Supplementary Material for OL016254 "Synthesis of Chiral Benzimidazolium Salts by an Amination/Ring Closure Sequence" by Rivas, F. R.; Riaz, U.; Giessert, A.; Smulik, J.; Diver, S. T.

Experimental Section

General Information. Reactions were conducted under an argon atmosphere unless otherwise noted. Toluene was distilled from CaH_2 immediately prior to use. Ethylene glycol dimethyl ether (DME), was distilled from sodium benzophenone ketyl prior to use. Pd_2dba_3 and (±)-BINAP were purchased from Strem Chemicals company. Sodium *tert*-butoxide (Na*t*-OBu) was purchased from Aldrich Chemical company and transferred inside a drybox to small vials that were then stored in a dessicator filled with anhydrous calcium sulfate, and weighed in the air. Aniline was treated with stannous chloride and distilled prior to use. Acetyl chloride, n-propionyl chloride, and benzoyl chloride were distilled prior to use. (*R*)-(-)-1-Amino-1-phenyl-2-methoxyethane was prepared as in ref. 1. 1-(*N*,*N*-Dimethylamino)-1'-(dicyclohexylphosphino) biphenyl was prepared as in ref. 2. All other reagents were purchased from Aldrich Chemical company and used without additional purification. Reactions were conducted in oven-dried, sealable Schlenk or pressure tubes equipped with a threaded teflon plug and magnetic stirbar. Column chromatography was carried out on Merck silica gel 60 (230-400 mesh). ^{1}H-NMR spectra were recorded at 400, or 500 MHz and ^{13}C-NMR spectra at either 75 or 125 MHz in the indicated solvent. ^{1}H-NMR spectra were referenced on the TMS signal for $CDCl_3$ solvent and at 1.93 ppm on the residual CHD_2CN for CD_3CN solvent. The ^{13}C-NMR spectra were referenced at 77.0 ppm for $CDCl_3$ and at 1.3 ppm for CD_3CN. Optical rotations were measured using the sodium D line in a thermostatted cell held at 25˚C. Enantiomeric and diastereomeric excesses were determined by HPLC using a Chiralcel OD-H column, *i*–propanol/hexane at the indicated ratio and rate, and UV-254 unless stated otherwise. Melting

points are uncorrected. IR spectra were obtained using Nicolet Impact series 420 IR. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA.

(2-Bromophenyl)-(*S*)-α-methylbenzylamine 1. Into an oven-dried 50 mL Schlenk tube equipped with magnetic stirbar and rubber septum was added 45.7 mg of Pd_2dba_3 (0.0499 mmol, 1.00 mol %), 62.3 mg of *rac*-BINAP (0.100 mmol, 2.00 mol %), and 625.0 mg of Na*t*-OBu (6.50 mmol, 1.30 eq.) under Ar. Toluene (7.0 mL) was added via an oven-dried syringe, followed by 0.77 mL of 98 % ee (*S*)-α-methylbenzyl-amine (6.0 mmol, 1.20 eq.) and 0.60 mL of 1,2-dibromobenzene (5.0 mmol, 1.00 eq.). The mixture was degassed, backfilled with Ar, sealed and then heated in an oil bath at 95˚C with stirring until the starting material had been completely consumed. The solution was then allowed to cool to room temperature, diluted with diethyl ether, filtered through a pad of celite and concentrated *in vacuo* (rotatory evaporator) to give a crude dark brown oil which was purified by flash chromatography (elution with 1% ethyl acetate/hexane) to provide 1.16 g of **1** (84.1%) as a clear oil. Analytical tlc (1% ethyl acetate/hexanes) R_f 0.22. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.33-7.28 (m, 4H), 7.24-7.20 (m, 1H), 6.97 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1H), 6.49 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1H), 6.36 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.70 (br d, *J* = 3.6 Hz, 1H), 4.51 (app quin, 1H), 1.57 (d, *J* = 7.2 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.5, 144.0, 132.2, 128.7, 128.3, 127.0, 125.7, 117.7, 112.6, 109.6, 53.5, 25.1; FT-IR (thin film, cm^{-1}) 3411, 3062, 3026, 2965, 2867, 1596, 1508, 1450, 1426, 1321, 1204, 744; High-resolution MS (EI^+, m/z) molecular ion calcd for $C_{14}H_{14}{}^{79}BrN$ 275.0310, found 275.0302 (^{79}Br), error 2.6 ppm; Enantiomeric excess determination by HPLC (0.5 mL/min, 10% *i*-propanol/hexane, t_R = 8.4 (*S*) and 11.7 (*R*) min) indicated 99% ee.

(2-Bromophenyl)-(*S*)-1-cyclohexylethylamine 2. Into an oven-dried 50 mL Schlenk tube equipped with magnetic stirbar and rubber septum was

added 91.6 mg of Pd_2dba_3 (0.100 mmol, 2.00 mol %), 186.8 mg of *rac*-BINAP (0.300 mmol, 6.00 mol %), and 672.7 mg of Na*t*-OBu (7.00 mmol, 1.40 eq.) under Ar. Toluene (15 mL) was added via an oven-dried syringe, followed by 0.820 mL of (*S*)-1-cyclohexylethyl-amine (5.52 mmol, 1.10 eq., 95 % ee) and 600 μL of 1,2-dibromobenzene (5.00 mmol, 1.00 eq.). The mixture was degassed, backfilled with Ar, sealed and then heated in an oil bath at 110˚C with stirring for 14 h. The solution was allowed to cool to room temperature, diluted with ether, extracted once with H_2O, filtered through a pad of Celite and concentrated *in vacuo* (rotatory evaporator) to give a crude dark brown oil. Filtration through a plug of silica gel using 1:1 CH_2Cl_2/hexane followed by concentration *in vacuo* gave an orange oil that was further purified by flash chromatography (elution with 0.5% ethyl acetate/hexane) to provide 892 mg of **2** (63.2%) as a clear oil. Analytical tlc (1% ethyl acetate/hexanes) R_f 0.27. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.13 (ddd, *J* = 7.8, 7.8, 1.3 Hz, 1H), 6.59 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.48 (ddd, *J* = 7.8, 7.8, 1.3 Hz, 1H), 4.22 (br d, *J* = 8.4 Hz, 1H), 3.35 (m, 1H), 1.85-1.66 (m, 5H), 1.53-1.43 (m, 1H), 1.31-0.98 (m, 5H), 1.15 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.6, 132.5, 128.4, 116.8, 111.5, 109.8, 53.1, 42.9, 29.6, 28.5, 26.6, 26.4, 26.3, 17.4; FT-IR (thin film, cm^{-1}) 3416, 3073, 2966, 2851, 2670, 1598, 1505, 1449, 1324, 1284, 1164, 738; High-resolution MS (EI^+, m/z) molecular ion calcd for $C_{14}H_{20}{}^{79}BrN$ 281.0779, found 281.0778 (^{79}Br), error 0.4 ppm; Enantiomeric excess determination by HPLC (0.25 mL/min, 10% *i*-propanol/hexane, t_R = 14.4 (*S*) and 15.6 (*R*) min) indicated 96% ee.

(2-Bromophenyl)-(*R*)-2-methoxy-1-phenylethylamine 3. Into an oven-dried 50 mL Schlenk tube equipped with magnetic stirbar and rubber septum was added 60.0 mg of Pd_2dba_3 (0.0655 mmol, 2.0 mol %) and 82.0 mg of *rac*-BINAP (0.132 mmol, 4.0 mol %). Toluene (10.0 mL) was added via an oven-dried syringe and the solution was heated in an oil bath at 80˚C for 15 min. The solution was then allowed to cool to room

temperature and 500.0 mg of (*R*)-(-)-1-amino-1-phenyl-2-methoxyethane (3.30 mmol, 1.0 eq.), 398 μL of 1,2-dibromobenzene (3.30 mmol, 1.0 eq.), and 478.4 mg of Na*t*-OBu (4.98 mmol, 1.5 eq.) were added under Ar. The mixture was degassed, backfilled with Ar, sealed and then heated in an oil bath at 80˚C with stirring for 48 h. The solution was allowed to cool to room temperature, diluted with ether, extracted once with H_2O, filtered through a pad of Celite and concentrated *in vacuo* (rotatory evaporator) to give a crude dark brown oil. Filtration through a plug of silica gel using 1:1 CH_2Cl_2/hexane followed by concentration *in vacuo* gave an orange oil that was further purified by flash chromatography (gradient elution with 1% ethyl acetate/hexane to 10 % ethyl acetate/hexane) to provide 986 mg of **3** (98%) as a clear oil. Analytical tlc (25% ethyl acetate/hexanes) R_f 0.53. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.0 Hz, 2H), 7.33 (t, *J* = 7.0, 2H), 7.26 (t, *J* = 7.0 Hz, 1H), 6.95 (t, *J* = 8.0 Hz, 1H). 6.51 (t, *J* = 8.0 Hz, 1H), 6.33 (d, *J* =8.0 Hz, 1H), 5.23 (br s, 1H), 4.55 (m, X of ABX, 1H), 3.67 (br d, A of ABX, 1H), 3.59 (br t, B of ABX, 1H), 3.41 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 144.3, 140.0, 132.2, 128.7, 128.2, 127.5, 126.6, 118.1, 113.0, 110.3, 76.8, 58.9, 58.0; FT-IR (thin film) 3397, 3062, 3027, 2926, 2859, 2826, 1596, 1505, 1452, 1322, 1118, 743 cm^{-1}; High-resolution MS (EI^+, m/z) molecular ion calcd for $C_{15}H_{16}{}^{79}BrNO$ 305.0415, found 305.0430 (^{79}Br), error 4.7 ppm; Low resolution MS (EI^+, m/z) 305.0 (M^+, ^{79}Br) 307.0 (M^+, ^{81}Br), $[\alpha]^{25}_D$ = +119 (c = 4.2, CH_2Cl_2).

***N,N'*-Bis (*S*)-α-methylbenzyl-1,2-diaminobenzene 4.** A flame-dried resealable 25 mL Schlenk flask equipped with a stirbar and rubber septum was cooled under vacuum and backfilled with argon. The flask was charged with 18.5 mg of Pd_2dba_3 (0.020 mmol, 4.0 mol %), 25.1 mg of *rac*-BINAP (0.040 mmol, 8.0 mol %) and 2.5 mL of toluene. The septum was replaced with a teflon screwcap and the mixture was degassed twice under high vacuum with an argon purge. The flask was sealed, and the mixture was heated at 130-135˚C in an oil bath for 15-20 min. After

cooling the mixture to room temperature, the teflon screwcap was replaced with a septum and then added 99.4 mg of NaO*t*-Bu (1.03 mmol, 2.05 equiv), 162 μL of (*S*)-α-methylbenzyl-amine (1.26 mmol, 2.50 eq., 98% ee), 139.3 mg of **1** (0.504 mmol, 1.00 eq.) and toluene (1.0 mL). The septum was replaced with a teflon screwcap and the mixture was degassed (4 times) under high vacuum with an argon purge. The flask was sealed, and the mixture was heated in an oil bath at 130-135˚C with stirring until the starting material had been completely consumed as judged by GC analysis. Reaction was completed in 1.5 h. The mixture was allowed to cool to room temperature, diluted with ether (5.0 mL), filtered through a celite pad, and concentrated *in vacuo* (rotatory evaporator). Flash chromatography of the dark colored residue (elution with 15-20 % CH_2Cl_2 and hexane) afforded 114 mg of **2** (71%) as a pale yellow oil. Analytical tlc (1:1 benzene/pentane) R_f 0.26. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 3.2 Hz, 4H), 7.30 (t, J = 3.2 Hz, 4H), 7.21 (t, J = 3.2 Hz, 2H), 6.56 (m, 2H), 6.43 (m, 2H), 4.48 (q, J = 6.8 Hz, 2H), 3.71 (br s, 2H), 1.56 (d, J = 6.8 Hz, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 145.2, 136.3, 128.6, 126.8, 125.9, 119.1, 113.6, 53.8, 25.2; FT-IR (thin film, cm^{-1}) 3350, 3059, 3026, 2964, 2863, 1599, 1509, 1492, 1449, 1434, 738, 699; High-resolution MS (EI^+, m/z) molecular ion calcd for $C_{22}H_{24}N_2$ 316.1939, found 316.1942, error 0.9 ppm; GC-MS (EI^+, m/z) 316 (M^+), 211 (M^+-105), 105 (M^+-211), 77 (M^+-229). Enantiomeric excess determination by HPLC (0.25 mL/min, 2.5% *i*-propanol/hexane, t_R = 26.0 (*S*,*S*), 30.5 (*S*,*R*), 31.0 (*R*,*R*) min) indicated 99% ee, > 95% de. $[\alpha]^{25}_D$ = +182 (c = 0.76, $CHCl_3$), $[\alpha]^{25}_D$ = +289 (c = 2.0, CH_2Cl_2).

***N*-Phenyl-*N'*-(*S*)-α-methylbenzyl-1,2-diaminobenzene 7.** Into an oven-dried 50 mL Schlenk tube equipped with magnetic stirbar and rubber septum was added 31.1 mg of Pd_2dba_3 (0.0340 mmol, 3.40 mol %) and 40.1 mg of 1-(*N*,*N*-dimethylamino)-1'-(dicyclohexylphosphino)biphenyl (0.102 mmol, 10.2 mol %). DME (4.0 mL) was added via an oven-dried syringe, and the solution was heated in an oil bath at 80˚C for 30 min. The

solution was then allowed to cool to room temperature and 119 μL of aniline (1.30 mmol, 1.30 eq.), 277.4 mg of **1** (1.00 mmol, 1.00 eq.), and 124.9 mg of Na*t*-OBu (1.30 mmol, 1.30 eq.) were successively added under Ar. The mixture was degassed, backfilled with Ar, and then heated in an oil bath at 80˚C with stirring for 30 min. The solution was allowed to cool to room temperature, diluted with ether, filtered through a pad of celite and concentrated *in vacuo* (rotatory evaporator) to give a crude dark brown oil. Purification by flash chromatography (elution with 0.5% EtOH in 2:3 benzene/pentane) provided 266 mg of **7** (92%) as a light yellow oil. Analytical tlc (2:3 benzene/pentane) R_f 0.18. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 4H), 7.25-7.20 (m, 3H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.62 (t, *J* = 7.5 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.10 (br s, 1H), 4.59 (br s, 1H), 4.48 (q, *J* = 6.7 Hz, 1H), 1.45 (d, *J* = 6.7 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$,) δ 145.9, 145.2, 143.3, 129.2, 128.5, 127.9, 126.8, 126.2, 125.8, 125.2, 119.2, 117.1, 115.2, 112.2, 53.3, 25.1; FT-IR (thin film, cm^{-1}) 3375, 3043, 2972, 2929, 2869,1596, 1520, 1498, 1455, 1303, 1281, 748, 699; High-resolution MS (EI^+, m/z) molecular ion calcd for $C_{20}H_{20}N_2$ 288.1626, found 288.1622, error 1.4 ppm. Enantiomeric excess determination by HPLC (0.5 mL/min, 10% *i*-propanol/hexane, t_R = 14.7 (*R*) and 15.9 (*S*) min) indicated 99% ee.

***N*-Phenyl-*N'*-(*S*)-1-cyclohexylethyl-1,2-diaminobenzene 9.** Into an oven-dried 20 mL pressure tube equipped with magnetic stirbar and rubber septum was added 15.6 mg of Pd_2dba_3 (0.017 mmol, 3.4 mol %) and 21.2 mg *rac*-BINAP (0.034 mmol, 6.8 mol %). Toluene (2.0 mL) was added via an oven-dried syringe, the rubber septum was replaced with a teflon screwcap, and the solution was heated in an oil bath at 80˚C for 15 min. The solution was then allowed to cool to room temperature and 59 μL of aniline (0.65 mmol, 1.3 eq.), 141.1 mg of **2** (0.500 mmol, 1.0 eq.), and 62.5 mg of Na*t*-OBu (0.65 mmol, 1.3 eq.) were added. The tube was sealed and heated in an oil bath at 110˚C with stirring for 2 h. The

solution was allowed to cool to room temperature, diluted with ether, washed once with water, filtered through a pad of Celite and concentrated *in vacuo* (rotatory evaporator) to give a crude dark brown oil. Purification by flash chromatography (elution with 1:3 benzene/pentane then 0.25 % EtOH in 1:2 benzene/pentane) provided 141 mg of **9** (96%) as a clear oil that turned light red after standing overnight. Analytical tlc (1:1 benzene/pentane) R_f 0.47. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.16 (t, J = 8.0 Hz, 2H), 7.10-7.05 (m, 2H), 6.78 (t, J = 7.5 Hz, 1H), 6.68-6.65 (m, 3H), 6.60 (t, J = 7.5 Hz, 1H), 4.97 (br s, 1H), 4.07 (br s, 1H), 3.32 (p, 1H), 1.80-1.67 (m, 3H), 1.64-1.55 (m, 2H), 1.39 (m, 1H), 1.26-0.89 (m, 5H), 1.05 (d, J = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 146.0, 144.0, 129.1, 127.7, 126.4, 125.8, 119.0, 116.0, 115.1, 111.0, 52.5, 42.9, 29.6, 28.4, 26.5, 26.4, 26.3, 17.3; FT-IR (thin film, cm^{-1}) 3373, 3043, 2965, 2923, 2850, 1600, 1514, 1496, 1449, 1302, 1278, 744, 693; High-resolution MS (EI^+, m/z) molecular ion calcd for $C_{20}H_{26}N_2$ 294.2096, found 294.2114, error 6.0 ppm; Enantiomeric excess determination by HPLC (0.5 mL/min, 10% *i*-propanol/hexane, t_R = 15.7 (*R*) and 19.4 (*S*) min) indicated 98% ee.

***N*-Phenyl-*N'*-(*R*)-2-methoxy-1-phenyl-ethyl-1,2-diaminobenzene 11.** Into an oven-dried 20 mL pressure tube equipped with magnetic stirbar and rubber septum was added 21.6 mg of Pd_2dba_3 (0.0236 mmol, 3.40 mol %) and 29.3 mg *rac*-BINAP (0.0471 mmol, 6.80 mol %). Toluene (2.8 mL) was added via an oven-dried syringe, the rubber septum was replaced with a teflon screwcap, and the solution was heated in an oil bath at 80˚C for 15 min. The solution was then allowed to cool to room temperature and 82 μL of aniline (0.90 mmol, 1.3 eq.), 212.1 mg of **3** (0.693 mmol, 1.00 eq.), and 86.6 mg of Na*t*-OBu (0.901 mmol, 1.30 eq.) were added under Ar. The tube was sealed and heated in an oil bath at 110˚C with stirring for 21 h. The solution was then allowed to cool to room temperature, diluted with ether, washed once with water, filtered through a pad of Celite and concentrated *in vacuo* (rotatory evaporator) to give a

crude dark brown oil. Purification by flash chromatography (elution with 40% CH_2Cl_2/hexane) provided a yellow oil that was further purified by flash chromatography (elution with 20 % diethyl ether/hexane) to provide 173 mg of **11** (78%) as a light yellow oil. Analytical tlc (20% diethyl ether/hexane) R_f 0.22. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.3 Hz, 2H), 7.32 (t, J = 7.3 Hz, 2H), 7.23 (t, J = 8.0 Hz, 3H), 7.12 (d, J = 7.6 Hz, 1H), 6.90-6.80 (m, 4H), 6.65 (t, J = 7.6 Hz, 1H), 6.43 (d, J = 7.6 Hz, 1H), 5.19 (br s, 1H), 5.00 (br s, 1H), 4.53 (br q, X of ABX, 1H), 3.54 (AB q, J_{AB} = 10.0 Hz, J_{AX} = 5.6 Hz, 1H), 3.51 (AB q, J_{AB} = 10.0 Hz, J_{BX} = 7.2 Hz, 1H), 3.23 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 145.7, 142.9, 140.6, 129.2, 129.1, 128.6, 127.4, 126.7, 125.5, 124.0, 119.3, 117.7, 115.7, 112.8, 76.9, 58.7, 57.9; FT-IR (thin film, cm^{-1}) 3372, 3044, 2926, 2891, 1598, 1513, 1497, 1305, 1116, 748, 701; High-resolution MS (EI^+, m/z) molecular ion calcd for $C_{21}H_{22}N_2O$ 318.1732, found 318.1742, error 3.2 ppm; $[\alpha]^{25}_D$ = +168 (c = 2.6, CH_2Cl_2).

General Procedure for The Synthesis of Benzimidazolium Salts: *N,N'*-Bis (*S*)-α-methylbenzyl-benzimidazolium chloride 5. To a 25 mL round-bottom flask equipped with a rubber septum and magnetic stirbar, 260.4 mg of **4** (0.823 mmol, 1.0 eq.) and $(EtO)_3CH$ (14 mL) were added. Then 70 μL of 12.1 N HCl (0.847 mmol, 1.0 eq.) was added dropwise using a graduated pipet. The resulting suspension was stirred at room temperature for 30 min under argon and then heated to 80˚C until condensation was observed on the neck of the flask. At this point the rubber septum was removed and the solution was allowed to stir open to the air for 2 h. After cooling to room temperature, the suspension obtained was diluted with diethyl ether (30 mL) and the supernatant was removed by decantation. The white solid obtained was washed five times with diethyl ether, then three times with hot toluene, followed by removal of residual solvents under high vacuum. The white solid was dried under vacuum (1 mm Hg) at 40˚C over P_2O_5 to provide 297 mg of **5** (99%), mp 242-243˚C. Analytical tlc (5:1 CH_2Cl_2/MeOH) R_f 0.37. ^{1}H-NMR (400 MHz, $CDCl_3$) δ

12.52 (s, 1H), 756-7.50 (m, 4H), 7.42-7.30 (m, 10H), 6.28 (q, *J* = 7.0 Hz, 2H), 2.34 (d, *J* = 7.0 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 142.4, 137.5, 131.0, 129.4, 129.0, 126.7, 126.6, 114.4, 59.2, 20.9; FT-IR (KBr, cm^{-1}) 3091, 3028, 2985, 2945, 2907, 1547, 1441, 1385, 1245, 751, 704; Low resolution FAB-MS molecular ion calcd for $C_{23}H_{23}N_2$(-Cl) 327.2, found 327.2 (M^+); Anal. Calcd. for $C_{23}H_{23}N_2Cl$: C, 76.12; H, 6.39; N, 7.72; Cl, 9.77, Found C, 76.06; H, 6.34; N, 6.60; Cl, 9.83. $[\alpha]^{25}_D$ = + 24 (c = 1.0 MeOH).

Bis (*S*)-α-methylbenzyl-benzimidazolium perchlorate 6. Obtained in 86% yield as white needles after recrystallization from toluene and minimum amount of acetonitrile, mp 200-201˚C. Analytical tlc (5:1 CH_2Cl_2/MeOH) R_f 0.57. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.93 (s, 1H), 744-7.30 (m, 14H), 6.06 (q, *J* = 7.0 Hz, 2H), 2.22 (d, *J* = 7.0 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 139.7, 137.4, 131.3, 129.5, 129.1, 126.9, 126.5, 114.6, 59.5, 20.5; FT-IR (KBr, cm^{-1}) 3130, 3065, 3031, 2988, 2946, 1553, 1455, 1212, 1095, 755, 701, 624; Anal. Calcd. for $C_{23}H_{23}N_2ClO_4$: C, 64.71; H, 5.43; N, 6.56, Found C, 64.79; H, 5.48; N, 6.60. $[\alpha]^{25}_D$ = + 23 (c = 2.0 MeCN).

1-(*S*)-α-Methylbenzyl-3-phenyl-benzimidazolium chloride 8. Obtained in 97% yield as white solid, mp 219-220˚C. Analytical tlc (5% CH_2Cl_2/hexane) R_f 0.41. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 12.08 (s, 1H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.73 (br d, 1H) 7.67 (M, 4H), 7.62-7.55 (M, 3H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.43-7.38 (m, 2H), 7.37-7.32 (m, 1H), 6.56 (q, *J* = 7.0 Hz, 1H), 2.37 (dd, *J* = 7.0, 2.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 142.8, 137.6, 133.3, 132.0, 131.0, 130.9, 130.9, 129.7, 129.4, 127.8, 127.6, 127.5, 125.3, 115.1, 114.1, 59.9, 20.8; FT-IR (KBr, cm^{-1}) 3101, 3036, 2982, 2935, 1593, 1549, 1497, 1405, 1251, 1230, 754, 696; Low resolution FAB-MS molecular ion calcd for $C_{21}H_{19}N_2$(-Cl) 299.2, found 299.2 (M^+); Anal. Calcd. for $C_{21}H_{19}ClN_2$: C, 75.33; H, 5.72; N, 8.37; Cl, 10.59, Found C, 75.37; H, 5.84; N, 8.34; Cl, 10.61. $[\alpha]^{25}_D$ = +85 (c = 0.7

MeOH).

1-(*S*)-1-Cyclohexylethyl-3-phenyl-benzimidazolium tetraphenylborate 10. The chloride salt did not precipitate out of solution by the general procedure. For isolation, the solution was concentrated *in vacuo* (rotatory evaporator) and the chloride salt was converted to the tetraphenylborate salt by anion exchange (see general procedure for anion exchange below). After recrystallization from ethyl acetate and minimun amount of CH_2Cl_2, **10** was obtained in 83% yield as colorless crystals, mp 201-202˚C. Analytical tlc (5% MeOH/CH_2Cl_2) R_f 0.63. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.58-7.52 (m, 2H), 7.50-7.42 (m, 4H), 7.38-7.28 (m,9H), 6.85 (t, *J* = 7.2 Hz, 8H), 6.82-6.75 (m, 6H), 6.43 (s, 1H), 3.86 (m, 1H), 1.86-1.73 (m, 3H), 1.69-1.58 (m, 2H), 1.38 (d, *J* = 7.0 Hz, 3H), 1.28-0.92 (m, 4H), 0.84-0.70 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 163.8, 139.1, 136.2, 132.1, 131.6, 131.1, 130.5, 129.6, 128.0, 127.7, 125.6, 125.5, 121.9, 114.5, 113.8, 63.0, 41.7, 29.5, 29.4, 25.5, 25.3, 17.2; FT-IR (KBr, cm^{-1}) 3109, 3054, 2998, 2983, 2927, 2827, 2852, 1549, 1479, 1424, 745, 734, 705, 693; Low resolution FAB-MS molecular ion calcd for $C_{21}H_{25}N_2$(-BPh_4) 305.2, found 305.2 (M^+); Anal. Calcd. for $C_{45}H_{45}BN_2$: C, 86.52; H, 7.26; N, 4.48, Found C, 86.40; H, 7.41; N, 4.49. $[\alpha]^{25}_D$ = + 2.9 (c = 2.1 MeCN).

1-(*R*)-2-Methoxy-1-(phenyl-ethyl)-3-phenyl-benzimidazolium chloride 12. For isolation the solution was concentrated *in vacuo* (rotatory evaporator) followed by recrystallization from CH_2Cl_2 and ethyl acetate to provide **12** in 91% yield as a white solid, mp 113-115˚C. Analytical tlc (5:1 CH_2Cl_2/MeOH) R_f 0.42. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 11.89 (s, 1H), 8.05 (d, *J* = 7.8 Hz, 2H), 7.75-7.68 (m, 5H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.59-7.49 (m, 3H), 7.45-7.36 (m, 3H), 6.27 (dd, X of AMX, *J* = 9.2, 3.6 Hz, 1H), 5.22 (dd, A of AMX, *J* = 11.2, 9.2 Hz, 1H), 4.23 (dd, M of AMX, *J* = 11.2, 3.6 Hz, 1H), 3.55 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.0, 133.6, 133.0, 131.4, 131.4, 130.6, 130.6, 129.6, 129.5, 128.0, 127.3, 127.1, 125.1, 114.6, 113.6, 71.9, 63.8, 59.3; FT-IR (KBr, cm^{-1}) 3104,

3039, 2934, 1598, 1551, 1497, 1472, 1229, 1090, 755, 695, 588; Low resolution FAB-MS molecular ion calcd for $C_{22}H_{21}N_2O$ (-Cl) 329.2, found 329.2 (M^+). $[\alpha]^{25}_D$ = + 63 (c = 1.1 MeOH). Satisfactory combustion analysis could not be obtained for this compound. Conversion of the chloride salt to the tetraphenylborate facilitated handling of this compound and gave good combustion analysis (see experimental procedure for anion exchange below): **1-(*R*)-2-methoxy-1-phenyl-ethyl-3-phenyl-benzimidazolium tetraphenylborate**, purified by recrystallization from CH_2Cl_2/ethyl ether, mp 181-182˚C. Analytical tlc (5% MeOH/CH_2Cl_2) R_f 0.70. ^{1}H-NMR (500 MHz, CD_3CN) δ 9.42 (s, 1H), 7.73 (m, 6H), 7.66-7.57 (m, 3H), 7.48-7.43 (m, 5H), 7.28 (m, 8H), 6.98 (t, *J* = 7.4 Hz, 8H), 6.83 (t, *J* = 7.4 Hz, 4H), 6.13 (dd, X of AMX, *J* = 7.8, 3.8 Hz, 1H), 4.29 (dd, A of AMX, *J* = 11.5, 7.8 Hz, 1H), 4.17 (dd, M of AMX, *J* = 11.5, 3.8 Hz, 1H), 3.41 (s, 3H); ^{13}C-NMR (125 MHz, CD_3CN) δ 164.8, 141.2, 136.7, 135.0, 133.9, 133.0, 132.4, 132.0, 131.4, 130.4, 130.2, 128.9, 128.5, 128.4, 126.6, 126.6, 122.7, 115.2, 114.8, 73.1, 63.1, 59.5; FT-IR (KBr, cm^{-1}) 3120, 3052, 3034, 2983, 1582, 1550, 1478, 1206, 749, 737, 706, 698; Anal. Calcd. for $C_{46}H_{41}BN_2O$: C, 85.18; H, 6.37; N, 4.32, Found C, 84.88; H, 6.40; N, 4.40. $[\alpha]^{25}_D$ = +31.6 (c = 2.1 MeCN).

***N*,*N*'-Bis-(*S*)-α-methylbenzyl-2-methyl-benzimidazolium chloride 19**. To a stirred solution of 155.6 mg of **4** (0.491 mmol, 1.0 eq.) in CH_2Cl_2 (2.0 mL) was added 86 μL of diisopropylethylamine (0.491 mmol, 1.0 eq.) at room temperature. The solution was stirred at this temperature for 10 min, then 35 μL of acetyl chloride (0.491, 1.0 eq.) was added and the resulting yellow solution was allowed to stir at room temperature for 10 h. The reaction mixture was diluted with diethyl ether (5.0 mL) and washed with brine (2 x 2.0 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated *in vacuo* (rotatory evaporator). Purification of the residue by flash chromatography (elution with 25% ethyl acetate/petroleum ether) provided 161 mg of **13** (91%) as a viscous oil. Analytical tlc (1:4 EtOAc and Hexane) R_f 0.71. Compound **13** was

identified by ^{1}H-NMR and used for the next step without further characterization.

To a stirred solution of 161.0 mg of **13** (0.449 mmol, 1.0 eq.) in anhydrous ethyl ether (1.5 mL) was added 774 μL of 1.0 M HCl in ethyl ether (0.774 mmol, 1.7 eq.) and resulting white precipitate was stirred at room temperature for 28 h. Hexane (2.0 mL) was added and the precipitates were removed by centrifugation. The supernatant was decanted and the solid obtained was dried under high vacuum to afford 153 mg of **15** (90%) as a white solid, mp 118-120˚C. Analytical TLC (4:1 CH_2Cl_2/MeOH) R_f 0.46. ^{1}H NMR (500 MHz, acetone-d_6) δ 7.59–7.35 (m, 14H), 6.62 (q, J = 7.0 Hz, 2H), 3.49 (s, 3H), 2.22 (d, J = 7.0 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 151.5, 136.5, 130.4, 129.3, 128.8, 126.6, 125.9, 114.6, 57.3, 19.1, 15.0; Low resolution FAB-MS molecular ion calcd for $C_{24}H_{25}N_2$(-Cl) 341.2, found 341.2 (M^+). $[\alpha]^{25}_D$= -129 (c = 0.51, CH_2Cl_2).

***N*,*N'*-Bis-(*S*)-α-methylbenzyl-2-ethyl-benzimidazolium chloride 20.**
To a stirred solution of 104 mg of **4** (0.329 mmol, 1.0 eq.) in CH_2Cl_2 (2.0 mL) was added 58 μL of diisopropylethylamine (0.33 mmol, 1.0 eq.), and 29 μL of n-propionyl chloride (0.33 mmol, 1.0 eq.) and the resulting yellow solution was stirred at room temperature for 2 h. The reaction mixture was diluted in diethyl ether (5 mL) and washed with brine (2 x 20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* (rotatory evaporator). Purification of the residue by flash chromatography (elution with 1:4 ethyl acetate/hexane) provided 106.5 mg of **14** (87%) as a colorless viscous oil. Analytical tlc (20% ethyl acetate/hexane) R_f 0.32. Compound **14** was identified by ^{1}H-NMR and used for the next step without further characterization.

To a stirred solution of 96.1 mg of **14** (0.258 mmol 1.0 eq.) in freshly distilled toluene (1.0 mL) was added 258 μL of 1.0 M HCl in ethyl ether (0.258 mmol, 1.0 eq.) and the resulting solution was stirred at room temperature for 24 hours. The supernatant was decanted and the solid

obtained washed with toluene, and dried under vacuum to afford 87.4 mg of **20** (87%), Analytical tlc (5:1 dichloromethane/methanol) R_f 0.61. ^{1}H-NMR (500 MHz, CD_3CN)δ 7.39-7.43 (m, 10H), 7.30-7.34 (m, 4H), 6.34 (q, *J* = 7.0 Hz, 2H), 3.53 (q, *J* = 8.0 Hz, 2H), 2.13 (d, *J* = 7.0 Hz, 6H), 1.31 (t, *J* = 8.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 155.7, 136.6, 130.2, 129.3, 128.9, 128.7, 128.1, 126.5, 125.9, 125.2, 114.9, 56.8, 20.0, 19.1, 12.3; FT-IR (KBr, cm^{-1}) 3063, 3029, 2989, 2942, 1634, 1500, 1473, 1384, 1135, 1117, 1074, 7545, 701; Low resolution FAB-MS molecular ion calcd for $C_{25}H_{27}N_2$(-Cl) 355.2, found 355.2 (M^+).$[\alpha]^{25}_D$ = -129.16 (c = 0.528, CH_2Cl_2).

***N,N'*-Bis-(*S*)-α-methylbenzyl-2-phenyl-benzimidazolium chloride 21**. To a stirred solution of 155.0 mg of **4** (0.489 mmol, 1.0 eq.) in CH_2Cl_2 (2.5 mL) was added 85 μL of diisopropylethylamine (0.488 mmol, 1 eq.) at room temperature. The solution was stirred at this temperature for 10 min, then 57 μL of benzoyl chloride (0.488 mmol, 1.0 eq.) was added and resulting yellow solution was stirred at room temperature for 7 h. The reaction mixture was diluted with diethyl ether (5.0 mL) and washed with saturated NaCl (2 x 2.0 mL) and water (2 x 1.0 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated *in vacuo* (rotatory evaporator). Purification of the residue by flash chromatography (elution with 25% ethyl acatate/petroleum ether) provided 155 mg of **15** (75%) as a viscous oil. Analytical tlc (1:4 ethyl acetate/hexane) R_f 0.25. Compound **15** was identified by ^{1}H NMR and used for the next step without further characterization.

To a stirred solution of 134.8 mg of **15** (0.321 mmol, 1.0 eq.) in anhydrous ethyl ether (1.5 mL) was added 337 μL of 1.0 M HCl in ethyl ether (0.337 mmol, 1.1 eq.) and resulting white precipitate was stirred at room temperature for 24 h. Hexane (2.0 mL) was added and the precipitates were removed by centrifugation. The supernatant was decanted and the solid was dried under high vacuum to afford 119 mg of

21 (84%) as white solid, mp 163-166˚C. Analytical tlc (1:1 CH_2Cl_2 /MeOH) R_f 0.71. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.22 (δ, 7.0 Hz, 1H), 7.93–7.84 (m, 2H), 7.64-7.63 (m, 1H), 7.51-7.48 (m, 3H), 7.39-7.38 (m, 3H), 5.98 (q, J = 7.0 Hz, 1H), 2.19 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 136.2, 133.5, 131.4, 130.7, 130.5, 129.5, 128.8, 127.0, 121.1, 115.6, 57.9, 20.4; Low resolution FAB-MS molecular ion calcd for $C_{29}H_{27}N_2$(-Cl) 403.2, found 403.2 (M^+). $[\alpha]^{25}_D$ = -229 (c = 0.68, CH_2Cl_2).

1-(*S*)-α-Methylbenzyl-2-methyl-3-n-butyl-benzimidazolium chloride 22. To a stirred solution of 263.0 mg of *N*-butyl-*N*'-(*S*)-α-methylbenzyl-1,2-diaminobenzene[4] (0.981 mmol, 1.0 eq.) in CH_2Cl_2 (5.0 mL) was added 206 μL of disopropylethylamine (1.18 mmol, 1.2 eq.) and 74 μL of acetyl chloride (1.04 mmol, 1.1 eq) at room temperature. After two hours of stirring at room temperature the reaction solution was diluted with diethyl ether (10 mL) and washed with brine (2 x 5 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated *in vacuo* (rotatory evaporator). Purification of the crude product by flash chromatography (elution with 20% ethyl acetate/hexane) provided 296.6 mg of **16** (97%) as a light yellow oil. Analytical TLC (1:4 ethyl acetate/hexane) R_f 0.20. Compound **16** was identified by ^{1}H-NMR and used for the next step without further characterization.

To a stirred solution of 117.5 mg of **16** (0.379 mmol, 1.0 eq.) in toluene (6.3 mL) was added 400 μL of 1.0 M HCl in diethyl ether (0.400 mmol, 1.06 eq.) and the resulting solution was stirred at room temperature for 2 h under Ar. After 2 h the reaction was heated to 80˚C until condensation was observed on the neck of the flask. At this point the rubber septum was removed and the solution was allowed to stir open to the air for 4 h. After cooling to room temperature the toluene was removed by decantation. The resulting white solid was washed with hot toluene (3 x 5.0 mL) by heating the flask to 80˚C until the solid became an oil. After cooling to room temperature the toluene was removed by

decantation. Evaporation of the residual toluene under high vacuum followed by drying under vacuum (1 mm Hg) at 40˚C over P_2O_5 provided 122.3 mg of **22** (98%) as a white foamy solid. Analytical tlc (5:1 CH_2Cl_2/MeOH) R_f 0.39. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.41-7.33 (m, 6H), 7.27 (d, *J* = 8.0 Hz, 1H), 6.35 (q, *J* = 7.5 Hz, 1H), 4.69 (m, 2H), 3.36 (s, 3H), 2.16 (d, *J* = 7.5 Hz, 3H), 1.93 (p, 2H), 1.48 (m, 2H), 1.00 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 151.1, 136.4, 131.5, 129.8, 129.2, 128.8, 126.5, 126.3, 126.2, 114.3, 112.7, 56.8, 46.3, 31.1,20.0, 18.6, 13.6, 12.9; FT-IR (KBr, cm^{-1}) 3057, 3029, 2959, 2933, 2872, 1508, 1470, 1384, 1140, 1063, 754, 705; Low resolution FAB-MS molecular ion calcd for $C_{20}H_{25}N_2$(-Cl) 293.2 found 293.2 (M^+). $[\alpha]^{25}_D$ = -76 (c = 1.5, CH_2Cl_2).

1-(*S*)-α-Methylbenzyl-2-phenyl-3-n-butyl-benzimidazolium chloride 23. To a stirred solution of 227.0 mg of *N*-butyl-*N*'-(*S*)-α-methylbenzyl-1,2-diaminobenzene[4] (0.846 mmol, 1.0 eq.) in CH_2Cl_2 (4.4 mL) was added 180 μL of disopropylethylamine (1.03 mmol, 1.2 eq.) and 103 μL of benzoyl chloride (0.888 mmol, 1.1 eq) at room temperature. After two hours of stirring at room temperature the reaction solution was diluted with diethyl ether (10 mL) and washed with brine (2 x 5 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated *in vacuo* (rotatory evaporator). Purification of the crude product by flash chromatography (elution with 20% ethyl acetate/hexane) provided 308.2 mg of **17** (98%) as a clear oil. Analytical tlc (1:4 ethyl acetate/hexane) R_f 0.58. Compound **17** was identified by ^{1}H-NMR and used for the next step without further characterization.

To a stirred solution of 133.6 mg of **17** (0.359 mmol, 1.0 eq.) in toluene (6.0 mL) was added 380 μL of 1.0 M HCl in diethyl ether (0.380 mmol, 1.06 eq.) and the resulting solution was stirred at room temperature for 12 h under argon. After 12 h the reaction was heated to 80˚C until condensation was observed on the neck of the flask. At this point the

rubber septum was removed and the solution was allowed to stir open to the air for 2 h. After cooling to room temperature the toluene was evaporated *in vacuo* (rotatory evaporator). The resulting white solid was washed with hot ethyl acetate (3 x 5 mL) by heating the flask to 80˚C until the solid became an oil. After cooling to room temperature the ethyl acetate was removed by decantation. Evaporation of the residual ethyl acetate under high vacuum followed by drying under vacuum (1 mm Hg) at 40˚C over P_2O_5 provided 122.8 mg of **23** (87%) as a white solid, mp 152 ˚C. Analytical tlc (5:1 CH_2Cl_2/MeOH) R_f 0.50. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 6.5 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.80-7.70 (m, 3H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.45-7.34 (m, 4H), 7.28 (m, 3H), 5.74 (q, *J* = 7.0 Hz, 1H), 4.59 (t, *J* = 8.0 Hz, 2H), 2.12 (d, *J* = 7.0 Hz, 3H), 1.85 (m, 2H), 1.29 (app sextet, *J* = 7.5 Hz, 2H), 0.83 (t, *J* = 7.5 Hz, 3H); ^{13}C-NMR (125 MHz, CD_3CN) δ 151.5, 137.8, 134.2, 133.1, 131.1, 131.0, 131.0, 130.9, 130.6, 129.9, 129.6, 127.9, 127.8, 127.7, 122.3, 116.0, 114.9, 58.2, 47.4, 31.7, 20.4, 18.3, 13.6; FT-IR (KBr, cm^{-1}) 3040, 3000, 2959, 2930, 2881, 1500, 1461, 1447, 1053, 1036, 762, 700; Low resolution FAB-MS molecular ion calcd for $C_{25}H_{27}N_2$(-Cl) 355.2 found 355.2 (M^+). $[\alpha]^{25}_D$ = -145 (c = 1.6, CH_2Cl_2).

1-(*S*)-α-Methylbenzyl-2,3-diphenyl-benzimidazolium chloride 24.

To a stirred solution of 100 mg of **7** (0.346 mmol, 1.0 eq.) in CH_2Cl_2 (2.0 mL) was added 51 µL of triethylamine (0.36 mmol, 1.1 eq.) and 43 µL benzoyl chloride (0.36 mmol, 1.1 eq.) sequentially at 23˚ C. The reaction was allowed to stir for 8 h at reflux. The reaction mixture was concentrated and dissolved in 10 mL Et_2O, washed with brine (10 mL), dried with $MgSO_2$, filtered, and concentrated *in vacuo* (rotatory evaporator). Purification of the residue by flash chromatography (elution with 25 % ethyl acetate/hexanes) provided 119 mg of **18** (87%) as a viscous oil. Compound **18** was identified by ^{1}H-NMR and used for the next step without further characterization.

To a stirred solution of 118 mg of **18** (0.300 mmol, 1.0 eq.) in 1.0 mL Et_2O was added 330 μL of 1.0 M HCL in Et_2O (0.330 mmol, 1.1 eq.) at 23˚ C and the resulting white precipitate was stirred for an additional 24 h. Hexane (3.0 mL) was added and the precipitate was removed by centrifugation. After removal of residual solvent under high vacuum, 82 mg of **24** (67%) was obtained as a white solid, mp 204-207˚ C. Analytical tlc (5:1 CH_2Cl_2/MeOH) R_f 0.56. ^{1}H-NMR (500 MHz, CD_3CN) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.73 (s, 2H), 7.64-7.36 (m, 15H), 5.92 (q, *J* = 7.5 Hz, 1H), 2.14 (d, 7.5 *J* = 7.5 Hz, 3H); ^{13}C-NMR (125 MHz, CD_3CN) δ 151.8, 137.6, 134.8, 133.8, 131.7, 130.9, 130.4, 130.3, 129.9, 129.6, 128.8, 128.3, 128.2, 127.8, 122.6, 116.1, 114.7, 58.7, 18.4; FT-IR (thin film, cm^{-1}) 3201, 3052, 2999, 2897, 1596, 1504, 1462, 1252, 1091, 1030, 750, 701; Low resolution FAB-MS molecular ion calcd. for $C_{27}H_{23}N_2$(-Cl) 375.2 found 375.2. $[\alpha]^{25}_D$ = -141 (c = 0.82, CH_2Cl_2).

General Procedure for Anion Exchange: *N,N'*-Bis (*S*)-α-methylbenzyl-benzimidazolium tetrafluoroborate 25. In an oven-dried 15 mL round bottom flask equipped with a magnetic stirbar and rubber septum 98.7 mg of **5** (0.272 mmol, 1 eq.) and CH_3CN (5.0 mL) were added. To the resulting suspension 28.5 mg of NH_4BF_4 (0.272 mmol, 1 eq.) were added and the suspension was stirred for 1 h at room temperature. Filtration of the suspension and concentration *in vacuo* (rotatory evaporator) gave a white solid that was dissolved in CH_2Cl_2, filtered through a small plug of silica gel, and concentrated again to give 109 mg of **25** (97%) as a white solid after drying over P_2O_5, mp 204-205˚C. Analytical tlc (5% MeOH/CH_2Cl_2) R_f 0.14. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.42-7.30 (m, 14H), 6.05 (q, *J* = 7.0 Hz, 2H), 2.23 (d, *J* = 7.0 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 139.8, 137.4, 131.2, 129.5, 129.1, 126.9, 126.5, 114.5, 59.5, 20.3; FT-IR (KBr, cm^{-1}) 3141, 3074, 2986, 1585, 1214, 1082, 1065, 1036, 756, 702; Anal. Calcd. for $C_{23}H_{23}N_2BF_4$: C, 66.69; H, 5.60; N, 6.76, Found C, 66.64; H, 5.73; N, 6.73. $[\alpha]^{25}_D$ = +22 (c = 2.2 MeOH).

***N,N'*-Bis (*S*)-(α-methylbenzyl)-benzimidazolium tetraphenylborate 26.** Obtained in 99% yield as a white solid. Recrystallization from toluene/acetonitrile gave white crystals, mp 169-170˚C. Analytical TLC (5% MeOH/CH_2Cl_2) R_f 0.54. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.47 (br s, 8H), 7.37 (t, *J* = 3.1 Hz, 6H), 7.27 (m, AA'BB', 2H), 7.09 (m, AA'BB', 2H), 7.03 (s, 1H), 7.00-6.93 (m, 12H), 6.84 (t, *J* = 7.1 Hz, 4H), 5,28 (q, *J* = 7.0 Hz, 2H), 1.69 (d, *J* = 7.0 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 164.0, 138.7, 136.2, 136.1, 130.6, 129.4, 129.2, 127.2, 126.1, 125.9, 122.0, 115.0, 58.9, 19.8; FT-IR (KBr, cm^{-1}) 3129, 3054, 2988, 1886, 1556, 1481, 1424, 1241, 756, 733, 700, 698, 612; Anal. Calcd. for $C_{47}H_{43}N_2B$: C, 87.29; H, 6.70; N, 4.33, Found C, 87.15; H, 6.77; N, 4.36. $[\alpha]^{25}_D$ = +17 (c = 3.3 MeCN).

1-(*S*)-(α-methylbenzyl)-3-phenyl-benzimidazolium tetraphenylborate 27. Isolated by recrystallization from toluene and minimum amount of acetonitrile. Obtained in 97% yield as white needles, mp 193-194˚C. Analytical TLC (5:1 CH_2Cl_2/MeOH) R_f 0.88. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.73 (m, 6H), 7.64-7.57 (m, 3H), 7.50-7.39 (m, 5H), 7.26 (m, 8H), 6.98 (t, *J* = 7.3 Hz, 8H), 6.83 (t, *J* = 7.3 Hz, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 164.8, 140.6, 139.0, 136.7, 134.0, 133.3, 132.0, 131.9, 131.4, 130.3, 130.1, 128.9, 128.4, 127.7, 126.6, 126.5, 122.7, 115.4, 114.9, 59.8, 21.5; FT-IR (KBr, cm^{-1}) 3116, 3062, 3003, 2982, 1582, 1551, 1482, 1425, 1223, 748, 738, 708, 698, 612; Anal. Calcd. for $C_{45}H_{39}BN_2$: C, 87.37; H, 6.35; N, 4.53, Found C, 87.46; H, 6.51; N, 4.54. $[\alpha]^{25}_D$ = + 39 (c = 4.6 MeCN).

***N,N'*-Bis (*S*)-(α-methylbenzyl)-1,3-dihydro-benzimidazol-2-one**. In an oven-dried 25 mL round bottom flask equipped with a magnetic stirbar and rubber septum was added 140.8 mg of **4** (0.445 mmol, 1.0 eq.), 101.2 mg of triethylamine (1.00 mmol, 2.3 eq.), and CH_2Cl_2 (5.0 mL). This solution was then cooled to 0˚C. In a separate oven-dried 10 mL round

bottom flask was placed 46.3 mg of triphosgene[3] (0.156 mmol, 0.35 eq.) dissolved in CH_2Cl_2 (5.0 mL) and transferred via syringe to the cold solution of **4** and triethylamine at 3.2 mL/hr using a syringe pump. After the addition was completed the flask was warmed to room temperature and stirred for an additional hour. The resulting solution was concentrated to dryness *in vacuo* (rotatory evaporator) and the crude product was redissolved in ethyl acetate and washed with $NaHSO_4$, $NaHCO_3$, saturated NaCl, and dried with Na_2SO_4. Purification by flash chromatography (elution with CH_2Cl_2 followed by 1% MeOH/CH_2Cl_2) gave a white solid with traces of a yellow impurity. Further purification by recrystallization using 3:2 ethyl acetate/hexane gave 135 mg of product (88%) as colorless needles, mp 177-178˚C. Analytical tlc (5:1 CH_2Cl_2/hexane) R_f 0.23. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 7.26 (t, J = 7.4 Hz, 1H), 6.79 (m 1H), 6.66 (m, 1H), 5.93 (q, J = 7.1 Hz, 1H), 1.91 (d, J = 7.1 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 154.1, 139.9, 128.6, 128.1, 127.4, 126.7, 120.6, 109.7, 50.7, 17.3, FT-IR (KBr) 3065, 2981, 2931, 1696, 1602, 1484, 1443, 1391, 1381, 1189, 1180, 1070, 754, 737, 702 cm^{-1}; Anal. Calcd. for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.4 8; N, 8.18, Found C, 80.46; H, 6.55; N, 8.24. Enantiomeric excess determination by HPLC (0.50 mL/min, 50% *i*-propanol/hexane, Whelk-O1 column, UV-290, t_R = 12.8 (*S,S*), 16.8 (*S,R*), 21.8 (*R,R*) min) indicated 99% ee and 99% de.

***N*-Butyl-*N'*-(R)-2-methoxy-1-phenyl-ethyl-1,2-diaminobenzene 28.**

Into an oven-dried 20 ml pressure tube equipped with magnetic stirbar and rubber septum was added 71.7 mg of Pd_2dba_3 (0.0783 mmol, 4.0 mol %) and 97.1 mg *rac*-BINAP (0.156 mmol, 8.0 mol %). Toluene (10.0 mL) was added via an oven-dried syringe, the rubber septum was replaced with a teflon screwcap, and the solution was heated in an oil bath at 130˚C for 15 min. The solution was then allowed to cool to room temperature and 600 mg of **3** (1.96 mmol, 1.0 eq.), 290 μL of n-butylamine (2.93 mmol, 1.5 eq.), and 378.1 mg of Na*t*-OBu (3.93 mmol, 2.0 eq.) were added. The

tube was sealed and heated in an oil bath at 130°C with stirring for 4 h. The solution was then allowed to cool to room temperature, diluted with diethyl ether, filtered through a pad of Celite, and concentrated *in vacuo* (rotatory evaporator) to give a crude dark brown oil. Purification by flash chromatography (elution with 20% diethyl ether/hexane) provided a yellow oil that was further purified by flash chromatography (gradient elution with pentane to 15%diethyl ether/pentane) to provide 203.6 mg of **28** (35%) as a light yellow oil. Analytical tlc (20% diethyl ether/hexane) R_f 0.31. ^{1}H-NMR (500 MHz, $CDCl_3$)δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 6.74 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.55 (t, *J* = 7.5 Hz, 1H), 6.38 (d, *J* = 7.5 Hz, 1H), 4.53 (br dd, X of ABX, 1H), 4.20 (br s, 1H), 3.64 (m, AB of ABX, 2H), 3.46 (br s, 1H), 3.39 (s, 3H), 3.13 (t, *J* = 7.0 Hz, 2H), 1.69 (m, 2H), 1.49 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 140.4, 138.3, 135.8, 128.6, 127.3, 126.8, 119.6, 118.3, 113.8, 111.1, 77.1, 58.6, 57.8, 44.1, 31.8, 20.5, 14.0; FT-IR (thin film, cm^{-1}) 3329, 3056, 3023, 2955, 2927, 2893, 2871, 1600, 1514, 1452, 1266, 1117, 735, 701; High resolution MS (EI^+,m/z) molecular ion calcd for $C_{19}H_{26}N_2O$ 298.2045, found 298.2021, error 8.2 ppm. $[\alpha]^{25}_D$ = +185 (c = 0.28, CH_2Cl_2).

1-(*R*)-2-Methoxy-1-(phenyl-ethyl)-2-methyl-3-butyl-benzimidazolium chloride 30. To a stirred solution of 76.6 mg of **28** (0.257 mmol, 1.0 eq.) in CH_2Cl_2 (2.0 mL) was added 43 μL of diisopropylethylamine (0.25 mmol, 1.0 eq.), and 18 μL of acetyl chloride (0.25 mmol, 1.0 eq.) and the resulting yellow solution was stirred at room temperature for 2 h. The reaction mixture was diluted in diethyl ether (5 mL) and washed with brine (2 x 20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* (rotatory evaporator). Purification of the residue by flash chromatography (gradient elution with hexane to 30% ethyl acetate /hexane) provided 80.0 mg of **29** (92%) as a clear viscous oil. Analytical tlc (20% diethyl ether/hexane) R_f 0.07. Compound **29** was identified by ^{1}H-NMR and used for the next step without further characterization.

To a stirred solution of 80.0 mg of **29** (0.235 mmol 1.0 eq.) in freshly distilled toluene (1.0 mL) was added 245 μL of 1.0 M HCl in diethyl ether (0.245 mmol, 1.1 eq.) and the resulting solution was heated to 80˚C until condensation was observed on the neck of the flask. At this point the solution was removed from the oil bath and allowed to stir for 24 hours at room temperature. The toluene was removed by decanting and the resulting brown oil was purified by reapeated hot ethyl acetate washings to afford 64.8 mg of **30** (77%) as a brown oil. Analytical tlc (5:1 methylene chloride/methanol) R_f 0.35. ^{1}H-NMR (500 MHz, $CDCl_3$)δ 7.70 (d, *J* = 8.5 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 6.32 (dd, X of AMX, *J* = 8.7, 4.1 Hz, 1H), 4.80 (m, 1H), 4.65 (m, 1H), 4.39 (dd, A of AMX, *J* = 10.0, 4.1 Hz, 1H), 4.33 (t, M of AMX, *J* = 10 Hz, 1H), 3.36 (s, 3H), 3.31 (s, 3H), 1.93 (m, 2H), 1.47 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 152.7, 132.8, 131.4, 130.0, 129.4, 129.2, 127.1, 126.2, 126.2, 114.5, 112.7, 70.9, 60.4, 59.4, 46.4, 31.1, 19.9, 13.6, 13.1; FT-IR (thin film, cm^{-1}) 3065, 3046, 2959, 2933, 2874, 1630, 1536, 1513, 1471, 1123, 758, 706; Low resolution FAB-MS molecular ion calcd for $C_{21}H_{27}N_2O$(-Cl) 323.2, found 323.2 (M^+). $[\alpha]^{25}_D$= -42 (c = 1.2, CH_2Cl_2).

***N,N'*-Bis (*S*)-(α-methylbenzyl)-benzimidazol-2-ylidene 31.**

Two oven-dried 50 mL Schlenk tubes were cooled under vacuum and backfilled with Ar. To one of the Schlenk tubes 11.1 mg of KO*t*-Bu (0.0989 mmol, 1.0 eq.) were added. Into the other 50 mL Schlenk tube 63.8 mg of **26** (0.0987 mmol, 1.0 eq.) were added. Both Schlenk tubes were evacuated under vacuum, backfilled with Ar, and then taken inside a glove box. To the Schlenk tube containing the KOt-Bu, 7.0 mL of dried THF were added and 1.5 mL of THF were added to the Schlenk tube containing **26**. The resulting solution of **26** was added dropwise using an oven-dried syringe to the suspension of KOt-Bu in THF at room temperature. After the addition of **26** was completed,the reaction mixture was stirred for 30 min. The suspension was filtered and the filtrate was

concentrated to dryness under vacuum inside the glove box. The resulting light yellow oil was redissolved in dried THF-d_8 and filtered again to obtain pure **31**. ^{1}H-NMR (500 MHz, THF-d_8) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.19-7.14 (m, 2H), 6.93 (m, 1H), 5.75 (q, *J* = 7.0 Hz, 1H), 2.10 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, THF-d_8) δ 224.0, 144.8, 136.5, 129.3, 128.0, 127.4, 121.9, 111.5, 58.2, 23.2.

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4) *N*-Butyl-*N*'-(*S*)-α-methylbenzyl-1,2-diaminobenzene was prepared in 77 % yield following the procedure reported in Rivas, F.M.; Riaz, U.; Diver, S.T. *Tetrahedron: Asymmetry* **2000**, *11*, 1703. Analytical tlc (1:4 ethyl acetate/hexane) R_f 0.62. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 7.5 Hz, 2H), 7.30 (dd, J = 7, 7.5 Hz, 2H), 7.21 (dd, J = 8, 7 Hz, 1H), 6.73 (dd, J = 7.5, 8 Hz, 1H), 6.67 (d, J = 7.5 Hz, 1H), 6.62 (t, J = 7.5 Hz, 1H), 6.43 (d, J = 7.5 Hz, 1H), 4.47 (ddd, J = 6, 6.5, 7 Hz, 1H), 3.62 (br s, 1H), 3.24 (br s, 1H), 3.11 (t, J = 7 Hz, 2H), 1.70-1.64 (m, 2H), 1.53 (d, J = 7 Hz, 3H), 1.48 (m, 2H), 0.992 (t, J = 7.5 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 145.2, 137.4, 136.2, 128.5, 126.7, 125.8, 119.0, 118.9, 113.1, 111.8, 53.6, 44.3, 31.9, 25.1, 20.5, 14.0; High resolution MS (EI^+, m/z) molecular ion calcd for $C_{18}H_{24}N_2$ 268.1939, found 268.1947, error 3.0 ppm. Enantiomeric excess determination by HPLC (0.5 mL/min, 10% *i*-propanol/hexane, t_R = 9.2 (*S*) and 10.7 (*R*) min) indicated 99% ee.