Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

The *iso*-VAPOL Ligand: Synthesis, Solid-State Structure and its Evaluation as a BOROX Catalyst

Anil K. Gupta, Xin Zhang, Richard J. Staples and William D. Wulff*

Department of Chemistry, Michigan State University, East Lansing, MI 48824

Supporting Information

Table of Contents

A. General Information S2

B. Synthesis of (*S*)-*iso*-VAPOL **3** (Scheme 3): S4

C. Synthesis of imines **30a-d, 34a-38a** S8

D. Synthesis of aziridines **33a-d, 39a-43a** (Table 1, 2, 3) S13

E. NMR analysis of a mixture of either (*S*)-**2** or (*S*)-**3** with $B(OPh)_3$ and imine **30c** (Fig 3) S23

F. X-ray structure of (*R*)-**2** and (*S*)-**3** (Fig 2) S25

G. References S29

A. General Information

All reactions were carried out in flame-dried glassware under an atmosphere of argon unless otherwise indicated. Triethylamine, dichloromethane and acetonitrile were distilled over calcium hydride under nitrogen. Tetrahydrofuran, dioxane and ether were distilled from sodium and benzophenone. Toluene was distilled from sodium under nitrogen. Hexanes and ethyl acetate were ACS grade and used as purchased.

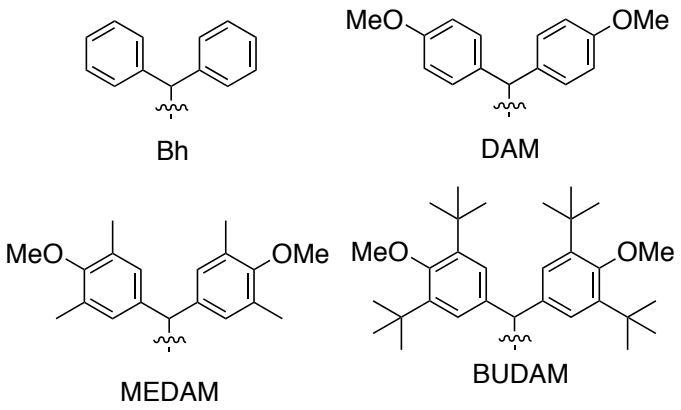
Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded in KBr matrix (for solids) and on NaCl disc (for liquids) on a Nicolet IR/42 spectrometer. ^{1}H NMR and ^{13}C NMR were recorded on a Varian 300 MHz or VXR-500 MHz spectrometer using $CDCl_3$ as solvent (unless otherwise noted) with the residual solvent peak as the internal standard (^{1}H NMR : 7.24 ppm, ^{13}C NMR : 77 ppm). Chemical shifts were reported in parts per million. Low-resolution Mass Spectrometry and High Resolution Mass Spectrometry were performed in the Department of Chemistry at Michigan State University. The crystallographic data of X-ray diffraction studies in this work were all collected at 173 K on a Brucker SMART 1000 CCD diffractometer at Michigan State University Crystallographic Research Center. Analytical thin-layer chromatography (TLC) was performed on Silicycle silica gel plates with F-254 indicator. Visualization was by short wave (254 nm) and long wave (365 nm) ultraviolet light, or by staining with phosphomolybdic acid in ethanol or with potassium permanganate. Column chromatography was performed with silica gel 60 (230 – 450 mesh).

HPLC analyses were peformed using a Varian Prostar 210 Solvent Delivery Module with a Prostar 330 PDA Detector and a Prostar Workstation. Chiral HPLC data for the aziridines were obtained using a CHIRALCEL OD-H column, CHIRALPAK AD column and PIRKLE COVALENT (R, R) WHELK-O 1 column.

Optical rotations were obtained on a Perkin-Elmer 341 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 20 °C and the concentrations are given in gram per 100 mL in ethyl acetate unless otherwise noted.

All reagents were purified by simple distillation or crystallization with simple solvents unless otherwise indicated. Ethyl diazoacetate **32**, triphenylborate, benzhydrylamine (distilled prior to use) obtained from Aldrich Chemical Co., Inc. and used as received. VAPOL and VANOL were made according to published procedure.[1] These ligands are also commercially available from Aldrich Chemical Co., Inc and Strem Chemicals. bis-(4-methoxyphenyl)methylamine (DAM amine)[2], bis-(3,5-dimethyl-4-methoxyphenyl) methanamine (MEDAM amine)[3], bis-(3,5-di-*tert*-butyl-4-methoxyphenyl) methanamine (BUDAM amine)[3] were made according to the published procedure.

Figure S1: Acronyms used for *N*-protecting groups.



Home-made Schlenk flask:

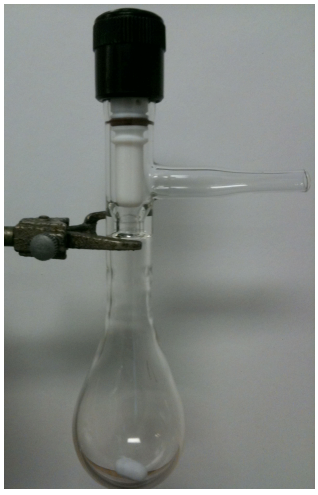
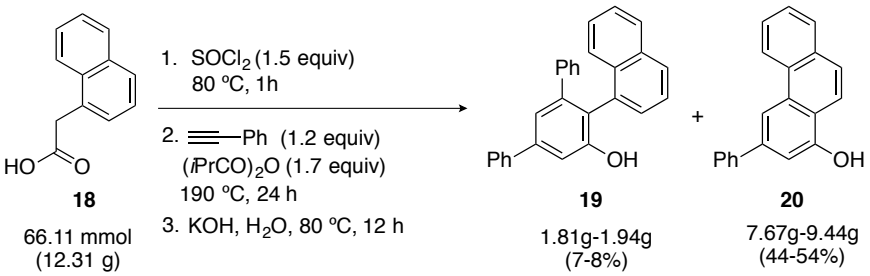


Figure S2: The Schlenk flask was prepared from a single-necked 25 mL pear-shaped flask that had its 14/20 glass joint replaced with a high vacuum threaded Teflon valve.

B. Synthesis of (*S*)-*iso*VAPOL 3

Preparation of ISOVAPOL monomer 20:



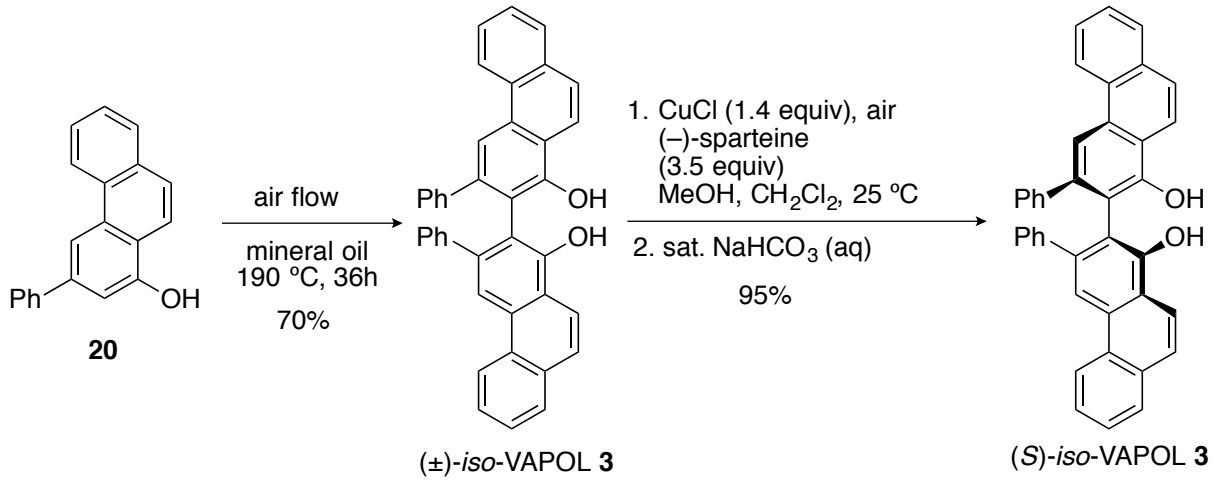
3-Phenyl-1-phenanthrol 20: The 1-naphthylacetic acid that was used was labeled as "plant cell culture tested, ≥95%) and was found not to contain any detectable amounts of 2-naphthylacetic acid. To a 250 mL flame-fried round bottom flask equipped with a large stir bar and a condenser all of which had been flushed with nitrogen was added 1-naphthylacetic acid **18** (12.31g, 66.11 mmol, 1 equiv.) and thionyl chloride (7.0 mL, 96 mmol, 1.5 equiv.). The mixture was heated at 80 °C for 1 h, and then all of the volatiles were carefully removed by high vacuum with a second trap to protect the pump. To the flask containing the resulting brown oil was added phenylacetylene (8.5 mL, 77 mmol, 1.2 equiv.) and *iso*-butyric anhydride (18 mL, 109 mmol, 1.7 equiv.) under nitrogen, and the resulting mixture heated to and stirred at 190 °C for 24 h with a nitrogen filled balloon attached to the septum on the top of the condenser via a needle. After the reaction mixture was cooled to room temperature, an aqueous KOH solution (25.91 g in 100 mL H_2O, 7 equiv.) was added slowly and the resulting mixture was heated to 80 °C for 12 h under nitrogen. The brown solution was then cooled to room temperature, and extracted with EtOAc (50 mL x 4, monitored by TLC). The combined organic layer was washed with brine (100 mL), and dried over $MgSO_4$, which removed via filter paper. The dark-brown solution was combined with silica gel (80 mL) and concentrated on a rotary evaporator. The residue was transferred to a silica gel column (60 x 350 mm) and eluted with 1:2 mixture of methylene chloride:hexanes under gravity. A first fraction containing several UV-active compounds was collected and discarded. A second fraction was collected which contained the by-product **19** (1.81 g, 4.86 mmol, 7%, mp. 82-84 °C). When the by-product had finished eluting, the eluent was changed to a 4:1 mixture of methylene chloride:hexanes and the third fraction was eluted under nitrogen pressure to afford the pure monomer product **20** (9.44 g, 34.92 mmol, 54%) as a yellow solid (m. p. = 177-178 °C). A second run under the same conditions gave 1.94 g of the by-product **19** (8%)

and 7.67 g of **20** (44%).

Spectral data for **19**: R_f = 0.71 in 1:3 EtOAc: hexane; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.87 (s, 1H), 7.00-7.03 (m, 2H), 7.05-7.07 (m, 2H), 7.31 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.36 (dd, *J* = 12.4, 1.8 Hz, 2H), 7.39-7.43 (m, 2H), 7.45 (td, *J* = 7.6, 1.3 Hz, 1H), 7.47-7.50 (m, 4H), 7.70-7.74 (m, 3H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 112.89, 121.32, 123.76, 125.54, 125.68, 126.30, 126.56, 126.87, 127.12, 127.53, 127.63, 128.50, 128.75, 128.83, 128.86, 129.86, 132.05, 132.36, 133.75, 140.47, 141.12, 142.26, 143.66, 153.88; IR (thin film) 3532 br, 3059 w, 1614 w, 1599 m, 1569 w, 1496 w, 1390 m, 1298 m, 1172 m cm^{-1}; HRMS (ESI-TOF) *m/z* 395.1405 [(M+Na$^+$); calcd. for $C_{28}H_{20}ONa$: 395.1412]

Spectral data for **20**: R_f = 0.65 (1:3 EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.37 (s, 1 H), 7.2 (s, 1 H), 7.41-7.38 (m, 1 H), 7.49 (t, 2 H, *J* = 7.3 Hz), 7.66-7.58 (m, 2 H), 7.75-7.73 (m, 3 H), 7.89 (d, 1 H, *J* = 7.8 Hz), 8.13 (d, 1 H, *J* = 9.0 Hz), 8.49 (s, 1H), 8.72 (d, 1 H, *J* = 8.1 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 110.12, 114.144, 119.76, 121.06, 123.15, 126.26, 126.62, 126.84, 127.49, 127.54, 128.70, 128.89, 130.20, 132.08, 132.48, 139.74, 141.32, 152.23; IR (KBr disc) 3521 s, 3059 w, 1619 w, 1601 m, 1569 w, 1405 w, 1277 w, 1227 w, 1152 w, 1138 m, 1076 m, 821 m, 749 s cm^{-1}; Mass spectrum *m/z* (% rel intensity) 270 (100) M$^+$, 241 (27), 165 (11), 135 (19), 120 (22), 77(10); Anal calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22; Found: C, 88.84; H, 5.21.

Preparation of (±) *iso*-VAPOL 3 and (*S*)- *iso*-VAPOL 3:



3,3'-diphenyl-2,2'-biphenanthrene-1,1'-diol (±)-3: To a 500 mL three-neck round bottom flask equipped with a stir bar and a 400 mm Allihn water cooled condenser was added 3-phenylphenanthren-1-ol **20** (4.02 g, 14.9 mmol) and light mineral oil (25 mL). The flask was transferred to oil bath at 190 °C. The stir bar in the oil bath was stopped before the flask was put into it to warm up for about 30 min until solid melted without any disturbance. A thick needle was introduced into the flask *via* the second neck to about 5 cm above the surface of reaction mixture and was used to provide a stream of house air, which was maintained at a flow rate of 0.15 – 0.20 L/min. The third neck was sealed with a rubber septum. Air f low was then introduced into the flask with a vigorous stirring of the reaction mixture. The reaction was kept at same temperature for 36 h. The flask was then cooled down to ambient temperature followed by the addition of hexanes (250 mL). The mixture was then stirred for 30 min. It was then kept at –20 °C for 12 h followed by suction filtration. It was then dried on high vacuum (0.5 mm Hg) for 2 h to afford the crude product as a yellow powder.

Purification by Crystallization: The crude product was then transferred to a 500 mL round bottom flask equipped with a condenser. The residue was rinsed with toluene (50 mL × 2) and transferred to the 500 mL round bottom flask. The resulted mixture was stirred and heated to boil while more toluene was added in 50 mL fraction till solid dissolved. The dark-brown solution was then cooled down to room temperature and kept at –20 °C overnight. The top solution was filtered without disturbing the precipitate over vacuum. A piece of new filter paper was then used to collect the brown crystal *via* suction filtration, washed by hexanes (20 mL × 2) and dried over vacuum to afford the first crop product (±)-**3** as an off- white solid (mp. 312-313 °C) in 50% yield (2.00 g, 3.73 mmol). The mother liquor was dried and the residue was crystallized in toluene (150mL) and cooled down to room temperature for 12 h followed by –20

°C overnight to afford second crop product (±)-**3** as an off-white solid (mp. 312-313 °C) in 20% yield (0.8 g, 1.49 mmol). The combined yield was 70% (2.80 g, 5.22 mmol).

Spectral data for (±)-**3**: R_f = 0.33 (1:9 EtOAc/hexanes) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.85 (s, 2 H), 6.73 (d, *J* = 7.1 Hz, 4H), 6.99 (t, *J* = 7.4 Hz, 4H), 7.06-7.11 (m, 2H), 7.59-7.65 (m, 4H), 7.83 (d, *J* = 9.1 Hz, 2H), 7.92-7.97 (m, 2H), 8.17 (s, 2H), 8.30 (d, *J* = 9.1 Hz, 2H), 8.58-8.62 (m, 2H); ^{13}C NMR (DMSO, 125 MHz) δ 114.98, 119.37, 121.15, 121.25, 123.15, 125.12, 126.16, 126.61, 126.64, 126.96, 128.31, 128.90, 129.63, 130.27, 131.70, 141.48, 141.68, 152.38; IR (KBr disc) 3521 vs, 3468 vs, 3059 w, 1616 w, 1594 m, 1566 w, 1509 w, 1482 w, 1393 m, 1362 m, 1253 m, 1224 s, 1195 w, 1141 m, 1076 w, 931 w, 866 w, 823 s, 752 s, 700 s cm^{-1} ; Mass spectrum *m/z* (% rel intensity) 538 (44) M^+, 537 (23), 370 (15), 269 (76), 241 (78), 231 (100), 215 (44), 77(2). Anal calcd for $C_{40}H_{26}O_2$: C, 89.19; H, 4.87; Found: C, 89.17; H, 4.89.

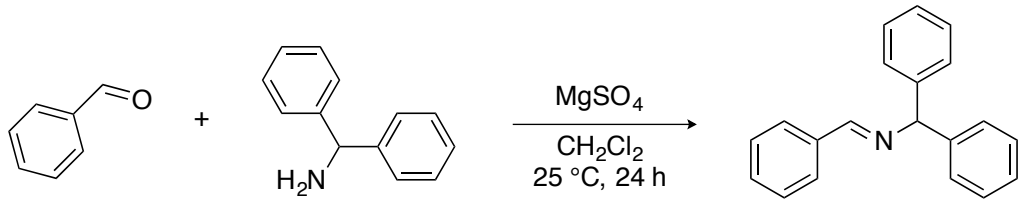
***(S)*-3,3'-diphenyl-2,2'-biphenanthrene-1,1'-diol 3:** To a 50 mL round bottomed flask was added CuCl (155 mg, 1.60 mmol), (–)-sparteine (760 mg, 3.20 mmol) and MeOH (30 mL). The reaction mixture was open to air and sonicated in an ultrasonic water bath for 0.5 h to afford a deep green solution. The flask was then sealed with a rubber septum and deoxygenated by purging with argon for 1 h (30 min in the solution and 30 min above the solution). To another 500 mL round bottomed flask equipped with a stir bar was added (±)-**3** (500 mg, 1.14 mmol) and CH_2Cl_2 (120 mL). The solution was purged with argon for 1 h as well (30 min in the solution and 30 min above the solution). The prepared Cu-sparteine complex solution was then transferred through a cannula to the solution of (±)-**3**. The mixed solution was then sonicated for 10 min and the flask was then covered with aluminum foil and allowed to stir at room temperature under slow constant flow of argon for 3 h. To the reaction mixture was added

saturated $NaHCO_3$ solution (10 mL) and the resulting mixture was stirred for 5 min. The mixture was then poured into a 500 mL separatory funnel with water (50 mL). The aqueous layer was then extracted with CH_2Cl_2 (50 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. The solution was then filtered through a short plug of dry silica gel (40 × 50 mm column) which was flushed with CH_2Cl_2 (100 mL) to give a light yellow solution with the Cu residue remaining on the top. The resulting solution was then concentrated *in vacuo* followed by exposure to high vacuum (0.05 mm Hg) for 30 min to afford the crude product as a dark yellow solid. Purification of the crude product by silica gel chromatography (40 mm × 300 mm column, 9:1 hexanes / EtOAc as eluent, dry loading) afforded pure *(S)-iso*-VAPOL **3** as an orange solid (mp. 315-316 ºC) in 95% yield (474 mg, 1.08 mmol). The optical purity of **3** was determined to be greater than 99% ee by HPLC analysis (Pirkle D-phenylglycine column, 75:25 hexane/*i*PrOH at 260nm, flow-rate: 2.0 mL/min). Retention times; R_t = 20.01 min ((*S*)-*iso*-VAPOL **3**) and R_t = 22.05 min ((*R*)-*iso*-VAPOL **3**).

Spectral data for (*S*)-**3**: Same as for (±)-**3**; $[\alpha]_D^{20}$ – 200.5 (*c* 1.0, EtOAc) on 99% ee material (HPLC).

C. Synthesis of imines 30a-d, 34a-38a.

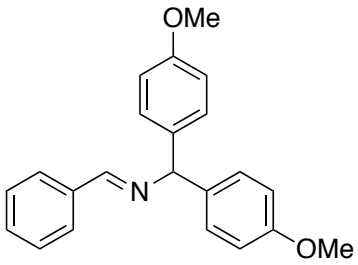
General Procedure for the synthesis of aldimines – Illustrated for the synthesis of *N*-benzylidene-1,1-diphenylmethanamine 30a.



30a

***N*-benzylidene-1,1-diphenylmethanamine 30a:** To a 50 mL flame-dried round bottom flask filled with argon was added benzhydryl amine (0.92 g, 5.00 mmol), $MgSO_4$ (1.0 g, 8.4 mmol, freshly flame-dried) and dry CH_2Cl_2 (15 mL). After stirring for 10 min, benzaldehyde (0.54 g, 5.05 mmol, 1.01 equiv) was added. The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was filtered through Celite and the Celite bed was washed with CH_2Cl_2 (10 mL × 3) and then the filtrate was concentrated by rotary evaporation to give the crude imine as an off-white solid. Crystallization (1:5 ethyl acetate/hexanes) and collection of the first crop afforded **30a** as white solid crystals (mp. 99-101 °C) in 80% isolated yield (1.09 g, 4 mmol).

Spectral data for **30a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.64 (s, 1H), 7.20-7.90 (m, 15H), 8.46 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 77.62, 126.69, 127.40, 128.15, 128.19, 128.24, 130.47, 136.07, 143.64, 160.48. These spectral data match those previously reported for this compound.[4]

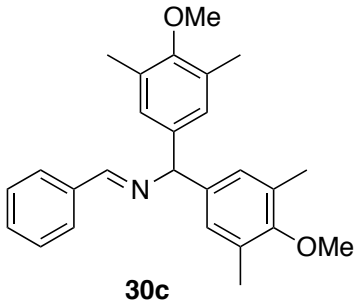


30b

***N*-benzylidene-bis(4-methoxyphenyl)methylamine 30b:** Imine **30b** was prepared according to the procedure described above for imine **30a**. Crystallization (1:25 CH_2Cl_2 / hexanes) and collection of the first crop afforded **30b** as white solid crystals (mp 60-61 ºC) in 91% isolated yield (1.51 g, 4.55 mmol).

Spectral data for **30b**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.76 (s, 6H), 5.51(s, 1H), 6.84 (d, 4H, J = 8.8 Hz), 7.25-7.27 (m, 4H), 7.37-7.40 (m, 3H), 7.79–7.82 (m, 2H), 8.37 (s, 1H); ^{13}C ($CDCl_3$, 75

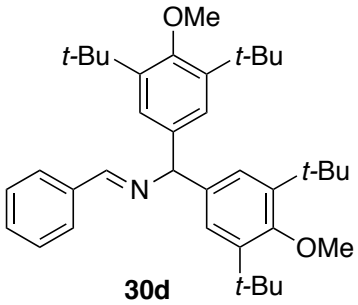
MHz) δ 55.17, 76.55, 113.71, 128.35, 128.43, 128.61, 128.70, 130.60, 136.28, 158.43, 160.24. These spectral data match those previously reported for this compound.[2]



30c

***N*-phenylmethylidene-*bis*(4-methoxy-3,5-dimethylphenyl) methyl amine 30c:** Imine **30c** was prepared according to the procedure described above for imine **30a**. Crystallization (1:9 CH_2Cl_2/hexanes) and collection of the first crop afforded **30c** as a white solid (mp 144-146 °C) in 90% isolated yield (1.74 g, 4.5 mmol).

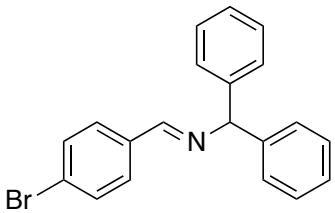
Spectral data for **30c**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.24 (s, 12H), 3.66 (s, 6H), 5.35 (s, 1H), 6.99 (s, 4H), 7.39-7.41 (m, 3H), 7.80–7.82 (m, 2H), 8.35 (s, 1H); ^{13}C ($CDCl_3$, 125 MHz) δ 16.22, 59.59, 77.41, 127.86, 128.46, 128.49, 130.61, 130.63, 136.45, 139.22, 155.84, 160.28; IR (thin film) 2944w, 1643vs, 1483vs cm^{-1}; Mass spectrum: *m/z* (% rel intensity) 387 M+ (3), 283 (100), 40 (17); Anal calcd for $C_{26}H_{29}NO_2$: C, 80.59; H, 7.54; N, 3.61. Found: C, 80.42; H, 7.24; N, 3.55. These spectral data match those previously reported for this compound.[5]



30d

***N*-benzylidene-1,1- bis(3,5-di-tert-butyl-4-methoxyphenyl) methanamine 30d:** Imine **30d** was prepared according to the procedure described above for imine **30a**. Crystallization (1:100 EtOAc/hexanes) and collection of the first crop afforded **30d** as white solid crystals (mp. 127-129 °C) in 90% isolated yield (2.5 g, 4.5 mmol).

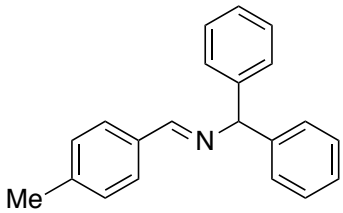
Spectral data for **30d**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.429 (s, 18H), 1.433 (s, 18H), 3.70 (s, 3H), 3.70 (s, 3H), 5.51 (s, 1H), 7.27 (s, 4H), 7.42–7.44 (m, 3H), 7.86–7.89 (m, 2H), 8.52 (s, 1H); ^{13}C ($CDCl_3$, 75 MHz) δ 32.08, 35.77, 64.13, 78.20, 126.02, 128.40, 128.47, 130.50, 136.55, 137.42, 143.10, 158.29, 160.23. These spectral data match those previously reported for this compound.[3]



34a

***N*-(4-bromobenzylidene)-1,1-diphenylmethanamine 34a:** Imine **34a** was prepared according to the procedure described above for imine **30a**. Crystallization (1:5 ethyl acetate/hexanes) and collection of the first crop afforded **34a** as white solid crystals (mp. 96-97 °C) in 75% isolated yield (1.31 g, 3.75 mmol).

Spectral data for **34a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.23 (s, 1H), 7.15-7.35 (m, 10H), 7.47 (d, *J* = 7 Hz, 2H), 7.64 (d, *J* = 7 Hz, 2H), 8.28 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 77.85, 127.05, 127.60, 128.46, 129.84, 131.75, 143.62, 159.51. These spectral data match those previously reported for this compound.[4]

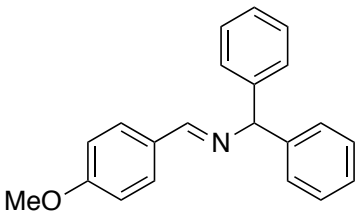


35a

***N*-(4-methylbenzylidene)-1,1-diphenylmethanamine 35a:** Imine **35a** was prepared according to the procedure described above for imine **30a**. Crystallization (1:5 ethyl acetate/hexanes) and collection of the first crop afforded **35a** as white solid crystals (mp. 73-74 °C) in 80% isolated yield (1.14 g, 4 mmol).

Spectral data for **35a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 3H), 5.64 (s, 1H), 7.26-7.48 (m, 12H), 7.80 (d, *J* = 8 Hz, 2H), 8.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 21.50, 76.57, 126.89,

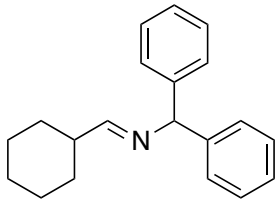
127.66, 128.38, 128.41, 129.21, 133.88, 141.01, 143.98, 160.67. These spectral data match those previously reported for this compound.[4]



36a

***N*-(4-methoxybenzylidene)-1,1-diphenylmethanamine 36a:** Imine **36a** was prepared according to the procedure described above for imine **30a**. Crystallization (1:5 ethyl acetate/hexanes) and collection of the first crop afforded **36a** as white solid crystals (mp. 108-109 °C) in 80% isolated yield (1.21 g, 4 mmol).

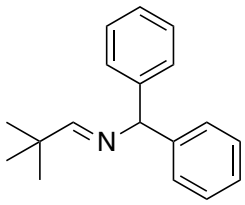
Spectral data for **36a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.82 (s, 3H), 5.55 (s, 1H), 6.91 (d, J = 8.8 Hz, 2H), 7.28-7.40 (m, 10H), 7.78 (d, J = 8.8 Hz, 2H), 8.34 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 55.32, 77.77, 113.88, 126.85, 127.67, 128.37, 129.99, 144.11, 160.01. These spectral data match those previously reported for this compound.[4]



37a

***N*-(cyclohexylmethylene)-1,1-diphenylmethanamine 37a:** Imine **37a** was prepared according to the procedure described above for imine **30a**. Crystallization (1:5 ethyl acetate/hexanes) and collection of the first crop afforded **37a** as white solid crystals (mp. 49-51 °C) in 70% isolated yield (0.97 g, 3.5 mmol).

Spectral data for **37a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10-1.90 (m, 10H), 2.20 (bs, 1H), 5.21 (s, 1H), 7.00-7.60 (m, 10H), 7.59 (d, J = 5.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 25.82, 26.41, 30.13, 43.91, 78.35, 127.20, 127.97, 128.73, 144.41, 169.51. These spectral data match those previously reported for this compound.[4]



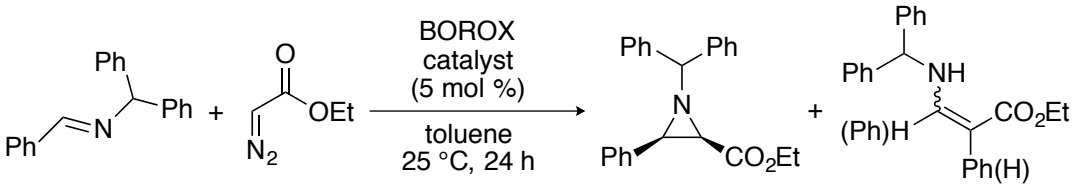
38a

***N*-(2,2-dimethylpropylidene)-1,1-diphenylmethanamine 38a:** Imine **38a** was prepared according to the procedure described above for imine **30a**. Crystallization (1:9 ethyl acetate/hexanes) and collection of the first crop afforded **38a** as white solid crystals (mp. 51-52 °C) in 50% isolated yield (0.63 g, 0.25 mmol).

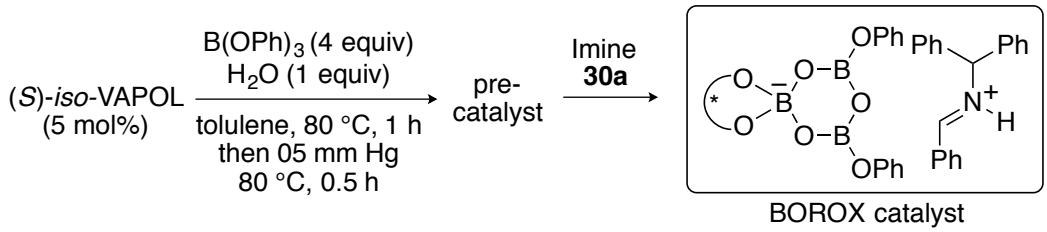
Spectral data for **38a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27 (s, 9H), 5.50 (s, 1H), 7.34 (t, *J* = 7 Hz, 2H), 7.44 (t, *J* = 7 Hz, 4H), 7.49 (d, *J* = 7 Hz, 4H), 7.85 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 26.94, 36.38, 77.36, 126.68, 127.44, 128.25, 144.23, 171.48. These spectral data match those previously reported for this compound.[4]

D. Synthesis of aziridines 33a-d, 39a-43a using (*S*)-*iso*-VAPOL and (*R*)-VANOL (*Table 1, 2 and 3*)

General Procedure for performing aziridination – Illustrated for the synthesis of *(2R,3R)*-ethyl 1-benzhydryl-3-phenylaziridine-2-carboxylate 33a.



30a **32** **33a** **A(B)**



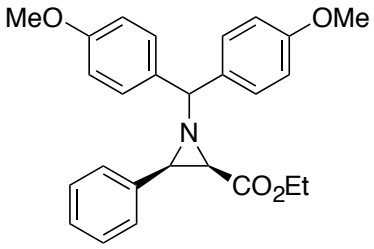
BOROX catalyst

***(2R,3R)*- ethyl 1-benzhydryl-3-phenylaziridine-2-carboxylate 33a:** To a 25 mL flame-dried home-made Schlenk flask (see Figure S2) equipped with a stir bar and flushed with argon was added (*S*)-*iso*-VAPOL (27 mg, 0.05 mmol), commercial $B(OPh)_3$ (58 mg, 0.2 mmol) and water (0.9 μL, 0.05 mmol). Under an argon flow through the side-arm of the Schlenk flask, dry toluene (2 mL) was added through the top of the Teflon valve to dissolve the two reagents. The flask was sealed by closing the Teflon valve, and then placed in an 80 ºC oil bath for 1 h. After 1 h, a vacuum (0.5 mm Hg) was carefully applied by slightly opening the Teflon valve to remove the volatiles. After the volatiles were removed completely, a full vacuum was applied and maintained for a period of 30 min at a temperature of 80 ºC (oil bath). The flask was then allowed to cool to room temperature and opened to argon through the side-arm of the Schlenk flask. To the flask containing the pre-catalyst was first added the aldimine **30a** (271 mg, 1 mmol) and then dry toluene (2 mL) under an argon flow through side-arm of the Schlenk flask. The reaction mixture was stirred for 5 min to give a light orange solution. To this solution was rapidly added ethyl diazoacetate (EDA) **32** (124 μL, 1.2 mmol) followed by closing the Teflon valve. The resulting mixture was stirred for 24 h at room temperature. Immediately upon addition of ethyl diazoacetate the reaction mixture became an intense yellow, which changed to light yellow towards the end of the reaction. The reaction was dilluted by addition of hexane (6 mL). The reaction mixture was then transferred to a 100 mL round bottom flask. The reaction flask was rinsed with dichloromethane (5 mL × 2) and the rinse was added to the 100 mL round bottom flask. The resulting solution was then concentrated *in vacuo* followed by exposure to high vacuum (0.05 mm Hg) for 1 h to afford the crude aziridine as an off-white solid.

A measure of the extent to which the reaction went to completion was estimated from the ^{1}H NMR spectrum of the crude reaction mixture by integration of the aziridine ring methine

protons relative to either the imine methine proton or the proton on the imine carbon. The *cis/trans* ratio was determined by comparing the ^{1}H NMR integration of the ring methine protons for each aziridine in the crude reaction mixture. The *cis* (J = 7-8 Hz) and the *trans* (J = 2-3 Hz) coupling constants were used to differentiate the two isomers. The yields of the acyclic enamine side products were determined by ^{1}H NMR analysis of the crude reaction mixture by integration of the *N*-H proton relative to that of the *cis*-aziridine methine protons with the aid of the isolated yield of the *cis*-aziridine. Purification of the crude aziridine by silica gel chromatography (35 mm × 400 mm column, 19:1 hexanes/EtOAc as eluent, under gravity) afforded pure cis-aziridine **33a** as a white solid (mp. 127.5-128.5 °C on 92% ee material) in 82% isolated yield (293 mg, 0.820 mmol); *cis/trans*: 50:1. Enamine side products: 3% yield of **A** and 7% yield of **B.** The optical purity of **33a** was determined to be 92% *ee* by HPLC analysis ((CHIRALCEL OD-H column, 90:10 hexanes/*i*PrOH at 222 nm, flow-rate: 0.7 mL/min): retention times; R_t = 9.01 min (major enantiomer, **33a**) and R_t = 4.67 min (minor enantiomer, *ent*-**33a**). The same reaction afforded aziridine **33a** in 87% yield and 89% ee using the (*R*)-VANOL boroxinate catalyst.

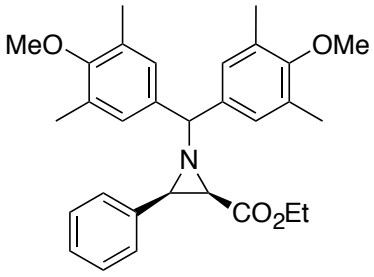
Spectral data for **33a**: R_f = 0.3 (1:9 EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.95 (t, 3H, J = 7.3 Hz), 2.64 (d, J = 6.8 Hz, 1H), 3.19 (d, J = 6.8 Hz, 1H), 3.91 (q, J = 7.1 Hz, 2H), 3.93 (s, 1H), 7.16-7.38 (m, 11H), 7.47 (d, J = 7.1 Hz, 2H), 7.58 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 13.93, 46.36, 48.01, 60.57, 77.68, 127.18, 127.31, 127.39, 127.52, 127.76, 127.78, 128.48, 135.00, 142.37, 142.49, 167.75; $[\alpha]_D^{20}$ + 33.4 (*c* 1.0, CH_2Cl_2) on 91% *ee* material (HPLC). These spectral data match those previously reported for this compound.[4]



33b

(*2R,3R*)-*Cis*-1-(*N*-1-*bis*(4-methoxyphenyl)methyl) -2-carboxyethyl-3-phenylaziridine 33b. Imine **30b** (332 mg, 1.00 mmol) was reacted according to the general procedure described above with (*S*)-*iso*-VAPOL as ligand. Purification of the crude aziridine by silica gel chromatography (35 mm × 350 mm column, 9:1 hexanes / EtOAc as eluent, after elution of the first fraction, which contains EDA and / or enamine side products, the eluent was changed to 5:1 hexanes / EtOAc) afforded pure aziridine **33b** as a white solid (mp 89.5-90.5 ºC) in 90% isolated yield (376 mg, 0.900 mmol); *cis/trans*: 50:1. Enamine side products: 6% yield of **A** and <1% yield of **B**. The optical purity of **33b** was determined to be 96% *ee* by HPLC analysis (CHIRALPAK AD column, 90:10 hexanes/*i*PrOH at 226nm, flow-rate: 1.0 mL/min): retention times; R_t = 8.78 min (major enantiomer, **33b**) and R_t = 15.49 min (minor enantiomer, *ent*-**33b**).

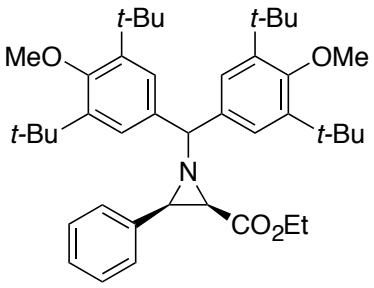
Spectral data for **33b**: R_f = 0.28 (1:5 EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.93 (t, 3H, *J* = 7.1 Hz), 2.59 (d, 1H, *J* = 6.8 Hz), 3.13 (d, 1H, *J* = 6.8 Hz), 3.67 (s, 3H), 3.75 (s, 3H), 3.81 (s, 1H), 3.91-3.98 (m, 2H), 6.74 (d, 2H, *J* = 8.8 Hz), 6.82 (d, 2H, *J* = 8.8 Hz), 7.14-7.24 (m, 3H), 7.31-7.35 (m, 4H), 7.43 (d, 2H, *J* = 8.8 Hz); ^{13}C ($CDCl_3$, 75 MHz) δ 13.94, 46.39, 48.02, 55.15, 55.22, 60.54, 76.44, 113.80, 127.27, 127.75, 127.79, 128.16, 128.49, 134.93, 135.13, 135.16, 158.61, 158.71, 167.83 (one sp^2 carbon not located); $[\alpha]_D^{20}$ +36.5 (*c* 1.0, EtOAc) on 94% ee material (HPLC). These spectral data match those previously reported for this compound.[2]



33c

***(2R,3R)-Cis*-1-(*N*-1-bis(4-methoxy-3,5-dimethylphenyl) methyl)-2-carboxyethyl-3-phenylaziridine 33c:** Imine **30c** (388 mg, 1.00 mmol) was reacted according to the general procedure described above with (*S*)-*iso*-VAPOL as ligand. Purification of the crude aziridine by silica gel chromatography (35 mm × 350 mm column, 9:1 hexanes / EtOAc as eluent, after elution of the first fraction, which contains EDA and / or enamine side products, the eluent was changed to 5:1 hexanes / EtOAc) afforded pure aziridine **33c** as a white solid (mp 107-108 ºC) in 96 % isolated yield (454 mg, 0.96 mmol).; *cis/trans*: ≥ 50:1. Enamine side products: 2% yield of **A** and 1% yield of **B.** The optical purity of **33c** was determined to be 98% *ee* by HPLC (CHIRALCEL OD-H column, 99:1 hexanes/*i*PrOH at 226 nm, flow-rate: 0.7 mL/min). Retention times; R_t = 8.96 min (major enantiomer, **33c**) and R_t = 12.85 min (minor enantiomer, *ent*-**33c**).

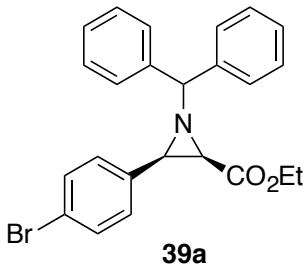
Spectral data for **33c**: R_f = 0.42 (1:9 EtOAc/hexane). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.98 (t, J = 7.1 Hz, 3H), 2.18 (s, 6H), 2.24 (s, 6H), 2.55 (d, J = 6.8 Hz, 1H), 3.10 (d, J = 6.6 Hz, 1H), 3.62 (s, 3H), 3.66 (s, 1H), 3.68 (s, 3H) 3.87-3.97 (m, 2H), 7.09 (s, 2H), 7.18 (s, 2H), 7.21 (d, J = 7.6 Hz, 2H), 7.35-7.37 (m, 3H); ^{13}C ($CDCl_3$, 125 MHz) δ 14.01, 16.16, 16.22, 46.26, 48.20, 59.52, 59.58, 60.47, 77.04, 127.21, 127.41, 127.70, 127.80,127.85, 130.59, 130.60, 135.33, 137.79, 137.96, 155.95, 156.10, 168.01. $[\alpha]_D^{20}$ +41.3 (*c* 1.0, EtOAc) on 99% ee material (HPLC). These spectral data match those previously reported for this compound.[5]



33d

(*2R,3R*)-ethyl-1-(bis(3,5-di-tert-butyl-4-methoxyphenyl) methyl)-3-phenylaziridine-2-carboxylate 33d: Imine **30d** (278 mg, 0.5 mmol) was reacted according to the general procedure described above with ((*S*)-*iso*-VAPOL as ligand. Purification of the crude aziridine by silica gel chromatography (35 mm × 350 mm column, 20:1 hexanes/EtOAc as eluent) afforded pure aziridine **33d** as a white solid (mp. 156-158 ºC) in 97% isolated yield (652 mg, 0.97 mmol).; *cis/trans*: ≥ 50:1. Enamine side products: <1% yield of **A** and <1% yield of **B.** The optical purity of **33d** was determined to be 96% *ee* by HPLC (Pirkle covalent (R,R) Whelk-O 1 column, 99:1 hexanes/*i*PrOH at 225 nm, flow-rate: 1.0 mL/min). Retention times; R_t = 9.72 min (major enantiomer, **33d**) and R_t = 5.38 min (minor enantiomer, *ent*-**33d**).

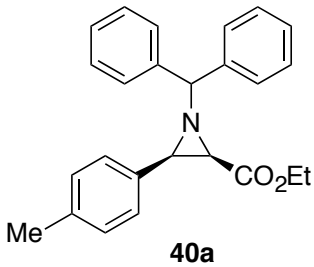
Spectral data for **33d:** R_f = 0.26 (20:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.97 (t, *J* = 7.1 Hz, 3H), 1.31 (s, 18H), 1.39 (s, 18H), 2.64 (d, *J* = 6.8 Hz, 1H), 3.15 (d, *J* = 6.8 Hz, 1H), 3.59 (s, 3H), 3.65 (s, 3H), 3.82 (s, 1H), 3.84-3.96 (m, 2H), 7.16-7.19 (m, 1H), 7.22-7.25 (m, 2H), 7.31 (s, 2H), 7.41 (s, 2H), 7.46 (d, *J* = 7.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.95, 32.04, 32.13, 35.71, 35.78, 46.35, 48.78, 60.50, 63.93, 64.01, 125.37, 125.49, 127.23, 127.58, 128.15, 135.35, 136.69, 136.85, 143.00, 143.08, 158.23, 158.25, 168.27 (one sp^3 carbon not located). $[\alpha]_D^{20}$ +5.5 (*c* 1.0, EtOAc) on 96% ee material (HPLC). These spectral data match those previously reported for this compound.[3]



39a

(*2R,3R*)-ethyl 1-benzhydryl-3-(4-bromophenyl)aziridine-2-carboxylate 39a: Imine **34a** (350 mg, 1.00 mmol) was reacted according to the general procedure described above with (*S*)-*iso*-VAPOL as ligand. Purification of the crude aziridine by silica gel chromatography (35 mm × 350 mm column, 9:1 hexanes/EtOAc as eluent) afforded pure aziridine **39a** as a white solid (mp. 150-151 °C) in 80% isolated yield (175 mg, 0.4 mmol). *cis/trans*: ≥ 50:1. Enamine side products: 2% yield of **A** and 6% yield of **B**. The optical purity of **39a** was determined to be 94% ee by HPLC analysis (CHIRALCEL OD-H column, 98:2 hexanes/*i*PrOH at 222 nm, flow-rate: 1.0 mL/min). Retention times, R_t = 14.31 min (major enaniomer, **39a**) and R_t = 5.56 min (minor enantiomer, *ent*-**39a**).

Spectral data for **39a**: R_f = 0.33 (1:9 EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.00 (t, *J* = 7.1 Hz, 3H), 2.66 (d, *J* = 6.8 Hz, 1H), 3.12 (d, *J* = 6.6 Hz, 1H), 3.92 (s, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 7.16-7.37 (m, 10H), 7.43 (d, *J* = 6.8 Hz, 2H), 7.56 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.98, 46.46, 47.33, 60.73, 77.58, 121.33, 127.12, 127.28, 127.41, 127.50, 128.52, 128.54, 129.54, 130.89, 134.03, 142.13, 142.30, 167.43; $[\alpha]_D^{20}$ +9.1 (*c* 1.0, CH_2Cl_2) on 94% *ee* material. These spectral data match those previously reported for this compound.[4]

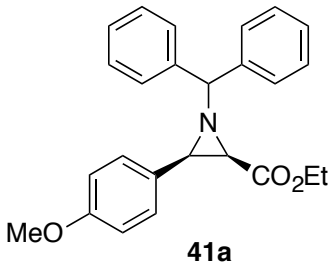


40a

(*2R,3R*)-ethyl 1-benzhydryl-3-p-tolylaziridine-2- carboxylate 40a: Imine **35a** (286 mg, 1.00 mmol) was reacted according to the general procedure described above with (*S*)-*iso*-VAPOL as the ligand. Purification of the crude aziridine by silica gel chromatography (35 mm × 350 mm column, 9:1 hexanes / EtOAc as eluent) afforded pure aziridine **40a** as a white solid (mp. 148-149 °C) in 82% isolated yield (304 mg, 0.820 mmol). *cis/trans*: ≥ 50:1. Enamine side products: 3% yield of **A** and 7% yield of **B**. The optical purity of **40a** was determined to be

94% ee by HPLC analysis (CHIRALCEL OD-H column, 90:10 hexanes/*i*PrOH at 222 nm, flow-rate: 0.7 mL/min). Retention times, R_t = 8.54 min (major enaniomer, **40a**) and R_t = 4.46 min (minor enantiomer, *ent*-**40a**).

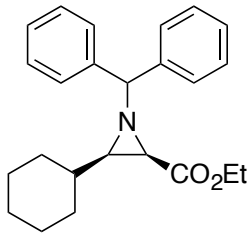
Spectral data for **40a:** R_f = 0.30 (1:9 EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.99 (t, *J* = 7.3 Hz, 3H), 2.27 (s, 3H), 2.62 (d, *J* = 6.8 Hz, 1H), 3.16 (d, *J* = 6.6 Hz, 1H), 3.91 (s, 1H), 3.93 (q, *J* = 7.3 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.15-7.34 (m, 8H), 7.46 (d, *J* = 6.8 Hz, 2H), 7.57 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 13.97, 21.12, 46.32, 48.00, 60.53, 77.72, 127.15, 127.20, 127.34, 127.51, 127.64, 128.45, 131.94, 136.88, 142.42, 142.53, 167.82; $[\alpha]_D^{20}$ +24.6 (*c* 1.0, CH_2Cl_2) on 94% *ee* material. These spectral data match those previously reported for this compound.[4]



41a

(*2R,3R*)-ethyl 1-benzhydryl-3-(4-methoxyphenyl)aziridine-2-carboxylate 41a[2]: Imine **36a** (302 mg, 1.00 mmol) was reacted according to the general procedure described above with (*S*)-*iso*-VAPOL as ligand. The silica gel for column chromatography was pre-conditioned by preparing a slurry in a 1:9 mixture of Et_3N:CH_2Cl_2 which was loaded into a column (35 mm × 350 mm), the solvent was drained and then the silica gel was dried by flushing with nitrogen for one hour. The silica gel column was then saturated with a 1:9 mixture of ethyl acetate:hexanes, the crude aziridine was loaded onto the column and then elution with the same solvent afforded pure aziridine **41a** as a white solid (mp. 136-137 °C) in 62% isolated yield (240 mg, 0.620 mmol). *cis/trans*: 9:1. Enamine side products: <1% yield of **A** and 6% yield of **B**. The optical purity of **41a** was determined to be 89 % ee by HPLC analysis (CHIRALCEL OD-H column, 95:5 hexanes/*i*PrOH at 222 nm, flow-rate: 0.7 mL/min). Retention times, R_t = 15.52 min (major enantiomer, **41a**) and R_t = 7.14 min (minor enantiomer, *ent*-**41a**).

Spectral data for **41a**: R_f = 0.2 (1:9 EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.00 (t, J = 7.3 Hz, 3H), 2.60 (d, J = 6.8 Hz, 1H), 3.14 (d, J = 6.9 Hz, 1H), 3.74 (s, 3H), 3.91 (s, 1H), 3.93 (q, J = 7.1 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 7.14-7.32 (m, 8H), 7.45 (d, J = 6.9 Hz, 2H), 7.57 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.99, 46.29, 47.70, 55.13, 60.52, 77.66, 113.18, 127.06, 127.15, 127.18, 127.34, 127.49, 128.44, 128.86, 142.39, 142.54, 158.85, 167.85; $[\alpha]_D^{20}$ +24.0 (*c* 1.0, CH_2Cl_2) on 89% *ee* material. These spectral data match those previously reported for this compound.[4]

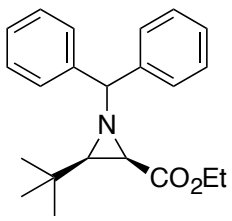


42a

(*2R,3R*)-ethyl 1-benzhydryl-3-cyclohexylaziridine-2-carboxylate 42a: Imine **37a** (278 mg, 1.00 mmol) was reacted according to the general procedure described above with (*S*)-*iso*-VAPOL as ligand. Purification of the crude aziridine by silica gel chromatography (35 mm × 350 mm column, 15:1 hexanes /EtOAc as eluent) afforded pure aziridine **42a** as a white solid (mp. 162.5-163 °C) in 72% isolated yield (262 mg, 0.72 mmol). *cis/trans*: ≥ 50:1. Enamine side products: 9% yield of **A** and 4% yield of **B**. The optical purity of **42a** was determined to be 79 % ee by HPLC analysis (CHIRALCEL OD-H column, 99:1 hexanes/*i*PrOH at 222 nm, flow-rate: 1.0 mL/min). Retention times, R_t = 6.88 min (major enaniomer, **42a**) and R_t = 3.41 min (minor enantiomer, *ent*-**42a**).

Spectral data for **42a**: R_f = 0.2 (1:15 EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.49 (dq, J = 10 Hz, 3 Hz, 1H), 0.90-1.66 (m, 10H), 1.23 (t, J = 7.1 Hz, 3H), 1.78 (dd, J = 7.1 Hz, 3.0 Hz, 1H), 2.24 (d, J = 6.8 Hz, 1H), 3.59 (s, 1H), 4.13-4.26 (m, 2H), 7.18-7.34 (m, 8H), 7.47 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.28, 25.35, 25.53,26.12, 30.10, 30.70, 36.26, 43.40, 52.12, 60.70, 78.17, 126.89, 127.05, 127.49, 128.27, 128.30, 128.36, 142.31, 142.71, 169.65;

$[\alpha]_D^{20}$ +112.6 (*c* 1.0, CH_2Cl_2) on 79% *ee* material. These spectral data match those previously reported for this compound.[4]



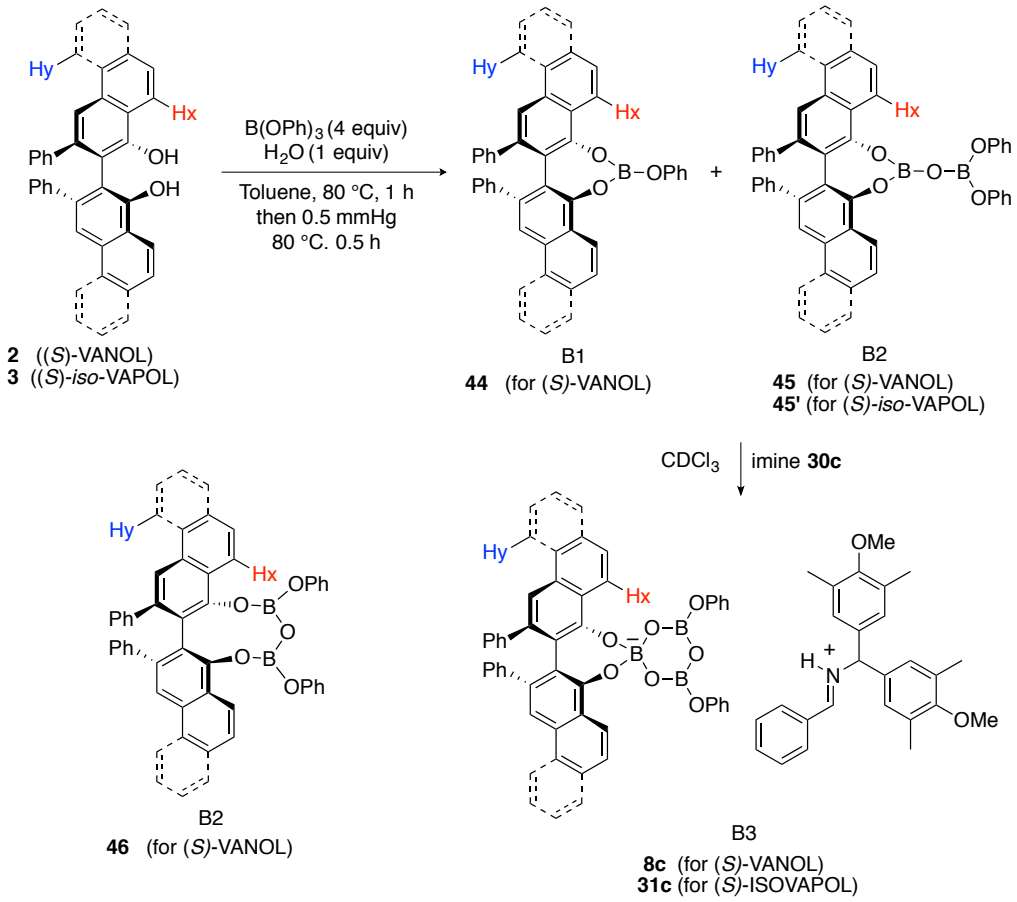
43a

(*2R,3R*)-ethyl 1-benzhydryl-3-tert-butylaziridine-2-carboxylate 43a: Imine **38a** (252 mg, 1.00 mmol) was reacted according to the general procedure described above with (*S*)-*iso*-VAPOL as ligand. Purification of the crude aziridine by silica gel chromatography (35 mm × 350 mm column, 9:1 hexanes / EtOAc as eluent) afforded pure aziridine **43a** as a white solid (mp. 149-150 °C) in 83% isolated yield (280 mg, 0.83 mmol). *cis/trans*: ≥ 50:1. Enamine side products: 6% yield of **A** and <1% yield of **B**. The optical purity of **43a** was determined to be 84 % ee by HPLC analysis (CHIRALCEL OD-H column, 99:1 hexanes/*i*PrOH at 222 nm, flow-rate: 1.0 mL/min). Retention times, R_t = 10.64 min (major enaniomer, **43a**) and R_t = 3.74 min (minor enantiomer, *ent*-**43a**).

Spectral data for **43a**: R_f = 0.33 (1:9 EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.73 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.79 (d, *J* = 7.3 Hz, 1H), 2.10 (d, *J* = 7.1 Hz, 1H), 3.63 (s, 1H), 4.07-4.18 (m, 1H), 4.22-4.33 (m, 1H), 7.21-7.37 (m, 6H), 7.43 (d, *J* = 6.8 Hz, 2H), 7.70 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.09, 27.39, 31.60, 43.37, 56.05, 60.59, 79.19, 126.84, 127.24, 127.37, 128.17, 128.20, 128.27, 142.60, 143.44, 169.74; $[\alpha]_D^{20}$ +133.0 (*c* 1.0, CH_2Cl_2) on 84% *ee* material. These spectral data match those previously reported for this compound.[4]

E. NMR analysis of a mixture of either (*S*)-VANOL or (*S*)-*iso*-VAPOL with $B(OPh)_3$, and imine 30c (*Figure 3)*

As shown in Figure 3 of this manuscript, a mixture of (*S*)-VANOL **2** and $B(OPh)_3$ results in a mixture containing predominantely the pyroborate B2 **45**, unreacted VANOL **2** and an unknown species (either **44** or **46**) when subjected to the pre-catalyst formation. Also, it was evident from the ^{1}H NMR and ^{11}B NMR that no boroxinate B3 **8c** was formed unless imine **30c** was added (characteristic peaks i.e. δ 8.55-8.56 ppm and δ 5.5-5.7 were missing in ^{1}H NMR and ^{11}B NMR respectively). Similar observations were made in the case of (*S*)-*iso*-VAPOL **3**. Unless otherwise noted, commercial $B(OPh)_3$ is used in all the experiments. Also, Ph_3CH is used as the internal standard.



Entry 1, Figure 3B: The ^{1}H NMR of pure (*S*)-VANOL **2** taken in $CDCl_3$.

Entry 2, Figure 3B: The pre-catalyst was made employing (*S*)-VANOL **2** (44 mg, 0.1 mmol), commercial $B(OPh)_3$ (116 mg, 0.4 mmol), water (1.8 μL, 0.1 mmol). To the flask containing the pre-catalyst was first added the Ph_3CH (12.22 mg, 0.05 mmol) and then $CDCl_3$ (1 mL) under an argon flow through side-arm of the Schlenk flask. The reaction mixture was then stirred for 10 min. The off-white colored solution was then directly transferred to a quartz NMR tube and was subjected to ^{1}H NMR and ^{11}B NMR analysis.

Entry 3, Figure 3B:

The pre-catalyst was made employing (*S*)-VANOL **2** (44 mg, 0.1 mmol), commercial $B(OPh)_3$ (116 mg, 0.4 mmol), water (1.8 μL, 0.1 mmol). To the flask containing the pre-catalyst was first added the imine **30c** (39 mg, 0.1 mmol), Ph_3CH (12.22 mg, 0.05 mmol) and then $CDCl_3$ (1 mL) under an argon flow through side-arm of the Schlenk flask. The reaction mixture was then stirred for 10 min. The red colored solution was then directly transferred to a quartz NMR tube and was subjected to ^{1}H NMR and ^{11}B NMR analysis.

Entry 4, Figure 3B: The ^{1}H NMR of pure (*S*)-*iso*-VAPOL **3** taken in $CDCl_3$.

Entry 5, Figure 3B: Same as entry 2 where (*S*)-*iso*-VAPOL **3** is used instead of (*S*)-VANOL **2**.

Entry 6, Figure 3B: Same as entry 2 where (*S*)-*iso*-VAPOL **3** is used instead of (*S*)-VANOL **2**.

F. Crystallographic structure information about (*R*)-VANOL 2 and (*S*)-*iso*-VAPOL 3

i) X-ray Structure of (*R*)-VANOL 2

A colorless needle crystal with dimensions 0.88 x 0.07 x 0.03 mm was mounted on a Nylon loop using very small amount of paratone oil.

Data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 1.0° per frame for 60 s. The total number of images was based on results from the program COSMO where redundancy was expected to be 4.0 and completeness to 0.83 Å to 100%. Cell parameters were retrieved using APEX II software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software which corrects for Lp. Scaling and absorption corrections were applied using SADABS multi-scan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F^2, SHELXL-97, which are incorporated in SHELXTL-PC V 6.10.

The structure was solved in the space group $P2_12_12_1$ (# 19). All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The Flack parameter is used to determine chirality of the crystal studied, the value should be near zero, a value of one is the other enantiomer and a value of 0.5 is racemic. The Flack parameter was refined to -0.2(4), this did not confirm the absolute stereochemistry. The absolute stereochemistry was confirmed by comparing the reported optical rotation. All drawings are done at 50% ellipsoids. The full structural parameters for **2** have been submitted in Cambridge Crystallographic Data Center (Reference numbers CCDC 1006298).

Table S1: Crystal data and structure refinement for (*R*)-**2**.

Empirical formula	C32 H22 O2
Formula weight	438.50

Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.3293(2) Å	α= 90°.
	b = 25.9756(4) Å	β= 90°.
	c = 32.3117(5) Å	γ = 90°.
Volume	6990.9(2) $Å^3$	
Z	12	
Density (calculated)	1.250 Mg/m^3	
Absorption coefficient	0.601 mm^{-1}	
F(000)	2760	
Crystal size	0.38 x 0.07 x 0.03 mm^3	
Theta range for data collection	2.18 to 68.40°.	
Index ranges	-10<=h<=10, -31<=k<=30, -38<=l<=37	
Reflections collected	47412	
Independent reflections	12725 [R(int) = 0.1171]	
Completeness to theta = 68.40°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9805 and 0.8057	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	12725 / 0 / 925
Goodness-of-fit on F^2	1.007
Final R indices [I>2sigma(I)]	R1 = 0.0659, wR2 = 0.1388
R indices (all data)	R1 = 0.1332, wR2 = 0.1717
Absolute structure parameter	-0.2(4)
Largest diff. peak and hole	0.264 and -0.282 e.Å^{-3}

ii) X-ray Structure of (*S*)-*iso*-VAPOL 3

A yellow needle crystal with dimensions 0.36 x 0.16 x 0.09 mm was mounted on a Nylon loop using very small amount of paratone oil.

Data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 0.5° per frame for 30 s. The total number of images was based on results from the program COSMO where redundancy was expected to be 4.0 and completeness of 100% out to 0.83 Å. Cell parameters were retrieved using APEX II software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software which corrects for Lp. Scaling and absorption corrections were applied using SADABS[4] multi-scan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F^2, SHELXL- 97, which are incorporated in SHELXTL-PC V 6.10.

The structure was solved in the space group $P2_1$(# 4). All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All drawings are done at 50% ellipsoids. The full structural parameters for **2** have been submitted in Cambridge Crystallographic Data Center (Reference numbers CCDC 1006299).

Table S2: Crystal data and structure refinement for (*S*)-**3**.

Empirical formula	C40 H26 O2	
Formula weight	538.61	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 12.6245(9) Å	α= 90°.
	b = 8.1476(6) Å	β= 114.0900(10)°.
	c = 14.5440(11) Å	γ = 90°.
Volume	1365.69(17) $Å^3$	
Z	2	
Density (calculated)	1.310 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	564	
Crystal size	0.36 x 0.16 x 0.09 mm^3	
Theta range for data collection	1.77 to 26.30°.	
Index ranges	-15<=h<=15, -10<=k<=10, -18<=l<=18	
Reflections collected	12067	
Independent reflections	5459 [R(int) = 0.0319]	
Completeness to theta = 26.30°	99.9 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9932 and 0.9719
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5459 / 1 / 381
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.0813
R indices (all data)	R1 = 0.0545, wR2 = 0.0888
Absolute structure parameter	-1.1(12)
Largest diff. peak and hole	0.190 and -0.143 e.$Å^{-3}$

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