Zinc-Catalyzed Enantioselective Hydrosilylation of Imines

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Supporting Information

General Information. Catalytic reactions were performed under nitrogen using standard Schlenk techniques. THF was distilled from sodium benzophenone ketyl under nitrogen. ZnEt$_2$ (1.1 M solution in toluene), hydrosilanes, and anhydrous methanol were purchased from Aldrich and used as received. Diamine ligands (L1–L4) were prepared according to the literature.\[^1\] Oximes were prepared from the corresponding ketones following a literature procedure.\[^2\] Phosphinylimines (1a–1h) were prepared from the corresponding oximes by modification of literature procedures.\[^3-5\] Flash chromatography was performed on silica gel from Merck (70–230 mesh). All $^1$H NMR and $^{13}$C NMR spectra were obtained on Varian Mercury 400 systems. $^{31}$P NMR spectra were obtained on a Unity Inova 500NB. Infrared spectra (IR) were obtained on a Nicolet 205 FT-IR and are recorded in cm$^{-1}$. Enantiomeric excess was determined by using a Younglin Acme 9000 Series HPLC with detection at 220 nm. GC analyses for the determination of reaction conversion were performed on a Younglin Acme 6000 Series. Racemates of N-phosphinylamines were prepared by reduction of the corresponding imines using LiAlH$_4$.

Preparation of ligand L4. To a suspension of K$_2$CO$_3$ (276 mg, 2.0 mmol) and (R,R)-(+) -1,2-diphenyl-1,2-ethylene diamine (106 mg, 0.5 mmol) in DMF (0.5 mL), was added 2-phenyl benzyl bromide (0.18 mL, 1.0 mmol) in DMF (1 mL). After stirring at room temperature, the reaction was quenched with water (2.0 mL). The resultant mixture was extracted with Et$_2$O (x 3), and the combined organic layers were washed
with water (x 3). The organic layer was dried over Na$_2$SO$_4$, concentrated, and the residue was purified by column chromatography (silica gel, hexanes/ethyl acetate (15/1)) to give **L4** (210 mg, 77% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32–7.14 (m, 18H), 7.11–7.02 (m, 6H), 6.80–6.78 (m, 4H), 3.50 (d, $J$ = 12.1 Hz, 2H), 3.42 (s, 2H), 3.29 (d, $J$ = 12.5 Hz, 2H), 1.65 (brs); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 142.2, 141.2, 141.1, 137.9, 130.7, 130.2, 129.2, 128.2, 127.5, 127.0, 126.9, 126.8, 69.1, 49.6; IR (KBr): 3308, 3023, 1599, 1452, 1102, 747, 699 cm$^{-1}$.

**General Procedure for the Preparation of Phosphinylimines (1a–1h).** Oxime (6.3 mmol) was added to an oven-dried round-bottom flask charged with a magnetic stir bar under N$_2$. Dry CH$_2$Cl$_2$ (50 mL) and hexanes (50 mL) were added to a reaction flask. Anhydrous triethylamine (1.00 mL, 7.1 mmol) was added to the reaction mixture, which was then cooled to -45 ºC. Chlorodiphenylphosphine (1.27 mL, 7 mmol) diluted with 5 mL of CH$_2$Cl$_2$ was added dropwise to the reaction solution over a period of 45 min. The reaction mixture was stirred at -45 ºC for 1 h, slowly warmed to room temperature, and then stirred overnight at room temperature. Insoluble salts (Et$_3$N·HCl) were filtered off and the filtrate was concentrated under vacuum. The residue was roughly purified by silica gel chromatography (CH$_2$Cl$_2$/acetone = 10/1) to give a solid which was washed with toluene/hexanes (3/1, 10 mL), filtered and dried under vacuum to give the product. The spectral characteristics of phosphinyl imines (1a, 1c–1h) were consistent with those reported previously in the literature.$^{[3-6]}$

![Diagram](https://via.placeholder.com/150)

(1b) white powder; 36% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96–7.91 (m, 6H), 7.59 (d, $J$ = 8.8 Hz, 2H) 7.45–7.40 (m, 6H), 2.93 (d, $J$ = 2.2 Hz, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 180.3 (d, $J$ = 6.9 Hz), 138.3 (d, $J$ = 24.4 Hz), 135.2, 133.9, 131.9–131.6 (m), 129.6, 128.6 (d, $J$ = 13.0 Hz), 127.7, 23.3 (d, $J$ = 12.2 Hz); $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ 20.3; Anal. Calcd. for C$_9$H$_{10}$N$_2$, C 60.32, H 4.30, N 3.52; Found C 60.40, H 4.28, N 3.34.

![Diagram](https://via.placeholder.com/150)

(1g) colorless viscous oil; 22% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97–7.88 (m, 4H), 7.48–7.44 (m, 2H), 7.43–7.27 (m, 9H), 3.50–3.43 (m, 1H), 1.28 (d, $J$ = 7.0 Hz, 6H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 192.5 (d, $J$ = 10.7 Hz), 139.0 (d, $J$ = 15.3 Hz), 135.4, 134.1, 131.3–131.2 (m), 130.9 (d, $J$ = 2.3 Hz), 130.0, 128.0–127.2 (m), 39.7 (d, $J$ = 16.0 Hz), 20.6; $^{31}$P NMR
General Procedure for the Enantioselective Hydrosilylation of N–Phosphinyl Imines (Table 2). To a solution of ligand L2 (8.6 mg, 0.022 mmol) in freshly distilled THF (0.4 mL), was added ZnEt₂ (0.02 mL, 1.1 M solution in toluene, 0.022 mmol) under nitrogen. The reaction mixture was stirred for 10 min, and a solution of phosphinyl imine (0.44 mmol) in THF (0.4 mL), PMHS (0.08 mL, 1.32 mmol), and anhydrous MeOH (0.2 mL) was added successively. The resulting solution was stirred for 12 h at room temperature and the reaction was monitored by TLC. After completion of the reaction, MeOH (10 mL) and 1 N NaOH in MeOH (0.2 mL) were added. The mixture was stirred for 30 min, filtered through a pad of celite, and concentrated under vacuum. Purification by silica gel chromatography (10% acetone/CH₂Cl₂) gave the corresponding phosphinyl amines. Configurations of phosphinylamines were determined by comparison of optical rotations or those of the corresponding primary amines with literature values.[7]

**(2a)**[^1] white powder; 86% yield; ¹H NMR (400 MHz, CDCl₃)  d 7.91–7.86 (m, 2H), 7.83–7.78 (m, 2H), 7.49–7.20 (m, 11H), 4.40–4.35 (m, 1H), 3.20–3.16 (m, 1H), 1.57 (d, J = 6.6 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) d 145.2, 133.9–132.6 (m), 132.1–131.6 (m), 128.7–128.5 (m), 127.3, 126.1, 51.4, 26.4 (d, J = 3.1 Hz); 97% ee by HPLC (Chiralcel OD-H Column, 2-propanol:hexanes = 10:90 (0.5 mL/min), minor isomer 11.0 min, major isomer 13.8 min).

**(2b)** white powder; 77% yield; ¹H NMR (400 MHz, CDCl₃)  d 7.90–7.85 (m, 2H), 7.79–7.74 (m, 2H), 7.49–7.32 (m, 8H), 7.14 (d, J = 8.4 Hz, 2H), 4.35–4.32 (m, 1H), 3.19–3.15 (m, 1H), 1.54 (d, J = 6.6 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) d 143.2 (d, J = 6.1 Hz), 133.6, 132.7–132.3 (m), 132.1–131.4 (m), 128.8–128.5 (m), 127.9, 121.0, 50.8, 26.2 (d, J = 3.8 Hz); ³¹P NMR (202 MHz, CDCl₃) d 23.6; IR (KBr): 3115, 1180 cm⁻¹; Anal. Calcd. for C₉H₁₀N₂, C 60.02, H 4.78, N 3.50; Found C 60.06, H 4.88, N 3.30; 97% ee by HPLC (Chiralcel OD-H Column, 2-propanol:hexanes = 5:95 (0.7 mL/min), minor isomer 14.0 min, major isomer 16.4 min).
(2c). \[\text{white powder; 83\% yield; }^1\text{H NMR (400 MHz, CDCl}_3)\] d 7.91–7.78 (m, 4H), 7.49–7.33 (m, 6H), 7.19 (d, \(J = 8.5\) Hz, 2H), 6.83 (d, \(J = 8.5\) Hz, 2H), 4.36–4.31 (m, 1H), 3.79 (s, 3H), 3.14–3.10 (m, 1H), 1.55 (d, \(J = 7.0\) Hz, 3H); \(^{13}\text{C}\{^1\text{H}\} \text{NMR (100 MHz, CDCl}_3)\] d 158.7, 137.4, 137.3–132.5 (m), 132.1–131.7 (m), 128.7–128.5 (m), 127.3, 114.0, 55.6, 50.8, 26.3 (d, \(J = 3.1\) Hz); 96\% ee by HPLC (Chiralpak AD-H Column, 2-propanol:hexanes = 10:90 (0.7 mL/min), major isomer 23.9 min, minor isomer 27.1 min).

(2d). \[\text{white powder; 82\% yield; }^1\text{H NMR (400 MHz, CDCl}_3)\] d 7.86–7.81 (m, 2H), 7.75–7.70 (m, 4H), 7.44–7.36 (m, 2H), 7.31–7.18 (m, 5H), 7.14–7.12 (m, 2H), 4.10–4.06 (m, 1H), 3.36–3.34 (m, 1H), 2.02–1.97 (m, 1H), 1.86–1.81 (m, 1H), 0.78 (t, \(J = 7.3\) Hz, 3H); \(^{13}\text{C}\{^1\text{H}\} \text{NMR (100 MHz, CDCl}_3)\] d 143.7 (d, \(J = 6.1\) Hz), 134.0, 132.7 (d, \(J = 9.9\) Hz), 132.0–131.8 (m), 131.5, 128.7–128.4 (m), 127.2, 126.7, 57.5, 32.9 (d, \(J = 3.8\) Hz), 11.1; 96\% ee by HPLC (Chiralcel OD-H Column, 2-propanol:hexanes = 5:95 (0.7 mL/min), major isomer 10.9 min, major isomer 15.1 min).

(2e). \[\text{white powder; 83\% yield; }^1\text{H NMR (400 MHz, CDCl}_3)\] d 8.01–7.95 (m, 4H), 7.67 (d, \(J = 7.3\) Hz, 1H), 7.52–7.42 (m, 6H), 7.26–7.16 (m, 3H), 4.67–4.58 (m, 1H), 3.17 (dd, \(J = 11.4, 5.6\) Hz, 1H), 2.96–2.89 (m, 1H), 2.77–2.69 (m, 1H), 2.63–2.56 (m, 1H), 2.01–1.91 (m, 1H); \(^{13}\text{C}\{^1\text{H}\} \text{NMR (100 MHz, CDCl}_3)\] d 144.8, 142.9, 132.5–132.1 (m), 128.8–128.7 (m), 127.9, 126.9, 124.8 (d, \(J = 6.9\) Hz), 57.2, 37.7 (d, \(J = 3.8\) Hz), 30.4; 98\% ee by HPLC (Chiralcel OD-H Column, 2-propanol:hexanes = 10:90 (0.5 mL/min), minor isomer 13.2 min, major isomer 19.3 min).

(2f). \[\text{white powder; 85\% yield; }^1\text{H NMR (400 MHz, CDCl}_3)\] d 7.99–7.94 (m, 4H), 7.70 (d, \(J = 7.7\) Hz, 1H), 7.51–7.41 (m, 6H), 7.24–7.12 (m, 2H), 7.03 (d, \(J = 7.1\) Hz, 1H), 4.35–4.27 (m, 1H), 3.21–3.17 (m, 1H), 2.82–2.65 (m, 2H), 2.16–2.05 (m, 1H), 1.96–1.68 (m, 3H); \(^{13}\text{C}\{^1\text{H}\} \text{NMR (100 MHz, CDCl}_3)\] d 138.8 (d, \(J = 78.4\) Hz), 137.5, 132.4 (d, \(J = 3.8\) Hz), 132.3 (d, \(J = 3.8\) Hz), 132.0, 129.2, 128.8–128.6 (m), 127.3, 126.4, 50.1, 33.7, 29.6, 20.3; 86\% ee by HPLC (Chiralpak AD-H Column, 2-propanol:hexanes = 10:90 (0.7 mL/min), major isomer 17.1 min, minor isomer 22.4 min).
(2g).<sup>9</sup> white powder; 74% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85–7.80 (m, 2H), 7.67–7.62 (m, 2H), 7.51–7.36 (m, 4H), 7.31–7.18 (m, 5H) 7.05 (d, J = 1.8 Hz, 2H), 3.94–3.87 (m, 1H), 3.38–3.34 (m, 1H), 2.04–2.00 (m, 1H), 1.01 (d, J = 6.6 Hz, 3H), 0.82 (d, J = 7.0 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 143.0 (d, J = 4.6 Hz) 132.8 (d, J = 9.2 Hz), 132.1–131.9 (m), 131.7 (d, J = 3.1 Hz), 131.3, 128.8–128.2 (m), 127.1, 127.0, 61.6, 36.1 (d, J = 4.6 Hz), 19.7; <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 23.6; IR (KBr): 3211, 1186 cm<sup>-1</sup>; HRMS m/z Calcd. for C<sub>22</sub>H<sub>24</sub>NOP (MH<sup>+</sup>) 350.1674, found 350.1677; 55% ee by HPLC (Chiralcel OD-H Column, 2-propanol:hexanes = 10:90 (0.5 mL/min), minor isomer 10.9 min, major isomer 12.0 min).

(2h).<sup>9</sup> white powder; 77% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95–7.84 (m, 4H), 7.49–7.40(m, 6H), 7.34 (d, J = 1.8 Hz, 1H), 6.27 (dd, J = 2.9, 1.8 Hz, 1H), 6.12(d, J = 2.9, 1H), 4. 40–4.36 (m, 1H), 3.19–3.15 (m, 1H), 1.60 (d, J = 7.0 Hz, 3H) <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 157.2 (d, J = 8.4 Hz), 141.9, 132.8–132.0 (m), 128.8–128.7 (m), 110.4, 105.5, 45.4, 23.4 (d, J = 3.4 Hz); <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 23.5; Anal. Calcd for C<sub>9</sub>H<sub>10</sub>N: C 69.45, H 5.83, N 4.50; Found C 69.51, H 5.95, N 4.35. ; 96 % ee by HPLC (Chiralpak AD-H Column, 2-propanol:hexanes = 10:90 (0.7 mL/min), major isomer 14.5 min, minor isomer 17.9 min).

**References**


