Supporting Information

for

A Method for the Asymmetric Hydrosilylation of N-Aryl Imines

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Complete experimental procedures and spectral data for compounds listed in Tables 1 and 2 and X-ray characterization data for compound **6** (13 pages).

General Methods. Toluene was distilled under nitrogen from sodium before use. Polymethylhydrosiloxane (PMHS, M_w=2200), ketones, and aryl amines were used as obtained from Aldrich. Dichloromethane was used as obtained. Isobutylamine was redistilled from CaH_2. (S,S)-Ethylene-bis(η^5-tetrahydroindenyl)titanium difluoride ((EBTHI)TiF_2, **1**) was prepared as previously described.[1] Flash chromatography was performed on E. M. Science Kieselgel 60 (230–400 mesh). Yields, unless otherwise stated, refer to isolated yields of compounds of greater than 95% purity as determined by ^{1}H NMR and GC analysis. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. New compounds were also characterized by elemental analysis (E & R Analytical Laboratory, Inc. or Atlantic Microlabs). All ^{1}H NMR spectra are reported in parts per million (ppm) downfield from tetramethylsilane. All ^{13}C NMR spectra are reported in ppm referenced to deuterochloroform (77.23 ppm). All melting points are uncorrected.

General procedures for the preparation of N-aryl imines.[2]
An oven-dried round bottom flask was equipped with a reflux condenser and placed under an argon atmosphere. Ketone (20 mmol), amine (25 mmol), and 5 Å molecular sieves (25 g, Aldrich) were dissolved/suspended in toluene (100 mL). The mixture was refluxed until consumption of the starting material was complete as determined by GC. The reaction mixture was cooled to room temperature, filtered through Celite, concentrated, and purified by Kugelrohr distillation. Imines were stored refrigerated in a nitrogen-filled glovebox. The E/Z ratio of the imine was determined by ^{1}H NMR and is >20/1 unless indicated otherwise.

General procedure for the reduction of N-aryl imines.
An oven-dried resealable Schlenk flask, under argon, was charged with (S,S)-(EBTHI)TiF_2 (8.8 mg, 0.025 mmol) and dry toluene(1 mL). To the resulting yellow solution $PhSiH_3$ (12 μL, 0.1 mmol), pyrrolidine (8 μL, 0.1 mmol) and methanol (4 μL, 0.1 mmol) were added via syringe. The mixture was stirred at 60 °C for 15-30 min resulting in a color change from yellow to green. PMHS (0.9 mL, 15 mmol) was added dropwise via syringe. The Schlenk flask was then sealed, cooled to room temperature, and brought into a nitrogen-filled glovebox; the imine (1.25 mmol) was added. The Schlenk flask was placed in a 60°C oil bath, at this point the color of the reaction mixture changed to red. To

this solution, isobutylamine (650 μl, 6.5 mmol) was slowly added over 13 h using a syringe pump. Once amine addition was complete, the color of the reaction mixture had often returned to green. GC analysis showed complete consumption of imine. The reaction mixture was cooled to room temperature and removed from the glovebox.

Workup procedure A: The reaction mixture was diluted with Et_2O (20 mL) and stirred with 1 M HCl (10 mL) for 0.5 h. The aqueous layer was separated and the ether layer discarded. The aqueous layer was made basic with 3 M NaOH and extracted with ether (3 x 15 mL). The combined ether layers were dried ($MgSO_4$) and concentrated in vacuo to yield the corresponding enantiomerically enriched amine. Workup procedure B: The reaction mixture was diluted with Et_2O (20 mL) and stirred with 1 M NaOH (25 mL) for 1h. The aqueous layer was separated and extracted with Et_2O (2 x 15 mL). The combined ether layers were washed with 1 M NaOH (10 mL) and brine (10 mL), dried ($MgSO_4$), and concentrated in vacuo. Column chromatography on deactivated silica using hexane as the eluant provided the corresponding enantiomerically enriched amine. Analysis of ee was performed by HPLC or GC using the conditions and columns indicated. In HPLC solvent consitions, "Mix" refers to a solution of 0.02% diethylamine and 2% isopropanol in hexane.

Racemic amines were prepared from the corresponding imines by reduction with sodium borohydride.

N-(1-Cyclohexyl-ethylidene)-aniline: (Table 1, entry 1) The general procedure for the preparation of imines yielded 2.31 g (57% yield) of the title compound as a colorless oil. ^{1}H NMR (300 MHz): δ 1.00–1.51 (m, 5H), 1.52–1.98 (m, 5H), 1.73 (s, 3H), 2.21–2.40 (m, 1H), 6.67 (d, J=7.6 Hz, 2H), 7.04 (t, J=7.1Hz, 1H), 7.25–7.30 (m, 2H). ^{13}C (75 MHz): δ 17.9, 25.6, 26.3, 30.4, 49.6, 119.5, 122.9, 129.0, 152.0, 175.8. IR (cm^{-1}): 1657. Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51. Found: C, 83.32; H, 9.78.

(S)-(+)-N-phenyl-1-(cyclohexyl)ethyl amine: The title compound was prepared by the general procedure for reduction of imines using workup procedure B (hexane) to produce a colorless oil (164 mg, 63% yield). Enantiomeric excess was determined to be >99% by HPLC on an OJ column (2% IPA, 1% mix, hexane at 0.7 mL/min). ^{1}H NMR (500 MHz): δ 0.90–1.28 (m,

6H), 1.11 (d, J=6.4 Hz, 3H), 1.40–1.49 (m, 1H), 1.63–1.86 (m, 5H), 3.31 (quint, J=6.1, 1H), 3.51 (br s, 1H), 6.52–6.70 (m, 3H), 7.15 (t, J=7.9 Hz, 2H).^{13}C (125 MHz): δ 17.6, 26.5, 26.7, 26.8, 28.6, 30.0, 43.1, 53.1, 113.1, 116.7, 129.4, 148.1. IR (cm^{-1}): 693, 747, 1254, 1320, 1449, 1509, 1600, 2852, 2927, 3018, 3051, 3408. Anal. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41. Found: C, 82.81; H, 10.39. $[\alpha]_D$ +16.9 (c 1.46, $CHCl_3$).

(S)-(+)-N-phenyl-1-(cyclohexyl)ethyl amine: Following the procedure of Wagaw et al.[3], an oven-dried Schlenk flask was charged with NaOtBu (67 mg, 0.70 mmol), $Pd_2(dba)_3$ (9 mg, 0.009 mmol), and (±) BINAP (12 mg, 0.019 mmol). After purging the Schlenk flask with argon, bromobenzene (55 μL, 0.52 mmol), (S)-(+)-1-cyclohexylethyl amine (90 μL, 0.61 mmol), and toluene (5 mL) were added. The Schlenk flask was placed in a 100 °C oil bath and heated until the reaction was complete as judged by GC analysis. After filtering the reaction mixture through Celite, a small aliquot was analyzed by HPLC and showed the same major enantiomer as the product formed from the general procedure for reduction of imines.

N-(1-Cyclohexyl-ethylidene)-4-anisidine: (Table 1, entry 2) The general procedure for preparation of imines yielded 2.73 g (63% yield) of the title compound as a yellow oil (6/1 E/Z ratio). ^{1}H NMR (500 MHz): δ 1.00–1.49 (m, 5H), 1.54–1.97 (m, 5H), 1.74 (s, 3H), 2.22–2.35 (m ,1H, major) 2.39–2.51 (m, 1H, minor), 3.78 (s, 3H, major), 3.79 (s, 3H, minor), 6.61(AB, J=9.1 Hz, 2H), 6.83 (AB, J=9.1 Hz, 2H). ^{13}C (125 MHz): δ 17.7, 26.3, 26.4, 30.5, 49.7, 55.6, 114.3, 120.7, 145.1, 155.7, 176.1. IR (cm^{-1}): 1660. Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15. Found: C, 77.81; H, 9.39.

(+)-N-(4-methoxyphenyl)-1-(cyclohexyl)ethyl amine: The title compound was prepared by the general procedure for reduction of imines using workup procedure A to produce a yellow oil (213 mg, 78% yield). Enantiomeric excess was determined to be >99% by GC on a B-PH column (130 °C). ^{1}H NMR (300 MHz): δ 1.00–1.34 (m, 5H), 1.08 (d, J=6.5 Hz, 3H), 1.37–1.49 (m, 1H), 1.61–1.81 (m, 5H), 3.12–3.27 (m, 2H), 3.74 (s, 3H), 6.54 (AB, 2H, J=9.0 Hz), 6.76 (AB, 2H, J=9.0 Hz). ^{13}C (75 MHz): δ 17.6, 26.6, 26.7, 26.9, 28.5, 30.1, 43.1, 54.3, 56.1, 114.7, 115.2, 142.5, 151.8. IR (cm^{-1}): 817, 1040, 1236, 1510, 2851, 2922, 3397. Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.93. Found: C, 77.16; H, 10.35. $[\alpha]_D$ +18.2 (c 0.99, $CHCl_3$).

N-(1-Cyclohexyl-ethylidene)-3-toluidine: (Table 1, entry 3) The general procedure for preparation of imines yielded 2.50 g (57% yield, 13/1 E/Z mixture) of the title compound as a colorless oil. ^{1}H NMR (300 MHz): δ 1.03–1.52 (m, 5H), 1.60–1.78 (m, 1H), 1.74 (s, 3H), 1.80–1.97 (m, 4H), 2.23–2.40 (m, 1H), 2.31 (s, 3H), 6.43–6.52 (m, 2H), 6.83 (dd, J=7.7, 0.6 Hz, 1H), 7.16 (t, J=7.7 Hz, 1H). ^{13}C (75 MHz): δ Major: 17.7, 21.5, 26.3, 26.8, 30.4, 49.4, 116.4, 120.1, 123.6, 128.7, 138.6, 151.9, 175.3; Minor: 21.6, 22.5, 25.5, 25.9, 28.4, 42.6, 112.3., 116.3, 120.0, 123.5, 139.0, 151.1, 175.8. IR (cm^{-1}): 1653. Anal. Calcd for $C_{15}H_{21}N$: C, 83.67; H, 9.83. Found: C, 83.75; H, 9.76.

(+)-N-(3-methylphenyl)-1-(cyclohexyl)ethyl amine: The title compound was prepared by the general procedure for reduction of imines using workup procedure A to produce a yellow oil (203 mg, 79% yield). Enantiomeric excess was determined to be >99% by GC on a BPH column (130 °C). ^{1}H NMR (300 MHz): δ 0.97–1.31 (m, 6H), 1.11 (d, J=6.6 Hz, 3H), 1.40–1.53 (m, 1H), 1.62–1.86 (m, 5H), 2.27 (s, 3H), 3.30 (quint, J=5.4 Hz, 1H), 4.13 (br s, 1H), 6.40–6.55 (m, 3H), 7.01–7.09 (m, 1H). ^{13}C (75 MHz): δ 18.0, 22.2, 26.8, 27.0, 27.1, 28.9, 30.3, 43.5, 53.5, 110.5, 114.3, 118.0, 129.6, 139.5, 148.4. IR (cm^{-1}): 691, 768, 1177, 1328, 1447, 1490, 1513, 1606, 2853, 2926, 3042, 3408. Anal. Calcd for $C_{15}H_{23}N$: C, 72.89; H, 10.67. Found: C, 72.69; H, 10.78. $[\alpha]_D$ +16.9 (c 1.04, $CHCl_3$).

N-(1-Cyclohexyl-ethylidene)-2-chloroaniline: (Table 1, entry 4) The general procedure for preparation of imines yielded 3.09 g (66% yield) of the title compound as a colorless oil. ^{1}H NMR (500 MHz): δ 1.20–1.41 (m, 3H), 1.47 (dq, J=12.0, 3.4 Hz, 2H), 1.58–1.75 (m, 1H), 1.72 (s, 3H), 1.81–1.89 (m, 2H), 1.94–2.01 (m, 2H), 2.37 (tt, J=11.6, 3.4 Hz, 1H), 6.70 (dd, J=7.6, 1.5 Hz, 1H), 6.95 (dt, J=7.9, 1.5 Hz, 1H), 7.17 (dt, J=7.6, 1.5 Hz, 1H), 7.33 (dd, J=7.9, 1.5 Hz). ^{13}C (125 MHz): δ 8.7, 26.3, 26.3, 30.4, 49.4, 120.9, 123.7, 123.9, 127.4, 129.8, 148.7, 178.2. IR (cm^{-1}): 1666. Anal. Calcd for $C_{14}H_{19}NCl$: C, 71.41; H, 7.64. Found: C, 71.32; H, 7.70.

N-(1-Cyclohexyl-ethylidene)-2-toluidine: (Table 1, entry 5) The general procedure for preparation of imines yielded 2.27 g (53% yield) of the title compound as a yellow-orange oil. ^{1}H NMR (300 MHz): δ 1.21–1.57 (m, 5H), 1.67 (s, 3H), 1.68–1.79 (m, 1H), 1.80–2.01 (m, 4H), 2.03 (s, 3H), 2.34(tt, J= 11.4, 3.3, 1H), 6.54 (d, J=7.7 Hz, 1 H), 6.95 (dt, J=7.5, 1.3 Hz, 1H), 7.06–7.18 (m, 2H).

^{13}C (75 MHz): δ 17.7, 18.1, 26.3, 30.6, 49.3, 118.7, 122.9, 126.5, 126.8, 130.3, 150.5, 175.1. IR (cm^{-1}): 1660. Anal. Calcd for $C_{15}H_{21}N$: C, 83.67; H, 9.83.

N-(2-methylcyclopent-2-enylidene)-4-anisidine: (Table 1, entry 6) The general procedure for preparation of imines yielded 1.30 g (32% yield) of the title compound as a yellow oil. ^1H NMR (300 MHz): δ 1.94 (s, 3 H), 2.38–2.46 (m, 4H), 3.78 (s, 3H), 6.67 (s, 1H), 6.81 (AB, J=9.3 Hz, 2H), 6.86 (AB, J=9.3 Hz, 2H). ^{13}C (75 MHz): δ 11.9, 28.2, 28.6, 55.5, 114.3, 121.1, 146.2, 146.6, 155.9, 179.5. IR (cm^{-1}): 1644. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51. Found: C, 77.83; H, 7.51.

(-)-(4-Methoxy-phenyl)-(2-methyl-cyclopent-2-enyl)-amine: The title compound was prepared by the general procedure for reduction of imines using 8.8 mg (0.0123 mmol) catalyst, 0.55 mL (9.2 mmol) PMHS, 91 mg (0.452 mmol) imine and 0.45 mL (4.5 mmol) isobutylamine. Workup procedure A produced the title compound as a yellow oil (90 mg, 90% yield). Enantiomeric excess was determined to be 98% by GC on a G-TA column (120 °C). ^1H NMR (300 MHz): δ 1.62–1.74 (m, 1H), 1.78 (s, 3H), 2.19–2.43 (m, 3H), 3.30 (br s, 1H), 3.74 (s, 3H), 4.22–4.32 (m, 1H), 5.52 (s, 1H), 6.52 (AB, J=9.1 Hz, 2H), 6.86 (AB, J=9.1 Hz, 2H). ^{13}C (75 MHz): δ 14.6, 30.2, 32.0, 56.1, 63.2, 114.8, 115.2, 127.8, 141.3, 142.6, 152.2. IR (cm^{-1}): 818, 1040, 1241, 1509, 2854, 2952, 3035, 3390. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43. Found: C, 76.56; H, 8.64. $[\alpha]_D$ –86.6 (c 1.19, $CHCl_3$).

N-(2-Octanylidene)-4-anisidine: (Table 1, entry 7) An oven-dried flask equipped with a Dean-Stark trap was charged with p-anisidine (7.5 g, 61 mmol), 2-octanone (8.0 mL, 50 mmol) and toluene (150 mL) under an argon atmosphere. After GC monitoring indicated the reaction was complete, the reaction mixture was concentrated and purified by Kugelrohr distillation to yield 6.89 g (62%) of the title compound as a yellow oil as a 2.6/1 E/Z mixture. ^1H NMR (500 MHz): δ Major: 0.85–0.94 (m, 3H), 1.31–1.41 (m, 5H), 1.61–1.74 (m, 2H), 1.78 (s, 3H), 2.16–2.19 (m, 1H), 2.37–2.42 (m, 2H), 3.78 (s, 3H), 6.63 (AB, J=8.6 Hz, 2H), 6.85 (AB, J=8.6 Hz, 2H); Minor: 0.81-0.85 (m, 3H), 1.13–1.27 (m, 2H), 1.42–1.50 (m, 2H), 3.75 (s, 3H) remainder obscured. ^{13}C (125 MHz): δ (mixture) 14.2, 14.3, 19.5, 22.6, 22.8, 26.2, 27.0, 29.2, 29.4, 31.6, 31.9, 34.1, 42.1, 55.6, 114.3, 120.7, 120.9, 145.0, 156.0, 172.8, 173.8. IR (cm^{-1}): 1656. Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.93. Found: C, 77.00; H, 9.77.

(+)-N-(2-Octanyl)-4-anisidine: The title compound was prepared by the general procedure for reduction of imines using workup procedure A to produce a yellow oil (199 mg, 70% yield). Enantiomeric excess was determined to be 88% by HPLC on an OJ column (0.5% IPA, 1% mix, and hexane at 1 mL/min). ^{1}H NMR (300 MHz): δ 0.81–0.97 (m, 4H), 1.17–1.52 (m, 10 H), 1.61–1.74(m, 2H), 1.78 (s, 3H), 2.10–2.19 (m, 2H), 2.38–2.42 (m, 2H), 3.78 (s, 3H), 6.64 (AB, J=8.6Hz, 2H), 6.84 (AB, J=8.6 Hz, 2H). ^{13}C (75 MHz): δ 14.4, 21.1, 23.0, 26.5, 29.7, 32.2, 37.6, 49.8, 56.1, 115.0, 115.3, 142.3, 152.1. IR (cm^{-1}): 819, 1048, 1180, 1235, 1511, 1617, 2855, 2927, 3023, 3372. Anal. Calcd for $C_{15}H_{25}NO$: C, 76.55; H, 10.71. Found: C, 76.65; H, 10.68. $[\alpha]_D$ + 6.2 (c 1.49, $CHCl_3$).

N-(6-Methyl-2-hept-6-enylidene)-4-anisidine: (Table 1, entry 8) The general procedure for preparation of imines yielded 2.40 g (52% yield) of the title compound as a yellow oil in a 2.3/1 E/Z ratio. ^{1}H NMR (300 MHz): δ 1.52 (s, 3H, minor), 1.65 (s, 3H, major), 1.71 (s, 3H, major), 1.78 (s, 3H, major), 2.13–2.22 (m, 2H), 2.30–2.51 (m, 2H), 3.72 (s, 1H, minor), 3.72 (s, 1H, major,), 4.95–5.01 (m, 1H, minor), 5.18–5.28 (m, 1H, major), 6.63 (AB, J=9 Hz, 2H), 6.84 (AB, J=9 Hz, 2H). ^{13}C (75 MHz): δ Major: 17.8, 19.5, 25.0, 25.8, 33.4, 41.7, 55.3, 114.1, 120.6, 123.4, 132.1, 144.8, 155.7, 171.9; Minor: 17.6, 25.4, 25.6, 26.1, 55.6, 114.1, 120.5, 122.8, 132.7, 144.4, 155.6, 172.6. IR (cm^{-1}): 1660. Anal. Calcd for $C_{15}H_{21}NO$: C, 76.88; H, 9.15. Found: C, 76.62; H, 9.16.

(+)-(4-methoxyphenyl)-(1,5-dimethyl-hex-4-enyl)amine: The title compound was prepared by the general procedure for reduction of imines using workup procedure A to produce a yellow oil (153 mg, 83% yield). Enantiomeric excess was determined to be 90% by HPLC on an OD column (0.3 % IPA, 1.5% mix, and hexane at 0.7 mL/min). ^{1}H NMR (300 MHz): δ 1.17 (d, J=6.3 Hz, 3H), 1.36–1.60 (m, 2H), 1.60 (s, 3H), 1.70 (s, 3H), 2.08 (q, J=7.4 Hz, 2H), 3.07 (br s, 1H), 3.38 (sextet, J=6.0 Hz, 1H), 3.75 (s, 3H), 5.13 (tt, J=7.2, 1.2 Hz, 1H), 6.55 (AB, J=9.0 Hz, 2H), 6.77 (AB, J=9.0 Hz, 2H). ^{13}C (75 MHz): δ 18.0, 21.1, 25.0, 26.0, 37.4, 49.3, 56.0, 114.8, 115.0, 124.2, 132.0, 142.0, 151.8. IR (cm^{-1}): . Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.93. Found: C, 77.13; H, 10.01. $[\alpha]_D$ + 10.0 (c 2.07, $CHCl_3$).

N-(1-Phenyl-ethylidene)-aniline: (Table 2, entry 1) The general procedure for preparation of imines yielded 2.02 g (52% yield) of the title compound as a white solid (mp: 33–34°C (lit.[4] 41°C)). ^{1}H NMR (500 MHz): δ

2.22 (s, 3H), 6.76–6.81 (m, 2H), 7.05–7.10 (m, 1H), 7.31–7.37 (m, 2H), 7.42–7.48 (m, 3H), 7.93–8.00 (m, 2H). ^{13}C (125 MHz): δ 17.6, 119.6, 123.4, 127.4, 128.6, 129.2, 130.7, 139.7, 151.9, 165.7. IR (cm^{-1}): 1629. Anal. Calcd for $C_{14}H_{21}N$: C, 86.12; H, 6.71. Found: C, 85.97; H, 6.71.

N-Phenyl-1-phenyl ethyl amine: The title compound was prepared according to the general procedure for the reduction of imines using workup procedure A to produce a yellow oil. Enantiomeric excess was determined to be 8% by GC analysis on a G-TA column (120°C).

N-(1-phenylpentylidene)-4-anisidine. (Table 2, entry 2) The general procedure for preparation of imines yielded 4.33g (85% yield) of the title compound as a yellow oil as a 6.4/1 E/Z mixture. ^{1}H NMR (500 MHz): δ Major: 0.79 (t, J= 7.5 Hz, 3H), 1.23 (sextet, J=7.7 Hz, 2H), 1.45 (quint, J=7.5 Hz, 2H), 2.62–2.69 (m, 2H), 3.82 (s, 3H), 6.73 (AB, J=8.5 Hz, 2H), 6.90 (AB, J=8.5 Hz, 2H), 7.41–7.48 (m, 3H), 7.84–7.93 (m, 2H); Minor: 0.93 (t, J=7.7 Hz, 2H), 1.57–1.64 (m, 2H), 3.71 (s, 3H), 6.58–6.70 (m, 2H), 7.09–7.14 (m, 1H), 7.22–7.26 (m, 1H), remainder are obscured. ^{13}C (125 MHz): δ 13.9, 23.0, 30.0, 30.4, 55.7, 114.0, 114.4, 120.6, 127.7, 128.0, 128.6, 130.3, 138.9, 144.9, 155.9, 170.8. IR (cm^{-1}): 1626. Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92. Found: C, 79.83; H, 7.92.

N-(4-Methoxyphenyl)-1-phenylpentyl amine. The application of the general procedure for the reduction of imines showed only 25% conversion to the title compound. Analysis of a small aliquot by HPLC using an OD column (1.5% IPA, 1% mix, and hexane at 0.7 mL/min) showed 6% ee.

N-(2',3'-Dihydroindenylidene)-4-anisidine: (Table 2, entry 3) The general procedure for preparation of imines yielded 2.99 g (63% yield) of the title compound as a yellow solid (mp: 71–73 °C). ^{1}H NMR (300 MHz): 1H 2.69–2.74 (m, 2H), 3.03–3.08 (m, 2H), 3.81 (s, 3H), 6.91 (s, 4H), 7.32–7.39 (m, 2H), 7.42–7.47 (m, 1H), 7.93 (d, J=7.6 Hz, 1H). ^{13}C (75 MHz): δ 28.4, 29.9, 55.6, 114.4, 121.4, 123.0, 125.9, 127.3, 132.0, 139.9, 145.6, 150.4, 156.3, 175.2. IR (cm^{-1}): 1640. Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37. Found: C, 81.18; H, 6.39.

(–)-N-(4-Methoxyphenyl)-aminoindan: The title compound was prepared by the general procedure for reduction of imines using workup procedure A to produce a yellow oil (248 mg, 82% yield). Enantiomeric excess was

determined to be 94% by HPLC analysis on a G-TA column (100°C). ^{1}H NMR (300 MHz): δ 1.59 (br s, 1H), 1.86–2.10 (m, 1 H), 2.52–2.68 (m, 1H), 2.86–2.95 (m, 1H), 2.95–3.13 (m, 1H), 3.81 (s, 3H), 5.00 (t, J= 6.7 Hz, 1H), 6.68 (AB, J=8.9 Hz, 2H), 6.81 (AB, J=8.9 Hz, 2H), 7.21–7.35 (m, 3H), 7.39–7.44 (m, 1H). ^{13}C (75 MHz): δ 30.4, 34.4, 56.0, 59.7, 114.8, 115.2, 124.4, 125.0, 126.0, 128.0, 142.2, 143.8, 145.0, 152.3. IR (cm^{-1}): 757, 820, 1038, 1233, 1510, 2830, 2847, 2935, 2993, 3023, 3066, 3373. Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16. Found: C, 80.12; H, 7.07. $[\alpha]_D$ – 44.5(c 1.04, $CHCl_3$).

N-(6'-Methoxy-3',4'-dihydronaphthalen-1'(2H)-ylidene)-4-anisidine:[5] (Table 2, entry 4) According to Periasammy's procedure[6] dichloromethane (25 mL), triethylamine (20 mmol), 6-methoxytetralone (10 mmol), and p-anisidine (12 mmol) were combined in an oven-dried flask under argon. $TiCl_4$ (5 mmol) was added dropwise over 15 min at 0°C. The resulting solution was allowed to warm to room temperature and was stirred for 9 h. The reaction mixture was quenched with a saturated potassium carbonate solution (30 mL), filtered, and the layers separated. The aqueous layer was extracted with methylene chloride (2 X 25 mL). The organic layers were combined, washed with brine (10 mL), and dried over $MgSO_4$. The solvent was removed in vacuo to yield the crude imine, which was purified by Kugelrohr distillation (3.54 g, 63% yield, yellow solid, mp: 114°C (lit[5]: 112.5–113°C)). ^{1}H NMR (500 MHz): 1.88 (quint, J=6.0 Hz, 2H), 2.52 (t, J=6.0 Hz, 2H), 2.86 (t, J=6.0 Hz, 2H), 3.81 (s, 3H), 3.84 (s, 3H), 6.62–6.94 (m, 2H), 6.75 (AB, J=8.6 Hz, 2H), 6.88 (AB, J=8.6 Hz, 2H), 8.25 (d, J=8.7 Hz, 1H). IR (cm^{-1}): 1625. Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81. Found: C, 76.76; H, 6.82.

N-(4-Methoxyphenyl)-6-methoxy-1,2,3,4-tetrahydro-1-naphthylamine: The application of the general procedure for the reduction of imines showed 67% conversion to the title compound. Analysis of a small aliquot by HPLC using an OD column (3% IPA, 1% mix, and hexane at 0.7 mL/min) showed 75% ee.

N-[1-(2'-Methylphenyl)-ethylidene]-aniline: (Table 2, entry 5) The general procedure for preparation of imines using 9.2 mmol ketone yielded 1.35 g (70% yield) of the title compound as a yellow oil in a 1.7/1 E/Z mixture. ^{1}H NMR (500 MHz): 2.09 (s, 3H, minor), 2.14 (s, 3H, major), 2.46 (s, 3H, minor), 2.50 (s, 3H, major) 6.64–6.67 (m, 0.5 H), 6.82–6.89 (m, 1.5 H), 6.98–7.03 (m,

1H), 7.04–7.12 (m, 2H), 7.22–7.29 (m, 2H), 7.22–7.41 (m, 2H). ^{13}C (125 MHz): δ (mixture) 20.0, 20.4, 21.4, 29.5, 119.4, 121.0, 123.6, 123.6, 125.5, 126.0, 127.2, 127.3, 128.2, 128.4, 128.8, 129.2, 130.3, 131.2, 133.1, 135.1, 141.7, 150.5, 151.4, 170.1, 171.2. IR (cm^{-1}): 1641. Anal. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22. Found: C, 85.78; H, 7.20.

N-Phenyl-1-(2'-methylphenyl)ethyl amine: The application of the general procedure for the reduction of imines showed 28% conversion to the title compound. Analysis of a small aliquot by HPLC using an OD column (0.3% isopropanol, 1.5% mix, and hexane at 0.7 mL/min) showed 9% ee.

Crystal data and structure refinement for compound **6**

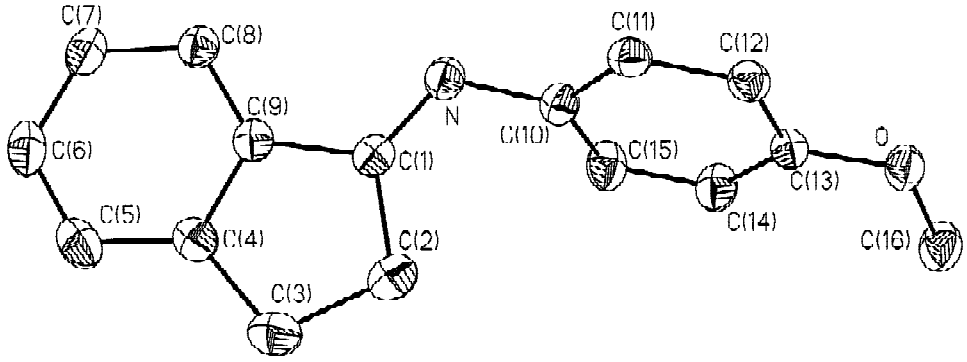

Figure S1: ORTEP Diagram of Compound **6**

Empirical formula	$C_{16}H_{15}NO$
Formula weight	237.29
Temperature	183(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a = 8.25140(10) Å α = 90.804 (2)°
	b = 8.7352(3) Å β = 114.299 (2)°
	c = 9.77970(10) Å γ = 99.761 (2)°
Volume	630.39 (2) $Å^3$
Z	2
Density (calculated)	1.250 Mg/m^3
Absorption coefficient	0.078 mm^{-1}
F(000)	252
Crystal size	0.15 x 0.38 x 0.38 mm

θ range for data collection	2.29 to 23.26°
Limiting indices	$-9 \le h \le 7$, $-9 \le k \le 9$, $-7 \le l \le 10$
Reflections collected	2558
Independent reflections	1739 (R_{int} = 0.0238)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1739 / 0 / 164
Goodness-of-fit on F^2	1.091
Final R indices [$I>2\sigma(I)$]	R1 = 0.0446, wR2 = 0.1064
R indices (all data)	R1 = 0.0500, wR2 = 0.1131
Extinction coefficient	0.071 (10)
Largest diff. peak and hole	0.147 and -0.156 eÅ^{-3}

Table S1: Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [Å^2 x 10^3]. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O	2550 (2)	5370 (2)	1836 (2)	43 (1)
N	5413 (2)	-86 (2)	2825 (2)	39 (1)
C(1)	6949 (3)	-97 (2)	2813 (2)	35 (1)
C(2)	8261 (3)	1232 (2)	2615 (3)	53 (1)
C(3)	9909 (3)	563 (3)	2732 (3)	54 (1)
C(4)	9470 (3)	-1128 (2)	3155 (2)	42 (1)
C(5)	10489 (3)	-2288 (3)	3355 (2)	51 (1)
C(6)	9797 (3)	-3779 (3)	3387 (2)	51 (1)
C(7)	8107 (3)	-4132 (2)	3223 (2)	46 (1)
C(8)	7085 (3)	-2989 (2)	3028 (2)	38 (1)
C(9)	7785 (2)	-1486 (2)	1533 (2)	35 (1)
C(10)	4704 (2)	1313 (2)	2540 (2)	37 (1)
C(11)	4514 (2)	2132 (2)	3682 (2)	36 (1)
C(12)	3788 (2)	3472 (2)	3398 (2)	36 (1)
C(13)	3227 (2)	4016 (2)	1981 (2)	35 (1)
C(14)	3358 (3)	3189 (2)	828 (2)	45 (1)
C(15)	4101 (3)	1848 (2)	1120 (2)	47 (1)
C(16)	2267 (3)	6119 (3)	488 (3)	53 (1)

Table S2: Bond lengths (Å)

O - C(13)	1.377 (2)	O - C(16)	1.429 (2)
N - C(1)	1.274 (2)	N - C(10)	1.425 (2)
C(1) - C(9)	1.471 (3)	C(1) - C(2)	1.520 (3)
C(2) - C(3)	1.532 (3)	C(3) - C(4)	1.509 (3)
C(4) - C(9)	1.390 (3)	C(4) - C(5)	1.393 (3)
C(5) - C(6)	1.382 (3)	C(6) - C(7)	1.389 (3)
C(7) - C(8)	1.383 (3)	C(8) - C(9)	1.390 (3)
C(10) - C(15)	1.387 (3)	C(10) - C(11)	1.394 (3)
C(11) - C(12)	1.384 (3)	C(12) - C(13)	1.387 (3)
C(13) - C(14)	1.382 (3)	C(14) - C(15)	1.393 (3)

Table S3: Bond angles (°)

C(13) - O - C(16)	117.4 (2)	C(1) - N - C(10)	118.7 (2)
N - C(1) - C(9)	123.7 (2)	N - C(1) - C(2)	129.1 (2)
C(9) - C(1) - C(2)	107.2 (2)	C(1) - C(2) - C(3)	106.6 (2)
C(4) - C(3) - C(2)	104.7 (2)	C(9) - C(4) - C(5)	119.7 (2)
C(9) - C(4) - C(3)	111.2 (2)	C(5) - C(4) - C(3)	129.1 (2)
C(6) - C(5) - C(4)	119.1 (2)	C(5) - C(6) - C(7)	120.9 (2)
C(8) - C(7) - C(6)	120.4 (2)	C(7) - C(8) - C(9)	118.6 (2)
C(4) - C(9) - C(8)	121.2 (2)	C(4) - C(9) - C(1)	110.3 (2)
C(8) - C(9) - C(1)	128.4 (2)	C(15)-C(10)-C(11)	118.4 (2)
C(15) - C(10) - N	121.5 (2)	C(11) - C(10) - N	120.0 (2)
C(12)-C(11)-C(10)	120.1 (2)	C(11)-C(12)-C(13)	121.0 (2)
O - C(13) - C(14)	124.6 (2)	O - C(13) - C(12)	115.9 (2)
C(14)-C(13)-C(12)	119.5 (2)	C(13)-C(14)-C(15)	119.3 (2)
C(10)-C(15)-C(14)	121.6 (2)		

Table S4: Anisotropic displacement parameters [$Å^2 \times 10^3$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O	52 (1)	40 (1)	46 (1)	11 (1)	25 (1)	19 (1)
N	45 (1)	36 (1)	41 (1)	6 (1)	20 (1)	11 (1)
C(1)	42 (1)	34 (1)	29 (1)	1 (1)	14 (1)	7 (1)
C(2)	58 (1)	39 (1)	65 (2)	9 (1)	29 (1)	5 (1)
C(3)	46 (1)	55 (1)	60 (2)	5 (1)	24 (1)	0 (1)
C(4)	38 (1)	50 (1)	36 (1)	4 (1)	14 (1)	9 (1)
C(5)	39 (1)	72 (2)	42 (1)	6 (1)	15 (1)	19 (1)
C(6)	59 (1)	59 (1)	39 (1)	10 (1)	19 (1)	33 (1)
C(7)	62 (1)	41 (1)	39 (1)	10 (1)	22 (1)	21 (1)
C(8)	45 (1)	39 (1)	33 (1)	5 (1)	17 (1)	11 (1)
C(9)	39 (1)	39 (1)	26 (1)	2 (1)	11 (1)	10 (1)
C(10)	39 (1)	33 (1)	38 (1)	3 (1)	16 (1)	7 (1)
C(11)	36 (1)	39 (1)	36 (1)	6 (1)	16 (1)	6 (1)
C(12)	38 (1)	35 (1)	36 (1)	0 (1)	18 (1)	5 (1)
C(13)	33 (1)	34 (1)	39 (1)	4 (1)	16 (1)	9 (1)
C(14)	58 (1)	48 (1)	32 (1)	10 (1)	19 (1)	21 (1)
C(15)	62 (1)	48 (1)	36 (1)	1 (1)	22 (1)	22 (1)
C(16)	65 (2)	51 (1)	50 (1)	17 (1)	27 (1)	26 (1)

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