[Supporting Information for:]

Enantioselective MSPV Reduction of Ketimines using 2-Propanol and (BINOL)Al^{III}

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General Procedures, Materials, and Instrumentations. All air- or water-sensitive reactions were carried out under nitrogen either in a Vacuum Atmospheres Company drybox or using standard Schlenk-line techniques. Triethylamine (Fisher Scientific) was dried over CaH_2 and vacuum-transferred into a Strauss flask. Toluene (Fisher Scientific) was dried over alumina and Q5 catalyst via the Dow-Grubbs solvent system[1] installed by Glass Contours (Laguna Beach, CA). 2-Propanol (Fisher Scientific) and 2-propan-2-*d*-ol (Aldrich Chemicals) were distilled over $Mg(O^iPr)_2$ and $Mg(O^iPr\text{-}2d)_2$, respectively. C_6D_6 (Cambridge Isotope Laboratories) was dried over sodium and benzophenone ketyl and vacuum-transferred into a Strauss flask. All solvents and reagents were saturated with nitrogen and stored in Strauss flasks prior to use. $CDCl_3$ (Cambridge Isotope Laboratories), enantiomerically pure samples of 2,2'-dihydroxy-1,1'-binapthyl (BINOL) (Sumikin Chemical Company, now Air Water Chemical, Inc. http://www.aw-chem.co.jp/e/index.html), and all other reagents (Aldrich Chemical Company) were purchased from commercial sources and used without further purification, unless otherwise noted.

^1H, ^2H, and ^{13}C NMR spectra were recorded on either a Varian INOVA 400 (400.63 MHz for ^1H, 100.74 MHz for ^{13}C) or a Varian INOVA 500 (499.6 MHz for ^1H, 76.7 MHz for ^2D, 125.6 MHz for ^{13}C) FT-NMR spectrometers. ^1H NMR data are reported as follows: chemical shift (multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant, and integration). ^1H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) using the residual solvent resonances as internal standards. Deuterium signals were externally referenced to $CDCl_3$ in CH_2Cl_2. ^{31}P NMR spectra were recorded on a Varian Mercury 400 FT-NMR spectrometer (162.0 MHz for ^{31}P NMR) and externally referenced to phosphoric acid in D_2O. ^{27}Al NMR spectra were recorded on a Varian INOVA 400 FT-NMR spectrometer (104.4 MHz for ^{27}Al) and externally referenced to concentrated $AlCl_3$ in D_2O. GC analyses of reaction mixtures were carried out on a Hewlett-Packard 5890A instrument equipped with a FID detector interfaced to an HP 3396A integrator. The column used was a 30-m HP-5 capillary column with a 0.32-mm inner diameter and a 0.25-μm film thickness (flow rate = 1.8 mL/min). GC conversions were determined through integration of the product and starting material peaks against 1,2,4,5-tetramethylbenzene (internal standard) using pre-established response factors. HPLC analyses were carried out on a computer-interfaced automated Agilent 1100 series HPLC equipped with a diode-array detector and ChemStation software. The column used was a 25-cm Chiralcel OD-H column (Daicel Chemical Industries, Ltd) with a 0.46-cm inner diameter. Retention times of enantiomerically enriched products were referenced to racemic samples prepared via sodium borohydride reduction of the starting imines.

General Procedure for the synthesis of imine starting materials. Imines **1**-**10** were synthesized following modified literature procedures.[2] Under bench-top conditions and in a 100-mL round-bottom flask equipped with a magnetic stir bar, the appropriate oxime (7.4 mmol) was combined with anhydrous toluene (10 mL) and anhydrous triethylamine (0.75 g, 7.4 mmol). The resulting mixture was stirred at room temperature and PPh_2Cl (1.6 g, 7.4 mmol) in anhydrous toluene (5 mL) was added drop-wise via addition funnel (~0.5 h addition time). Upon completion, the reaction was stirred for an additional hour at room temperature after which precipitate was filtered from the reaction using a Büchner funnel. Solvents were removed from the filtrate using a rotary evaporator, leaving a pale yellow crude reaction product. Subsequent purification via column chromatography on silica gel (15 cm × 5 cm) with acetone/CH_2Cl_2 eluants (10/90-50/50) afforded the pure products as white to off-white solids except **10**, which was a pale yellow oil (yield = 35-60 %).

General procedure for optimization of the MSPV reduction of 1. In the drybox, an 8-mL vial equipped with a magnetic stir bar was charged with (*S*)-BINOL (0.16 – 0.19 mmol). Anhydrous toluene (1 – 3 mL) was added followed by $AlMe_3$ (0.16 – 0.19 mmol) and the vial was capped with a Teflon-lined silicone septa. The resulting cloudy mixture was stirred for 0.5 h when 2-propanol was added. The ensuing homogeneous reaction was allowed to stir at room temperature for an additional 0.5 h, taken out of the drybox, and then heated to 60 °C in a Thermolyne Type 17600 Dri-Bath block heater equipped with an aluminum heating block containing a 4 × 3 bank of [20 mm diameter × 50 mm depth] wells. A solution of the imine (0.16 mmol) in toluene (1 mL) was then added via a gas-tight syringe and the resulting yellow solution was stirred for an additional 20 h at 60 °C. A 100-μL fraction was taken via gas-tight syringe, diluted in CH_2Cl_2 (3 mL), and extracted with water (3 × 5 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, and directly analyzed via GC and HPLC. GC temperature program: Initial temp = 50 °C, initial time = 5 min; ramp rate = 10 °C/min, final temp =

250 °C, final time = 20 min (imine retention time = 31.4 min; amine retention time = 30.6 min; BINOL retention time = 28.4 min). HPLC conditions are listed below.

General procedure for the MSPV reduction of imines. In the drybox, an 8-mL vial equipped with a magnetic stir bar was charged with (*S*)-BINOL (54 mg, 0.19 mmol). Anhydrous toluene (1 mL) was added followed by $AlMe_3$ (18.5 µL, 0.19 mmol) and the vial was capped with a Teflon-lined silicone septa. The resulting cloudy mixture was stirred for 0.5 h when 2-propanol (50 µL, 0.64 mmol) was added. The ensuing homogeneous reaction was allowed to stir at room temperature for an additional 0.5 h, taken out of the drybox, and then heated to 60 °C in a Thermolyne Type 17600 Dri-Bath block heater equipped with an aluminum heating block containing a 4 × 3 bank of [20 mm diameter × 50 mm depth] wells. A solution of the imine (0.16 mmol) in toluene (1 mL) was then added via a gas-tight syringe and the resulting yellow solution was stirred for an additional 20 h at 60 °C. The reaction was cooled to room temperature, diluted with CH_2Cl_2 (20 mL), and washed with H_2O (3 × 50 mL) and saturated aqueous NaCl (50 mL). The organics were then dried over anhydrous Na_2SO_4, filtered over a Büchner funnel, and evaporated to dryness on a rotary evaporator. Crude reaction mixtures were then purified via chromatography on silica gel (25 cm × 2 cm) with acetone/CH_2Cl_2 eluants (10/90 – 50/50). Stereochemical assignments of the products were made via comparison to literature precedents (*vide infra*).

***N*-(1-Phenylethyl)-*P*,*P*-diphenylphosphinamide (11)**.[3,4] A white solid (yield = 85%, ee = 96% (Table 2, entry 1)). ^{1}H NMR (400.64 MHz, $CDCl_3$): δ 1.50 (d, *J* = 6.8 Hz, 3 H), 3.18 (b s, 1 H), 4.31 (m, 1 H), 7.16-7.42 (m, 8 H), 7.72-7.86 (m, 4 H). ^{13}C{^{1}H} NMR (100.73 MHz, $CDCl_3$): δ 26.2 (d, *J* = 3.0 Hz), 51.2, 126.1, 127.3, 128.5-128.8 (m), 131.9-132.2 (m), 132.6, 132.7, 145.2 (d, *J* = 6.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23. GC-MS (EI): Calculated for $C_{21}H_{22}NPO$ 321.35; Found = 321. HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 0.5 mL/min, detector set at 254 nm. Major isomer retention time = 13.5 min, minor isomer retention time = 16.7 min.

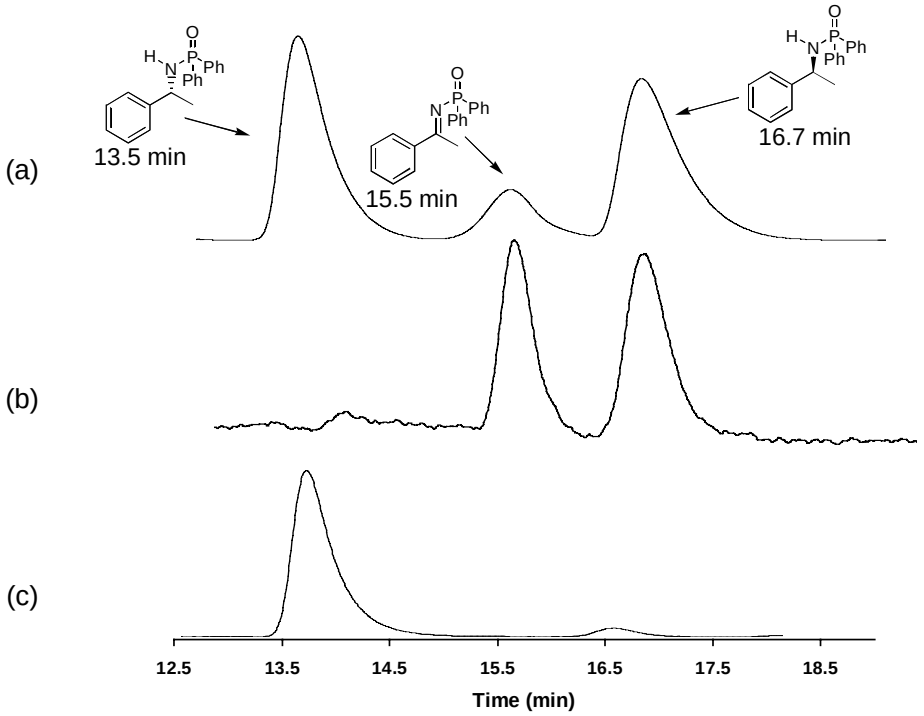

Figure S1. Chiral HPLC traces of **11**: (a) crude reaction mixture from the $NaBH_4$ reduction of **1**, (b) crude reaction mixture from the (*R*)-BINOL/$AlMe_3$/^{i}PrOH reduction of **1** (Table 3, entry 5), and (c) purified product from (*S*)-BINOL/$AlMe_3$/^{i}PrOH reduction of **1** (Table 2, entry 1). The large extinction coefficient of the imine starting material exaggerates its presence vs. that of the amine products in (a) and (b).

***N*-(1-Phenylpropyl)-*P*,*P*-diphenylphosphinamide(12)**.[3,4] A white solid (yield = 85%, ee = 95% (Table 2, entry 2)). ^{1}H NMR (499.48 MHz, $CDCl_3$): δ 0.72 (t, *J* = 7.5 Hz, 3 H), 1.74-1.97 (m, 2.5 H); 3.18 (b s, 1 H), 4.01-4.04 (m, 1 H), 7.06-7.43 (m, 10 H) 7.67-7.81 (m, 4 H). ^{13}C{^{1}H} NMR (100.74 MHz, $CDCl_3$): δ 10.8, 32.8, 57.3, 126.7, 127.3, 128.4, 128.6-128.7 (m), 131.9-132.1 (m), 132.8, 132.9, 143.7. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23. GC-MS (EI): Calculated for $C_{21}H_{22}NPO$

335.38; Found = 334. HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 0.5 mL/min, detector set at 254 nm. Major isomer retention time = 12.9 min, minor isomer retention time = 16.6 min.

***N*-(1-Phenylbutyl)-*P,P*-diphenylphosphinamide(13)**.[5] An off-white solid (yield = 84%, ee = 94% (Table 2, entry 3)). ^{1}H NMR (400.63 MHz, $CDCl_3$): δ 0.75 (t, *J* = 7.2 Hz, 3 H), 1.08-1.18 (m, 2 H), 1.72-1.86 (m, 2 H), 3.18 (b s, 1 H), 4.08 (m, 1 H), 7.06-7.42 (m, 11 H), 7.66-7.81 (m, 4 H). $^{13}C\{^{1}H\}$ NMR (100.74 MHz, $CDCl_3$): δ 14.0, 19.6, 42.2, 55.9, 126.6, 127.3, 128.4-128.7 (m), 131.9-132.1 (m), 132.6-132.9 (m), 143.1. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 23. GC-MS (EI): Calculated for $C_{22}H_{24}NPO$ = 349.41; Found = 348. HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 1.0 mL/min, detector set at 254 nm. Major isomer retention time = 4.9 min, minor isomer retention time = 5.8 min.

***N*-(1-Phenyl-2-methylpropyl)-*P,P*-diphenylphosphinamide (14)**.[6] A white solid (yield = 79%, ee = 96% (Table 2, entry 4)). ^{1}H NMR (400.63 MHz, $CDCl_3$): δ 0.78 (d, *J* = 7.2 Hz, 3 H), 0.98 (d, *J* = 6.8 Hz, 3H), 1.97 (m, 1 H), 3.37 (m, 1 H), 3.87 (m, 1 H), 7.03 (d, *J* = 6.8 Hz, 2 H), 7.17-7.45 (m, 9 H), 7.60-7.91 (m, 4 H). $^{13}C\{^{1}H\}$ NMR (100.73 MHz, $CDCl_3$): δ 19.4, 35.8, 35.1, 61.5 (d, *J* = 1.5 Hz), 126.8, 127.0, 127.1, 128.2-128.3 (m), 128.6-128.7 (m), 131.7-132.0 (m), 132.7, 132.9, 143.1 (d, *J* = 3.8 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 23. GC-MS (EI): Calculated for $C_{22}H_{24}NPO$ = 349.41; Found = 348. HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 1.0 mL/min, detector set at 254 nm. Minor isomer retention time = 6.4 min, major isomer retention time = 7.8 min.

***N*-(1-(1-Napthyl)ethyl)-*P,P*-diphenylphosphinamide (15)**.[7] An off-white solid (yield = 80%, ee = 98% (Table 2, entry 5)). ^{1}H NMR (400.63 MHz, $CDCl_3$): δ 1.63 (d, *J* = 6.4 Hz, 3 H), 3.33 (b s, 1 H), 5.16 (m, 1 H), 7.19-7.44 (m, 10 H), 7.56 (d, *J* = 6.8 Hz, 1 H), 7.62-7.87 (m, 6 H). $^{13}C\{^{1}H\}$ NMR (100.73 MHz, $CDCl_3$): δ 26.4, 47.4, 122.6, 123.2, 125.7, 125.8, 126.3, 128.0, 128.5-129.0 (m), 132.1-132.5 (m). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 24. GC-MS (EI): Calculated for $C_{24}H_{22}NPO$ = 371.41; Found = 371. HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 1.0 mL/min, detector set at 254 nm. Major isomer retention time = 8.8 min, minor isomer retention time = 11.7 min.

***N*-(1-(2-Napthyl)ethyl)-*P,P*-diphenylphosphinamide (16)**.[7] An off-white solid (yield = 75%, ee = 96% (Table 2, entry 6)). ^{1}H NMR (499.48 MHz, $CDCl_3$): δ 1.69 (d, *J* = 6.5 Hz, 3 H), 3.33 (b s, 1 H), 4.58 (b s, 1 H) 7.28-7.53 (m, 9 H), 7.67 (s, 1 H), 7.80-7.97 (m, 7 H). $^{13}C\{^{1}H\}$ NMR (100.74 MHz, $CDCl_3$): δ 26.1, 51.4, 124.5, 124.7, 126.0, 126.4, 127.8, 128.1, 128.6-128.8 (m), 132.0-132.3 (m), 132.6-132.8 (m), 135.5. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 23. GC-MS (EI): Calculated for $C_{24}H_{22}NPO$ = 371.41; Found = 371. HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 1.0 mL/min, detector set at 254 nm. Major isomer retention time = 10.2 min, minor isomer retention time = 11.0 min.

***N*-[2-(*E*-4-Phenyl-but-3-enyl)]-*P,P*-diphenylphosphinamide (17)**.[5] An off-white solid (yield = 84%, ee = 94% (Table 2, entry 7)). ^{1}H NMR (499.48 MHz, $CDCl_3$): δ 1.37 (d, *J* = 6.0 Hz, 3 H), 2.88 (b s, 1 H), 3.91 (m, 1 H), 6.17 (dd, J_1 = 16.0 Hz, J_2 = 5.0 Hz, 1 H), 6.37 (d, *J* = 16.0 Hz, 1 H), 7.15-7.44 (m, 11 H), 7.87 (b m, 4 H). $^{13}C\{^{1}H\}$ NMR (125.60 MHz, $CDCl_3$): δ 24.3, 49.3, 126.6, 127.8, 128.6-128.8 (m), 129.9, 132.0-132.2 (m), 132.5-132.7 (m), 133.6, 136.9. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 23. GC-MS (EI): Calculated for $C_{22}H_{22}NPO$ 347.39; Found = 347. HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 1.0 mL/min, detector set at 254 nm. Major isomer retention time = 7.2 min, minor isomer retention time = 8.4 min.

***N*-[2-(4-Phenyl-but-3-ynyl)]-*P,P*-diphenylphosphinamide (18)**.[8] A pale yellow solid (yield = 80%, ee = 94% (Table 2, entry 8)). ^{1}H NMR (499.48 MHz, $CDCl_3$): δ 1.62 (d, *J* = 6.5 Hz, 3 H), 3.26 (m. 1 H), 4.29 (m, 1 H), 7.19-7.52 (m, 11 H), 7.72-7.95 (m, 4 H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 24. GC-MS (EI): Calculated for $C_{22}H_{24}NPO$ = 345.37; Found = 345. HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 1.0 mL/min, detector set at 254 nm. Major isomer retention time = 7.2 min, minor isomer retention time = 8.4 min.

***N*-(1-cyclohexylethyl)-*P,P*-diphenylphosphinamide (19)**.[5] An off-white solid (yield = 84%, ee = 94% (Table 2, entry 9)). ^{1}H NMR (400.63 MHz, $CDCl_3$): δ 1.15-1.48 (m, 6 H), 1.52-1.95 (m, 8 H), 2.56 (m, 1 H), 3.01 (m, 1 H), 7.38-7.58 (m, 6 H), 7.72-7.90 (m, 4 H). $^{13}C\{^{1}H\}$ NMR (125.60 MHz, $CDCl_3$): δ 25.6, 25.9, 26.3, 27.3, 28.4, 30.0, 52.4, 128.8-129 (m), 130.0, 131.2-131.3 (m), 132.0-132.2 (m), 132.3-132.4 (m), 135.2. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 27. HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 1.0 mL/min, detector set at 254 nm. Major isomer retention time = 11.05 min, minor isomer retention time = 11.8 min.

***N*-(3-octyl)-*P,P*-diphenylphosphinamide (20)**. A pale yellow oil (yield: 84%; ee: 93% (Table 2, entry 10)). ^{1}H NMR (400.63 MHz, $CDCl_3$): δ 0.79-1.50 (m, 16 H), 2.64 (m, 1 H), 2.93 (m, 1 H), 7.20-7.51 (m, 6 H), 7.82-7.86 (m, 4 H). $^{13}C\{^{1}H\}$ NMR (100.74 MHz, $CDCl_3$): δ 9.8, 14.2, 22.7, 25.3, 29.5 (d, *J* = 5.3 Hz), 31.9, 36.3 (d, *J* = 5.3 Hz), 52.9, 128.5-129.0 (m), 131,1, 131.9, 132.2-132.5 (m). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 22. GC-MS (EI): Calculated for $C_{20}H_{28}NPO$ 329.42;

Found = 329. HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 1.0 mL/min, detector set at 254 nm. Major isomer retention time = 8.6 min, minor isomer retention = 10.9 min.

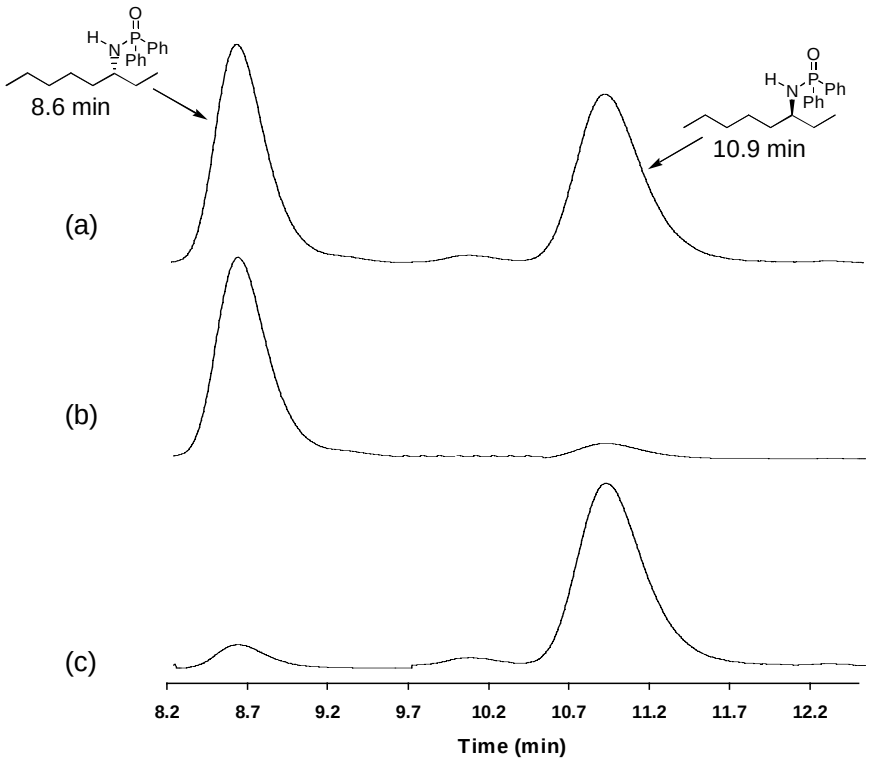

Figure S2. Chiral HPLC traces of **20**: (a) crude reaction mixture from the $NaBH_4$ reduction of **10**, (b) purified product from (*S*)-BINOL/$AlMe_3$/^{i}PrOH reduction of **10**, and (c) crude reaction mixture from (*R*)-BINOL/$AlMe_3$/^{i}PrOH reduction of **10**.

Large scale MSPV reduction of 1 and BINOL recovery and recycling. A flame-dried 100-mL Schlenk flask equipped with a magnetic stir bar was charged with (*S*)-BINOL (1.08 g, 3.8 mmol). The flask was evacuated and back-filled with nitrogen in triplicate, and anhydrous toluene (33 mL) was added via cannula under nitrogen. $AlMe_3$ (2.0 M solution in toluene, 1.9 mL, 3.8 mmol) was slowly added (over 1 minute) via a gas-tight syringe and the ensuing cloudy white mixture was stirred for 0.5 h. Anhydrous 2-propanol (1 mL, 12.8 mmol) was then added to the reaction via syringe to give a homogeneous, colorless solution, which was then allowed to stir for an additional 0.5 h. The reaction vessel was heated to 60 ^{o}C via an oil bath and **1** (1.0 g, 3.2 mmol) in anhydrous toluene (5 mL) was added to give a bright yellow solution. After 20 h stirring at 60 ^{o}C, heating was stopped and CH_2Cl_2 (100 mL) was added. The resulting mixture was extracted with aqueous KOH (5 wt% in water, 3 × 50 mL) and the aqueous layers were combined and set aside (*vide infra*). The organic layer was dried over anhydrous Na_2SO_4, and solvent was removed. Crude reaction product was purified by chromatography on silica (acetone/CH_2Cl_2, 40/60) to give pure (*R*)-**11**[3] as a white solid (0.88 g, 86% yield, 96% ee) as well as (*S*)-BINOL (0.1 g).

The aqueous layer (*vide supra*) was acidified with 2 N HCl (~ 100 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered over a Buchner funnel. The filtrate was evaporated on a rotary evaporator and the resulting crude product was further dried *in vacuo* to leave (*S*)-BINOL as a white solid (0.90 g, 83% recovery). Importantly, in the purification of the amine (*vide supra*) an additional crop of (*S*)-BINOL (0.1 g) was collected to give a total yield of 93% of recovered (*S*)-BINOL. This sample was used in a subsequent reduction of **1** following the procedure out line above to give the chiral product **11** in 95% ee (90% conversion of **1**).

Synthesis of deuterated amines. The general reaction set-up for the deuteration of **1** followed that of the general imine reduction strategy (*vide supra*) but with a larger amount of the imine (150 mg, 0.48 mmol). All other reagents were scaled accordingly with anhydrous 2-propan-2-*d*-ol being used in place of 2-propanol as the reducing agent. The crude reaction mixture was purified via column chromatography on silica gel (25 cm × 2 cm) with acetone/CH_2Cl_2 (40/60) eluant to yield (*R*)-**11**-*d* as a white solid (116 mg, 75% yield, 96% ee, Figure S3). ^{1}H NMR (499.48 MHz, $CDCl_3$): δ 1.58 (s, 3H), 3.59 (b, 1H), 7.27-7.40 (m, 7H), 7.47-7.53 (m, 4H), 7.82-7.86 (m, 2H), 7.93-7.96 (m, 2 H). ^{13}C{^{1}H} NMR (125.60 MHz, $CDCl_3$):

δ 26.1 (d, *J* = 2.5 Hz), 51.1 (t, *J* = 19.6 Hz), 126.2, 127.4, 128.7-128.8 (m), 132.1-132.3 (m), 132.7, 132.8, 145.2 (d, *J* = 7.2 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 24 (s). $^{2}H\{^{1}H\}$ NMR (CH_2Cl_2): δ 4.30 (s). GC-MS (EI): Calculated for $C_{20}H_{19}DNPO$ = 322.36; Found = 322. HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 0.5 mL/min, detector set at 254 nm. Major isomer retention time = 13.8 min, minor isomer retention time = 17.2 min.

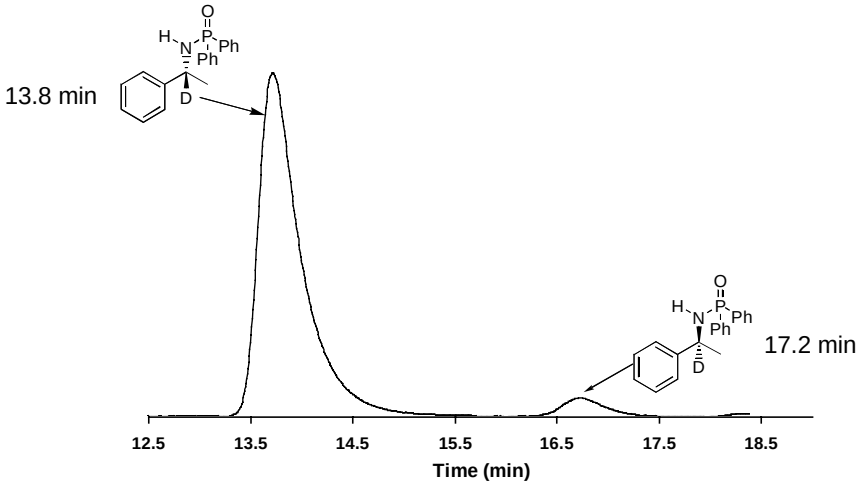

Figure S3. Chiral HPLC traces of the purified product from the reduction of **1** with (*S*)-BINOL/$AlMe_3$/2-propan-2-*d*-ol.

The product (*S*)-**20**-*d* could be synthesized in 93% ee following an analogous manner implementing (*R*)-BINOL/$AlMe_3$ in the reduction of **10** (Figure S4). ^{1}H NMR (400.64 MHz, $CDCl_3$): δ 0.75-1.48 (m, 16 H), 2.45 (m, 1 H), 7.23-7.51 (m, 6 H), 7.80-7.86 (m, 4 H). $^{13}C\{^{1}H\}$ NMR (100.74 MHz, $CDCl_3$): δ 9.8, 14.2, 22.7, 25.3, 29.8, 31.9, 36.1, 51.7 128.0-129.2 (m), 131.3-132.5 (m). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 17 ppm. $^{2}H\{^{1}H\}$ NMR (CH_2Cl_2): δ 3.47 (s). GC-MS (EI): Calculated for $C_{20}H_{19}DNPO$ = 330.42; Found = 330. HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 1.0 mL/min, detector set at 254 nm.

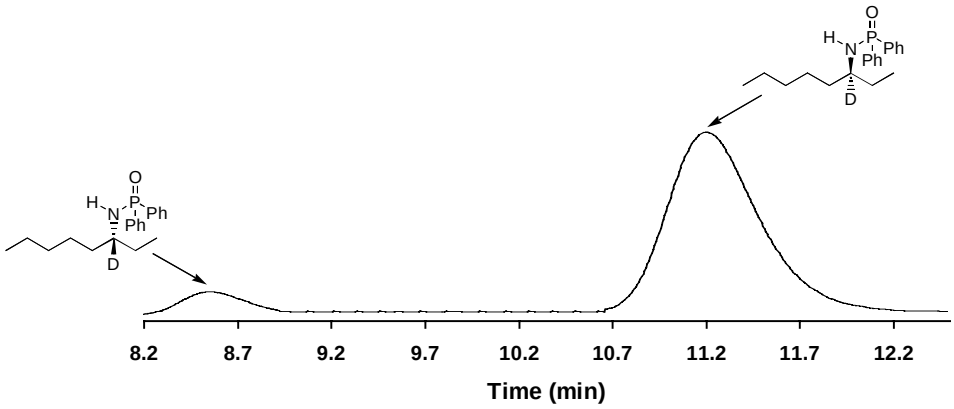

Figure S4. Chiral HPLC traces of the purified product from the reduction of **10** with (*R*)-BINOL/$AlMe_3$/2-propan-2-*d*-ol.

Procedure for ^{27}Al NMR experiment. In a drybox, to a 4-mL vial equipped with a magnetic stir bar was added (*S*)-BINOL (96 mg, 0.32 mmol), C_6D_6 (1 mL), and $AlMe_3$ (33 μL, 0.32 mmol via a gas-tight syringe). The ensuing cloudy mixture was stirred for 0.5 h when 2-propanol (50 μL, 0.32 mmol) was added. The resulting homogeneous reaction was stirred for an additional 0.5 h when compound **1** was added. The reaction instantaneously turned bright yellow and was stirred for 1 h at room temperature after which it was transferred to a gas-tight NMR tube and directly analyzed by NMR spectroscopy. ^{27}Al NMR: δ 45 (b). $^{31}P\{^{1}H\}$ NMR: δ 22 (s). The parent imine exhibits a single resonance ($^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 17) in its ^{31}P NMR spectrum.

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