Supporting Information for: Dynamic Kinetic Asymmetric Cycloaddition of Isocyanates to Vinylaziridines

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General remarks

Anhydrous diethyl ether, methylene chloride, and acetonitrile were dried by passage through an aluminum column. Methanol was dried by distillation from sodium methoxide. Solvents were degassed by freeze-thaw techniques under vacuum.¹ Enantiomeric excesses of the imidazolidin-2-ones were determined by chiral HPLC compared to racemic samples prepared by the standard procedure with triphenylphosphine as the ligand. All isocyanates were purchased from Aldrich and used without further purification. 1-Amino-3-buten-2-ol,^{2a} *N*-tosyl-2-vinylaziridine,^{2b} (η^3 -C₃H₅Pd)₂,^{2c} and ligands **4**^{2d} and **5**^{2e} were prepared by literature procedures. All compounds are >95% pure by proton NMR unless otherwise noted.

Flash chromatography was performed on silica (EM Science, Kieselgel 60, 230-400mesh, ASTM) or neutral alumina (Fluka, Aluminum Oxide, type 507, Brockmann grade III, 6% hydrate) using compressed air. TLC was performed using glass-backed plates coated with 0.2mm silica (Merck, DC-Platten, Kieselgel; 60 F₂₅₄) or plastic backed plates coated with 0.2mm neutral alumina (EM, 60 F₂₅₄, Type E). Chiral HPLC analysis was performed on Daicel Chiralpack columns, eluting with heptane/2-propanol mixtures using a Thermo Separation Products Spectra SERIES P100 or P200 instruments. NMR spectra were carried out on a Varian GEM-300 (300MHz), Mercury 400 (400MHz), or Unity 500 (500MHz) instruments and are calibrated to TMS or residual solvent peaks. Optical rotation was measured on a Jasco DIP-1000 digital polarimeter in 5 cm cells at room temperature.

Part A: Synthesis of Vinylaziridines

N-Benzyl-2-vinylaziridine

1-Benzylamino-3-buten-2-ol was synthesized by a procedure adapted from Saavedra.³ A flame dried 250ml RB flask was charged with 1-amino-3-buten-2-ol (7.98g, 91.7mmol) and flushed with argon. Anhydrous methanol (92ml) followed by benzaldehyde (14ml, 14.6g, 137mmol) were added to the above amino alcohol, and the resulting homogeneous solution was stirred for 1.5h at room temperature. The solution was placed in an ice bath and NaBH₄ (5.21g, 137mmol) was added in small portions. After stirring for an additional 3h at ambient temperature, the solution was concentrated in vacuo to a heterogeneous oil. Methylene chloride (500ml) was added to the oil, and the organic phase was washed with aqueous NaHCO₃ sat. (1x250ml). The organic layer was extracted with aqueous 1M HCl (2x250ml), and the acidic aqueous extract was washed with methylene chloride (1x150ml). After basifying the acidic aqueous layer with aqueous 4M NaOH (150ml), the resulting heterogeneous solution was extracted with methylene chloride (2x250ml). The final organic extract was dried with MgSO₄, filtered and concentrated in vacuo to yield 1-benzylamino-3-buten-2-ol as a clear colorless oil (15.15g, 93%). ¹H NMR (CDCl₃ 200MHz) δ 7.20-7.40 (m, 5H), 5.82 (ddd, *J*=5.4, 10.4, 17.2Hz, 1H), 5.31 (dt, *J*=1.6, 17.2Hz, 1H), 5.24 (dt, *J*=1.4, 10.4Hz, 1H), 4.10-4.25 (m, 1H), 3.70-3.80 (m, 2H), 2.40-2.80 (m, 4H). ¹³C NMR (CDCl₃ 50MHz) δ 139.83, 138.90, 128.42, 128.07, 127.05, 115.42, 70.54, 54.11, 53.42. IR (neat) 3309,

3086, 3028, 2836, 1496, 1454, 1319, 1142, 1111, 1-66, 1029, 992, 923, 734, 699 cm^{-1} . HRMS (EI) calcd for $\text{C}_{11}\text{H}_{15}\text{NO}$ ($\text{M}^+ + \text{H}$) 178.1232 found 178.1232.

N-Benzyl-2-vinylaziridine was synthesized from a modified procedure of Lindstrom *et al*, and Sauleave *et al*.⁴ An oven dried 500ml R.B. flask was charged with Ph_3PBr_2 (25.0g, 59.2mmol), attached a 125ml addition funnel and flushed with argon. Anhydrous acetonitrile (200ml) was added followed by diisopropylethylamine (21.6ml, 16.0g, 124mmol). 1-Benzylamino-3-buten-2-ol (9.53g, 53.8mmol) dissolved in anhydrous acetonitrile (75ml) was added dropwise to the above solution at room temperature over a 20min period. The clear yellow-orange solution was stirred for 18h at room temperature under N_2 . Approximately 80% of the solution was removed in vacuo after which diethyl ether (250ml) was added. The heterogeneous mixture was vigorously stirred for 30min and filtered. The solids were washed with copious amounts of diethyl ether, and the filtrate was concentrated to a heterogeneous oil. This precipitation and wash was repeated twice with 1 diethyl ether : 1 petroleum ether to afford an oily solid after careful concentration in vacuo. *N*-Benzyl-2-vinylaziridine was isolated from the oily mixture via silica chromatography (1st 20% Et_2O in PE and 2nd 14% Et_2O in PE) as a slightly yellow clear oil (5.3g, 62%). This aziridine can be stored for months at -20°C in a desiccator without significant thermal decomposition. $d=0.946 \text{ g/ml}$ ^1H NMR (CDCl_3 300MHz) δ 7.20-7.40 (m, 5H), 5.59 (ddd, $J=7.8, 10.2, 17.7\text{Hz}$, 1H), 5.30 (dd, $J=1.2, 17.1\text{Hz}$, 1H), 5.11 (dd, $J=1.2, 10.5\text{Hz}$, 1H), 3.52 (d, $J=13.5\text{Hz}$, 1H), 3.46 (d, $J=13.8\text{Hz}$, 1H), 1.98-2.05 (m, 1H), 1.84 (d, $J=3.0\text{Hz}$, 1H), 1.63 (d, $J=6.3\text{Hz}$, 1H). ^{13}C NMR (CDCl_3 75MHz) δ 138.94, 138.18, 128.26, 127.73, 126.89, 116.24, 64.31, 41.32, 35.27. IR (neat) 3029, 2980, 2909, 2828, 1638, 1496, 1453, 1358, 1342, 1254, 1151, 1027, 989, 911, 733, 698 cm^{-1} . HRMS (EI) calcd for $\text{C}_{11}\text{H}_{13}\text{N}$ (M^+) 159.1048 found 159.1042.

N-(*o*-Nitro-benzyl)-2-vinyl-aziridine

1-(*o*-Nitro-benzylamino)-3-buten-2-ol was synthesized by the same procedure as for previous amino alcohol with *o*-nitrobenzaldehyde and isolated as a yellow solid (76%). Mp $64-68^\circ\text{C}$ ^1H NMR (CDCl_3 300MHz) δ 7.96 (d, $J=8.1\text{Hz}$, 1H), 7.54-7.64 (m, 2H), 7.39-7.48 (m, 1H), 5.83 (ddd, $J=17.1, 10.2, 5.4\text{Hz}$, 1H), 5.33 (dt, $J=17.1, 1.5\text{Hz}$, 1H), 5.16 (dt, $J=10.5, 1.4\text{Hz}$, 1H), 4.3-4.5 (m, 1H), 4.07 (s, 2H), 2.4-3.0 (m, 3H) 1.80 (bs, 1H). ^{13}C NMR (CDCl_3 75MHz) δ 149.09, 138.47, 135.11, 133.20, 131.27, 128.16, 124.83, 115.79, 70.77, 54.28, 50.55. IR (KBr –Neat) 3111, 2847, 1523, 1430, 1342, 1113, 1075, 1001, 943, 857, 793, 745, 702 cm^{-1} . HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_3$ ($\text{M}^+ + \text{H}$) 223.1083 found 223.1083

N-(*o*-Nitro-benzyl)-2-vinyl-aziridine was synthesized by the same procedure as for the previous aziridine from 1-(*o*-nitrobenzylamino)-3-buten-2-ol and isolated as a clear colorless oil (74%) after silica chromatography (30% Et_2O in PE). ^1H NMR (CDCl_3 400MHz) δ 8.03 (dd, $J=8.1, 1.2\text{Hz}$, 1H), 7.94-8.00 (m, 1H), 7.62-7.68 (m, 1H), 7.38-7.44 (m, 1H), 5.63 (ddd, $J=17.2, 10.4, 7.6\text{Hz}$, 1H), 5.35 (d, $J=17.2\text{Hz}$, 1H), 5.17 (d, $J=10.4\text{Hz}$, 1H), 4.04 (d, $J=17.2\text{Hz}$, 1H), 3.73 (d, $J=16.8\text{Hz}$, 1H), 2.0-2.2 (m, 1H), 1.96 (d, $J=3.2\text{Hz}$, 1H), 1.71 (d, $J=6.4\text{Hz}$, 1H). ^{13}C NMR (CDCl_3 100MHz) δ 147.57, 137.74, 135.48, 133.63, 129.57, 127.48, 124.55, 116.88, 61.00, 41.65, 35.75. IR (KBr –Neat) (KBr – Neat) 2983, 1611, 1525, 1342, 1304, 1033, 990, 914, 858, 809, 790, 729 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$ ($\text{M}^+ + \text{H}$) 205.0977 found 205.0982.

N-Benzyl-2-methyl-2-vinylaziridine

A 10ml flame dried test tube was charged with $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (31mg, 30 μmol), PPh_3 (39mg, 0.15mmol), flushed with argon and degassed and anhydrous CH_2Cl_2 (7.5ml) was added. After stirring for 10min at room temperature, isoprene monoepoxide (292_1, 250mg, 2.97mmol) and benzyl isocyanate (362_1, 336mg, 0.252mmol) were added dropwise in the respected order. After stirring for 18h in a seal tube of argon at room temperature, the solvent was removed in vacuo, and 3-benzyl-4-methyl-4-vinyl-oxazolidin-2-one was isolated via silica chromatography (40% DCM, 5% EtOAc in PE) as a yellow oily solid (470mg, 85%). ^1H NMR (CDCl_3 300MHz) δ 7.20-7.40 (m, 5H), 5.76 (dd, $J=17, 11\text{Hz}$, 1H), 5.28 (d, $J=11\text{Hz}$, 1H), 5.23 (d, $J=18\text{Hz}$, 1H), 4.50 (d, $J=16\text{Hz}$, 1H), 3.96-4.18 (m, 3H), 1.25 (s, 3H). ^{13}C NMR (CDCl_3 75MHz) δ 158.16, 138.62, 137.99, 128.37, 127.86, 127.34, 117.35, 73.88, 62.01, 44.49, 21.40. IR (KBr -Neat) 2979, 1753, 1432, 1400, 1362, 1310, 1163, 1083, 1060, 1040, 1015, 931, 763, 731, 706 cm^{-1} . HRMS (EI) calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ (M^+) 217.1103 found 217.1097.

2-Benzylamino-2-methyl-3-buten-1-ol was synthesized by a modified procedure published by Groneberg and coworkers.⁵ A 250ml R.B. flask was charged with 3-benzyl-4-methyl-4-vinyl-oxazolidin-2-one (4.65g, 21.4mmol), aqueous 50% NaOH (30ml), MeOH (30ml) and EtOH (10ml). The solution was refluxed for 1/2h at which point no starting oxazolidinone was present by TLC. Most of the alcohol was removed in vacuo and water (250ml) was added. The aqueous portion was extracted with CH_2Cl_2 (3x100ml). The organic portion was washed with aqueous 0.1M NaOH (1x100ml) and extracted with aqueous 1M HCl (3x100ml). The acidic aqueous extract was washed with CH_2Cl_2 (1x100ml), basified with aqueous 50% NaOH (25ml), and extracted with CH_2Cl_2 (3x100ml). The final organic extract was washed with 0.1M NaOH brine (1x100ml), dried with Na_2SO_4 , filtered and concentrated in vacuo to a tan clear oil (3.83g, 94%). ^1H NMR (CDCl_3 400MHz) δ 7.20-7.40 (m, 5H), 5.85 (dd, $J=18, 11\text{Hz}$, 1H), 5.24 (dd, $J=11, 1\text{Hz}$, 1H), 5.12 (dd, $J=18, 1\text{Hz}$, 1H), 3.65 (d, $J=12\text{Hz}$, 1H), 3.61 (d, $J=12\text{Hz}$, 1H), 3.44 (d, $J=10\text{Hz}$, 1H), 3.40 (d, $J=10\text{Hz}$, 1H), 1.24 (s, 3H). ^{13}C NMR (CDCl_3 100MHz) δ 141.98, 140.60, 128.45, 128.21, 127.01, 114.89, 68.04, 58.45, 46.77, 21.04. IR (KBr -Neat) 3301, 3085, 3064, 3029, 2975, 2928, 2866, 1453, 1414, 1049, 921, 731, 698 cm^{-1} . LRMS $\text{C}_{12}\text{H}_{17}\text{NO}$ ($\text{M}^+ + \text{H}$) 191.0, ($\text{M}^+ - \text{CH}_2\text{OH}$) 160.0, ($\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2^+$) 160.0, ($\text{C}_6\text{H}_5\text{CH}_2^+$) 91.0.

N-Benzyl-2-methyl-2-vinylaziridine was synthesized by a modification of several published procedures.⁶ A flame dried 10ml RB flask was charged with 2-benzylamino-2-methyl-but-3-en-1-ol (250mg, 1.31mmol), flushed with argon and anhydrous diethyl ether (5ml) was added. Chlorosulfonic acid (104_1, 183mg, 1.57mmol) was added at 0 $^\circ\text{C}$, and the resulting heterogeneous solution was vigorously stirred at 0 $^\circ\text{C}$ for 1.5h and at room temperature for 1h. The solid was collected by filtration, washed with copious amounts of anhydrous diethyl ether, and dried under high vacuum overnight to afford the sulfonate salt as a white powder in ~90% purity (351mg, ~98%). The crude sulfonate salt was used in the next reaction without further purification. ^1H NMR (DMSO 500MHz) δ 8.95-9.05 (bs, 2H), 7.35-7.55 (m, 5H), 6.03 (dd, 17.5, 11.5Hz, 1H), 5.45-5.55 (m, 2H), 4.00-4.15 (m, 3H), 3.88 (d, $J=11.0\text{Hz}$, 1H), 1.56 (s, 3H).

A flame dried 100ml R.B. flask was charged with the previously synthesized salt (784mg, 2.89mmol), flushed with argon, and anhydrous diethyl ether (50ml) was added. While vigorously stirring the heterogeneous solution at room temperature, $n\text{BuLi}$ (1.6M in hexanes, 3.6ml, 5.8

mmol) was added dropwise. The solution was vigorously stirred for 3h at room temperature, at which point an additional 70ml of ether was added. The organic portion was washed with H₂O (1x50ml), Brine (1x40ml), dried with Na₂SO₄, filtered and concentrated in vacuo to a yellow oil. *N*-Benzyl-2-methyl-2-vinylaziridine was purified by neutral alumina chromatography (Brockmann Grade III, 6% hydrate, 3.5% Et₂O in petroleum ether) and isolated as a clear and colorless oil (218mg, 44%). The aziridine readily decomposes at -10°C and should be used immediately. ¹H NMR (CDCl₃ 300MHz) δ 7.5-7.1 (m, 5H), 5.84 (dd, 17.4, 10.5Hz, 0.63H) other epimer 5.66 (17.4Hz, 10.5Hz, 0.37H), 5.27-5.02 (m, 2H), 3.67-3.57 (m, 2H), 1.99 (s, 1H), 1.66 (s, 0.63H) other epimer 1.51 (s, 0.37H), epimers 1.37 and 1.36 (s each, 3H total). ¹³C NMR (CDCl₃ 75MHz) δ Both epimers: 144.23, 140.04, 139.975, 136.67, 128.12, 127.47, 127.32, 126.51, 56.97, 56.63, 41.71, 41.05, 22.81, 12.91. (KBr –Neat) 3087, 3064, 3030, 2971, 2924, 2850, 1637, 1496, 1453, 1381, 1355, 1152, 1074, 1028, 995, 910, 732, 696 cm⁻¹. HRMS (EI) calcd for C₁₂H₁₅N (M⁺) 173.1204 found 173.1206.

***N*-(p-Methoxyphenyl)-2-vinylaziridine**

The procedure of Buchwald and coworkers⁷ was adapted for the synthesis of *N*-(p-methoxyphenylamino)-3-buten-2-ol. A flame dried 20ml test tube was charged with CuI (219mg, 1.15mmol), K₃PO₄ (4.9g, 23mmol) and 4-iodoanisole (2.7g, 12mmol). After flushing with argon, isopropyl alcohol (10ml), ethylene glycol (1.3ml, 23mmol) and 1-amino-3-buten-2-ol (1.0g, 12mmol) were added in the respected order. The tube was sealed under argon with a septa and stirred vigorously at 80 °C for 18h. The tube was allowed to cool to room temperature at which point water (50ml) was added. The aqueous heterogeneous mixture was extracted with Et₂O (4x100ml). The combined organic extracts were dried with Na₂SO₄, filtered and concentrated in vacuo to a purple oil. *N*-(p-Methoxyphenylamino)-3-buten-2-ol was isolated via silica chromatography (10-35% EtOAc in PE) as a green to tan oil (1.52g, 68%). ¹H NMR (CDCl₃ 300MHz) δ 6.74-6.84 (m, 2H), 6.58-6.68 (m, 2H), 5.90 (ddd, *J*=6, 11, 17Hz, 1H), 5.35 (dt, *J*=2, 17Hz, 1H), 5.22 (dt, *J*=1, 11Hz, 1H), 4.2-4.4 (m, 1H), 3.75 (s, 3H), 3.0-3.4 (m, 4H). ¹³C NMR (CDCl₃ 75MHz) δ 152.43, 142.00, 138.41, 116.11, 114.85, 114.77, 71.05, 55.06, 50.66. IR (KBr –Neat) 3388 bs, 2935, 2833, 1514, 1464, 1236, 1180, 1118, 1038, 925, 821, 733. HRMS (EI) calcd for C₁₁H₁₅NO₂ (M⁺) 193.1103 found 193.1102.

N-(p-Methoxyphenyl)-2-vinylaziridine was synthesized by the same procedure used for *N*-benzyl-2-vinylaziridine with *N*-(p-methoxyphenylamino)-3-buten-2-ol and isolated via neutral alumina chromatography (Brockmann Grade III, 6% hydrate, 2-6% Et₂O in Pentane) as a tan to yellow oil in reasonable purity (~11% yield and 90% pure by ¹H NMR) and used in the next step without further purification. ¹H NMR (CDCl₃ 300MHz) δ 6.88-6.96 (m, 2H), 6.77-6.82 (m, 2H), 5.54-5.72 (m, 1H), 5.44 (dd, *J*=1, 17Hz, 1H), 5.21 (dd, *J*=1, 10Hz, 1H), 3.75 (s, 3H), 2.54-2.63 (m, 1H), 2.25 (d, *J*=6Hz, 1H), 2.21 (d, *J*=3Hz, 1H). ¹³C NMR (CDCl₃ 75MHz) δ 155.01, 147, 137.52, 121.27, 116.77, 114.12, 55.37, 41.35, 35.13. IR (KBr –Neat) 3038, 2983, 2834, 1507, 1464, 1348, 1273, 1241, 1181, 1109, 1037, 989, 948, 917, 832, 799. HRMS (EI) calcd for C₁₁H₁₃NO (M⁺) 175.0997 found 175.1003.

Part B: Dynamic Kinetic Cycloaddition of Isocyanates to Vinylaziridines

Typical Procedure for the Palladium Catalyzed Dynamic Kinetic Asymmetric Cycloaddition of Isocyanates to VinylAziridines:

This procedure is a modified procedure published by Trost *et al* and Alper *et al*.⁸ A flame dried 10ml test tube was charged with $[(^3\text{C}_3\text{H}_5)\text{PdCl}]_2$ (2 mol % to aziridine), and ligand **5** (6 mol % to aziridine). The tube was flushed with argon and anhydrous and degassed methylene chloride (0.12M to aziridine) was added. After stirring for ~10min at room temperature, glacial acetic acid (10 mol % to aziridine) was added and stirring continued for another 10min. at room temperature. The aziridine was added to the homogeneous orange solution followed by the isocyanate (1 eq to aziridine) dropwise. The solution was stirred in an argon sealed test tube at room temperature until all aziridine was consumed by TLC. The homogeneous yellow to orange solution was concentrated to an oil, and the imidazolidin-2-one was isolated via chromatography. For scale up procedures, the isocyanate should be carefully added to the catalyst solution in a room temperature water bath to control the exothermic addition.

Table 2 Entry 1: (+)-(S)-1-Benzyl-3-phenyl-4-vinyl-imidazolidin-2-one

This reaction with *N*-benzyl-2-vinylaziridine and phenylisocyanate was complete in 2h, and the imidazolidin-2-one was isolated via silica chromatography (40% methylene chloride, 5% ethyl acetate in petroleum ether) as a yellow cloudy oil which solidified upon standing to an off white solid (99%). Chiralpak AD HPLC (10% 2-propanol in *n*-Heptane 1ml/min 254nm) shows 82% ee favoring 15.52 min over 19.02min. Mp=63-65°C. ¹H NMR (CDCl₃ 500MHz) δ 7.50-7.45 (m, 2H), 7.35-7.28 (m, 7H), 7.05 (t, *J*=7.5Hz, 1H), 5.77 (ddd, *J*=17.5,10.5,7.5Hz, 1H), 5.27 (d, *J*=17.5Hz, 1H), 5.20 (d, *J*=10.0Hz, 1H), 4.63-4.60 (m, 1H), 4.53 (d, *J*=15.0Hz, 1H), 4.42 (d, *J*=15.0Hz, 1H), 3.52 (t, *J*=9.0Hz, 1H), 3.04 (dd, *J*=8.5, 6.0Hz, 1H). ¹³C NMR (CDCl₃ 125MHz) δ 157.84, 139.12, 136.74, 136.35, 128.62, 128.54, 128.15, 127.52, 123.18, 120.40, 118.49, 56.37, 48.37, 47.99. IR (KBr –Neat) 2942, 1691, 1593, 1487, 1426, 1275, 1252, 1202, 926, 760, 695cm⁻¹. HRMS (EI) calcd for C₁₈H₁₈N₂O (M⁺) 278.1419 found 278.1415. Anal calcd for C₁₈H₁₈N₂O: C: 77.67, H: 6.52, N: 10.06, found C: 77.73, 6.25, 10.19. Recrystallization in 15% 2-propanol in *n*-heptane affords enantiomerically pure (+)-(S)-1-Benzyl-3-phenyl-4-vinyl-imidazolidin-2-one [α]_D^{25.8} = + 40.8° (c=1.14 in CHCl₃).

Table 2 Entry 2: 3-Benzoyl-1-benzyl-4-vinyl-imidazolidin-2-one

This reaction with *N*-benzyl-2-vinylaziridine and benzoylisocyanate was complete in 8h, and the imidazolidin-2-one via silica chromatography (40% DCM, 5% EtOAc in PE) was isolated as a yellow oil, (94%). Chiralpak AD HPLC (10% 2-propanol in *n*-heptane, 1ml/min, 254nm) shows 13% ee in favor of 12.53min over 17.92min. ¹H NMR (CDCl₃ 300MHz) δ 7.61-7.67 (m, 2H), 7.21-7.54 (m, 8H), 5.87 (ddd, *J*=7, 11, 17Hz, 1H), 5.36 (d, *J*=17Hz, 1H), 5.26 (d, *J*=11Hz, 1H), 4.92-5.02 (m, 1H), 4.42 (d, *J*=15Hz, 1H), 4.38 (d, *J*=15Hz, 1H), 3.54 (t, *J*=9Hz, 1H), 3.09 (dd, *J*=5,9Hz, 1H). ¹³C NMR (CDCl₃ 75MHz) δ 170.01, 154.10, 135.56, 134.99, 134.81, 131.40, 128.79, 128.71, 128.16, 127.94, 127.52, 117.84, 53.54, 47.58, 46.71. IR (KBr –Neat) 3062,

3031, 2924, 1732, 1667, 1490, 1425, 1338, 1248, 1179, 1157, 1079, 1029, 929, 800, 747, 718, 697, 662, 616 cm^{-1} . HRMS (EI) calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2$ (M^+) 306.1368 found 306.1365.

Table 2 Entry 3: (+)-(S)-1-Benzyl-3-(4-methoxy-phenyl)-4-vinyl-imidazolidin-2-one

This reaction with *N*-benzyl-2-vinylaziridine and *p*-methoxyphenylisocyanate was complete in 2h, and the imidazolidin-2-one via silica chromatography (40% DCM, 5% EtOAc in PE to 60% DCM, 5% EtOAc in PE) was isolated as a yellow oil which solidified to an off white solid upon standing, (99%). Chiralpak AD HPLC (20% 2-propanol in *n*-heptane, 1ml/min, 254nm) shows 90% ee in favor of 21.74min over 27.63min. $[\alpha]_{\text{D}}^{26.2} = +18.1^\circ$ ($c=1.68$ in CHCl_3 , 90% ee). ^1H NMR (CDCl_3 400MHz) δ 7.24-7.38 (m, 7H), 6.84-6.90 (m, 2H), 5.75 (ddd, $J=17.6$, 10.0, 7.6Hz, 1H), 5.22 (d, $J=17.2$ Hz, 1H), 5.17 (d, 10.4Hz, 1H), 4.48-4.58 (m, 2H), 4.39 (d, $J=15.2$ Hz, 1H), 3.78 (s, 3H), 3.50 (t, $J=9.2$ Hz, 1H), 3.02 (dd, $J=8.8$, 6.8Hz, 1H). ^{13}C NMR (CDCl_3 100MHz) δ 158.40, 156.01, 136.87, 136.46, 132.08, 128.60, 128.17, 127.48, 123.20, 118.81, 113.89, 57.41, 55.37, 48.18, 48.12. IR (KBr –Neat) 2938, 1702, 1514, 1487, 1439, 1356, 1245, 1180, 1035, 911, 828, 733, 701 cm^{-1} . HRMS (EI) calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$ (M^+) 308.1525 found 308.1529.

Table 2 Entry 4: (-)-(S)-1,3-Dibenzyl-4-vinyl-imidazolidin-2-one

This reaction with *N*-benzyl-2-vinylaziridine and benzylisocyanate was complete in 18h, and the imidazolidin-2-one via silica chromatography (40% DCM, 5% EtOAc in PE) was isolated as a cloudy oil (98%). Chiralpak AD HPLC (3% 2-propanol in *n*-heptane, 1ml/min, 220nm) shows 95% ee in favor of 37.31min over 34.99min. $[\alpha]_{\text{D}}^{26.9} = -35.1^\circ$ ($c=1.36$ in CHCl_3 , 94% ee by AD HPLC). ^1H NMR (CDCl_3 400MHz) δ 7.20-7.40 (m, 10H), 5.63 (ddd, $J=16.8$, 10.0, 8.8Hz, 1H), 5.22 (dd, $J=10.0$, 1.2Hz, 1H), 5.15 (d, $J=17.2$ Hz, 1H), 4.85 (d, $J=15.2$ Hz, 1H), 4.45 (d, $J=14.8$ Hz, 1H), 4.38 (d, $J=14.4$ Hz, 1H), 3.93 (d, $J=15.2$ Hz, 1H), 3.79 (q, $J=8.4$ Hz, 1H), 3.28 (t, $J=8.8$ Hz, 1H), 2.86 (dd, $J=8.8$, 7.6Hz, 1H). ^{13}C NMR (CDCl_3 100MHz) δ 160.50, 137.24, 137.10, 136.11, 128.57, 128.56, 128.46, 128.11, 127.39, 127.28, 119.72, 55.99, 48.28, 48.22, 45.49. IR (KBr –Neat) 3031, 2952, 2858, 1694, 1495, 1489, 1447, 1425, 1358, 1243, 910, 732, 702, 648 cm^{-1} . HRMS (EI) calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$ (M^+) 292.1576 found 292.1587.

Table 2 Entry 5: (+)-(S)-1-Benzyl-3-(2,4-dimethoxy-phenyl)-4-vinyl-imidazolidin-2-one

This reaction with *N*-benzyl-2-vinylaziridine and *o,p*-dimethoxyphenylisocyanate was complete in 18h, and the imidazolidin-2-one via silica chromatography (50% DCM, 5% EtOAc in PE to 50% DCM, 5% EtOAc in diethyl ether) was isolated as a yellow oil, (96%). Chiralcel OJ HPLC (10% 2-propanol in *n*-heptane, 1ml/min, 254nm) shows 91% ee in favor of 21.38min over 25.05min. $[\alpha]_{\text{D}}^{25.2} = +19.0^\circ$ ($c=0.753$ in CHCl_3 , 91% ee). ^1H NMR (CDCl_3 400MHz) δ 7.2-7.4

(m, 5H), 7.11 (d, $J=8.4\text{Hz}$, 1H), 6.49 (d, $J=2.8\text{Hz}$, 1H), 6.45 (dd, $J=8.4$, 2.4Hz , 1H), 5.73 (ddd, $J=17.2$, 9.6 , 8.4Hz , 1H), 5.00-5.60 (m, 2H), 4.56 (d, 15.2Hz , 1H), 4.42 (q, $J=8\text{Hz}$, 1H), 4.34 (d, $J=14.8\text{Hz}$, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.49 (t, $J=8.8\text{Hz}$, 1H), 3.02 (dd, $J=8.4$, 7.6Hz , 1H). ^{13}C NMR (CDCl₃ 100MHz) δ 159.96, 159.80, 156.82, 137.32, 136.89, 131.35, 128.50, 128.14, 127.30, 119.99, 118.75, 104.10, 99.57, 58.90, 55.59, 55.41, 48.60, 48.18. IR (KBr –Neat) 2938, 2839, 1699, 1613, 1588, 1514, 1441, 1424, 1308, 1283, 1245, 1209, 1160, 1034, 911, 732 cm^{-1} . HRMS (EI) calcd for C₂₀H₂₂N₂O₃ (M⁺) 338.1630 found 338.1637.

Table 2 Entry 6: (+)-(S)-1-Benzyl-3-(4-methylsulfanyl-phenyl)-4-vinyl-imidazolidin-2-one

This reaction with *N*-benzyl-2-vinylaziridine and *p*-methylthiophenylisocyanate was complete in 2h, and the imidazolidin-2-one was isolated via silica chromatography (45% methylene chloride with 5% EtOAc in petroleum ether) as a white cloudy oil that solidifies upon standing, (85%). Chiralpak AD HPLC (20% 2-propanol in *n*-heptane, 1ml/min, 254nm) shows 85% ee in favor of 22.77min over 29.87min. $[\alpha]_{\text{D}}^{26.4} = +11.6^\circ$ ($c=1.05$ in CHCl₃, 92.5% ee by AD HPLC). Mp= 50-53°C. ^1H NMR (CDCl₃ 500MHz) δ 7.24-7.45 (m, 9H), 5.75 (ddd, $J=17.0$, 10.0 , 7.5Hz , 1H), 5.26 (d, $J=17.5\text{Hz}$, 1H), 5.21 (d, $J=10.5\text{Hz}$, 1H), 4.60 (dd, $J=14.5$, 6.0Hz , 1H), 4.52 (d, $J=14.5\text{Hz}$, 1H), 4.41 (d, $J=15.0\text{Hz}$, 1H), 3.52 (t, $J=9.0\text{Hz}$, 1H), 3.04 (dd, $J=9.0\text{Hz}$, 6.0Hz , 1H), 2.45 (s, 3H). ^{13}C NMR (CDCl₃ 125MHz) δ 157.76, 136.88, 136.66, 136.20, 132.19, 128.65, 128.15, 127.89, 127.56, 121.00, 118.70, 56.45, 48.07, 48.00, 16.82. IR (KBr –Neat) 2924, 1697, 1498, 1429, 1356, 1328, 1270, 1202, 1154, 1093, 995, 955, 921, 826, 812, 746, 703 cm^{-1} .

Table 2 Entry 7: (S)-1-Benzyl-4-methyl-3-phenyl-4-vinyl-imidazolidin-2-one

This reaction with *N*-benzyl-2-methyl-2-vinylaziridine and phenylisocyanate was complete in 2h, and the imidazolidin-2-one was isolated via neutral alumina chromatography (Brockmann grade III, 6% hydrate, 13% EtOAc in petroleum ether) as a clear tan oil (60%). Chiralpak AD HPLC (10% 2-propanol in *n*-heptane, 1ml/min, 254nm) shows 80% ee in favor of 15.90min over 20.59min. ^1H NMR (CDCl₃ 300MHz) δ 7.1-7.4 (m, 10H), 6.05 (dd, $J=17.4$, 10.8Hz , 1H), 5.17 (d, $J=10.8\text{Hz}$, 1H), 5.12 (d, $J=17.7\text{Hz}$, 1H), 4.52 (d, $J=14.7\text{Hz}$, 1H), 4.45 (d, $J=14.7\text{Hz}$, 1H), 3.19 (d, $J=8.7\text{Hz}$, 1H), 3.11 (d, $J=8.7\text{Hz}$, 1H), 1.38 (s, 3H). ^{13}C NMR (CDCl₃ MHz) δ 158.66, 141.38, 137.24, 137.01, 128.58, 128.50, 128.13, 127.44, 126.92, 125.74, 115.32, 60.74, 55.90, 48.00, 21.91. IR (KBr –Neat) 2881, 1697, 1598, 1497, 1439, 1344, 1344, 1175, 931, 754, 738, 695 cm^{-1} . HRMS (EI) calcd C₁₉H₂₀N₂O (M⁺) 292.1576, found 292.1574.

Table 2 Entry 8: (+)-(S)-1-(2-Nitro-benzyl)-3-phenyl-4-vinyl-imidazolidin-2-one

This reaction with *N*-(*o*-nitrobenzyl)-2-vinylaziridine and phenylisocyanate was complete in 2h, and the imidazolidin-2-one via silica chromatography (40% DCM, 5% EtOAc in PE) was isolated as a yellow cloudy oil (99%). Chiralcel OJ HPLC (20% 2-propanol in *n*-heptane, 1ml/min, 254nm) shows 83% ee in favor of 37.78min over 32.52min. $[\alpha]_{\text{D}}^{24.8} = +18.4^\circ$ ($c=0.991$

in CHCl₃, 83% ee). ¹H NMR (CDCl₃ 400MHz) _ 8.01 (d, *J*=8.4Hz, 1H), 7.58-7.64 (m, 2H), 7.42-7.52 (m, 3H), 7.32 (t, *J*=8.4Hz, 2H), 7.07 (t, *J*=7.6Hz, 1H), 5.82 (ddd, *J*=17.2, 10.0, 7.2Hz, 1H), 5.32 (d, *J*=17.2Hz, 1H), 5.26 (d, *J*=10.4Hz, 1H), 4.78-4.88 (m, 2H), 4.68-4.76 (m, 1H), 3.68 (t, *J*=8.8Hz, 1H), 3.19 (dd, *J*=8.8, 6.0Hz, 1H). ¹³C NMR (CDCl₃ MHz) _ 158.07, 148.55, 138.78, 135.99, 133.65, 132.91, 129.93, 128.61, 128.30, 124.84, 123.43, 120.93, 118.79, 56.42, 49.22, 45.07. IR (KBr –Neat) 3065, 2983, 2935, 2872, 1705, 1599, 1529, 1502, 1431, 1357, 1253, 1046, 990, 933, 856, 790, 756, 729, 692 cm⁻¹. HRMS (EI) calcd for C₁₈H₁₇N₃O₃ (M⁺) 323.1270 found 323.1268.

Table 2 Entry 9: (+)-(S)-3-(4-Methoxy-phenyl)-1-(2-nitro-benzyl)-4-vinyl-imidazolidin-2-one

This reaction with *N*-(*o*-nitrobenzyl)-2-vinylaziridine and *p*-methoxy-phenylisocyanate was complete in 2h, and the imidazolidin-2-one via silica chromatography (50% DCM, 5% EtOAc in PE) was isolated as a yellow oil (99%). Chiralpak AD HPLC (20% 2-propanol in *n*-heptane, 1ml/min, 254nm) shows 82% ee in favor of 36.72min over 39.21min. [α]_D^{23.5} = +8.7° (*c*=1.2 in CHCl₃, 82% ee). ¹H NMR (CDCl₃ 300MHz) _ 8.01 (d, *J*=8.1Hz, 1H), 7.62 (d, *J*=4.5Hz, 2H), 7.30-7.48 (m, 3H), 6.84-6.92 (m, 2H), 5.80 (ddd, *J*=17.4, 9.9, 7.5Hz, 1H), 5.27 (d, *J*=16.8, 1H), 5.23 (*J*=10.2Hz, 1H), 4.85 (d, *J*=16.8Hz, 1H), 4.78 (d, *J*=16.8Hz, 1H), 4.62 (q, *J*=7.8Hz, 1H), 3.78 (s, 3H), 3.66 (t, *J*=9.0Hz, 1H), 3.17 (dd, *J*=8.7, 6.6Hz, 1H). ¹³C NMR (CDCl₃ 75MHz) _ 158.60, 156.22, 148.60, 136.14, 133.62, 133.05, 131.74, 130.02, 128.26, 124.81, 123.20, 119.10, 113.94, 57.45, 55.38, 49.32, 45.17. IR (KBr –Neat) 2935, 1702, 1610, 1578, 1514, 1488, 1437, 1357, 1296, 1246, 1181, 1035, 931, 857, 829, 790, 731 cm⁻¹. HRMS (EI) calcd C₁₉H₁₉N₃O₄ (M⁺) 353.1376 found 353.1373.

Table 2 Entry 10: (S)-1-(4-Methoxy-phenyl)-3-phenyl-4-vinyl-imidazolidin-2-one

This reaction with *N*-(*p*-methoxyphenyl)-2-vinylaziridine and phenylisocyanate was complete in 18h, and the imidazolidin-2-one via silica chromatography (30% DCM, 5% EtOAc in PE) was isolated as white solid (52%). Chiralpak AD HPLC (10% 2-propanol in *n*-heptane, 1ml/min, 254nm) shows 74% ee in favor of 39.28min over 46.27min. ¹H NMR (CDCl₃ 400MHz) _ 7.44-7.52 (m, 4H), 7.31-7.37 (m, 2H), 7.10 (tt, *J*=1.2, 7.2Hz, 1H), 6.91 (d, *J*=9.2Hz, 2H), 5.87 (ddd, *J*=7.2, 10.0, 17.2Hz, 1H), 5.39 (d, *J*=17.2Hz, 1H), 5.30 (d, *J*=10.4Hz, 1H), 4.79 (dd, *J*=7.6, 16.4Hz, 1H), 4.10 (t, *J*=9.2Hz, 1H), 3.80 (s, 3H), 3.63 (dd, *J*=6.0, 8.8Hz, 1H). ¹³C NMR (CDCl₃ 125MHz) _ 155.63, 155.35, 138.64, 136.16, 133.10, 128.60, 123.75, 121.16, 119.95, 119.31, 114.10, 56.08, 55.47, 49.10. IR (KBr –Neat) 2924, 1697, 1518, 1410, 1359, 1285, 1239, 934, 824, 770, 744, 691 cm⁻¹. HRMS (EI) calcd for C₁₈H₁₈N₂O₂ (M⁺) 294.1368 found: 294.1363.

Table 2 Entry 11: (S)-3-Phenyl-1-(toluene-4-sulfonyl)-4-vinyl-imidazolidin-2-one

This reaction with *N*-tosyl-2-vinylaziridine and phenylisocyanate was complete in 2h, and the imidazolidin-2-one via silica chromatography (35% DCM, 5% EtOAc in PE) was isolated

as pale white solid, (61%). Chiralpak AD HPLC (20% 2-propanol in n-heptane, 1ml/min, 254nm) shows 65% ee in favor of 16.72min over 20.22min. The product can be recrystallized into white needles with 20% 2-propanol in n-heptane without any increase in ee. Mp 141-143°C. ¹H NMR (CDCl₃ 300MHz) δ 7.96 (d, *J*=8.4Hz, 2H), 7.20-7.40 (m, 6H), 7.11 (t, *J*=6.9Hz, 1H), 5.73 (ddd, *J*=17.4, 10.2, 7.8Hz, 1H), 5.28 (d, *J*=16.8, 1H), 5.26 (d, *J*=10.2Hz, 1H), 4.67 (q, *J*=8.1Hz, 1H), 4.11 (t, *J*=9.0Hz, 1H), 3.71 (dd, *J*=9.3, 5.4Hz, 1H), 2.43 (s, 3H). ¹³C NMR (CDCl₃ 75MHz) δ 151.80, 144.99, 136.77, 134.65, 134.36, 129.65, 128.76, 128.26, 125.12, 121.80, 120.27, 56.48, 47.50, 21.61. IR (KBr –Neat) 2363, 2346, 1715, 1598, 1497, 1365, 1224, 1187, 1172, 1114, 1094, 810, 748, 706, 693, 664 cm⁻¹. HRMS (EI) calcd for C₁₈H₁₈N₂O₃S (M⁺) 342.1038 Found 342.1037. Anal. Calcd for C₁₈H₁₈N₂O₃S: C: 63.14, H: 5.30, N: 8.18, Found C: 63.31, H: 5.28, N: 8.16.

Part C: Conversion of Imidazolidin-2-ones to Diamines

N¹-Benzyl-N²-phenyl-but-3-ene-1,2-diamine (8a)

This reduction is a modified procedure from the published one of Kavrakova and Lyapova.⁹ A oven dried 25ml R.B. flask was charged with LiAlH₄ (41mg, 1.1mmol) and flushed with argon. Anhydrous diethyl ether (15ml) followed by imidazolidin-2-one **6a** (100mg, 0.36mmol) as a solid were added. The heterogeneous solution was stirred at reflux for 2.5h at which point no starting imidazolidin-2-one was present by TLC. Water (100_1), aqueous 4M NaOH (100_1), and H₂O (200_1) were added dropwise at 0 °C in the respected order. The mixture was vigorous stirred for 15min. The mixture was diluted with diethyl ether (15ml), dried with Na₂SO₄, filtered and concentrated in vacuo to a cloudy yellow oil. 1-Benzyl-3-phenyl-2-vinylimidazolidin was clean by ¹H NMR and taken into the next step without further purification. ¹H NMR (CDCl₃ 300MHz) δ 7.2-7.4 (m, 5H), 7.18 (t, *J*=8.4Hz, 2H), 6.69 (t, *J*=7.5Hz, 1H), 6.54 (d, *J*=7.8Hz, 2H), 5.90 (ddd, *J*=6.6, 10.5, 17.1Hz, 1H), 5.30, (d, *J*=17.1Hz, 1H), 5.18 (d, *J*=10.2Hz, 1H), 4.29 (d, *J*=5.1Hz, 1H), 4.18 (dd, *J*=6.6, 11.1Hz, 1H), 3.92 (d, *J*=4.8Hz, 1H), 3.77 (d, *J*=12.9Hz, 1H), 3.70 (d, *J*=12.9Hz, 1H), 3.05 (dd, *J*=6.0, 9.3Hz, 1H), 2.86 (dd, *J*=4.2, 9.6Hz, 1H). ¹³C NMR (CDCl₃ MHz) δ 146.48, 139.12, 138.28, 128.97, 128.60, 128.41, 127.26, 116.59, 115.91, 112.19, 71.53, 60.61, 59.40, 58.44. IR (KBr –Neat) 3062, 3028, 2920, 2801, 1599, 1507, 1454, 1364, 1208, 1156, 1029, 993, 911, 747, 693 cm⁻¹. GCMS calcd for C₁₈H₂₀H₂ (M⁺) 264 found 264, (M⁺ - H) 263.

This hydrolysis for the formation of diamine **8a** is a modified procedure from the one published by Hesse and coworkers.¹⁰ A 25ml R.B. flask was charged with the imidazolidine **7a** (all material from the previous step), H₂NOH·HCl (125mg, 1.8mmol) and aqueous 0.01% HCl (10ml). The heterogeneous mixture was stirred at 60°C for 1h at which point an aliquot partitioned between EtOAc and aqueous Na₂CO₃ sat. showed no starting imidazolidine by TLC. Aqueous 0.5M HCl (50ml) was added to the homogeneous solution, and the resulting mixture was washed with CHCl₃ (2x40ml). The aqueous portion was carefully basified with copious amounts of solid Na₂CO₃ and extracted with CHCl₃ (5x40ml). The organic extracts were dried with Na₂SO₄, filtered and concentrated in vacuo to yield clean diamine **8a** as a cloudy yellow oil (82.1mg, 91% for both steps). ¹H NMR (CDCl₃ 400MHz) δ 7.28-7.34 (m, 5H), 7.14 (t, *J*=8.0Hz, 2H), 6.68 (t, *J*=7.2Hz, 1H), 6.63 (d, *J*=7.6Hz, 2H), 5.76 (ddd, *J*=5.6, 10.4, 17.2Hz, 1H), 5.27 (d, *J*=16.0Hz, 1H), 5.16 (d, *J*=10.0Hz, 1H), 4.34 (bs, 1H), 3.90-4.00 (m, 1H), 3.82 (d, *J*=13.2Hz,

1H), 3.78 (d, $J=13.6\text{Hz}$, 1H), 2.84 (dd, $J=4.8, 12.0\text{Hz}$, 1H), 2.78 (dd, $J=7.2, 12.0\text{Hz}$, 1H), 1.50 (bs, 1H). ^{13}C NMR (CDCl₃ MHz) δ 147.78, 140.08, 138.38, 129.05, 128.42, 128.03, 127.01, 117.32, 116.27, 113.57, 55.37, 53.63, 52.91. IR (KBr –Neat) 3396, 3052, 3026, 2898, 2835, 1602, 1504, 1453, 1430, 1317, 1120, 993, 922, 749, 693 cm^{-1} .

(+)-(S)-N,N-Dibenzyl-but-3-ene-1,2-diamine (8b)

This reduction is a modified procedure from the published one of Kavrakova and Lyapova.⁹ A oven dried 50ml R.B. flask was charged with LiAlH₄ (130mg, 3.4mmol) and flushed with argon. Anhydrous diethyl ether (20ml) was added followed by imidazolidin-2-one **6b** (250mg, 0.86mmol) dissolved in 10ml of anhydrous diethyl ether dropwise at room temperature. The heterogeneous solution was stirred at reflux for 20h at which point no starting imidazolidin-2-one was present by TLC. Water (150_l), aqueous 4M NaOH (150_l), and water (250_l) were added dropwise in the respected order at room temperature. The mixture was vigorously stirred for another 15min. The mixture was diluted with methylene chloride (45ml), dried with Na₂SO₄, filtered and concentrated in vacuo to a colorless oil. 1,3-Dibenzyl-4-vinylimidazolidine **7b** was clean by ^1H NMR and taken into the next step without further purification. ^1H NMR (CDCl₃ 300MHz) δ 7.1-7.4 (m, 10H), 5.84 (ddd, $J=8.1, 9.9, 17.4\text{Hz}$, 1H), 5.24 (d, $J=17.1\text{Hz}$, 1H), 5.14 (d, $J=9.9\text{Hz}$, 1H), 4.00 (d, $J=13.2\text{Hz}$, 1H), 3.6-3.8 (m, 3H), 3.2-3.4 (m, 3H), 3.08 (dd, $J=7.2, 9.6\text{Hz}$, 1H), 2.63 (dd, $J=8.1, 9.3\text{Hz}$, 1H). ^{13}C NMR (CDCl₃ 75MHz) δ 139.34, 138.97, 138.89, 128.55, 128.47, 128.20, 128.15, 126.90, 126.80, 117.02, 76.16, 66.98, 59.78, 58.68, 56.84. IR (KBr –Neat) 3063, 3028, 2915, 2797, 1494, 1454, 1358, 1308, 1170, 1072, 1028, 992, 922, 737, 698 cm^{-1} . HRMS (EI) calcd for C₁₉H₂₂N₂ ($\text{M}^+ - \text{H}$) 277.1705 found 277.1720.

This hydrolysis is a modified procedure from the one published by Hesse and coworkers.¹⁰ A 50ml R.B. flask was charged with the imidazolidine **7b** (all material from the previous step, H₂NOH·HCl (297mg, 4.3mmol) and aqueous 0.01% HCl (25ml). The heterogeneous mixture was stirred at 60°C for 1h at which point an aliquot partitioned between EtOAc and aqueous Na₂CO₃ sat. showed no starting imidazolidine by TLC. Aqueous 0.5M HCl (100ml) was added to the homogeneous solution, and the resulting solution was washed with CHCl₃ (2x50ml). The aqueous portion was carefully basified with copious amounts of solid Na₂CO₃ and extracted with CHCl₃ (7x50ml). The organic extracts were dried with Na₂SO₄, filtered and concentrated in vacuo to yield clean diamine **8b** as a yellow cloudy oil (214mg, 94% for both steps). $[\alpha]_D^{25.3} = +16.3$ ($c=1.12$ in CHCl₃, 95% ee). ^1H NMR (CDCl₃ 300MHz) δ 7.1-7.4 (m, 10H), 5.66 (ddd, $J=7.8, 9.9, 17.1\text{Hz}$, 1H), 5.20 (d, $J=17.1\text{Hz}$, 1H), 5.18 (d, $J=10.5\text{Hz}$, 1H), 3.85 (d, $J=13.2\text{Hz}$, 1H), 3.73 (s, 2H), 3.62 (d, $J=13.2\text{Hz}$, 1H), 3.19 (dd, $J=7.8, 12.9\text{Hz}$, 1H), 2.69 (dd, $J=5.1, 11.7\text{Hz}$, 1H), 2.61 (dd, $J=8.1, 12.0\text{Hz}$, 1H), 1.66 (bs, 2H). ^{13}C NMR (CDCl₃ 75MHz) δ 140.64, 140.41, 139.59, 128.33, 128.16, 128.03, 126.84, 116.95, 60.27, 53.73, 53.59, 51.13. IR (KBr –Neat) 3312, 3062, 3027, 2828, 1495, 1453, 1114, 1028, 994, 921, 735, 698 cm^{-1} . HRMS (EI) calcd for C₁₈H₂₂N₂ ($\text{M}^+ - \text{CH}_2\text{NHCH}_2\text{C}_6\text{H}_5$) 147.1048 found 147.1048, ($\text{CH}_2\text{NHCH}_2\text{C}_6\text{H}_5^+$) calcd 120.0811 found 120.0827, ($\text{CH}_2\text{C}_6\text{H}_5^+$) calcd 91.0546 found 91.0570.

Part D: Synthesis of SALEN ligand 10

SALEN LIGAND (+)-(S)-10

This procedure is a modified one published by Choi, Dondoni, Lakshmi and coworkers.¹¹ Two 10ml test tubes were charged with diamine **8b** (A: 75mg, 0.28mmol, B: 50mg, 0.15mmol), Pd(OH)₂/C 20wt % (A: 30mg, B: 16mg), and anhydrous methanol (A: 7ml, B: 4ml). The tubes were sealed with a septa and a needle was inserted. The tubes were placed in a parr apparatus and stirred under 85 psi of H₂ after flushing 4 times with 85 psi of H₂. The reaction was monitored by removing a 1ml aliquot from reaction B that was filtered through a cotton plug, protonated with concentrated HCl (100_1), concentrated in vacuo, and subsequently examined by ¹H NMR. The olefin was completely hydrogenated and the benzyl groups were removed at room temperature at 26h under 85 psi of H₂. Reaction A was filtered through a cotton plug, and plug of solid Na₂SO₄ to furnish a clear homogeneous solution of the diamine **9** in MeOH. Reaction B was filtered by the same procedure as A and protonated with concentrated HCl (100_1). The resulting solution of B was concentrated in vacuo to afford a NMR sample of the HCl salt of diamine **9**: ¹H NMR (D₂O, 300MHz) _ 3.42-4.47 (m, 1H), 3.20 (d, *J*=6.3Hz, 2H), 1.59-1.72 (m, 2H), 0.91 (t, *J*=7.5Hz, 3H).

The methanol filtrate of reaction A was stirred at 60 °C and salicylaldehyde (66_1, 76mg, 0.62mmol) was added. The solution was stirred for 2h at which point the clear bright yellow solution was concentrated in vacuo to a bright yellow oil. The oil was taken up in anhydrous acetonitrile (60ml) and washed with hexane (5x40ml). The acetonitrile layer was filtered through a cotton plug and concentrated in vacuo to a bright yellow oil. The oil was further concentrated at 60 °C and 8 torr for 5h to afford the SALEN ligand **10** in ~80% purity by ¹H NMR as a bright yellow oil (67.5mg, ~60% considering 80% purity). [α]_D^{27.0} = +173 (c=0.660 in CHCl₃, 95% ee ~80 pure). (lit^{11a} [α]_D = +223 (c=0.72 in CHCl₃)) ¹H NMR (CDCl₃ 400MHz) _ 13.2 (bs, 2H), 8.31 (s, 1H), 8.30 (s, 1H), 7.18-7.32 (m, 4H), 6.90-6.96 (m, 2H), 6.82-6.88 (m, 2H), 3.93 (dd, *J*=4.4, 16.8Hz, 1H), 3.69 (dd, *J*=7.6, 12.0Hz, 1H), 3.36-3.47 (m, 1H), 1.65-1.90 (m, 2H), 0.95 (t, *J*=7.2Hz, 3H). ¹³C NMR (CDCl₃ 100MHz) _ 166.36, 165.06, 161.01, 132.31, 132.28, 131.50, 131.42, 118.63, 118.60, 116.90, 116.88, 71.65, 64.41, 27.06, 10.57. IR (KBr -Neat) 3420 bs, 2970, 2925, 2880, 2850, 1631, 1580, 1498, 1460, 1279, 1151, 756 cm⁻¹. HRMS (EI) calcd for C₁₈H₂₀N₂O₂ (M⁺) 296.1525 found 296.1516.

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