Highly Enantioselective Diethylzinc Addition to Imines Employing Readily Available *N*-Monosubstituted Amino Alcohols

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(Supporting Information)

General: NMR spectra were recorded on a Bruker-200 or 300MHz spectrometer. Elemental analysis was carried out using Carlo Erba-1106 Analyzer. EI Mass spectra were recorded on VG-7010E. IR spectra were recorded on MicroLab MX. Optical rotation were recorded on PE polarimeter 241. HPLC analysis was performed on Beckman 110B chromatography with Beckman 168 variable wavelength detector. Chiralpak AD column was purchased from Daicel Chemical Industries, LTD. All reactions involving air and moisture sensitive were carried out under a dry argon atmosphere using standard Schlenk line techniques. Toluene and THF were dried with sodium/ benzophenone. CH₂Cl₂ was dried with CaH₂. Petroleum ether (PE) and ethyl acetate for column chromatography were distilled before use.

Materials: All starting materials were purchased from Acros and used directly. The *N*-diphenylphosphinoylimines **4a**,^{1-3,5} **4b**,³⁻⁵ **4c**,^{2,3,7} **4d**,^{4,5} **4e**,^{6,8} were prepared according to the literature.¹⁻⁸

General experimental for preparation of (1R, 2S)-*N*-aryl-1,2-diphenyl-2-aminoethanol (3a-3f) and (1R, 2S)-*N*-methyl-*N*-aryl-1,2-diphenyl-2-aminoethanol (2a-2g):

A solution of (1R,2S)-1,2-diphenyl-2-aminoethanol (5 mmol) and aryl aldehyde (5 mmol) in anhydrous ethanol was stirred for 2-12h at room temperature, then added sodium borohydride (8 mmol). The reaction mixture was stirred for 2h at rt. and quenched with 2M HCl, and then removed the ethanol. The residue was neutralized with aqueous NaOH (0.5 M, 20 mL). The mixture was

extracted with dichloromethane (20mL×3), and the combined organic layer was washed with water for three times. The organic layer was dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure. Purification of the crude product on silica chromatography or by crystallization gave **3a-3f**.

A mixture of **3** (3 mmol) and methanoic acid (5 mL) was stirred for 0.5 h at room temperature, and then added aqueous formaldehyde (30%, 5 mL). The mixture was refluxed for 10h, and then removed the remaining excess formaldehyde by rotary evaporator. The resulting residue was dissolved in NaOH (0.5M, 10 mL) and was extracted with dichloromethane (15mL×3), and the combined organic layer was washed with aqueous saturated NaCl. The organic layer was dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure. Purification of the crude product on silica chromatography or by crystallization gave **2a-2g**.

(1R,2S)-N-methyl-N-4'-methoxybenzyl-1,2-diphenyl-2-aminoethanol (2a).

This compound was obtained as a white solid (0.991 g) in 95% yield. Mp 83-84°C; $[\alpha]_D^{25} = -68.5$ (c = 1.01, CHCl₃); IR (NUJOL, cm⁻¹) 3491 (OH), 1611, 1514, 1459 (O-CH₃), 1251 (C-O-C), 700 (CH₂); ¹HNMR (200 MHz, CDCl₃): (ppm) 2.28 (3H, s, CH₃), 2.83-3.02 (1H, s, br, OH), 3.29 (1H, d, J= 13.3Hz, PhCHN), 3.59-3.64 (2H, m, NCH₂Ar), 3.79 (3H, s, CH₃), 5.37 (1H, d, J= 5.6 Hz, PhCHOH), 6.77-7.24 (14H, m, Ar-H); ¹³CNMR (75 MHz, CDCl₃) δ(ppm) 38.8 (CH₃), 55.2 (CH₃), 58.8 (NCH₂), 72.6 (NCH), 74.4 (HOCH), 113.5 (Ar), 126.6 (Ar), 127.1 (Ar), 127.4 (Ar), 127.7 (Ar), 127.8 (Ar), 129.6 (Ar), 129.9 (Ar), 130.8 (Ar), 135.9 (Ar), 141.8 (Ar), 158.6 (Ar); MS(Cl): m/e 28, 77 (C₆H₅⁺), 91 (PhCH₂⁺), 121 (C₈H₉O⁺), 240 (M+1-PhCH₂⁺-OH). Anal. calcd for C₂₃H₂₅NO₂: C, 79.51; H, 7.25; N, 4.03. Found: C, 79.50; H, 7.11; N, 4.10.

(1R,2S)-N-methyl-N-4'-Benzoylbenzyl-1,2-diphenyl-2-aminoethanol (2b):

This compound was obtained as a white solid (1.143 g) in 90% yield. Mp 93-94°C; $[\alpha]_D^{25} = -58.0$ (c = 1.00, CHCl₃); IR (NUJOL, cm⁻¹) 3431(OH), 1511, 1459 (N-CH₃), 1237 (C-O-C), 1022 (C-O-C), 704 (CH₂); ¹HNMR (300 MHz, CDCl₃) (ppm) 2.30 (s, 3H, CH₃), 2.90 (1H, s, br, OH), 3.27 (1H, d, J=13.8Hz, CHN), 3.63 (2H, m, NCH₂Ph), 5.07 (2H, s, OCH₂Ph), 5.39 (1H, d, J= 5.7Hz, CHOH), 6.88-7.46 (19H, m, Ar-H); ¹³CNMR (75 MHz, CDCl₃) δ(ppm) 38.9 (CH₃), 58.8 (NCH₂), 70.0 (OCH₂), 72.6 (NCH), 74.5 (HOCH), 114.5 (Ar), 126.5 (Ar), 127.0 (Ar), 127.4 (Ar), 127.4 (Ar), 127.7 (Ar), 127.8 (Ar), 127.9 (Ar), 128.5 (Ar), 129.5 (Ar), 129.8 (Ar), 131.2 (Ar), 135.9 (Ar), 137.1

(Ar), 141.7 (Ar), 157.8 (Ar); MS (CI): m/e 91 (PhCH_2^+ , 100), 316 ($\text{M}+1\text{-PhCH}_2^+\text{-OH}$), 197. Anal. calcd for $\text{C}_{29}\text{H}_{29}\text{NO}_2$: C, 82.24; H, 6.90; N, 3.31. Found: C, 82.23; H, 7.00; N, 3.45.

(1R,2S)-N-methyl-N-2',4',6'-trimethylbenzyl-1,2-diphenyl-2-aminoethanol (2c):

This compound was obtained as a white solid (1.002 g) in 93% yield. Mp 95-96 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25} = -66.7$ ($c = 1.01$, CHCl_3); IR (NUJOL, cm^{-1}) 3532 (OH), 1611, 1455 (N-CH₃), 701 (CH₂); ^1H NMR (300 MHz $\square$ CDCl_3) $\square$ (ppm) 2.17 (9H, s, PhCH_3), 2.29 (3H, s, CH_3), 2.83-2.89 (1H, s, br, OH), 3.46-3.57 (2H, m, NCH_2Ph), 3.71 (1H, d, $J = 6.4\text{Hz}$, NCHPh), 5.42 (1H, d, $J = 6.4\text{Hz}$, CHOH), 6.8 (s, 2H, Ar-H), 7.19-7.36 (10H, m, Ar-H); ^{13}C NMR (50 MHz, CDCl_3) δ (ppm) 19.9 (CH_3), 20.6 (CH_3), 36.4 (CH_3), 53.6 (NCH_2), 72.5 (NCH), 76.9 (HOCH), 126.2 (Ar), 126.8 (Ar), 127.2 (Ar), 127.5 (Ar), 127.9 (Ar), 128.0 (Ar), 128.7 (Ar), 129.4 (Ar), 131.5 (Ar), 135.7 (Ar), 136.0 (Ar), 137.8 (Ar), 141.6 (Ar); MS (CI): m/e 77, 91 (PhCH_2^+), 133 [CH_2 (2,4,6-trimethyl benzene), 100], 252 ($\text{M}+1\text{-PhCH}_2^+\text{-OH}$, 36).

(1R,2S)-N-methyl-N-2'-bromobenzyl-1,2-diphenyl-2-aminoethanol (2d):

This compound was obtained as a viscid liquid (1.069 g) in 90% yield. $[\alpha]_{\text{D}}^{25} = -33.7$ ($c = 0.986$, CHCl_3); IR (neat, cm^{-1}) 3565, 3449 (OH), 1449 (N-CH₃), 703 (CH₂); ^1H NMR (300 MHz $\square$ CDCl_3) $\square$ (ppm) 2.31 (3H, s, CH_3), 2.90 (1H, s, br, OH), 3.62-3.66 (2H, m, NCH_2Ph), 3.71 (1H, d, $J = 6.0\text{ Hz}$, NCHPh), 5.42 (1H, d, $J = 6.0\text{Hz}$, CHOH), 7.16-7.52 (14H, m, Ar-H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 39.1 (CH_3), 58.8 (NCH_2), 69.9 (OCH_2), 72.8 (NCH), 75.2 (HOCH), 124.1 (Ar), 126.6 (Ar), 126.9 (Ar), 127.2 (Ar), 127.3 (Ar), 127.5 (Ar), 127.8 (Ar), 127.9 (Ar), 128.2 (Ar), 129.0 (Ar), 129.6 (Ar), 130.5 (Ar), 132.6 (Ar), 135.9 (Ar), 138.1 (Ar), 141.7 (Ar); MS (CI): m/z , 77, 91, 118, 169 ($\text{CH}_2\text{Ph}^{79}\text{Br}$, 77), 171 ($\text{CH}_2\text{Ph}^{81}\text{Br}$, 77), 288 ($\text{M}+1\text{-PhCH}_2^+\text{-OH}$, 100), 290 (98).

(1R,2S)-N-methyl-N-3'-chlorobenzyl-1,2-diphenyl-2-aminoethanol (2e):

This compound was obtained as a viscid liquid (0.895 g) in 85% yield. $[\alpha]_{\text{D}}^{25} = -135.9$ ($c = 0.504$, CHCl_3); IR (neat, cm^{-1}) 3563 (OH), 3446 (OH), 1596, 1450 (N-CH₃), 705 (CH₂); ^1H NMR (300 MHz $\square$ CDCl_3) $\square$ (ppm) 2.06 (3H, s, CH_3), 2.68 (1H, s, br, OH), 3.05 (1H, d, $J = 13.8\text{ Hz}$, NCH_2Ph), 3.37 (1H, d, $J = 13.8\text{ Hz}$, NCH_2Ph), 3.46 (1H, d, $J = 6.7\text{ Hz}$, NCHPh), 5.06 (1H, d, $J = 6.7\text{ Hz}$, CHOH), 6.73-7.18 (14H, m, Ar-H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 34.8 (CH_3), 55.0 (NCH_2), 68.8 (NCH), 70.5 (HOCH), 122.6 (Ar), 122.7 (Ar), 123.1 (Ar), 123.4 (Ar), 123.6 (Ar), 123.9 (Ar), 124.0 (Ar), 124.6 (Ar), 125.4 (Ar), 125.5 (Ar), 130.1 (Ar), 131.6 (Ar), 137.3 (Ar), 137.7 (Ar); MS (CI): m/z 42, 77, 91, 105, 118, 125 ($\text{CH}_2\text{Ph}^{35}\text{Cl}$, 100), 127 ($\text{CH}_2\text{Ph}^{37}\text{Cl}$, 33), 244 ($\text{M}+1\text{-PhCH}_2^+\text{-OH}$, 80),

246 (26);

(1R,2S)-N-methyl-N-4'-chorobenzyl-1,2-diphenyl-2-aminoethanol (2f):

This compound was obtained as a white solid (0.896 g) in 85% yield. Mp 102-103 °C; $[\alpha]_D^{25} = -65.0$ (c = 1.01, CHCl₃); IR (NUJOL, cm⁻¹) 3488 (OH), 1401, 1455 (N-CH₃), 703 (CH₂); ¹HNMR (200 MHz, CDCl₃) (ppm) 2.26 (3H, s, CH₃), 3.29 (1H, d, J=13.7 Hz, NCHPh), 3.58-3.66 (2H, m, NCH₂Ph), 5.35 (1H, d, J= 6.30 Hz, CHOH), 6.97-7.27 (14H, m, Ar-H); ¹³CNMR (75 MHz, CDCl₃) δ(ppm) 38.7 (CH₃), 58.7 (NCH₂), 72.6 (NCH), 74.3 (HOCH), 126.6 (Ar), 127.2 (Ar), 127.6 (Ar), 127.8 (Ar), 127.9 (Ar), 128.3 (Ar), 129.5 (Ar), 129.9 (Ar), 132.5 (Ar), 135.5 (Ar), 137.4 (Ar), 141.8 (Ar); MS (CI): m/z 77, 91, 118, 125 (CH₂Ph³⁵Cl, 100), 127(CH₂Ph³⁷Cl, 33), 244 (M+1-PhCH₂⁺-OH, 80), 246 (26); Anal. calcd for C₂₂H₂₂ClNO: C, 75.09; H, 6.30, N, 3.98. Found: C, 75.08; H, 6.29; N, 4.04 .

(1R,2S)-N-methyl-N-piperonyl-1,2-diphenyl-2-aminoethanol (2g):

This compound was obtained as a white solid (0.886 g) in 80% yield. Mp 105-106 °C; $[\alpha]_D^{25} = -74.5$ (c = 0.746, CHCl₃); IR (NUJOL, cm⁻¹) 3484 (OH), 1489, 1448, 1450 (O-CH₂), 1459 (N-CH₃), 1245(C-O-C), 1038 (C-O-C), 705 (CH₂); ¹HNMR (300 MHz, CDCl₃) (ppm) 2.30 (3H, s, CH₃), 3.26 (1H, d, J=12.0 Hz, NCHPh), 3.57-3.67 (2H, m, NCH₂Ph), 5.40 (1H, s, CHOH), 5.95 (2H, s, O-CH₂-O), 6.70-6.73 (3H, m, ArH) 7.14-7.28 (10H, m, ArH); ¹³CNMR (75 MHz, CDCl₃) δ(ppm) 38.7 (CH₃), 59.2 (NCH₂), 72.7 (NCH), 74.3 (HOCH), 100.8 (O-C-O), 107.7 (Ar), 109.0 (Ar), 121.7 (Ar), 126.5 (Ar), 127.2 (Ar), 127.4 (Ar), 127.7 (Ar), 127.8 (Ar), 129.5 (Ar), 129.8 (Ar), 132.8 (Ar), 135.8 (Ar), 141.7 (Ar), 146.4 (Ar), 147.5 (Ar); MS (CI): m/z 77, 91, 105, 135 (BnOCH₂O⁺, 100), 254 (M+1-PhCH₂⁺-OH, 39); Anal. calcd for C₂₃H₂₃NO₃: C, 76.43; H, 6.41; N, 3.88. Found: C, 76.18; H, 6.37; N, 4.00.

(1R,2S)-N-4'-methoxybenzyl-1,2-diphenyl-2-aminoethanol (3a):

This compound was obtained as a white solid (1.249 g) in 75% yield. Mp 156-158 °C; $[\alpha]_D^{25} = +18.9$ (c = 1.02, CHCl₃); IR (NUJOL, cm⁻¹) 3085, 3028, 1611, 1513, 1452 (O-CH₃), 1247 (C-O-C), 699 (CH₂); ¹HNMR (300 MHz, CDCl₃): (ppm) 3.26 (1H, d, J= 13.1 Hz), 3.68 (1H, d, J= 13.1 Hz), 3.81(3H, s), 3.94 (1H, d, J=5.7 Hz), 4.87 (1H, d, J=5.7 Hz), 6.84 (2H, d, J=8.7 Hz), 7.09-7.31(12H, m); ¹³CNMR (75 MHz, DMSO) δ(ppm) 50.0 (CH₃), 55.3 (NCH₂), 67.5 (NCH), 76.6 (HOCH), 113.8 (Ar), 126.9 (Ar), 127.2 (Ar), 127.3 (Ar), 127.8 (Ar), 128.9 (Ar), 129.2 (Ar), 132.8 (Ar), 141.3 (Ar),

143.6 (Ar), 158.3 (Ar); MS (CI): m/z 121 ($\text{C}_8\text{H}_9\text{O}^+$), 226 ($\text{M}+1\text{-PhCH}_2^+\text{-OH}$), 334 ($\text{M}+1$); Anal. calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_2$: C, 79.25; H, 6.95; N, 4.20. Found: C, 78.95; H, 6.88; N, 4.46.

(1R,2S)-N-4'-Benzoxylbenzyl-1,2-diphenyl-2-aminoethanol (3b):

This compound was obtained as a white solid (1.452 g) in 71% yield. Mp 182-183 $^\circ$; $[\alpha]_D^{25} = +18.3$ (c = 0.378, CHCl_3); IR (NUJOL, cm^{-1}) 3082, 3028, 1513, 1611, 1451, 1248 (C-O-C), 1010 (C-O-C), 699 (CH_2); ^1H NMR (300 MHz $\square$ CDCl_3): (ppm) 3.53 (1H, d, $J = 13.1$ Hz), 3.73 (1H, d, $J = 13.1$ Hz), 3.96 (1H, d, $J = 5.4$ Hz), 4.97 (1H, s), 5.03 (2H, s), 6.91 (2H, d, $J = 8.7$ Hz), 7.11-7.43 (19H, m); MS (CI) m/z 91 (PhCH_2^+), 197 ($\text{CH}_2\text{PhOBn}^+$), 302 ($\text{M}+1\text{-PhCH}_2^+\text{-OH}$); Anal. calcd for $\text{C}_{28}\text{H}_{27}\text{NO}_2$: C, 82.12; H, 6.65; N, 3.42. Found: C, 82.39; H, 6.75; N, 3.61.

(1R,2S)-N-2',4',6'-trimethylbenzyl-1,2-diphenyl-2-aminoethanol (3c):

This compound was obtained as a white solid (1.259 g) in 73% yield. Mp 124-125 $^\circ$; $[\alpha]_D^{25} = +9.6$ (c = 1.00, CHCl_3); IR (NUJOL, cm^{-1}) 3395 (OH), 3341, 3061, 3032, 1454, 702 (CH_2); ^1H NMR (300 MHz $\square$ CDCl_3): (ppm) 2.16 (6H, s, 2 CH_3), 2.26 (3H, s, CH_3), 3.54 (1H, d, $J = 11.6$ Hz, ArCH_2N), 3.62 (1H, d, $J = 11.6$ Hz, ArCH_2N), 3.98 (1H, d, $J = 6.4$ Hz, PhCHN), 4.79 (1H, d, $J = 6.4$ Hz, PhCHOH), 6.83 (2H, s, Ar-H), 7.19-7.37 (10H, m, Ar-H); ^{13}C NMR (75 MHz, DMSO) δ (ppm): 19.0 (CH_3), 20.8 (CH_3), 45.1 (NCH_2), 70.0 (NCH), 77.1 (HOCH), 127.1 (Ar), 127.4 (Ar), 127.9 (Ar), 128.1 (Ar), 128.7 (Ar), 128.8 (Ar), 133.9 (Ar), 135.7 (Ar), 136.7 (Ar), 142.2 (Ar), 143.8 (Ar); MS (CI): m/z 106 (PhCHO^+), 133 [CH_2 (2,4,6-trimethyl benzene)], 238 ($\text{M}+1\text{-PhCH}_2^+\text{-OH}$), 346 ($\text{M}+1$).

(1R,2S)-N-2'-bromolbenzyl-1,2-diphenyl-2-aminoethanol (3d):

This compound was obtained as a white solid (1.489 g) in 78% yield. Mp 147-148 $^\circ$; $[\alpha]_D^{25} = +27.9$ (c = 0.816, CHCl_3); IR (NUJOL, cm^{-1}) 3301, 3189, 3086, 3064, 3030, 1452, 702 (CH_2); ^1H NMR (300 MHz $\square$ CDCl_3): (ppm) 3.64 (1H, d, $J = 13.6$ Hz), 3.79 (1H, d, $J = 13.6$ Hz), 3.89 (1H, d, $J = 6.0$ Hz), 4.86 (1H, d, $J = 6.0$ Hz), 7.11-7.50 (15H, m); MS (CI) m/z, 77, 91, 118, 169 ($\text{CH}_2\text{Ph}^{79}\text{Br}-1$), 171 ($\text{CH}_2\text{Ph}^{81}\text{Br}-1$), 274 ($\text{M}+1\text{-PhCH}_2^+\text{-OH}$), 276; Anal. calcd for $\text{C}_{21}\text{H}_{20}\text{BrNO}$: C, 65.98; H, 5.27; N, 3.66. Found: C, 66.08; H, 5.27; N, 4.01.

(1R,2S)-N-3'-chorobenzyl-1,2-diphenyl-2-aminoethanol (3e):

This compound was obtained as a white solid (1.146 g) in 68% yield. Mp 152-153 $^\circ$; $[\alpha]_D^{25} = +24.4$ (c = 0.814, CHCl_3); IR (NUJOL, cm^{-1}) 3317 (OH), 3085, 3030, 1401, 1451, 1426, 703 (CH_2);

^1H NMR (300 MHz $\square$ CDCl_3): (ppm) 3.51 (1H, d, $J=13.7$ Hz), 3.71 (1H, d, $J=13.7$ Hz), 3.90 (1H, d, $J=6.0$ Hz), 4.87 (1H, d, $J=6.0$ Hz), 7.04-7.34 (14H, m); MS (CI): m/z 91, 125 ($\text{CH}_2\text{Ph}^{35}\text{Cl}$), 127 ($\text{CH}_2\text{Ph}^{37}\text{Cl}$), 230 ($\text{M}+1\text{-PhCH}_2^+\text{-OH}$), 232, 338 ($\text{M}+1$); Anal. calcd for $\text{C}_{21}\text{H}_{20}\text{ClNO}$: C, 74.66; H, 5.97; N, 4.15. Found: C, 74.54; H, 6.02; N, 4.43.

(1R,2S)-*N*-4'-chorobenzyl-1,2-diphenyl-2-aminoethanol (3f):

This compound was obtained as a white solid (1.095 g) in 65% yield. Mp 174-175 $\square$; $[\alpha]_D^{25} = +25.0$ ($c = 0.786$, CHCl_3); IR (NUJOL, cm^{-1}) 3310 (OH), 3085, 3028, 1400, 701 (CH_2); ^1H NMR (300 MHz $\square$ CDCl_3): (ppm) 3.53 (1H, d, $J=13.5$ Hz), 3.76 (1H, d, $J=13.5$ Hz), 3.91 (1H, d, $J=5.7$ Hz), 4.96 (1H, d, $J=3.6$ Hz), 7.10-7.32 (14H, m); MS (CI): m/z 125 ($\text{CH}_2\text{Ph}^{35}\text{Cl}$), 127 ($\text{CH}_2\text{Ph}^{37}\text{Cl}$), 230 ($\text{M}+1\text{-PhCH}_2^+\text{-OH}$), 232, 338 ($\text{M}+1$); Anal. calcd for $\text{C}_{21}\text{H}_{20}\text{ClNO}$: C, 74.66; H, 5.97; N, 4.15. Found: C, 74.44; H, 6.04; N, 4.36.

Typical Experimental Procedure for the Enantioselective Addition of Diethylzinc to *N*-Diphenylphosphinoyl benzalimine (4a, 0.1 mmol) in the presence of 3c (0.1mmol): Imine **4a**

(30.5 mg, 0.1 mmol) and amino alcohol **3c** (34.5 mg, 0.1 mmol) was dissolved in toluene (2 mL) under argon. To the mixture was added Et_2Zn in hexane (1 M, 0.5 mL, 0.5 mmol) at rt. After stirred for 48 h, the reaction was quenched with saturated aqueous ammonium chloride, and the aqueous layer was extracted with CH_2Cl_2 . The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4 . After evaporation of the solvent, the residue was purified through column chromatography on silica gel to give **5a** as a white solid (30.8 mg). Yield, 92%, Mp 121-123 $\square$; ^1H NMR (300 MHz, CDCl_3) δ 1.80-1.95 (m, 3H, $J=7.4$ Hz, CH_3CH_2), 1.98-2.10 (m, 1H, CH_2CH_3), 3.32 (m, 1H, NH), 4.10 (m, 1H, CHNH), 7.15-7.46 (m, 11H, Ar-H), 7.78-7.89 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, CDCl_3) δ 10.5 (CH_3), 32.5 (CH_2), 57.1 (CHNH), 125.0 (Ar), 126.4 (Ar), 126.6 (Ar), 127.0 (Ar), 128.1 (Ar), 128.3 (Ar), 128.4 (Ar), 128.5 (Ar), 131.6 (Ar), 131.7 (Ar), 131.8 (Ar), 132.4 (Ar), 132.6 (Ar), 143.4 (Ar); MS (CI): 334 (M-H), 306 (M- CH_2CH_3), 258 (M-Ph), 216 (Ph_2PONH^+), 201 (Ph_2PO^+); IR (NUJOL) cm^{-1} : 3135 (NH), 1188 (P=O). The enantiomeric excess of 97% with *R*-isomer major was determined by HPLC (Chiracel AD column, hexane/ propan-2-ol= 80: 20; flow rate 1 mL/ min; *R*-isomer, t_R 8.66 min and *S*-isomer, t_R 11.60 min).

Enantioselective Addition of Diethylzinc to *N*-Diphenylphosphinoyl benzalimine (4a, 1 mmol) in the presence of 3c (1 mmol): Imine **4a** (305.0 mg, 1 mmol) and amino alcohol **3c** (345.1 mg, 1

mmol) was dissolved in toluene (20 mL) under argon. Et₂Zn in hexane (1 M, 5 mL, 5 mmol) was dropped slowly to the mixture at 0-5 °C. After stirred for 48 h at rt., the reaction was quenched with saturated aqueous ammonium chloride, and the aqueous layer was extracted with CH₂Cl₂ (30mL×3). The combined organic layer was washed with brine, and dried over anhydrous Na₂SO₄. After evaporation of the solvent, the residue was purified through column chromatography on silica gel to give **5a** as a white solid (324.8 mg). Yield, 97%. The enantiomeric excess of 98% with *R*-isomer major was determined by HPLC (Chiracel AD column, hexane/ propan-2-ol= 80: 20 ; flow rate 1 mL/ min; *R*-isomer, *t_R* 7.05 min and *S*-isomer, *t_R* 9.28 min).

***N*-[1-(4-Methoxyphenyl)propyl]-*P,P*-diphenylphosphinoylamide (5b).** This compound was obtained as a white solid (32.5 mg) in 89% yield. Mp 130-131 °C; ¹HNMR (300 MHz, CDCl₃) δ 1.77-1.86 (m, 1H, CH₂CH₃), 1.96-2.05 (m, 1H, CH₂CH₃), 3.31 (m, 1H, NH), 3.81 (s, 3H, CH₃O), 4.04-4.07 (m, 1H, CHNH), 6.83 (d, 2H, *J*= 8.7Hz, Ar-H), 7.09 (d, 2H, *J*= 8.7Hz, Ar-H), 7.28-7.48 (m, 6H, Ar-H), 7.79-7.88 (m, 4H, Ar-H); ¹³CNMR (75 MHz, CDCl₃) δ 10.6 (CH₃), 32.3 (CH₂), 55.2 (CH₃O), 56.6 (CHNH), 113.7 (Ar), 127.5 (Ar), 128.1 (Ar), 128.2 (Ar), 128.3 (Ar), 128.5 (Ar), 131.6 (Ar), 131.7 (Ar), 131.8 (Ar), 132.4 (Ar), 132.6 (Ar), 135.5 (Ar), 158.4 (Ar); MS (CI): 365 (M⁺), 336 (M-CH₂CH₃), 201 (Ph₂PO⁺), 164 (M- Ph₂PO); IR (NUJOL) cm⁻¹: 3203 (NH), 1182 (P=O). The enantiomeric excess of 97% with *R*-isomer major was determined by HPLC (Chiracel AD column, Hexane/ propan-2-ol= 80: 20; flow rate 1 mL/ min; *R*-isomer, *t_R* 10.54 min and *S*-isomer, *t_R* 13.15min)

***N*-Piperonyl-*P,P*-diphenylphosphinamide (5c).** This compound was obtained as a white solid (34.7 mg) in 92% yield .Mp 154-155 °C; ¹HNMR (300 MHz, CDCl₃) δ 6.08-6.09 (m, 2H, OCH₂O), 6.90-6.96 (m, 1H, Ar-H), 7.35-7.63 (m, 8H, Ar-H), 7.90-7.97 (m, 4H, Ar-H), 9.18 (d, 1 H, *J_{H-P}*= 33.0 Hz, CH=N); ¹³CNMR (75 MHz, CDCl₃) δ 101.9 (OCH₂O), 106.8 (Ar), 107.2 (Ar), 108.3 (Ar), 128.3 (Ar), 128.4 (Ar), 128.5 (Ar), 128.6 (Ar), 128.8 (Ar), 130.7 (Ar), 131.0 (Ar), 131.4 (Ar), 131.5 (Ar), 131.6 (Ar), 131.8 (Ar), 132.3 (Ar), 133.9 (Ar), 148.5 (Ar), 152.5 (Ar), 171.8 (C=N); MS (CI) *m/e* 349 (M⁺), 272 (M-Ph), 202 (Ph₂POH⁺), 201 (Ph₂PO⁺); IR (NUJOL) cm⁻¹ 1616 (C=N), 1270 (C-O), 1200 (P=O). The enantiomeric excess of 97% with *R*-isomer major was determined by HPLC (Chiracel AD column, Hexane/ propan-2-ol= 80: 20; flow rate 1 mL/ min; *R*-isomer, *t_R* 8.32 min and *S*-isomer, *t_R* 13.82 min)

***N*-[1-(4-Methylphenyl)propyl]-*P,P*-diphenylphosphinoylamide (5d)**

This compound was obtained as a white solid (33.3 mg) in 95% yield. Mp 107-110 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.45 (t, 3H, *J* = 7.4 Hz, CH₂CH₃), 1.78-1.90 (m, 1H, CH₂CH₃), 1.95-2.09 (m, 1H, CH₂CH₃), 2.35 (s, 3H, CH₃Ar), 3.30-3.33 (m, 1H, NH), 4.05-4.14 (m, 1H, CHNH), 7.06 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.12 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.35-7.48 (m, 6H, Ar-H), 7.75-7.89 (m, 4H, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ 10.5 (CH₃), 21.0 (CH₃Ar), 32.4 (CH₂), 56.9 (CHNH), 126.3 (Ar), 128.1 (Ar), 128.3 (Ar), 128.4 (Ar), 129.1 (Ar), 131.6 (Ar), 131.7 (Ar), 131.8 (Ar), 132.4 (Ar), 132.5 (Ar), 132.6 (Ar), 136.6 (Ar), 140.4 (Ar); MS (CI): 320 (M-CH₂CH₃), 201 (Ph₂PO⁺), 148 (M-Ph₂PO); IR (NUJOL) cm⁻¹: 3224 (NH), 1185 (P=O). The enantiomeric excess of 98% with *R*-isomer major was determined by HPLC (Chiracel AD column, Hexane/ propan-2-ol = 92: 8; flow rate 1 mL/ min; *R*-isomer, *t_R* 7.79 min and *S*-isomer, *t_R* 9.44 min)

***N*-(3-Methylphenylidene)-*P,P*-diphenylphosphinamide (5e).** This compound was obtained as a white solid (30.1 mg) in 86% yield. Mp 116-118 °C; ¹H NMR (300 MHz, CDCl₃) δ 2.45 (s, 3H, CH₃Ar), 7.40-7.51 (m, 8H, Ar-H), 7.69-7.99 (m, 6H, Ar-H), 9.30 (d, 1H, *J*_{H-P} = 33.0 Hz, CH=N), ¹³C NMR (75 MHz, CDCl₃) δ 21.2 (CH₃Ar), 127.8 (Ar), 128.3 (Ar), 128.5 (Ar), 128.7 (Ar), 130.2 (Ar), 131.4 (Ar), 131.6 (Ar), 131.7 (Ar), 131.8 (Ar), 132.1 (Ar), 133.7 (Ar), 134.5 (Ar), 138.7 (Ar), 173.8 (C=N), 173.9 (C=N); MS (CI) *m/e* 319 (M⁺), 242 (M-Ph), 216 (Ph₂PONH⁺), 202 (Ph₂POH⁺), 201 (Ph₂PO⁺); IR (NUJOL) cm⁻¹ 1628 (C=N), 1200 (P=O). The enantiomeric excess of 96% with *R*-isomer major was determined by HPLC (Chiracel AD column, Hexane/ propan-2-ol = 90: 10; flow rate 1 mL/ min; *R*-isomer, *t_R* 5.82 min and *S*-isomer, *t_R* 9.59 min)

References and Notes

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