, 1.5, 0.6 Hz, 1H, *ArH*), 2.80-2.52 (m, 2H, CH₃CHP(O)), 2.47-2.38 (m, 1H, CH₃CHP), 2.02-1.79 (m, 5H, CH₃CHP(O) and CHCH₂CH₂), 1.73-1.59 (m, 2H, CHCH₂CH₂), 1.34-1.24 (m, 1H, CHCH₂CH₂), 1.26 (d, *J*_{H-P} = 13.8 Hz, *J* = 7.0 Hz, 3H, CH₃CHP(O)), 1.24 (d, *J*_{H-P} = 17.6 Hz, *J* = 7.0 Hz, 3H, CH₃CHP(O)), 1.03 (dd, *J*_{H-P} = 9.2 Hz, *J* = 7.2 Hz, 3H, CH₃CHP), 1.00-0.86 (m, 1H, CHCH₂CH₂), 0.81 (dd, *J*_{H-P} = 17.3 Hz, *J* = 7.4 Hz, 3H, CH₃CHP); ¹³C NMR (100 MHz, C₆D₆) δ 144.1 (dd, *J*_{C-P} = 37.4, 9.7 Hz), 139.3 (dd, *J*_{C-P} = 82.7, 33.6 Hz), 134.2 (dd, *J*_{C-P} = 10.6, 2.5 Hz), 130.6 (d, *J*_{C-P} = 2.3 Hz), 128.1 (d, *J*_{C-P} = 10.6 Hz), 36.8 (d, *J*_{C-P} = 1.9 Hz), 36.6 (dd, *J*_{C-P} = 67.1, 5.3 Hz), 36.3 (d, *J*_{C-P} = 6.4 Hz), 34.8 (d, *J*_{C-P} = 13.6 Hz), 34.6 (d, *J*_{C-P} = 11.1 Hz), 32.0 (dd, *J*_{C-P} = 8.1, 1.8 Hz), 31.7 (dd, *J*_{C-P} = 68.0, 0.9 Hz), 31.5 (d, *J*_{C-P} = 9.9 Hz), 20.3 (d, *J*_{C-P} = 35.9 Hz), 18.3 (d, *J*_{C-P} = 3.7 Hz), 17.3 (d, *J*_{C-P} = 8.7 Hz), 12.8 (dd, *J*_{C-P} = 3.0, 0.9 Hz); NMR ³¹P (162 MHz, C₆D₆) δ 62.4 (d, *J* = 5.1 Hz), 9.7 (d, *J* = 5.1 Hz); HRMS (MAB) [*M*]⁺: calcd 322.16154 *m/z*, found: 322.1610 *m/z*; IR (Neat) 2923, 2860, 1446, 1157, 756, 737, 672 cm⁻¹. Elementary Analysis calcd for C₁₈H₂₈P₂O: C, 67.07; H, 8.75 found: C, 67.23; H, 8.98.

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***N*-[(1*S*)-1-phenylpropyl]-*P,P*-diphenyl-phosphinic amide (**24**).** The general procedure was followed. Yield 96%, enantiomeric excess (98% ee) was determined by HPLC analysis (Chiralpak AD, 80:20 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**24** t_r = 8.7 min, (*S*)-**24** t_r = 11.7 min). mp 118-119 °C; R_f 0.45 (100% AcOEt); $[\alpha]_D^{20}$ -53.1 (c 2.54, MeOH); ^1H NMR (400 MHz, CDCl_3) δ 7.87 (ddt, J = 12.2, 6.7, 1.5 Hz, 2H), 7.76 (ddt, J = 12.2, 6.7, 1.5 Hz, 2H), 7.52-7.35 (m, 4H), 7.36-7.21 (m, 5H), 7.18-7.13 (m, 2H), 4.11 (qd, J = 9.8, 5.8 Hz, 1H), 3.23 (dd, J = 9.5, 6.3 Hz, 1H), 2.07-1.96 (m, 1H), 1.90-1.78 (m, 1H), 0.79 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, CHCl_3) δ 143.5 (d, $J_{\text{C-P}}$ = 5.5 Hz), 133.2 (d, $J_{\text{C-P}}$ = 129.0 Hz), 132.4 (d, $J_{\text{C-P}}$ = 9.0 Hz), 132.0 (d, $J_{\text{C-P}}$ = 131.8 Hz), 131.7 (d, $J_{\text{C-P}}$ = 9.0 Hz), 131.6 (d, $J_{\text{C-P}}$ = 2.8 Hz), 131.5 (d, $J_{\text{C-P}}$ = 2.2 Hz), 128.3, 128.2 (d, $J_{\text{C-P}}$ = 12.5 Hz), 128.1 (d, $J_{\text{C-P}}$ = 12.5 Hz), 126.9, 126.4, 57.0 (d, $J_{\text{C-P}}$ = 6.2 Hz), 32.4 (d, $J_{\text{C-P}}$ = 3.5 Hz), 10.5 (d, $J_{\text{C-P}}$ = 2.8 Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 22.9; IR (neat) 3141, 1456, 1437, 1195, 1179, 1106, 904, 751, 720, 695 cm^{-1} .

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***N*-[(1*S*)-1-(4-Methylphenyl)propyl]-*P,P*-diphenylphosphinic amide (**25**).** The general procedure was followed. Yield 94%, enantiomeric excess (98% ee) was determined by HPLC analysis (Chiralpak AD, 80:20 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**25** t_r = 8.6 min, (*S*)-**25** t_r = 10.4 min). mp 125-126 °C; R_f 0.45 (100% AcOEt); $[\alpha]_D^{20}$ -55.7 (c 1.86, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.87 (ddt, J = 12.2, 6.7, 1.5 Hz, 2H), 7.77 (ddt, J = 12.2, 6.7, 1.5 Hz, 2H), 7.51-7.39 (m, 4H), 7.34 (tdd, J = 8.0, 3.3, 1.5 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 7.8 Hz, 2H), 4.06 (qd, J = 9.8, 5.8 Hz, 1H), 3.20 (dd, J = 9.5, 6.3 Hz, 1H), 2.34 (s, 3H), 2.07-1.95 (m, 1H), 1.89-1.76 (m, 1H), 0.77 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CHCl₃) δ 140.4 (d, J_{C-P} = 6.2 Hz), 136.4, 133.3 (d, J_{C-P} = 128.3 Hz), 132.1 (d, J_{C-P} = 74.2 Hz), 132.0 (d, J_{C-P} = 129.7 Hz), 131.9 (d, J_{C-P} = 74.2 Hz), 131.6 (d, J_{C-P} = 2.1 Hz), 131.5 (d, J_{C-P} = 2.1 Hz), 129.0, 128.2 (d, J_{C-P} = 12.5 Hz), 128.1 (d, J_{C-P} = 12.5 Hz), 126.3, 56.8 (d, J_{C-P} = 6.2 Hz), 32.3 (d, J_{C-P} = 2.8 Hz), 20.9 (d, J_{C-P} = 6.9 Hz), 10.5 (d, J_{C-P} = 2.8 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 22.9; IR (Neat) 3135, 1451, 1436, 1179, 1089, 1060, 722, 693 cm⁻¹.

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***N*-[*(1S)*-1-(3-Methylphenyl)propyl]-*P,P*-diphenylphosphinic amide (26).** The general procedure was followed. Yield 96%, enantiomeric excess (97% ee) was determined by HPLC analysis (Chiralpak AD, 80:20 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**26** t_r = 6.3 min, (*S*)-**26** t_r = 10.2 min). mp 98-99 °C; ; R_f 0.45 (100% AcOEt); $[\alpha]_D^{20}$ -37.6 (c 1.90, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.85 (ddt, J = 12.0, 6.7, 1.5 Hz, 2H), 7.75 (ddt, J = 12.0, 6.7, 1.5 Hz, 2H), 7.48-7.35 (m, 4H), 7.31 (td, J = 7.8, 3.3 Hz, 2H), 7.17 (d, J = 7.4 Hz, 1H), 6.97 (d, J = 7.7 Hz, 1H), 6.91 (s, 1H), 4.04 (qd, J = 9.5, 6.1 Hz, 1H), 3.34 (dd, J = 9.4, 6.9 Hz, 1H), 2.29 (s, 3H), 2.07-1.94 (m, 1H), 1.88-1.76 (m, 1H), 0.77 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CHCl₃) δ 143.3 (d, J_{C-P} = 6.2 Hz), 137.8, 133.2 (d, J_{C-P} = 128.3 Hz), 132.1 (d, J_{C-P} = 80.5 Hz), 132.0 (d, J_{C-P} = 128.3 Hz), 131.9 (d, J_{C-P} = 80.5 Hz), 131.6 (d, J_{C-P} = 2.8 Hz), 131.5 (d, J_{C-P} = 2.8 Hz), 128.3 (d, J_{C-P} = 12.5 Hz), 128.2, 128.1 (d, J_{C-P} = 12.5 Hz), 127.7, 127.2 (d, J_{C-P} = 2.8 Hz), 123.4, 57.1 (d, J_{C-P} = 7.6 Hz), 32.3 (d, J_{C-P} = 2.8 Hz), 21.3 (d, J_{C-P} = 6.2 Hz), 10.5 (d, J_{C-P} = 2.8 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 23.0; IR (Neat) 3155, 1448, 1437, 1185, 1107, 915, 717, 691 cm⁻¹.

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***N*-[*(1S)*-1-(4-Chlorophenyl)propyl]-*P,P*-diphenylphosphinic amide (**27**).** The general procedure was followed. Yield 97%, enantiomeric excess (97% ee) was determined by HPLC analysis (Chiralpak AD, 80:20 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**27** t_r = 10.9 min, (*S*)-**27** t_r = 12.6 min). mp 156-157 °C; R_f 0.45 (100% AcOEt); $[\alpha]_D^{20}$ -62.1 (c 2.08, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.86 (ddt, J = 12.0, 6.7, 1.8 Hz, 2H), 7.73 (ddt, J = 12.0, 6.7, 1.8 Hz, 2H), 7.52-7.40 (m, 4H), 7.33 (td, J = 7.4, 3.2 Hz, 2H), 7.26 (dt, J = 8.7, 2.2 Hz, 2H), 7.08 (dt, J = 8.4, 2.1 Hz, 2H), 4.09 (qd, J = 9.3, 6.5 Hz, 1H), 3.22 (dd, J = 8.4, 6.3 Hz, 1H), 2.04-1.92 (m, 1H), 1.86-1.73 (m, 1H), 0.79 (t, J = 7.3, 3H); ¹³C NMR (100 MHz, CHCl₃) δ 141.9 (d, J_{C-P} = 5.5 Hz), 132.6, 132.0 (d, J_{C-P} = 129.0 Hz), 132.0 (d, J_{C-P} = 63.8 Hz), 131.9 (d, J_{C-P} = 63.8 Hz), 131.8 (d, J_{C-P} = 129.0 Hz), 131.7, 131.6, 128.4, 128.3 (d, J_{C-P} = 12.5 Hz), 128.2 (d, J_{C-P} = 12.5 Hz), 127.8, 56.3 (d, J_{C-P} = 6.2, Hz), 32.3 (d, J_{C-P} = 4.2 Hz), 10.3; ³¹P NMR (162 MHz, CDCl₃) δ 23.0; IR (Neat) 3132, 1462, 1194, 1180, 1109, 1091, 1013, 897, 721, 693 cm⁻¹.

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***N*-[(1*S*)-1-(4-Bromophenyl)propyl]-*P,P*-diphenylphosphinic amide (**28**).** The general procedure was followed. Yield 97%, enantiomeric excess (96% ee) was determined by HPLC analysis (Chiralpak AD, 80:20 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**28** t_r = 11.3 min, (*S*)-**28** t_r = 12.9 min). mp 158-161 °C; R_f 0.45 (100% AcOEt); $[\alpha]_D^{20}$ -65.4 (c 1.86, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.85 (dd, J = 11.7, 7.0 Hz, 2H), 7.72 (dd, J = 11.7, 7.0 Hz, 2H), 7.52-7.36 (m, 6H), 7.32 (td, J = 7.4, 3.3 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 4.06 (qd, J = 9.5, 6.3 Hz, 1H), 3.28 (dd, J = 7.3 Hz, 1H), 1.97 (sept, J = 7.2 Hz, 1H), 1.79 (sept, J = 7.2 Hz, 1H), 0.79 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CHCl₃) δ 142.5 (d, J_{C-P} = 4.9 Hz), 132.8 (d, J_{C-P} = 126.9 Hz), 132.0 (d, J_{C-P} = 63.1 Hz), 131.9 (d, J_{C-P} = 63.1 Hz), 131.8 (d, J_{C-P} = 126.9 Hz), 131.7, 131.6, 131.4, 128.4 (d, J_{C-P} = 12.5 Hz), 128.2, 128.2 (d, J_{C-P} = 12.5 Hz), 120.7, 56.4 (d, J_{C-P} = 6.9 Hz), 32.3 (d, J_{C-P} = 2.8 Hz), 10.4 (d, J_{C-P} = 3.5 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 23.0; IR (Neat) 3134, 1461, 1437, 1194, 1179, 1109, 1067, 926, 842, 720, 693 cm⁻¹.

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***N*-[(1*S*)-1-(4-Methoxyphenyl)propyl]-*P,P*-diphenylphosphinic amide (**29**).** The general procedure was followed but with a 40 h reaction time. Yield 91%, enantiomeric excess (98% ee) was determined by HPLC analysis (Chiralpak AD, 80:20 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**29** t_r = 11.0 min, (*S*)-**29** t_r = 13.5 min). mp. 130-131 °C; R_f 0.35 (100% AcOEt); $[\alpha]_D^{20}$ -52.6 (c 1.89, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.86 (ddt, J = 11.8, 6.7, 1.4 Hz, 2H), 7.76 (ddt, J = 11.8, 6.7, 1.4 Hz, 2H), 7.50-7.34 (m, 4H), 7.33 (tdt, J = 7.6, 3.3, 1.5 Hz, 2H), 7.08 (dt, J = 8.7, 2.1 Hz, 2H), 6.82 (dt, J = 8.7, 2.1 Hz, 2H), 4.05 (qd, J = 9.5, 5.8 Hz, 1H), 3.79 (s, 3H), 3.21 (t, J = 7.3 Hz, 1H), 2.06-1.94 (m, 1H), 1.86-1.74 (m, 1H), 0.76 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CHCl₃) δ 158.4, 135.5 (d, J_{C-P} = 5.5 Hz), 133.2 (d, J_{C-P} = 127.6 Hz), 132.1 (d, J_{C-P} = 75.6 Hz), 132.0 (d, J_{C-P} = 127.6 Hz), 132.0 (d, J_{C-P} = 75.6 Hz), 131.6, 131.5, 128.3 (d, J_{C-P} = 12.5 Hz), 128.1 (d, J_{C-P} = 12.5 Hz), 127.5, 113.6, 56.5 (d, J_{C-P} = 5.5 Hz), 55.1 (d, J_{C-P} = 8.3 Hz), 32.3 (d, J_{C-P} = 2.8 Hz), 10.5 (d, J_{C-P} = 2.1 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 22.8; IR (Neat) 3146, 1512, 1451, 1437, 1246, 1195, 1176, 752, 693 cm⁻¹.

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***N*-[(1*S*)-1-Benzo[1,3]dioxol-5-yl-propyl]-*P,P*-diphenylphosphinic amide (**30**).** The general procedure was followed but with a 40h reaction time. Yield 93%, enantiomeric excess (98% ee) was determined by HPLC analysis (Chiralpak AD, 80:20 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**30** t_r = 10.8 min, (*S*)-**30** t_r = 16.6 min). mp 115-116 °C; R_f 0.45 (100% AcOEt); $[\alpha]_D^{20}$ -63.3 (c 2.49, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.85 (ddt, J = 11.8, 6.9, 1.5 Hz, 2H), 7.75 (ddt, J = 11.8, 6.9, 1.5 Hz, 2H), 7.48-7.36 (m, 4H), 7.35-7.29 (m, 2H), 6.68 (s, 1H), 6.67 (d, J = 6.3 Hz, 1H), 6.55 (dd, J = 8.0, 1.8 Hz, 1H), 5.90 (t, J = 1.5 Hz, 2H), 4.00 (qd, J = 9.4, 5.9 Hz, 1H), 3.28 (dd, J = 8.8, 6.3 Hz, 1H), 2.02-1.90 (m, 1H), 1.82-1.69 (m, 1H), 0.76 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CHCl₃) δ 147.6, 146.3, 137.4 (d, J_{C-P} = 5.5 Hz), 133.1 (d, J_{C-P} = 128.3 Hz), 132.0 (d, J_{C-P} = 72.1 Hz), 132.0 (d, J_{C-P} = 128.3 Hz), 131.9 (d, J_{C-P} = 72.1 Hz), 131.6, 131.5, 128.3 (d, J_{C-P} = 12.5 Hz), 128.1 (d, J_{C-P} = 12.5 Hz), 119.9, 107.9, 106.6 (d, J_{C-P} = 6.2, Hz), 100.8, 56.8 (d, J_{C-P} = 7.6 Hz), 32.4 (d, J_{C-P} = 2.8 Hz), 10.5 (d, J_{C-P} = 3.5 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 22.8; IR (Neat) 3148, 1437, 1244, 1178, 1107, 1040, 930, 721, 693 cm⁻¹.

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***N*-[(1*S*)-1-(1-Naphthyl)propyl]-*P,P*-diphenylphosphinic amide (**31**).** The general procedure was followed. Yield 93%, enantiomeric excess (97% ee) was determined by HPLC analysis (Chiralpak AD, 90:10 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**31** t_r = 13.9 min, (*S*)-**31** t_r = 23.6 min). mp 139-140 °C; R_f 0.45 (100% AcOEt); $[\alpha]_D^{20}$ +38.4 (c 2.03, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.88 (dd, J = 11.7, 7.6 Hz, 2H), 7.82 (d, J = 8.0 Hz, 1H), 7.76 (t, J = 8.0 Hz, 1H), 7.70 (dd, J = 12.0, 7.7 Hz, 2H), 7.56 (d, J = 7.0 Hz, 1H), 7.51-7.25 (m, 7H), 7.20-7.13 (m, 2H), 5.05-4.94 (m, 1H), 3.56 (d, J = 5.6 Hz, 1H), 2.08 (qn, J = 7.2 Hz, 2H), 0.85 (t, J = 7.3, 3H); ¹³C NMR (100 MHz, CHCl₃) δ 139.7 (d, J_{C-P} = 5.5 Hz), 133.6, 133.2 (d, J_{C-P} = 126.9 Hz), 132.0 (d, J_{C-P} = 59.0 Hz), 131.9 (d, J_{C-P} = 59.0 Hz), 131.8 (d, J_{C-P} = 126.9 Hz), 131.7, 131.4 (d, J_{C-P} = 2.8 Hz), 130.5, 128.6, 128.3 (d, J_{C-P} = 12.5 Hz), 128.0 (d, J_{C-P} = 12.5 Hz), 127.5, 125.8, 125.3, 125.2, 123.2, 122.8, 52.5 (d, J_{C-P} = 6.2 Hz), 32.3, 10.5 (d, J_{C-P} = 2.8 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 23.2; IR (Neat) 3147, 1437, 1178, 912, 776, 722, 695 cm⁻¹.

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***N*-[*(1S)*-1-(2-Naphthyl)propyl]-*P,P*-diphenylphosphinic amide (**32**).** The general procedure was followed. Yield 96%, enantiomeric excess (97% ee) was determined by HPLC analysis (Chiralpak AD, 80:20 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**32** t_r = 9.2 min, (*S*)-**32** t_r = 12.8 min). mp 144-145 °C; R_f 0.45 (100% AcOEt); $[\alpha]_D^{20}$ -62.5 (c 1.80, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 7.4 Hz, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.84-7.72 (m, 6H), 7.52 (s, 1H), 7.49-7.34 (m, 6H), 7.26 (td, J = 7.6, 2.8 Hz, 2H), 4.28 (qd, J = 9.5, 6.3 Hz, 1H), 3.45 (s(br), 1H), 2.11 (sept, J = 7.0 Hz, 2H), 1.94 (sept, J = 7.0 Hz, 2H), 0.81 (t, J = 7.4, 3H); ¹³C NMR (100 MHz, CHCl₃) δ 140.6 (d, J_{C-P} = 5.5 Hz), 133.2 (d, J_{C-P} = 127.6 Hz), 133.1, 132.5, 132.1 (d, J_{C-P} = 77.0 Hz), 132.0 (d, J_{C-P} = 77.0 Hz), 131.9 (d, J_{C-P} = 127.6 Hz), 131.7, 131.5, 128.3 (d, J_{C-P} = 12.5 Hz), 128.3, 128.1 (d, J_{C-P} = 12.5 Hz), 127.7, 127.5, 125.9, 125.6, 125.4, 124.4, 57.2 (d, J_{C-P} = 1.4 Hz), 32.2 (d, J_{C-P} = 2.8 Hz), 10.5 (d, J_{C-P} = 2.8 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 23.1; IR (Neat) 3146, 1437, 1197, 1181, 1107, 921, 745, 693 cm⁻¹.

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***N*-[*(1S)*-1-(2-Furyl)propyl]-*P,P*-diphenylphosphinic amide (**X**).** The general procedure was followed except that ligand **1** 3 mol% and Cu(OTf)₂ 2.5 mol% at -15°C are used. Yield 97%, enantiomeric excess (96% ee) was determined by HPLC analysis (Chiralpak AS, 85:15 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**33** *t*_r = 33.9 min, (*S*)-**33** *t*_r = 41.0 min). mp 98-99 °C; R_f 0.35 (100% AcOEt); [α]_D²⁰ -61.3 (c 1.81, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.88 (m, 4H), 7.48-7.34 (m, 6H), 7.31 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.23 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.04 (d, *J* = 3.2, 1H), 4.16 (qd, *J* = 8.5, 5.9 Hz, 1H), 3.30 (t, *J* = 8.9 Hz, 1H), 2.05-1.83 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CHCl₃) δ 155.3 (d, *J*_{C-P} = 6.9 Hz), 141.4, 133.0 (d, *J*_{C-P} = 130.4 Hz), 132.0 (d, *J*_{C-P} = 74.2 Hz), 131.9 (d, *J*_{C-P} = 74.2 Hz), 131.9 (d, *J*_{C-P} = 130.4 Hz), 131.7, 131.6, 128.3 (d, *J*_{C-P} = 12.5 Hz), 128.2 (d, *J*_{C-P} = 12.5 Hz), 109.9 (d, *J*_{C-P} = 6.2 Hz), 106.1 (d, *J*_{C-P} = 2.8 Hz), 50.6 (d, *J*_{C-P} = 4.9 Hz), 29.8 (d, *J*_{C-P} = 2.8 Hz), 10.1 (d, *J*_{C-P} = 2.8 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 22.9; IR (Neat) 3180, 1434, 1175, 1123, 1008, 892, 723, 693 cm⁻¹.

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***N*-[(1*S*)-1-Cyclopropylpropyl]-*P,P*-diphenylphosphinic amide (**34**).** The general procedure was followed. Yield 95%, enantiomeric excess (94% ee) was determined by HPLC analysis (Chiralpak AD, 80:20 hexanes:*i*-PrOH, 1.0 mL/min: (*S*)-**34** t_r = 7.9 min, (*R*)-**34** t_r = 9.4 min). The absolute configuration was determined by comparison with the literature of the optical rotation of the deprotected hydrochloride amine.²⁶ mp 132-133 °C ; R_f 0.60 (100% AcOEt); $[\alpha]_D^{20}$ +23.2 (c 1.90, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (ddt, J = 11.7, 6.9, 1.7 Hz, 2H), 7.86 (ddt, J = 11.7, 6.9, 1.7 Hz, 2H), 7.50-7.37 (m, 6H), 2.87 (t, J = 6.9 Hz, 1H), 2.37 (qnd, J = 8.8, 6.1 Hz, 1H), 1.65 (qn, J = 7.4 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H), 0.86-0.76 (m, 1H), 0.50-0.35 (m, 2H), 0.25-0.12 (m, 2H); ¹³C NMR (100 MHz, CHCl₃) δ 133.3 (d, J_{C-P} = 129.0 Hz), 133.1 (d, J_{C-P} = 129.0 Hz), 132.0 (d, J_{C-P} = 27.7 Hz), 132.0 (d, J_{C-P} = 9.0 Hz), 131.4(2), 128.2 (d, J_{C-P} = 12.5 Hz), 128.1 (d, J_{C-P} = 12.5 Hz), 57.6 (d, J_{C-P} = 2.8 Hz), 30.6 (d, J_{C-P} = 5.5 Hz), 17.4 (d, J_{C-P} = 4.2 Hz), 10.0 (d, J_{C-P} = 2.8 Hz), 3.9 (d, J_{C-P} = 36.6 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 21.6; IR (Neat) 3186, 1434, 1184, 1165, 1106, 1050, 692 cm⁻¹; LRMS (APCI) $[M+H]^+$: 300 m/z .

***N*-[(1*S*)-1-(2-Methoxyphenyl)propyl]-*P,P*-diphenylphosphinic amide (35).** The general procedure was followed. Yield 97%, enantiomeric excess (95%) was determined by HPLC analysis of the purified product on chiral stationary phase (Chiralpak AD, 90:10 Hexane:*i*-PrOH, 1mL/min): (*R*)-**35** t_r = 22.0 min, (*S*)-**35** t_r = 27.9 min). mp 118-119 °C; R_f 0.50 (100% EtOAc); $[\alpha]_D^{20}$ -10.5° (c 1.01, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.84 (dd, J = 10.3, 8.3 Hz, 2H), 7.74 (dd, J = 10.7, 8.2 Hz, 2H), 7.49-7.35 (m, 4H), 7.35-7.25 (m, 2H), 7.21 (t, J = 7.7 Hz, 1H); 6.98-6.91 (m, 1H), 6.90-6.79 (m, 2H), 4.15 (ddt, J = 9.6, 9.6, 7.8 Hz, 1H), 4.00 (t, J = 9.6, 9.6, 1H), 2.07-1.83 (m, 2H), 0.77 (td, J = 7.5, 1.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.4, 134.1 (d, J_{C-P} = 127.9 Hz), 133.0 (d, J_{C-P} = 9.5 Hz), 132.8 (d, J_{C-P} = 130.2 Hz), 132.2 (d, J_{C-P} = 9.5 Hz), 132.0 (d, J_{C-P} = 2.7 Hz), 131.9 (d, J_{C-P} = 2.5 Hz), 131.7 (d, J = 5.5 Hz), 128.9 (d, J = 12.0 Hz), 128.7 (d, J = 10.8 Hz), 128.5, 121.0, 111.4, 55.8, 55.6, 31.4 (d, J_{C-P} = 3.4 Hz), 11.6; ³¹P NMR (121.5 MHz, CDCl₃) δ 23.6; IR (neat) 3185 (br), 3057, 2963, 1601, 1493, 1462, 1438, 1240, 1191, 1122, 1110, 909, 723, 697 cm⁻¹; LRMS (APCI) $[M+H]^+$: 366 m/z .

***N*-[(1*S*)-1-(2-chlorophenyl)propyl]-*P,P*-diphenylphosphinic amide (**36**).** The general procedure was followed. Yield 96%, enantiomeric excess (91%) was determined by HPLC analysis of the purified product on chiral stationary phase (Chiralpak AS, 80:20 Hexane:*i*-PrOH, 1mL/min): (*R*)-**36** t_r = 10.7min, (*S*)-**36** t_r = 17.1 min). mp 140-142 °C; R_f 0.50 (100% EtOAc); $[\alpha]_D^{20}$ 14.2° (c 1.05, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.90-7.80 (m, 2H), 7.75-7.67 (m, 2H); 7.52-7.36 (m, 4H), 7.34-7.12 (m, 6H), 4.49 (tdd, J = 10.4, 7.1, 7.1 Hz, 1H), 3.60 (dd, J = 9.9, 6.5 Hz, 1H,), 1.80-2.05 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 140.9 (d, J_{C-P} = 4.8 Hz), , 132.8 (d, J_{C-P} = 128.5 Hz), 132.4 (d, J_{C-P} = 9.9 Hz), 132.4, 131.7 (d, J_{C-P} = 9.6 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 131.6 (d, J_{C-P} = 130.8 Hz), 131.5 (d, J_{C-P} = 2.5 Hz), 129.6, 128.3 (d J_{C-P} = 18.1 Hz), 128.3, 127.0 (d, J_{C-P} = 3.3 Hz), 126.8, 54.5, 34.4 (d, J_{C-P} = 3.8 Hz), 10.5; ³¹P NMR (162 MHz, CDCl₃) δ 23.0; IR (neat) 3171 (br), 3059, 2966, 1438, 1185, 1123, 1110, 909, 752, 724, 696 cm⁻¹; LRMS (APCI) calcd for C₂₁H₂₁ClNOP [M+H]⁺: 370 m/z . found 370 m/z .

***N*-[(1*S*)-1-(2-methylphenyl)propyl]-*P,P*-diphenylphosphinic amide (**37**).** The general procedure was followed. Yield 97%, enantiomeric excess (99%) was determined by HPLC analysis of the purified product on chiral stationary phase (Chiralpak AD, 90:10 Hexane:*i*-PrOH, 1mL/min): (*R*)-**37** t_r = 15.9 min, (*S*)-**37** t_r = 27.2 min). mp 134-135 °C; R_f 0.59 (100% EtOAc); $[\alpha]_D^{20}$ +15.8° (c 1.08, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.87 (dd, J = 11.6, 7.0 Hz, 2H), 7.69 (dd, J = 11.9, 7.5 Hz, 2H), 7.50-7.19 (m, 8H), 7.12 (t, J = 7.3 Hz, 1H), 7.00 (d, J = 7.4 Hz, 1H), 4.34 (tdd, J = 9.7, 7.1, 7.1 Hz, 1H), 3.36 (t, J = 7.6 Hz, 1H), 2.01-1.69 (m, 5H), 1.88 (t, J = 7.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 142.3 (d, J_{C-P} = 5.2 Hz), 134.7, 133.2, (d, J_{C-P} = 127.7 Hz), 132.5 (d, J_{C-P} = 9.8 Hz), 131.8 (d, J_{C-P} = 131.0 Hz), 131.7 (d, J_{C-P} = 9.3 Hz), 131.7 (d, J_{C-P} = 2.4 Hz), 131.5 (d, J_{C-P} = 2.4 Hz), 130.0, 128.3 (d, J_{C-P} = 12.6 Hz), 128.0 (d, J_{C-P} = 12.7 Hz), 126.5, 126.2, 125.1, 52.2, 32.6 (d, J_{C-P} = 3.5 Hz), 18.9; IR (neat) 3182 (br), 3056, 2963, 1438, 1189, 1122, 1110, 909, 725, 697 cm⁻¹; LRMS (APCI) $[M+H]^+$: 350 m/z .

***N*-[(1*S*)-1-phenylethyl]-*P,P*-diphenyl-phosphinic amide (**6**).** The general procedure was followed. Yield 87%, enantiomeric excess (97% ee) was determined by HPLC analysis (Chiralpak AS, 80:20 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**6** t_r = 8.8 min, (*S*)-**6** t_r = 12.6 min). The absolute configuration of the major isomer was determined by comparison of optical rotation with the literature.¹⁶ mp 178-179 °C; R_f 0.25 (100% EtOAc); $[\alpha]_D^{20}$ -35.5 (c 0.78, MeOH); ^1H NMR (300 MHz, CDCl_3) δ 7.92 (ddd, J = 11.8, 8.3, 1.4 Hz, 2H), 7.82 (ddd, J = 11.9, 8.3, 1.4 Hz, 2H), 7.51-7.22 (m, 11H), 4.40 (ddq, J = 6.7, 5.6, 2.9 Hz, 1H), 3.24 (dd, J = 9.4, 5.6 Hz, 1H), 1.58 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.4 (d, $J_{\text{C-P}}$ = 6.7 Hz), 133.6 (d, $J_{\text{C-P}}$ = 129.0 Hz), 132.7 (d, $J_{\text{C-P}}$ = 39.8 Hz), 132.5 (d, $J_{\text{C-P}}$ = 39.6 Hz), 132.5 (d, $J_{\text{C-P}}$ = 129.6 Hz), 132.2 (d, $J_{\text{C-P}}$ = 7.0 Hz), 132.2 (d, $J_{\text{C-P}}$ = 6.1 Hz), 129.0, 128.9 (d, $J_{\text{C-P}}$ = 13.1 Hz), 128.8 (d, $J_{\text{C-P}}$ = 12.6 Hz), 127.5, 126.4, 51.4 (d, $J_{\text{C-P}}$ = 1.0 Hz), 26.4 (d, $J_{\text{C-P}}$ = 3.3 Hz); ^{31}P NMR (121.5 MHz, CDCl_3) δ 23.7; IR (neat) 3152 (br), 1435 (m), 1177 (s), 751 (s), 725 (s), 691 (s); LRMS (APCI) $[M+H]^+$: 322 m/z .

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***N*-[*(1S)*-1-(3-Methylphenyl)ethyl]-*P,P*-diphenylphosphinic amide (**38**).** The general procedure was followed Yield 80%, enantiomeric excess (92% ee) was determined by HPLC analysis (Chiralpak AD-H, 90:10 hexanes:*i*-PrOH, 1.0 mL/min: (+)-**38** t_r = 12,8 min, (-)-**38** t_r = 18,9 min). mp 133-135°C; R_f = 0.5 (100% EtOAc); $[\alpha]_D^{20}$ -38.4 (c 0.57, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.90 (ddd, J = 13,2, 7,9, 2,2 Hz, 2H), 7.87 (ddd, J = 12,0, 6,8, 1,5 Hz, 2H), 7.47-7.36 (m, 6H), 7.27-7.18 (m, 1H), 7.11-7.05 (m, 3H), 4.35 (ddq, J = 9,6, 6,8, 2,8 Hz, 1H), 3.23 (dd, J = 9,6, 6,0 Hz, 1H), 2.32 (s, 3H), 1.56 (d, J = 6,7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.5 (d, J_{C-P} = 8,4 Hz), 138.5, 133.7 (d, J_{C-P} = 128,0 Hz), 132.7 (d, J_{C-P} = 44,2 Hz), 132.6 (d, J_{C-P} = 44,1 Hz), 132.6 (d, J_{C-P} = 130,4 Hz), 132.2 (d, J_{C-P} = 6,3 Hz), 132.2 (d, J_{C-P} = 6,0 Hz), 128,9, 128,9 (d, J_{C-P} = 12,4 Hz), 128,8 (d, J_{C-P} = 12,7 Hz), 128,3, 127,2, 51,5 (d, J_{C-P} = 1,1 Hz), 26,4 (d, J_{C-P} = 3,2 Hz), 21,9; ³¹P NMR (121,5 MHz, CDCl₃) δ 23,7; IR (neat) 3138 (br), 1435, 1179 (br), 1125, 1108, 1085, 997, 976, 896, 791, 748, 721, 691; LRMS (APCI) $[M+H]^+$: 336 m/z .

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***N*-[(1*S*)-1-furylethyl]-*P,P*-diphenyl-phosphinic amide (39).** The general procedure was followed. Yield 90%, enantiomeric excess (89% ee) was determined by HPLC analysis (Chiralpak AD-H, 90:10 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**39** t_r = 16.5 min, (*S*)-**39** t_r = 21.2 min). The absolute configuration of the major isomer was determined by comparison of optical rotation with the literature. mp 128-130°C; R_f 0.5 (100% EtOAc); $[\alpha]_D^{20}$ -49.9 (c 0.84, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.98-7.87 (m, 4H), 7.52-7.41 (m, 6H), 7.35 (dd, J = 1.8, 0.8 Hz, 1H), 6.29 (dd, J = 3.2, 1.8 Hz, 1H), 4.41 (ddq, J = 6.9, 6.5, 3.1 Hz, 1H), 3.19 (dd, J = 9.4, 6.5 Hz, 1H), 1.60 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.4 (d, J_{C-P} = 10.3 Hz), 142.1, 133.4 (d, J_{C-P} = 128.4 Hz), 132.7 (d, J_{C-P} = 56.3 Hz), 132.6 (d, J_{C-P} = 56.2 Hz), 132.3 (d, J_{C-P} = 130.8 Hz), 132.3 (d, J_{C-P} = 2.8 Hz), 132.2 (d, J_{C-P} = 4.5 Hz), 128.9 (d, J_{C-P} = 12.6 Hz), 110.6, 105.7, 45.6 (d, J_{C-P} = 0.5 Hz), 23.5 (d, J_{C-P} = 2.9 Hz); ³¹P NMR (121.5 MHz, CDCl₃) δ 23.7; IR (neat) 3144 (br), 1438, 1189 (br), 1152, 1108, 1008, 997, 979, 915, 728, 689; LRMS (APCI) $[M+H]^+$: 312 m/z . Elementary Analysis calcd C: 69.45, H: 5.83, N: 4.50, found C: 69.21, H: 5.90, N: 4.50.

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***N*-[*(1S)*-1-(3-Methoxyphenyl)ethyl]-*P,P*-diphenylphosphinic amide (**43**).** The general procedure was followed. Yield 88%, enantiomeric excess (92%) was determined by HPLC analysis of the purified product on chiral stationary phase (Chiralpak AD, 90:10 Hexane:*i*-PrOH, 1mL/min): (*R*)-**43** t_r = 16.5 min, (*S*)-**43** t_r = 28.2 min). mp 115-118 °C; R_f 0.42 (100% EtOAc); $[\alpha]_D^{20}$ -28.5° (c 1.08, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.94-7.75 (m, 4H), 7.50-7.28 (m, 6H), 7.21 (t, J = 7.9 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.83 (t, J = 2 Hz, 1H), 6.76 (dd, J = 8.1, 2.3 Hz, 1H), 4.34 (ddq, J = 9.4, 9.4, 6.7 Hz, 1H), 3.75 (s, 3H), 3.38 (dd, J = 8.3, 6.2 Hz, 1H), 1.55 (d, J = 6.7 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 160.1, 147.3 (d, J_{C-P} = 6.8 Hz), 133.6 (d, J_{C-P} = 128.0 Hz), 132.8 (d, J_{C-P} = 9.6 Hz), 132.6 (d, J_{C-P} = 128.9 Hz), 132.3 (d, J_{C-P} = 9.5 Hz), 132.2 (d, J_{C-P} = 2.7 Hz), 132.1 (d, J_{C-P} = 2.6 Hz), 130.0, 128.9 (d, J_{C-P} = 6.5 Hz), 128.8 (d, J_{C-P} = 6.0 Hz), 118.7, 112.6, 112.4, 55.6, 51.4, 26.3 (d, J_{C-P} = 3.2 Hz); ³¹P NMR (121.5 MHz, CDCl₃) δ 23.8; IR (neat) 3168 (br), 3060, 2970, 1601, 1488, 1464, 1438, 1254, 1189, 1122, 1109, 731, 698 cm⁻¹; LRMS (APCI) [M+H]⁺: 352 m/z .

The ee of compound **43** can be enriched from 92% to 99% by slow recrystallization (over 5 days) in *tert*-butyl methyl ether in 67% yield.

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(1S)-1-(3-Methoxyphenyl)ethylamine trifluoroacetic acid salt (46). To a stirred solution of **43** (323 mg, 0.919 mmol) in methanol (1.5 mL) was added concentrated hydrochloric acid (350 μ L, 4.200 mmol) at room temperature. After 4 h the mixture was diluted with water (10 mL) and treated with a solution of sodium hydroxide (1M) until pH 12. The product was extracted with CH_2Cl_2 (3x) and the combined organic layers were dried over Na_2SO_4 . Trifluoroacetic acid was added before the evaporation of the solvent. The purification of the organic salt by silica gel column chromatography (10:90 MeOH: CH_2Cl_2) afforded **46** (246 mg; quantitative) as a clear oil which can solidify slowly to a white solid. mp 140-142 $^\circ\text{C}$; R_f 0.23 (10:90 MeOH: CH_2Cl_2); $[\alpha]_D^{20}$ -11.3 (c 0.94, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 8.25 ((br)s, 3H), 7.23 (t, J = 7.8 Hz, 1H), 6.92 (s, 1H), 6.90 (d, J = 8 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 4.16 (q, J = 6.6 Hz, 1H), 3.73 (s, 3H), 1.52 (d, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 162.5 (q, J = 35.6 Hz), 160.4, 139.9, 130.5, 119.2, 116.8 (q, J = 291.7 Hz), 115.3, 112.2, 55.5, 51.9, 20.5; ^{19}F NMR (282 MHz, CDCl_3) δ -76.4; IR (neat) 3401 (br), 2944 (br), 1668 (s), 1605 (s), 1184 (s), 1134 (s), 1044 (m), 599 (m); LRMS (APCI) $[\text{M}-\text{CF}_3\text{CO}_2]^+$: 152 m/z .

Enantiomeric excess of **46** (99% ee) was determined on the *N*-[1-(3-Methoxy-phenyl)-ethyl]-benzamide (**47**) derivative by HPLC analysis (Chiralpak AD, 90:10 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**47** t_r = 12.5 min, (*S*)-**47** t_r = 19.1 min)

47

(1S)-1-(3-Methoxyphenyl)-N,N-dimethyl ethylamine trifluoroacetic acid salt (48). Compound **46** (219 mg, 0.828 mmol) was dissolved in an aqueous solution (37% w/w) of formaldehyde (250 μ L, 3.060 mmol) followed by the addition of formic acid (350 μ L, 9.277 mmol). The mixture was heated to 100 °C for 7h. The reaction was cooled down and quenched with aqueous NaOH (1M). The mixture was extracted with CH₂Cl₂ (3x) and the combined organic layers were dried over Na₂SO₄. Before the evaporation of the solvent on the rotavap, trifluoroacetic acid was added. The purification of the organic salt by silica gel column chromatography (10:90 MeOH:CH₂Cl₂) afforded **48** (206 mg; 86%) as a clear oil. R_f 0.32 (10:90 MeOH: CH₂Cl₂); [α]_D²⁰ -17.5 (*c* 1.63, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 12.56 (s, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 2 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 4.20 (q, *J* = 6.3 Hz, 1H), 3.81 (s, 1H), 2.77 (s, 3H), 2.63 (s, 3H), 1.74 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.2 (q, *J* = 38.8 Hz), 160.1, 135.1, 130.2, 120.6, 115.6, 115.1 (q, *J* = 289.2 Hz), 113.8, 66.0, 55.2, 41.2, 39.3, 16.6; ¹⁹F NMR (282 MHz, CDCl₃) δ -78.4; IR (neat) 3402 (br), 3002 (br), 2650 (br), 1675 (s), 1603 (m), 1469 (m), 1201 (s), 1131 (s); LRMS (APCI) [M-CF₃CO₂]⁺: 180 *m/z*.

49

(1S)-1-(3-Hydroxyphenyl)-N,N-dimethyl ethylamine (49). To a solution of **48** (197 mg, 0.672 mmol) in CH₂Cl₂ (2 mL) was added dropwise at -78 °C BBr₃ (320 μ L, 3.385 mmol). The mixture was stirred 30 min at -78°C and then 4h at room temperature. The reaction was quenched with a saturated solution of NaHCO₃. The pH was adjusted to pH 9 and the product was extracted with CH₂Cl₂ (10x). The combined organic layers were dried over Na₂SO₄. Concentration and purification by silica gel on column chromatography (20:80 MeOH:CH₂Cl₂) afforded **49** (101 mg, 84%) as a white solid. mp 97-98 °C. *R*_f 0.23 (30:70 MeOH:CH₂Cl₂); [α]_D²⁰ -42.3 (*c* 1.42, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.13 (t, *J* = 7.8 Hz, 1H), 6.86 (t, *J* = 2.0 Hz, 1H), 6.80 (s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 3.37 (q, *J* = 6.8 Hz, 1H), 2.26 (s, 6H), 1.41 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.0, 142.8, 129.3, 119.3, 115.2, 114.9, 65.9, 42.5, 19.0 ; IR (neat) 2976 (m), 2900 (br), 1676 (w), 1587 (s), 1457 (s), 1279 (s), 1158 (m), 911, (m), 785 (m), 702 (m); LRMS (APCI) [M+H]⁺: 166 *m/z*.

42

***N*-((1*S*)-7-[[*tert*-butyl(dimethyl)silyl]oxy]-1-phenylheptyl)-*P,P*-diphenylphosphinic amide (42).**

In a disposable borosilicate tube capped with a septum [(6-iodohexyl)oxy](*t*-butyl)dimethylsilane (685 mg, 2 mmol, 6 equiv), diethylzinc (1 mL, 10 mmol, 30 equiv) and CH₂Cl₂ (2 mL) were irradiated 2.5 h by a sun-lamp (OSRAM Ultra Vitalux, 300W) at room temperature under argon. Complete conversion of the iodide was monitored by injection (GC) of an hydrolyzed aliquot. The colorless solution was transferred in a 10 mL round bottomed flask and vacuum was applied (0.5 mm Hg) during 2 h at 50 °C to remove excess of diethylzinc and drive the equilibrium towards the formation of the desired diorganozinc. Meanwhile, ligand **10** (5.5 mg, 0.016 mmol, 0.05 equiv) and Cu(OTf)₂ (12 mg, 0.033 mmol, 0.10 equiv) were dissolved in toluene (1 mL), stirred for 1 h at room temperature. The diorganozinc species in toluene (1 mL) was cannulated onto the catalyst solution and the resulting dark gray heterogeneous solution stirred 20 min at room temperature and 10 min at 0 °C. A cold (0 °C) suspension of diphenylphosphinoylimine **5** (100 mg, 0.33 mmol, 1.00 equiv) in toluene (2 mL + 1 mL to rinse) was transferred (Teflon cannula) to the catalyst solution. After stirring for 40 h at 0 °C, the reaction was quenched with saturated NH₄Cl and the aqueous layer was extracted rapidly with CH₂Cl₂ (3x). The combined organic layers were dried over Na₂SO₄. Concentration and purification by silica gel column chromatography (50:50 EtOAc:hexane) afforded (**42**). (92 mg, 52 %) as a white solid. Enantiomeric excess (89% ee) was determined by HPLC analysis (Chiralpak AD-H, 90:10 hexanes:*i*-PrOH, 1.0 mL/min: (+)-**42** *t*_r = 6.7 min, (-)-**42** *t*_r = 11.4 min). mp 114-116 °C; *R*_f 0.30 (50:50 EtOAc:hexane); [α]_D²⁰ -11.4 (*c* 1.0, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.85 (ddd, *J* = 11.9, 9.5, 1.6 Hz, 2H), 7.74 (ddd, *J* = 12.0, 8.4, 1.4 Hz, 2H), 7.55-7.37 (m, 4H), 7.35-7.19 (m, 5H), 7.15-7.04 (m, 2H), 4.13 (ddt, *J* = 9.5, 9.7, 2.2 Hz, 1H), 3.52 (t, *J* = 6.6 Hz, 2H), 3.52 (dd, *J* = 9.7, 6.3 Hz, 1H), 1.98-1.90 (m, 1H), 1.84-1.72 (m, 1H), 1.50-1.33 (m, 2H), 1.30-1.0 (m, 6H), 0.87 (s, 9H), 0.02 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 144.3 (d, *J*_{C-P} = 6.7 Hz), 133.6 (d, *J*_{C-P} = 127.9 Hz), 132.7 (d, *J*_{C-P} = 62.0 Hz), 132.5 (d, *J*_{C-P} = 56.4 Hz), 132.4 (d, *J*_{C-P} = 130.7 Hz), 132.2 (d, *J*_{C-P} = 9.3 Hz), 132.1 (d, *J*_{C-P} = 9.3 Hz), 128.9, 128.8 (d, *J*_{C-P} = 13.9 Hz), 128.7 (d, *J*_{C-P} = 13.9 Hz), 127.5, 126.8, 63.6, 56.2, 40.1 (d, *J*_{C-P} = 3.7 Hz), 33.2, 29.6, 26.5, 26.4, 26.0, 18.8, -4.8; ³¹P NMR (121.5 MHz, CDCl₃) δ 23.7; IR (neat) 3210 (br), 1436 (m), 1183 (m), 749 (s), 720 (s), 691 (s); LRMS (APCI) [M+H]⁺: 522 *m/z*; Elementary Analysis calcd C: 71.36, H: 8.50, N: 2.68, found C: 71.16, H: 9.08, N: 2.70s.

Racemic

Enantio enriched Mixture

40

***N*-[*(1S)*-1-phenylpentyl]-*P,P*-diphenyl-phosphinic amide (**40**).** In the same flask, ligand **10** (11 mg, 0.033 mmol, 0.05 equiv) and (CuOTf)₂•toluene (18 mg, 0.033 mmol, 0.05 equiv) were dissolved in toluene (2 mL). The resulting dark green heterogeneous solution was stirred for 1 h at room temperature the neat dibutylzinc (230 μ L, 1.32 mmol, 2.00 equiv) was added at room temperature and the resulting dark red suspension was stirred for 20 min at room temperature and an additional 10 min at 0 °C. A cold (0 °C) suspension of diphenylphosphinoylimine **5** (245 mg, 0.80 mmol, 1.00 equiv in toluene (3 mL + 1 mL to rinse) was transferred (Teflon cannula) to the catalyst solution. After stirring for 20 h at 0 °C, the reaction was quenched with saturated NH₄Cl and the aqueous layer was extracted rapidly with CH₂Cl₂ (3x). The combined organic layers were dried over Na₂SO₄. Concentration and purification by silica gel column chromatography (100% EtOAc) afforded (**40**) (222 mg, 92 %) as a white solid. Enantiomeric excess (92% ee) was determined by HPLC analysis (Chiralpak AD, 80:20 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**40** *t*_r = 7.1 min, (*S*)-**40** *t*_r = 9.7 min). The absolute configuration of the major isomer was tentatively assigned by comparison of the optical rotation with the other aryl-phosphonic amides. mp 119-120°C; *R*_f 0.40 (100% EtOAc); [α]_D²⁰ -43.0 (*c* 0.58, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.84 (ddd, *J* = 11.8, 8.3, 1.6 Hz, 2H), 7.73 (ddd, *J* = 11.9, 8.2, 1.3 Hz, 2H), 7.47-7.34 (m, 2H), 7.31-7.20 (m, 4H), 7.15-7.12 (m, 2H), 4.12 (ddt, *J* = 8.6, 6.6, 2.0 Hz, 1H), 3.38 (dd, *J* = 9.6, 6.5 Hz, 1H), 1.96 (m, 1H), 1.79 (m, 1H), 1.21 (m, 3H), 1.07 (m, 1H), 0.77 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.4 (d, *J*_{C-P} = 5.6 Hz), 133.7 (d, *J*_{C-P} = 127.8 Hz), 132.7 (d, *J*_{C-P} = 56.6 Hz), 132.6 (d, *J*_{C-P} = 56.5 Hz), 132.5 (d, *J*_{C-P} = 130.0 Hz), 132.1 (d, *J*_{C-P} = 7.3 Hz), 132.1 (d, *J*_{C-P} = 9.6 Hz), 128.8, 128.8 (d, *J*_{C-P} = 14.2 Hz), 128.6 (d, *J*_{C-P} = 14.3 Hz), 127.4, 126.9, 56.2, 39.9 (d, *J*_{C-P} = 3.7 Hz), 28.7, 22.8, 14.3; ³¹P NMR (91 MHz, CDCl₃) δ 23.7; IR (neat) 3152 (br), 1435 (m), 1177 (s), 751 (s), 725 (s), 691 (s); LRMS (APCI) [M+H]⁺: 364 *m/z*.

41

***N*-[(1*S*)-2-methyl-1-phenylpropyl]-*P,P*-diphenyl-phosphinic amide (41).** In the same flask, ligand **10** (5.5 mg, 0.016 mmol, 0.05 equiv) and Cu(OTf)₂ (12 mg, 0.033 mmol, 0.1 equiv) were dissolved in toluene (2 mL). The resulting dark green heterogeneous solution was stirred for 1 h at room temperature the neat diisopropylzinc (200 μ L, 5M in Et₂O, 1 mmol, 3.00 equiv) was added at room temperature and the resulting dark red suspension was stirred for 20 min at room temperature and an additional 10 min at 0 °C. A cold (0 °C) suspension of diphenylphosphinoylimine **5** (100 mg, 0.33 mmol, 1.00 equiv) in toluene (3 mL + 1 mL) was transferred (Teflon cannula) to the catalyst solution. After stirring for 20 h at 0 °C, the reaction was quenched with saturated NH₄Cl and the aqueous layer was extracted rapidly with CH₂Cl₂ (3x). The combined organic layers were dried over Na₂SO₄. Concentration and purification by silica gel column chromatography (50:50 EtOAc:hexanes) afforded (**41**) as a white solid (98 mg, 84 % yield). The ee was determined to be 97 %(*S*) by HPLC analysis (Chiralpak OD, 95:5 hexanes:*i*-PrOH, 1.0 mL/min: (*R*)-**41** *t*_r = 11.8 min, (*S*)-**41** *t*_r = 13.7 min). The absolute configuration of the major isomer was tentatively assigned by comparison with the other addition products. mp 150-152 °C; R_f 0.35 (100% EtOAc); [α]_D²⁰ -17.6 (*c* 0.05, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.84 (ddd, *J* = 12.3, 7.4, 1.4 Hz, 2H), 7.66 (ddd, *J* = 11.6, 7.6, 1.7 Hz, 2H), 7.51-7.37 (m, 4H), 7.28-7.21 (m, 5H), 7.08-7.04 (m, 2H), 3.91 (dd, *J* = 16.1, 8.7 Hz, 1H), 3.35 (m, 1H), 2.01 (ddq, *J* = 8.7, 6.5, 6.2 Hz, 1H), 1.0 (d, *J* = 6.5 Hz, 3H), 0.81 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.3 (d, *J*_{C-P} = 3.9 Hz), 133.8 (d, *J*_{C-P} = 120.8 Hz), 132.9 (d, *J*_{C-P} = 63.4 Hz), 132.5 (d, *J*_{C-P} = 63.1 Hz), 132.7 (d, *J*_{C-P} = 120.8 Hz), 132.1 (d, *J*_{C-P} = 12.9 Hz), 128.8 (d, *J*_{C-P} = 25.1 Hz), 128.6 (d, *J*_{C-P} = 25.4 Hz), 128.5, 127.4, 127.2, 61.7, 36.1 (d, *J*_{C-P} = 4.1 Hz), 19.7 (d, *J*_{C-P} = 1.4 Hz); ³¹P NMR (121.5 MHz, CDCl₃) δ 24.0; IR (neat) 3203 (br), 1437(m), 1181 (s), 753 (s), 723 (s), 690 (s); LRMS (APCI) [M+H]⁺: 350 *m/z*.

22

***N*-(2-Chloro-benzylidene)-diphenylphosphinoylamide (22).** The *N*-diphenylphosphinoylimine was prepared according to the literature procedure.³ R_f 0.42 (100% EtOAc); mp 109-111 °C; ^1H NMR (300 MHz, C_6D_6) δ 10.00 (d, $J = 31.3$ Hz, 1H), 8.18-8.05 (m, 5H), 7.13-7.06 (m, 6H), 6.92-6.89 (m, 1H), 6.84-6.75 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 170.6 (d, $J_{\text{C-P}} = 6.5$ Hz), 137.1 (d, $J_{\text{C-P}} = 228$ Hz), 134.4, 133.8, 133.6 (d, $J_{\text{C-P}} = 25$ Hz), 132.4 (d, $J_{\text{C-P}} = 9.0$ Hz), 132.1 (d, $J_{\text{C-P}} = 2.4$ Hz), 130.7, 129.7, 129.0 (d, $J_{\text{C-P}} = 12.3$ Hz), 127.3; ^{31}P NMR (162 MHz, C_6D_6) δ 23.7; IR (neat) 3441 (br), 3058, 1612, 1590, 1438, 1207, 1124, 832 cm^{-1} ; LRMS (APCI) $[\text{M}+\text{H}]^+$: 340 m/z .

21

***N*-(2-Methoxy-benzylidene)-diphenylphosphinoylamide (21).** The *N*-diphenylphosphinoylimine was prepared according to the literature procedure.³ R_f 0.29 (100% EtOAc); mp 133-136 °C; ^1H NMR (400 MHz, C_6D_6) δ 10.25 (d, $J = 32.3$ Hz, 1H), 8.33 (dd, $J = 7.7, 1.8$ Hz, 1H), 8.23-8.15 (m, 4H), 7.10-7.02 (m, 7H), 6.75 (t, $J = 7.6$ Hz, 1H), 6.29 (d, $J = 8.4$ Hz, 1H), 3.02 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 167.1 (d, $J_{\text{C-P}} = 6.7$ Hz), 158.5, 132.3 (d, $J_{\text{C-P}} = 124.5$ Hz), 132.2, 129.3 (d, $J_{\text{C-P}} = 8.9$ Hz), 128.6 (d, $J_{\text{C-P}} = 1.9$ Hz), 125.7 (d, $J_{\text{C-P}} = 12.2$ Hz), 122.2 (d, $J_{\text{C-P}} = 24.8$ Hz), 117.8, 108.6 (d, $J_{\text{C-P}} = 2.0$ Hz), 52.1; ^{31}P NMR (162 MHz, C_6D_6) δ 23.6; IR (neat) 3437 (br), 3056, 1609, 1595, 1438, 1250, 1200, 1124, 841, 699 cm^{-1} ; LRMS (APCI) $[\text{M}+\text{H}]^+$: 336 m/z .

23

***N*-(2-Methyl-benzylidene)-diphenylphosphinoylamide (23).** The *N*-diphenylphosphinoylimine was prepared according to the literature procedure.³ R_f 0.34 (100% EtOAc); ^1H NMR (400 MHz, C_6D_6) δ 9.74 (d, $J = 32.5$ Hz, 1H), 8.19-8.12 (m, 4H), 8.00 (dd, $J = 7.3, 1.5$ Hz, 4H), 7.10-7.03 (m, 6H), 6.98-6.90 (m, 2H), 6.72 (d, $J = 7.1$ Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.0 (d, $J_{\text{C-P}} = 7.6$ Hz), 138.4, 132.0 (d, $J_{\text{C-P}} = 126.2$), 131.4 (d, $J_{\text{C-P}} = 13.8$ Hz), 130.2, 129.2 (d, $J_{\text{C-P}} = 8.9$ Hz), 128.8 (d, $J_{\text{C-P}} = 2.2$ Hz), 128.6, 127.0, 125.9, (d, $J_{\text{C-P}} = 12.3$ Hz), 123.5, 16.4 (d, $J_{\text{C-P}} = 6.5$ Hz); ^{31}P NMR (162 MHz, C_6D_6) δ 23.5; IR (neat) 3437 (br), 3056, 1613, 1594, 1569, 1438, 1198, 1124, 843, 697 cm^{-1} ; LRMS (APCI) $[\text{M}+\text{H}]^+$: 320 m/z .

50

***N*-(3-Methoxy-benzylidene)-diphenylphosphinoylimide (50).** The *N*-diphenylphosphinoylimine was prepared according to the literature procedure.³ R_f 0.33 (100% EtOAc); ^1H NMR (400 MHz, C_6D_6) δ 9.43 (d, $J = 31.8$ Hz, 1H), 8.18-8.11 (m, 4H), 7.31 (t, $J = 1.9$ Hz, 1H), 7.22 (d, $J = 7.5$ Hz, 1H), 7.07-7.00 (m, 7H), 6.89 (t, $J = 7.9$ Hz, 1H), 6.77 (dd, $J = 8.3, 2.3$ Hz, 1H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 174.5 (d, $J_{\text{C-P}} = 7.4$ Hz), 160.7, 138.2 (d, $J_{\text{C-P}} = 24.7$ Hz), 134.0 (d, $J_{\text{C-P}} = 125.6$ Hz), 132.4 (d, $J_{\text{C-P}} = 9.0$ Hz), 132.0 (d, $J_{\text{C-P}} = 2.4$ Hz), 130.3, 129.0 (d, $J_{\text{C-P}} = 12.3$), 123.8, 120.6, 114.2, 55.3; ^{31}P NMR (162 MHz, C_6D_6) δ 23.5; IR (neat) 3439 (br), 3056, 1619, 1581, 1438, 1270, 1202, 1125, 838, 727, 699 cm^{-1} ; LRMS (APCI) $[\text{M}+\text{H}]^+$: 336 m/z .

^1H , ^{31}P and ^{13}C NMR Spectra of selected compounds

^1H NMR (300 MHz)

¹³C NMR (75 MHz)

¹H NMR (400 MHz)

^1H NMR (300 MHz)

^1H NMR (300 MHz)

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