Supporting Information for:

Catalytic Asymmetric Aziridination with Aryl Borate Catalysts Derived from VAPOL and VANOL Ligands

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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 pentane/methylene chloride mixtures. Ethyl diazoacetate was used as purchased from Aldrich. 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 purified by recrystallization from pentane/methylene chloride if desired.

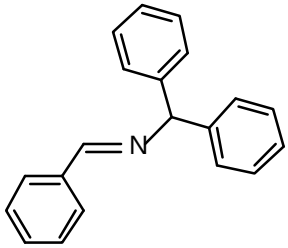
Melting points were determined on a Hoover Unimelt apparatus and are not corrected. IR spectra were taken on a Nicolet 20SX FTIR instrument. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz or a Bruker 500 MHz instrument in $CDCl_3$ unless otherwise noted. $CDCl_3$ was also used as the internal standard for both ^{1}H NMR (δ = 7.24) and ^{13}C NMR (δ = 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 phosphomolybdic acid in ethanol. Flash column chromatography was performed with E. Merck 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-H column.

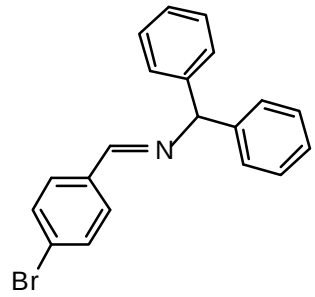
Optical rotations were obtained on a Perkin-Elmer 141 polarimeter at a wavelength of 589 nm (sodium D line) using a 1.0 decimeter cell with a total volume of 1.0 mL. Specific rotations are reported in degrees per decimeter at 23 °C and the concentrations are given in grams per 100 mL in methylene chloride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

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 over a few minutes 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 imines **1a-1f**, **1h**-**1i** as crude solids. These imines were then recrystallized from pentane:CH_2Cl_2. Imine **1g** 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.



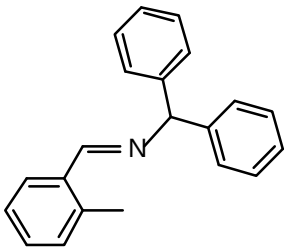
(1a)

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



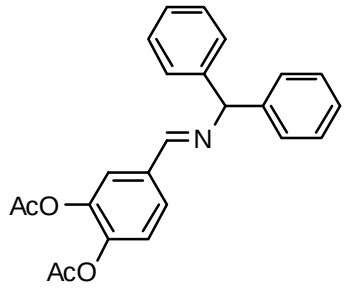
(1b)

N-(4-Bromobenzylidene)-1,1-diphenylmethylamine[3] **(1b)** 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).



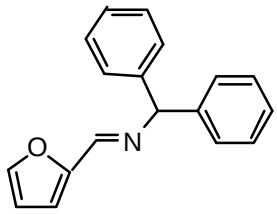
(1c)

N-(*o*-Tolylbenzylidene)-1,1-diphenylmethylamine[4] **(1c)** White crystal: mp 99-100 °C (Pentane/CH_2Cl_2); ^{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).



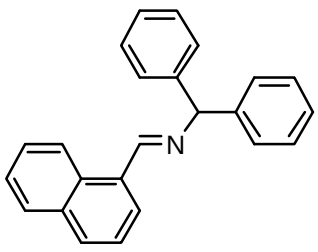
(1d)

N-(3,4-benzylidene)-1,1-diphenylmethylamine (1d) White solid: mp 138-139 °C (pentane/CH_2Cl_2): IR (film) 1775 cm^{-1}, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 2.30 (s, 3H), 5.62 (s, 1H), 7.24 (m, 3H), 7.33 (t, 4H, J = 8 Hz), 7.38 (d, 4H, J = 8 Hz), 7.68 (d,d, 1H J = 8 Hz, 2 Hz), 7.77 (d, 1H, J = 2 Hz), 8.37 (s, 1H); ^{13}C NMR (100.6 MHz) δ 20.64, 20.70, 77.62, 122.88, 123.60, 126.99, 127.11, 127.68, 128.50, 135.16, 142.44, 143.59, 144.07, 158.85, 168.02, 168.22; mass spectrum (EI) *m/z* (relative intensity): 387 M^+ (10), 167 (100); *m/z* calcd for $C_{24}H_{21}NO_4$ 387.1471; found 387.1469. Anal calcd for $C_{24}H_{21}NO_4$: C, 74.46; H, 5.47; N, 3.62. Found: C, 74.17; H, 5.66; N, 3.58.



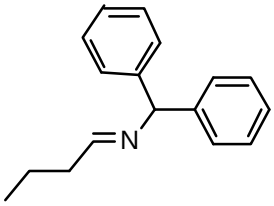
(1e)

N-(Furan-2-ylmethylidine)-1,1-diphenylmethylamine[2] **(1e);** White crystal: ^1H 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).



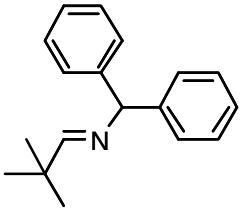
(1f)

N-(1-Naphthylidene)-1,1-diphenylmethylamine (1f) White solid: mp 105 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.62 (s, 1H), 7.18-7.55 (m, 12 H), 7.84-7.91 (m, 3H), 9.00 (s, 1H), 9.06 (d, 1H, J = 7 Hz).



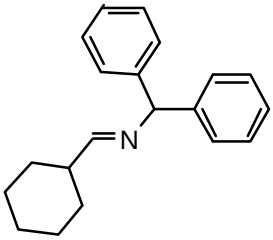
(1g)

N-Propylidine-1,1-diphenylmethylamine[4] **(1g)** 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).



(1h)

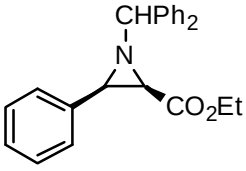
N-(1,1-dimethylethylidene)-1,1-diphenylmethylamine (1h) White solid: mp 51-51.5 °C (pentane): IR (film) 1666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 9H), 5.50 (s, 1H), 7.34 (t, 2H, J = 7 Hz), 7.44 (t, 4H, J = 7 Hz), 7.49 (d, 4H, J = 7 Hz), 7.85 (s, 1H); ^{13}C NMR (100.6 MHz) δ 26.94, 36.38, 77.36, 126.68, 127.44, 128.25, 144.23, 171.48; mass spectrum (EI) *m/z* (relative intensity): 251 M^{+} (<1), 167 (100); *m/z* calcd for $C_{18}H_{21}N$ 251.1674, found 251.1665. Anal calcd for $C_{18}H_{21}N$: C, 86.08; H, 8.43; N, 5.58. Found: C, 85.82; H, 8.58; N, 5.53.



(1i)

N-(Cyclohexylmethylidene)-1,1-diphenylmethylamine (1i)[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 catalysts: To a flame-dried Schlenk flask cooled under argon was added either 54 mg (0.10 mmol) of VAPOL (S or R) or 44 mg (0.10 mmol) of VANOL (S or R) which was then dissolved in 2 mL of CH_2Cl_2. To this flask either 300 µL of 1M BH_3-THF (0.30 mmol) or 0.30 mmol of the respective borate 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 **9** was then used by dissolving in appropriate solvent and transferring to the reaction flask.

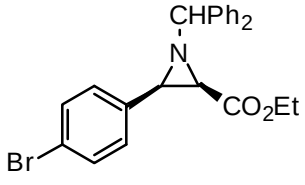


(3a)

A typical asymmetric aziridination procedure for cis-aziridines : Cis-1-(N-1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-phenylaziridine[4] **(3a)**

The catalyst **9** from 54 mg (0.10 mmol) of S-VAPOL was dissolved in 1 mL of CH_2Cl_2 and transferred via syringe to a 10 mL flame dried flask with stir bar at room temperature. Imine **1a** (279 mg, 1.0 mmol) was then dissolved in 1 mL of CH_2Cl_2 and added via syringe to the catalyst

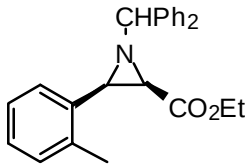
solution. Stirring for 10 minutes gave an orange solution. To this solution was then rapidly added 115 μL (1.1 mmol) of ethyl diazoacetate (EDA) by syringe. Bubbling was observed a few seconds after EDA addition and continued for about 15 minutes. The reaction was monitored by TLC and stopped after 30 minutes. The reaction contents were then transferred to a 100 mL RB flask, diluted with 25 mL of hexanes and the solvent removed by rotary evaporation to give the crude aziridine as a off-white solid. The *cis/trans* ratios were found by comparing the ^{1}H 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 (**4a** and **5a**) were also determined by ^{1}H NMR of the crude reaction mixture by N-H proton integration relative to the integration of the aziridine methine protons. The crude aziridine was purified by column chromatography (50 mm column, 6" SiO_2, 9:1 hexanes:ethyl acetate) to give aziridine **3a** as a white solid (289 mg, 0.81 mmol) in 81 % isolated yield. An optical purity of 95 % *ee* was determined by HPLC analysis using a chiralcel OD-H column with 9:1 hexanes:2-propanol as the eluent, flow rate = 0.7 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: R_t = 4.25 min (minor enantiomer) and R_t = 7.68 min (major enantiomer). *Cis/trans* ratio: >50:1. Side products: 4.3 % **4a** and 1.4 % **5b**. All characterization details for **3a** can be found in reference 4.



(3b)

Cis-1-(1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-(*p*-Bromophenyl)-aziridine[4] (3b)

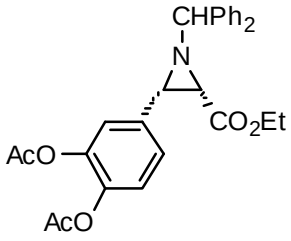
A similar procedure for the synthesis of **3a** was followed with the following differences: the reaction was run for 5 hours. Product **3b** was obtained as a white solid (395 mg) in 91 % isolated yield. An optical purity of 98 % *ee* was determined by HPLC analysis (OD-H column, 9:1 hexanes:2-propanol), flow rate = 1.0 mL/min. Retention times: R_t = 3.25 min (minor) and R_t = 5.13 min (major). *Cis/trans* ratio: >50:1. Side products: 3.4 % **4b** and 2.2 % **4b**. All characterization details for **3b** can be found in reference 4.



(3c)

Cis-1-(N-1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-(*o*-tolyl)-aziridine[4] **(3c)**

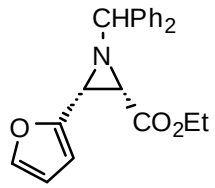
A similar procedure for the synthesis of **3a** was followed with the following differences: a reaction time of 14 hours was found. Product **3c** was obtained as a white solid (270 mg) in 69 % isolated yield. An optical purity of 94 % *ee* was determined by HPLC analysis (OD-H column, 99:1 hexanes:2-propanol), flow rate = 1.0 mL/min. Retention times: R_t = 5.7 min (minor) and R_t = 6.9 min (major). *Cis/trans* ratio: >50:1. Side products: 11.1 % **4c** and 7.1 % **5c**. All characterization details for **3c** can be found in reference 4.



(3d)

Cis-1-(1,1-diphenylmethyl)-(2S)-carboxyethyl-(3S)-(2,3-diacetoxyphenyl)-aziridine (3d) A similar procedure for the synthesis of **3a** was

followed with the following differences: the reaction was run at 1 M in imine (5.00 g, 12.91 mmol) and 2.5 mol % of R-VAPOL (174 mg) was used as the chiral ligand. Column chromatography was performed with 3:7 ethyl acetate:hexanes. Product **3d** was obtained as a white solid (5.20 g) in an 85 % isolated yield. An optical purity of 96 % *ee* was determined by HPLC analysis (OD-H column, 19:1 hexanes/2-propanol), flow-rate 2.0 mL/min. Compound recrystallized from 300 mL of 10:1 hexanes/CH_2Cl_2 to give 4.43 g of 99 % ee material. Retention times: R_t = 7.5 min (minor) and R_t = 9.5 min (major). Cis/trans ratio >50:1. Side products: <1 % **4d** and <1 % **5d**. m.p. 141-143 °C (hexanes/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (t, 3H, J = 7 Hz), 2.24 (s, 3H), 2.25 (s, 3H), 2.68 (d, 1H, J = 7 Hz), 3.18 (d, 1H, J = 7 Hz), 3.95 (s, 1H), 3.95 (m, 2H), 7.07 (d, 1H, J = 9 Hz), 7.19 (m, 1H), 7.28 (m, 7H), 7.45 (d, 2H, J = 7 Hz), 7.81 (d, 2H, J = 7 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 13.84, 20.64, 46.57, 47.03, 60.89, 77.49, 122.75, 122.78, 126.05, 127.18, 127.30, 127.45, 127.61, 128.55, 128.65, 133.97, 141.35, 141.57, 142.21, 167.45 168.07, 168.24; IR (thin film, cm^{-1}) 3030(w), 2980(w), 1770(s), 1731(s), 1600(m); mass spectrum (EI) *m/z* (relative intensity): 474 M+1 (21), 306 (12), 195 (10), 167 (100); m/z calcd for $C_{28}H_{27}NO_6$ 474.1903, found 474.1903. Anal calcd for $C_{28}H_{27}NO_6$: C, 71.02; H, 5.75; N, 2.96. Found: C, 71.23; H, 5.88; N, 2.94. Specific rotation: $[\alpha]^{23}_D$ = -17.3° (*C* = 1 from CH_2Cl_2) on 99 % *ee* material (HPLC).

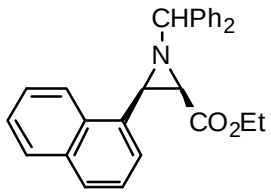


(3e)

Cis-1-(1,1-diphenylmethyl)-(2S)-carboxyethyl-(3S)-(2'-furyl)-aziridine[4]

(3e)

A similar procedure for the synthesis of **3a** was followed with the following differences: The reaction was run in toluene solvent with R-VANOL (0.10 mmol, 44 mg) as the chiral ligand. The catalyst/imine solution was cooled to 0 °C, the EDA added, and the reaction was run for 16 hours at that temperature. Product **3e** was obtained as a white solid (191 mg) in 55 % isolated yield. An optical purity of 93 % *ee* was determined by HPLC analysis (OD-H column, 9:1 hexanes:2-propanol), flow rate = 1.0 mL/min. Retention times: R_t = 4.2 min (minor) and R_t = 8.6 min (major). *Cis/trans* ratio: >50:1. Side products: <1 % **4e** and <1 % **5e**. All characterization details for **3e** can be found in reference 4.



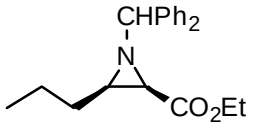
(3f)

Cis-1-(1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-1'-naphthylaziridine

(3f)

A similar procedure for the synthesis of **3a** was followed with the following differences: the reaction was run for 12 hours. Product **3f**

was obtained as a white solid (355 mg) in an 87 % isolated yield. An optical purity of 92 % *ee* was determined by HPLC analysis (OD-H column, 9:1 hexanes/2-propanol), flow-rate 1.0 mL/min. Retention times: R_t = 2.3 min (minor) and R_t = 3.5 min (major). *Cis/trans* ratio >50:1. Side products: 3.8 % **4f** and 0.3 % **5f**. m.p. 152-154 °C (hex/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.65 (t, 3H, J = 7 Hz), 2.94 (d, 1H, J = 7 Hz), 3.75 (m, 2H), 3.77 (d, 1H, J = 7 Hz), 4.10 (s, 1H), 7.22 (m, 1H), 7.30 (m, 3H), 7.38 (m, 3H), 7.48 (m, 2H), 7.58 (d, 2H, J = 7 Hz), 7.70 (m, 4H), 7.81 (d, 1H, J = 7 Hz), 8.12 (d, 1H, J = 7 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 13.55, 45.98, 46.36, 60.35, 77.91, 122.93, 125.29, 125.40, 125.82, 126.51, 127.10, 127.14, 127.58, 127.85, 128.48, 128.54, 130.48, 131.38, 133.01, 142.22, 142.45, 167.75; IR (thin film, cm^{-1}) 3030(w), 2980(w), 1737(s), 1598(m), 1191(s); mass spectrum (EI) *m/z* (relative intensity): 407 M^+ (5), 240 (59), 167 (100), 139 (9); *m/z* calcd for $C_{28}H_{25}NO_2$ 407.1885, found 407.1881. Anal calcd for $C_{28}H_{25}NO_2$: C, 82.59; H, 6.19; N, 3.44. Found: C, 81.86; H, 6.37; N, 3.26. Specific rotation: $[\alpha]^{23}_D$ = -9.6° (*C* = 1 from CH_2Cl_2) on 92 % *ee* material (HPLC).

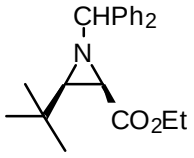


(3g)

Cis-1-(1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-n-propylaziridine[4]

(3g)

A similar procedure for the synthesis of **3a** was followed with the following differences: the reaction was run in toluene solvent with S-VAPOL (0.10 mmol, 54 mg) as the chiral ligand. The catalyst/imine solution was cooled to 0 °C and the EDA added. A 4 hour reaction time was allowed at 0 °C and then the reaction was warmed to 23 °C for another 16 hours. Product **3g** was obtained as a white solid (175 mg) in 54 % isolated yield. An optical purity of 91 % *ee* was determined by HPLC analysis (OD-H column, 99:1 hexanes:2-propanol), flow rate = 1.0 mL/min. Retention times: R_t = 3.9 min (minor) and R_t = 6.4 min (major). *Cis/trans* ratio: >50:1. Side products: 8.3 % **4g** and 9.2 % **5g**. All characterization details of **3g** can be found in reference 4.

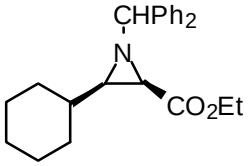


(3h)

Cis-1-(1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-t-butylaziridine (3h)

A similar procedure for the synthesis of **3a** was followed with the following differences: the reaction solvent was toluene and the chiral ligand used was 44 mg (0.10 mmol) of S-VANOL. A 4 hour reaction time was allowed at 0 °C and then the reaction was warmed to 23 °C for another 1 hour. Product **3h** was obtained as a white solid (260 mg) in an 77 % isolated yield. An optical purity of 97 % *ee* was determined by HPLC analysis (OD-H column, 99:1 hexanes/2-propanol), flow-rate 1.0 mL/min. Retention times: R_t = 5.1 min (minor) and R_t = 8.7 min (major). *Cis/trans* ratio >50:1. Side products: <1 % **4h** and <1 % **5h**. White

solid: mp 149-150 °C (pentane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.70 (s, 9H), 1.29 (t, 3H, J = 7 Hz), 1.76 (d, 1H, J = 7 Hz), 2.16 (d, 1H, J = 7 Hz), 3.59 (s, 1H), 4.09 (m, 1H), 4.24 (m, 1H), 7.20 (m, 2H), 7.28 (m, 4H), 7.40 (d, 2H, J = 7 Hz), 7.67 (d, 2H, J = 7 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.09, 27.39, 31.59, 43.37, 60.58, 79.19, 126.83, 127.24, 127.36, 128.17, 128.19, 128.26, 142.07, 143.43, 169.72; mass spectrum (EI) *m/z* (relative intensity): 338 M+1 (14), 195 (15), 167 (100); *m/z* calcd for $C_{22}H_{27}NO_2$ 338.2120, found 338.2124. Anal calcd for $C_{22}H_{27}NO_2$: C, 78.30; H, 8.06; N, 4.15. Found: C, 78.27; H, 8.27; N, 4.13. Specific rotation: $[\alpha]^{23}_{D}$ = +49.1° (*C* = 1 from CH_2Cl_2) on 92 % *ee* material (HPLC).



(3i)

Cis-1-(1,1-diphenylmethyl)-(2R)-carboxyethyl-(3R)-cyclohexylaziridine (3i)

A similar procedure for the synthesis of **3a** was followed with the following differences: the reaction was run in CH_2Cl_2 solvent with S-VAPOL (0.10 mmol, 54 mg) as the chiral ligand. An 8 hour reaction time at room temperature was allowed. Product **3i** was obtained as a white solid (269 mg) in 74 % isolated yield. An optical purity of 94 % *ee* was determined by HPLC analysis (OD-H column, 99:1 hexanes:2-propanol), flow rate = 1.0 mL/min. Retention times: R_t = 3.5 min (minor) and R_t = 5.8

min (major). *Cis/trans* ratio: 38:1. Side products: <1 % **4i** and <1 % **5i**. All characterization details of **3i** can be found in reference 4.

Procedure for the hydrogenation of 3d to give D-phenyl alanine ethyl ester (10) and hydrolysis to give L-DOPA (11) Aziridine **3d** (5.20 g, 11.0 mmol) with 96 % *ee* was crystallized once from CH_2Cl_2/hexanes (1:10, 275 mL total) to give 4.43 g (9.36 mmol) of a white cotton-like solid which was determined to be 99 % *ee* by chiral HPLC. This enriched **3d**, 1.00 g (2.11 mmol) was then dissolved in a 200 mL solution of formic acid (5 v/v %) in methanol and added via cannula to 1.00 g (9.40 mmol) of palladium black in 100 mL of the 5 % formic acid/methanol solution. The reaction stirred for 24 hours until completion by TLC (product stained orange with a ninhydrin solution) and was worked-up by gravity filtration, rotary evaporation and stirring in 100 mL saturated carbonate solution for 1 hour followed by partitioning into two successive extractions with 100 mL methylene chloride. 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 silica gel with CH_2Cl_2:MeOH 20:1 as the eluent. Product **10** was a clear, colorless oil 0.470 g (1.52 mmol) (72 % yield). This amino ester **10** was immediately taken on to the next step.

Compound **10** was dissolved in 15 mL of acetone with stir bar and cooled to 0 °C in an ice bath. Then, by syringe, 4 mL of 3 N HCl was added over a few minutes. The reaction was warmed to room temperature and then refluxed at 80 °C for 20 hours until complete by TLC (ninhydrin

stain, DOPA a characteristic gray/blue). The reaction flask was cooled and then the solvent was removed by rotary evaporation to give a yellow oil. The product L-DOPA (**11**) was isolated by ion-exchange chromatography: DOWEX 1X8-100 (basic) 50-100 mesh resin packed with water. Crude compound **11** was added and washed off with water as the eluent. L-DOPA was isolated as a film 0.113 g (60 % yield) and ^{1}H NMR and ^{13}C NMR spectra matched the literature.[7] Specific rotation was found to be: $[\alpha]^{23}_{D}$ = – 8.0° (*C* = 1 from 1 N HCl) was compared to an authentic sample from Aldrich: $[\alpha]^{23}_{D}$ = –8.2° (*C* = 1 from 1 N HCl). This corresponds to a 98 % *ee*.

References

[1] D. Armesto, M. J. Ortiz, R. Perez-Ossorio, *J. Chem. Soc. Perkin Trans. I* **1986**, 2021-2026.

[2] G. Cainelli, D. Giacomini, A. Trere, P. P. Boyl, *J. Org. Chem.* **1996**, *61,* 5134-5139.

[3] D. Green, G. Patel, S. Elgendy, J. A. Baban, G. Claeson, V. V. Kakkar, J. Deadman, *Tetrahedron* **1994**, *50,* 5099-5108.

[4] J. A. Antilla, W. D. Wulff, *J. Am. Chem. Soc.* **1999**, 5099-5100.

[5] L. Casarrubois, J. A. Perez, M. Brookhart, J. L. Templeton, *J. Org. Chem.* **1996**, *61,* 8358-8359.

[6] A. Lopez, M. Moreno-Manas, R. Pleixats, A. Roglans, J. Ezquerra, C. Pedregal, *Tetrahedron* **1996**, *52,* 8365-8386.

[7] The Aldrich Library of ^{1}H NMR and ^{13}C NMR Spectra.