Supplementary Material for

Catalytic Asymmetric Aziridination with a Chiral VAPOL-Boron Lewis Acid

Jon C. Antilla and William D. Wulff*

Department of Chemistry

Searle Chemistry Laboratory

The University of Chicago

Chicago, Illinois 60637

Experimental procedures and spectral data for all new compounds.

All experiments were performed under an argon atmosphere. Flasks were flame-dried and cooled under argon before use. Methylene chloride and toluene were distilled from calcium hydride under nitrogen. Hexanes and ethyl acetate were ACS grade and used as purchased. Reagents were purified by simple distillation or recrystallization with appropriate solvents. Imines were purified by recrystallization from absolute ethanol or pentane/methylene chloride mixtures. Ethyl diazoacetate was used as purchased from Aldrich except in one case of purification by column chromatography. Borane-THF was used as purchased from Aldrich. VAPOL was purified by column chromatography with 9:1 hexanes:ethyl acetate. All aldimines were synthesized by a known procedure.[1] Aziridines were purified by column chromatography with hexanes/ethyl acetate and further by recrystallization from pentane/methylene chloride if desired.

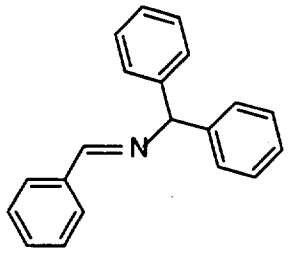
Melting points were determined on a Hoover Unimelt apparatus and are not corrected. IR spectra were taken on a Nicolet 20SX FTIR instrument. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz or a Bruker 500 MHz instrument in $CDCl_3$ unless otherwise noted. $CDCl_3$ was also used as the internal standard for both ^{1}H NMR ($\delta = 7.24$) and ^{13}C NMR ($\delta = 77.0$). Low-resolution mass spectra and high-resolution mass spectra were performed at the University of Illinois, Urbana, IL. Elemental analysis were performed by Galbraith Laboratories, Inc.,

Knoxville, TN. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel plates with F-254 indicator. Visualization was by long wave ultraviolet light, exposure to iodine vapor, or by staining with *p*-anisaldehyde in ethanol/sulfuric acid or phosphobolybdic acid in ethanol. Flash column chromatography was performed with E. Merch silica gel 60 (230-400 mesh).

HPLC was carried out using a Waters M-45 Solvent Delivery System equipped with a Waters Model U6K Universal Liquid Chromatograph Injector, a Waters Model 440 Absorbance detector, and a Spectra-Physics Chromjet Integrator. Chiral HPLC data was obtained through the use of a Diacel Chiralcel OD column.

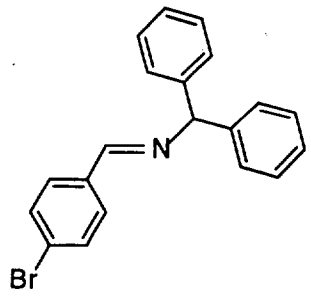
Optical rotations were obtained on a Perkin-Elmer 141 polarimeter at a wavelength of 589 nm (sodium D line) using a 1.0 decimeter cell with a total volume of 1.0 mL. Specific rotations are reported in degrees per decimeter at 23 °C and the concentrations are given in grams per 100 mL in methylene chloride.

A typical experimental procedure for the synthesis of all aldimines: Aldehydes and N-diphenylmethylamine were distilled before use. Solid aldehydes were used as purchased from Aldrich. The N-diphenylmethylamine was typically dissolved in 50 mL of CH_2Cl_2 for each 30 mmol of amine. To this stirred flask, a quantity of 4 g of $MgSO_4$ was added. After 10 min. of stirring, the same 30 mmol quantity of aldehyde was added slowly by syringe. The reaction was stirred from 4 to 16 hours while being monitored by TLC for loss of starting material. Upon completion the reaction contents were gravity filtered and concentrated by rotary evaporation to give the crude imine **8a-8g**, and **8i** as crude solids. These were then recrystalized from EtOH and in one case from pentane:CH_2Cl_2. Imine **8h** was a liquid at room temperature and was used without further purification. All imine yields were from 60-88 % after a single crop upon recrystallization.



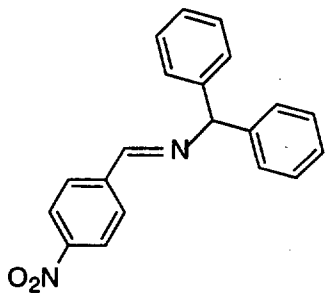
(8a)

N-Benzylidene-1,1-diphenylmethylamine (8a)[2] White crystal; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.64 (s, 1H), 7.2-7.9 (m, 15H), 8.46 (s, 1H).



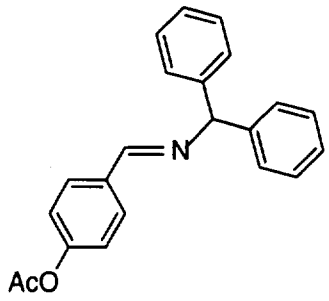
(8b)

N-(4-Bromobenzylidene)-1,1-diphenylmethylamine (8b)[3] White crystal: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.23 (s, 1H), 7.15-7.35 (m, 10 H), 7.47 (d, 2H, J = 7 Hz), 7.64 (d, 2H, J = 7 Hz), 8.28 (s, 1H).



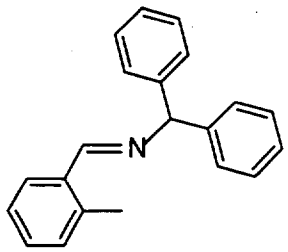
(8c)

N-(4-Nitrobenzylidene)-1,1-diphenylmethylamine (8c)[3] Off-white crystal: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.76 (s, 1H), 7.3-7.4 (m, 10H), 8.08 (d, 2H, J = 8 Hz), 8.31 (d, 2H, J = 8 Hz), 8.52 (s, 1H).



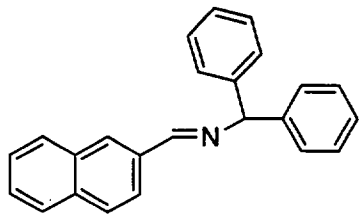
(8d)

N-(4-Acetoxybenzylidene)-1,1-diphenylmethylamine (8d)[4] White crystal: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 5.69 (s, 1H), 7.00 (d, 2H, J = 8 Hz), 7.18 (d, 2H, J = 8 Hz), 7.25-7.45 (m, 8H), 7.93 (Br d, 2H), 8.42 (s, 1H).



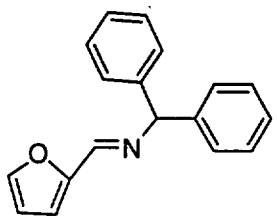
(8e)

N-(*o*- Tolylbenzylidene)-1,1-diphenylmethylamine (8e) White crystal: mp 99-100 °C (EtOH); IR (film) 1640 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.48 (s, 3H), 5.52 (s, 1H), 7.1-7.4 (m, 12H), 7.93 (d, 1H, J = 7 Hz), 8.67 (s, 1H). ^{13}C NMR (125.8 MHz) δ = 60.63, 77.92, 127.13, 127.34, 128.45, 128.31, 130.61, 138.28, 139.88, 144.74, 161.56.



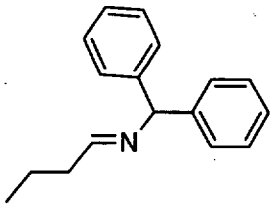
(8f)

N-(2-Naphthylidene)-1,1-dipenylmethylamine (8f) White crystal: mp 149-150 °C ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.62 (s, 1H), 7.1-7.5 (m, 12H), 7.81 (m, 3H), 8.02 (s, 1H), 8.10 (d, 1H, J = 7 Hz), 8.52 (s, 1H).



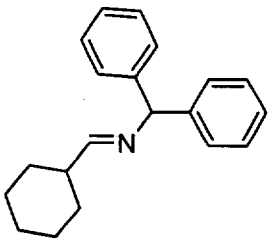
(8g)

N-(Furan-2-ylmethylidine)-1,1-diphenylmethylamine (8g)[2] White crystal: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.51 (s, 1H), 6.40 (d,d. 1H, J = 2 Hz and J = 3.5 Hz), 6.73 (d, 1H, J = 3.5 Hz), 7.1-7.35 (m, 10H), 7.46 (d, 1H, J = 2 Hz), 8.12 (s, 1H).



(8h)

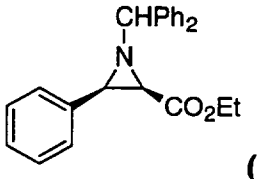
N-Propylidine-1,1-diphenylmethylamine (8h) light yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.95 (t, 3H, J = 7.5 Hz), 1.60 (q, 2H, J = 7.5 Hz), 2.33 (d,t. 2H, J = 7.5 Hz and J = 5 Hz), 5.35 (s, 1H), 7.1-7.4 (m, 10H), 7.84 (t, 1H, J = 5 Hz).



(8i)

N-(Cyclohexylmethylidene)-1,1-diphenylmethylamine (8i)[2] white crystal: ^{1}H NMR (500 MHz, $CDCl_3$)): δ = 1.1-1.9 (m, 10H), 2.20 (bs, 1H), 5.21 (s, 1H), 7.0-7.6 (m, 10H), 7.59 (d, 1H, J = 5.5 Hz).

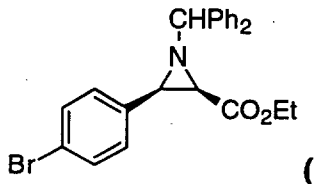
Experimental procedure to form the boron-VAPOL catalyst (14) To a flame-dried Schlenk flask cooled under argon was added 54 mg of S or R-VAPOL (0.10 mmol) which was dissolved in 2 mL of CH_2Cl_2. To this flask 300 μL of 1M BH_3-THF (0.30 mmol) was added. This stirred mixture was heated to 55°C for 1 hour and then a vacuum (0.5 mm Hg) was applied for one-half hour with continual heating at 55°C. The catalyst **14** was then used by dissolving in appropriate solvent and transfering to reaction flask.



(10a)

A typical asymmetric aziridination procedure for cis-aziridines : Cis-1-(N-1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-phenylaziridine (10a) The catalyst **14** from 54 mg (0.10 mmol) of S-VAPOL was dissolved in 1 mL of toluene and transferred via syringe to a 10 mL flame dried flask with stir bar at room temperature. To this flask was first added 115 μL (1.1 mmol) of ethyl diazoacetate by syringe. After five min of stirring 271 mg (1.00 mmol) of imine **8a** in 1 mL of toluene was added via syringe pump addition over 3 hours. Two additional hours of stirring were allowed before the reaction contents were diluted with 10 mL of ethyl ether and washed twice with 20 mL portions of brine. The organic layer was dried over $MgSO_4$, gravity filtered, and concentrated by rotary evaporation to give the crude aziridine as a off-white solid. The cis/trans ratios were found by comparing the ^1H NMR integration values for the relative aziridine methine protons. The cis (7-8 Hz) and the trans (2-3 Hz) coupling constants were used to differentiate the two isomers. Acyclic enamine products (**11a-i**, **12a-i**) were also determined by ^1H NMR of the crude reaction mixture with the N-H proton integration relative to the integration of the aziridine methine protons. The solid crude reaction mixture was purified by column chromatography (50 mm column, 6" SiO_2, 9 :1

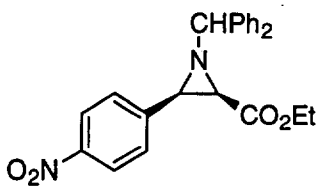
hexanes:ethyl acetate) to give aziridine **10a** as a white solid (275 mg) in 77 % isolated yield. An Optical purity of 97 % ee was determined by HPLC analysis using a chiralcel OD column with 9:1 hexanes:2-propanol as the eluent, flow rate = 1.0 mL/min. The respective racemic aziridine was made with BF_3-Et_2O as the catalyst[5] under similar reaction conditions for confirmation of retention times. Retention times: t_r = 5.4 min (minor enantiomer) and t_r = 10.5 min (major enantiomer) were found by chiral HPLC. Cis/trans ratio: >50:1. Side products: <1 % **11a** and <1 % **12a**. White solid, mp 127.5-128.5 (hex/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (t, 3H, J = 7 Hz), 2.76 (d, 1H, J = 7 Hz), 3.30 (d, 1H, J = 7 Hz), 4.00 (m, 2H), 4.08 (s, 1H), 7.25 (m, 2H), 7.33 (m, 5H), 7.41 (t, 2H, J = 7 Hz), 7.49 (d, 2H, J = 7 Hz), 7.57 (d, 2H, J = 7 Hz), 7.69 (d, 2H, J = 7 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 13.88, 46.34, 47.98, 60.48, 77.64, 127.17, 127.17, 127.27, 127.35, 127.49, 127.71, 127.74, 128.43, 135.00, 142.35, 142.48, 167.65. IR (thin film, cm^{-1}) 3030 (m), 2981 (m), 1737 (s), 1600 (s), 1200 (s), 1097 (s). MS (EI) m/z (relative intensity): 357 M^+ (<1), 190 (100), 167 (60), 117 (34); m/z calcd for $C_{24}H_{23}NO_2$ 357.1729, found 357.1738. Anal calcd for $C_{24}H_{23}NO_2$: C, 80.64; H, 6.48; N, 3.92. Found: C, 80.92; H, 6.70; N, 3.88. Specific rotation: $[\alpha]^{23}_D$ = +38.2° C=2 (CH_2Cl_2).



(10b)

Cis-1-(1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-(*p*-Bromophenyl)-aziridine (10b) The same procedure as with **10a** was followed with these changes: 350 mg (1.00 mmol) of Imine **8b** was dissolved in 3 mL of toluene and added to 54 mg (0.10 mmol) of the S-VAPOL derived catalyst **14**/ ethyl diazo acetate mixture in 1 mL of toluene. The reaction stopped 1 hour after the 3 hour syringe pump addition (rxn time 4 hours). The product was a white solid (278 mg) in 64 % isolated yield and an optical purity of 97 % ee. Cis/trans ratio: 16:1. Side products: 2.0 % **11b** and 3.9 % **12b**. Chiral HPLC: t_r = 5.3 min (minor isomer) and t_r = 11.2 min (major isomer). White solid, mp 150-151 °C (hex/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.07 (t, 3H, J = 7 Hz), 2.74 (d, 1H, J = 7 Hz), 3.19 (d, 1H, J = 7 Hz), 4.00 (q, 2H, J = 7 Hz), 4.01 (s, 1H), 7.23 (t, 1H, J = 7 Hz), 7.29-7.45 (m, 9H), 7.50 (d, 2H, J = 7 Hz), 7.65 (d, 2H, J = 7 Hz). ^{13}C NMR

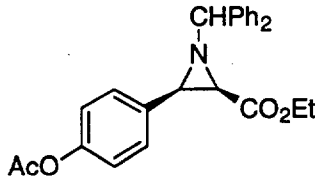
(125.8 MHz, $CDCl_3$): δ 13.96, 46.44, 47.31, 60.67, 77.55, 121.31, 127.11, 127.25, 127.40, 127.46, 128.49, 129.52, 130.86, 134.06, 142.12, 142.29, 167.37. IR (thin film, cm^{-1}) 1734 (s), 1201 (s), 1067 (m). MS (EI) m/z (relative intensity): 437 M^+ (<1, ^{81}Br), 435 M^+ (<1, ^{79}Br), 270 (42) ^{81}Br, 268 (43) ^{79}Br, 167 (100) ^{81}Br, 165 (19) ^{79}Br; m/z calcd for $C_{24}H_{22}NO_2{}^{81}Br$ 437.0813, found 437.0817. Anal calcd for $C_{24}H_{22}NO_2Br$: C, 66.06; H, 5.27; N, 3.09. Found: C, 66.06; H, 5.08; N, 3.21. Specific rotation: $[\alpha]^{23}_D$ = +10.9° C=2 (CH_2Cl_2).



(10c)

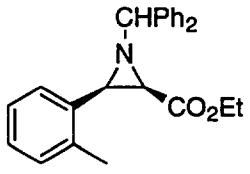
Cis-1-(1,1-diphenylmethyl)-(2R)-carboxyethyl-(3r)-(*p*- Nitrophenyl)-aziridine (10c)

The same procedure as with **10a** was followed with the these changes: 316 mg (1.00 mmol) of imine **8c** was dissolved in 2 mL toluene and added to the catalyst **14** derived from 54 mg (0.10 mmol) of S-VAPOL in 1 mL of toluene with 115 μL (1.1 mmol) of ethyl diazoacetate at 0 °C. After 3 hours of syringe pump addition of the imine at 0 °C the reaction was warmed back to room temperature and stirred for another 21 hours (24 hr rxn time). An isolated yield of 68 % (272 mg) was found with an optical purity of 91 % ee. Cis/trans ratio: 11:1. Side products: <1 % **11c** and <1 % **12c**. Chiral HPLC: t_r = 9.0 min (minor isomer) and t_r = 12.2 min (major isomer). Off-white solid, mp 133-135 °C (hex/EtOAc); ^1H NMR (500 MHz, $CDCl_3$): δ = 1.06 (t, 3H, J = 7 Hz), 2.84 (d, 1H, J = 7 Hz), 3.30 (d, 1H, J = 7 Hz), 3.98 (q, 2H, J = 7 Hz), 4.04 (s, 1H), 7.23 (t, 1H, J = 7 Hz), 7.29 (m, 3H), 7.38 (t, 2H, J = 7 Hz), 7.55 (d, 2H, J = 8 Hz), 7.63 (m, 4H), 8.15 (d, 2H, J = 8 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.96, 29.64, 46.88, 47.02, 60.89, 123.00, 127.02, 127.34, 127.40, 127.64, 128.57, 128.60, 128.74, 141.09, 142.03, 142.49, 166.92. IR (thin film, cm^{-1}) 2980 (w), 1742 (s), 1605 (s), 1520 (s), 1346 (s), 1340 (s), 1202 (s). MS (EI) m/z (relative intensity): 402 M^+ (<1), 167 (100), 165 (12), 152 (8), 89 (3); m/z calcd for $C_{24}H_{22}N_2O_4$ 402.1580, found 402.1574. Anal calcd for $C_{24}H_{22}N_2O_4$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.58; H, 5.71; N, 6.82. Specific Rotation: $[\alpha]^{23}_D$ = -10.0° C=1 (CH_2Cl_2).



(10d)

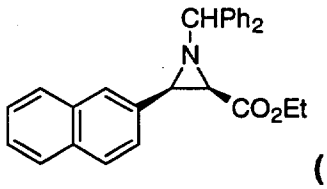
Cis-1-(N-1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-(*p*- acetoxyphenyl)-aziridine (10d) The same procedure as with **10a** was followed with the these changes: 329 mg (1.00 mmol) of imine **8d** was added in 1 mL of toluene by syringe pump for 3 hours to the 54 mg (0.10 mmol) of S-VAPOL derived catalyst **14**/ethyl diazoacetate 1.15 μL (1.1 equ.) mixture in 1 mL of toluene at room temperature. The reaction was stirred for another 13 hours to completion (16 hour rxn time). An isolated yield of 67 % (278 mg) with a 96 % ee was found. Cis/trans ratio: 40:1. Side products: 3.6 % **11d** and 3.0 % **12d**. Chiral HPLC retention times: t_r = 7.5 min (minor isomer) and 10.9 min (major isomer). White solid, mp 148-150 °C (hex/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05 (t, 3H, J = 7 Hz), 2.29 (s, 3H), 2.74 (d, 1H, J = 7 Hz), 3.26 (d, 1H, J = 7 Hz), 3.99 (q, 2H, J = 7 Hz), 4.00 (s, 1H), 7.05 (d, 2H, J = 7 Hz), 7.24 (t, 1H, J = 7 Hz), 7.31 (m, 3H), 7.39 (t, 2H, J = 8 Hz), 7.48 (d, 2H, J = 8 Hz), 7.53 (d, 2H, J = 8 Hz), 7.68 (d, 2H, J = 8 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$): 13.85, 20.69, 46.34, 47.11, 60.56, 77.53, 120.87, 127.08, 127.14, 127.40, 128.40, 128.45, 132.52, 142.20, 142.30, 149.87, 167.50, 169.22. IR (thin film, cm^{-1}) 3062 (w), 2990 (w), 1752 (s), 1738 (s), 1199 (s). MS (EI) m/z (relative intensity): 415 M^+ (2), 248 (93), 206 (100), 167 (71), 165 (23), 133 (20); m/z calcd for $C_{26}H_{25}NO_4$ 415.1784, found 415.1786. Anal calcd for $C_{26}H_{25}NO_4$: C, 75.16; H, 6.06; N, 3.37. Found: C, 74.99; H, 6.20; N, 3.28. Specific rotation: $[\alpha]^{23}_D$ = +29.9° C=1 (CH_2Cl_2).



(10e)

Cis-1-(N-1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-(*o*- tolyl)-aziridine (10e) The same procedure as with **10a** was followed with the these changes: Imine **8e**, 607 mg (2 mmol),

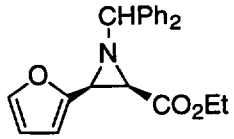
was added in 4 mL of toluene by 3 hour syringe pump addition to the 54 mg (0.10 mmol) of S-VAPOL derived catalyst **14**/ethyl diazoacetate 230 μL (2.2 mmol) mixture in 1 mL of toluene at room temperature (5 mol % in catalyst). The reaction was allowed to stir for another 21 hours to completion (24 hr rxn time). The reaction gave 784 mg of **10e** as a white solid in 51 % yield and an optical purity of 98 % ee. Cis/trans ratio: 3:1. Side products: 8.1 % **11e** and 6.5 % **12e**. Chiral HPLC: t_r = 6.7 min (minor isomer) and t_r = 8.5 min (major isomer) with 40:1 hexanes:2-propanol as the eluent. mp 162-163 °C (hex/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (t, 3H, J = 7 Hz), 2.43 (s, 3H), 2.86 (d, 1H, J = 7 Hz), 3.34 (d, 1H, J = 7 Hz), 4.00 (q, 2H, J = 7 Hz), 4.07 (s, 1H), 7.15 (d, 1H, J = 7 Hz), 7.22 (m, 2H), 7.28 (m, 1H), 7.38 (m, 3H), 7.45 (t, 2H, J = 7 Hz), 7.65 (d, 2H, J = 7 Hz), 7.68 (d, 1H, J = 7 Hz), 7.75 (d, 2H, J = 7 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 13.73, 18.70, 45.53, 46.81, 60.33, 77.76, 125.26, 127.04, 127.06, 127.43, 127.63, 128.39, 128.41, 128.44, 129.01, 133,05, 135.90, 142.33, 142,48, 167.80. IR (thin film, cm^{-1}) 3054 (M), 2982 (m), 1740 (s), 1600 (m), 1184 (s). MS (EI) m/z (relative intensity): 371 M^+ (<1), 204 (100), 167 (43), 131 (41); m/z calcd for $C_{25}H_{25}NO_2$ 371.1889, found 371.1888. Anal calcd for $C_{25}H_{25}NO_2$: C, 80.83; H, 6.78; N, 3.37. Found: C, 80.84; H, 6.94; N, 3.64. Specific rotation: $[\alpha]^{23}_D$ = +37.0° C=2 (CH_2Cl_2).



(10f)

Cis-1-(1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-2'-naphthylaziridine (10f) The same procedure as with **10a** was followed with the these changes: Imine **8f**, 321 mg (1.00 mmol), was dissolved in 1 mL of CH_2Cl_2 and added by syringe pump over 3 hours to the 27 mg of S-VAPOL (0. 050 mmol) derived catalyst **14**/ethyl diazoacetate 115 μL (1.1 mmol) mixture in 1 mL of CH_2Cl_2 at room temperature. The reaction was stopped 1 hour later (4 hour rxn time) to provide the title compound in a 70 % isolated yield (285 mg) with an optical purity of 97 % ee. Cis/trans ratio: 30:1. Side products: 1.5 % **11f** and 1.4 % **12f**. Chiral HPLC: t_r = 5.5 min (minor isomer) and 10.9 min (major isomer). White solid; m.p. 150-153 °C (hex/EtOAc); ^{1}H NMR (500

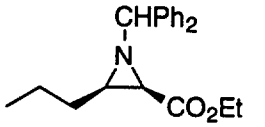
MHz, $CDCl_3$): δ 1.00 (t, 3H, J = 7 Hz), 2.84 (d, 1H, J = 7 Hz), 3.43 (d, 1H, J = 7 Hz), 3.95 (q, 2H, J = 7 Hz), 4.09 (s, 1H), 7.22 (t, 1H, J = 7 Hz), 7.32 (m, 3H), 7.42 (t, 2H, 7 Hz), 7.45 (m, 2H), 7.61 (m, 3H), 7.72 (d, 2H, 8 Hz), 7.85 (m, 3H), 7.97 (s, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 13.90, 46.70, 48.19, 60.56, 77.71, 125.07, 126.76, 125.82, 126.82, 127.22, 127.25, 127.32, 127.37, 127.48, 127.59, 127.84, 128.45, 128.47, 132.62, 132.84, 132.93, 142.33, 142.44, 167.66. IR (thin film, cm^{-1}) 3040 (w), 3000 (w), 1735 (s), 1599 (m), 1192 (s). MS (EI) m/z (relative intensity): 407 M^+ (3), 240 (91), 167 (100), 140 (9); m/z calcd for $C_{28}H_{25}NO_2$ 407.1889, found 407.1889. Specific rotation: $[\alpha]^{23}_D$ = -6.9° C=1 (CH_2Cl_2).



(10g)

Cis-1-(1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-(2'-furyl)-aziridine (10g) The same procedure as with **10a** was followed with the these changes: Imine **8g**, 261 mg (1.00 mmol), was dissolved in 4 mL of toluene and added by syringe pump over 3 hours to the 54 mg of (0.10 mmol) S-VAPOL derived catalyst **14**/ethyl diazoacetate 115 μL (1.1 mmol) mixture at room temperature. The reaction was stopped 5 hours later (8 hour rxn time) and a 55 % yield of **10g** (191 mg) was obtained with an optical purity of 94.5 % ee. Cis/trans ratio: 16:1. Side products: <1 % **11g** and <1 % **12g**. Chiral HPLC: t_r = 5.2 min (minor isomer) and t_r = 11.8 min (major isomer). White solid, m.p 104-105 °C (hex/EtOAc); ^1H NMR (500 MHz, $CDCl_3$): δ 1.17 (t, 3H, J = 7 Hz), 2.73 (d, 1H, J = 7 Hz), 3.17 (d, 1H, J = 7 Hz), 3.97 (s, 1H), 4.12 (m, 2H), 6.32 (m, 1H), 6.36 (d, 1H, J = 4 Hz), 7.22-7.37 (m, 7H), 7.51 (d, 2H, J = 7 Hz), 7.58 (d, 2H, J = 7 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$): 14.01, 41.64, 45.40, 60.83, 77.47, 107.99, 107.38, 127.25, 127.31, 127.39, 127.40, 128.42, 128.47, 141.91, 141.97, 142.07, 149.56, 167.44. IR (thin film, cm^{-1})

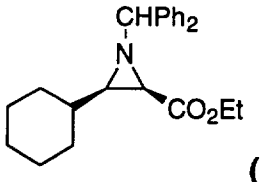
3100 (m), 1738 (s), 1208 (s), 710 (m). MS (EI) m/z (relative intensity): 347 M^+ (<1), 180 (100), 167 (71), 152 (26), 97 (12); m/z calcd for $C_{22}H_{21}NO_3$ 347.1521, found 347.1528. Anal calcd for $C_{22}H_{21}NO_3$ C, 76.06; H, 6.09; N, 4.03. Found: C, 75.80; H, 6.26; N, 3.97. Specific rotation: $[\alpha]^{23}_D$ = +7.1° C=1 (CH_2Cl_2).



(10h)

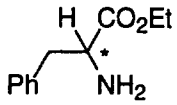
Cis-1-(1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-n-propylaziridine (10h) The same procedure as with **10a** was followed with the these changes: Imine **8h**, 237 mg (1.00 mmol), was dissolved in 1 mL of toluene and added by syringe pump over 3 hours to the 54 mg (0.10 mmol) of S-VAPOL derived catalyst **14**/ethyl diazoacetate 115 µL (1.1 mmol) mixture at 0 °C. The reaction was allowed to warm to room temperature and stopped 4 hours later (7 hour rxn time) and a 54 % yield (128 mg) of **10h** was obtained with an optical purity of 91 % ee. Cis/trans ratio: >50:1. Side products: 9.6 % **11h** and 6.4 % **12h**. Chiral HPLC: t_r = 4.9 min (minor isomer) and t_r = 10.4 min (major isomer). White solid, mp 104-105 °C (hex/EtOAc); ^1H NMR (500 MHz, $CDCl_3$): δ 0.74 (t, 3H, J = 7 Hz), 1.05 (m, 1H), 1.10 (m, 1H), 1.25 (t, 3H, J = 7 Hz), 1.45 (m, 1H), 1.52 (m, 1H), 2.05 (q, 1H, J = 7 Hz), 2.28 (d, 1H, J = 7 Hz), 3.66 (s, 1H), 4.17 (m, 2H), 7.27 (m, 2H), 7.33 (m, 4H), 7.39 (d, 2H, J = 7 Hz), 7.49 (d, 2H, J = 7 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$): 13.57, 14.21, 20.26, 29.85, 43.32, 46.62, 60.62, 77.88, 126.94, 127.10, 127.30, 127.82, 128.27, 128.29, 142.42, 142.77, 169.46. IR (thin film, cm^{-1}) 3040 (m), 2959 (m), 1732 (s), 1194 (s). MS (EI) m/z (relative intensity): 323 M^+ (2), 167 (100), 156 (91), 152 (15), 128 (23) 82 (17); m/z calcd for $C_{21}H_{25}NO_2$ 323.1889, found 3231888. Anal calcd for $C_{21}H_{25}NO_2$

C, 77.98; H, 7.79; N, 4.33. Found: C, 78.06; H, 7.94; N, 4.21. Specific rotation: $[\alpha]^{23}_{D}$ = +89.5° C=1 (CH_2Cl_2).



(10i)

Cis-1-(1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-cyclohexylaziridine (10i) The same procedure as with **10a** was followed with the these changes: Imine **8i**, (1.00 mmol) was dissolved in 1 mL of toluene and added by syringe pump over 2 hours to the 54 mg (0.10 mmol) of the S-VAPOL derived catalyst **14**/ethyl diazoacetate 115 µL (1.1 mmol) mixture at room temperature. The reaction was stopped 1 hour after the slow addition (3 hour rxn time) and a 72 % yield (261 mg) of **10i** was obtained with an optical purity of 96 % ee. Cis/trans ratio: 35:1. Side products: <1 % **11i** and <1 % **12i**. Chiral HPLC: t_r = 9.9 min (minor isomer) and t_r = 16.72 min (major isomer) with 40:1 hexanes:2-propanol as the eluent. White solid, mp 162.5-163 °C (hex/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.52 (d,q. 1H, J = 3 Hz, J = 10 Hz), 0.95-1.66 (m, 10H), 1.28 (t, 3H, J = 7 Hz), 1.83 (d,d. 1H, J = 3 Hz, J = 7 Hz), 2.29 (d, 1H, J = 7 Hz), 3.63 (s, 1H), 4.25 (m, 2H), 7.24 (m, 2H), 7.31 (m, 4H), 7.37 (m, 2H), 7.45 (d, 2H, J = 7 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$): 14.27, 25.34, 25.53, 30.11, 30.71, 36.27, 43.39, 52.12, 60.67, 78.18, 126.80, 126.82, 127.06, 127.49, 128.26, 128.30, 128.35, 142.33, 142.72, 169.63. IR (thin film, cm^{-1}) 2927 (m), 2917 (m), 2850 (m), 1731 (s), 1190 (s), 1180 (s). MS (EI) m/z (relative intensity): 363 M^+ (1), 196 (100), 167 (64), 102 (18), 95 (29). Anal calcd for $C_{24}H_{29}NO_2$ C, 79.44; H, 8.07; N, 3.64. Found: C, 79.30; H, 8.04; N, 3.85. Specific rotation: $[\alpha]^{23}_{D}$ = +137.3° C=1 (CH_2Cl_2).



(15a)

Procedure for the hydrogenation of 10a to give D-phenyl alanine ethyl ester (15a)[6] Aziridine **10a** with 97 % ee was recrystallized once from CH_2Cl_2/pentane (1:15) to give a white cotton-like solid which was determined to be 99.2 % ee by chiral HPLC. This enriched **10a**, 125 mg (0.50 mmol) was then dissolved in a 5 mL solution of formic acid (5 v/v %) in methanol and added via cannula to 0.016 g (0.15 mmol) of palladium black in 0.5 mL of the 5 % formic acid/methanol solution. The reaction stirred for 24 hours and was worked-up by gravity filtration, rotary evaporation and stirring in 25 mL saturated carbonate solution for 1 hour followed by partitioning into two successive 20 mL methylene chloride extraction's. The organic layers were combined, dried over $MgSO_4$, and reduced by rotary evaporation to give the crude amino acid ethyl ester. This ester was purified by column chromatography on SiO_2 with acetonitrile:MeOH 20:1 as the eluent. Compound **15a** was found in an 80 % yield (54 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.22 (t, 3H, J = 7Hz), 1.72 (br s, 2H), 2.85 (d,d. 1H, J = 8 Hz and J = 13.5 Hz), 3.07 (d,d. 1H, J = 13.5 Hz and J = 5 Hz), 3.71 (d,d. 1H, J = 8 Hz and J = 5 Hz), 4.14 (q, 2H, J = 7Hz), 7.15-7.35 (m, 5H). Specific rotation found: $[\alpha]^{23}_D$ = -23.0° C=3.2 (EtOH). Literature[7] rotation: $[\alpha]^{23}_D$ = +23.8° C=3.2 (EtOH) for L-phenyl alanine ethyl ester.

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