Supporting Information

A General, Highly Enantioselective Method for the Synthesis of D and L α-Amino Acids and Allylic Amines

Young K. Chen, Alice E. Lurain, and Patrick J. Walsh*

Contribution from the P. Roy and Diane T. Vagelos Laboratories, University of Pennsylvania, Department of Chemistry, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323.

(*S*)-3-Cyclopropyl-1-phenyl-prop-2-en-1-ol (2). General Procedure A: To a stirred solution of Cy_2BH (22.0 mmol) in hexanes (40 mL) prepared according to Oppolzer's procedure was added cyclopropylacetylene (1.87 mL, 22.0 mmol) dropwise (Caution: exothermic!).[1] The homogenous reaction mixture was stirred for 15 min at room temperature, then cooled to -78 °C. Et_2Zn (3.08 g, 25.0 mmol) in hexanes (10 mL) or Me_2Zn in toluene (12.5 mL, 2.0 M) was added followed by (-)-MIB (96 mg, 2.0 mol%, 0.4 mmol). The reaction was transferred into a 0 °C bath, and benzaldehyde (2.03 mL, 20 mmol) was added over 30 min. The reaction was stirred at 0 °C for 2 hours and quenched with 5 mL of H_2O. After stirring for 1 hour, $MgSO_4$ was added and the content of the flask was filtered and thoroughly rinsed with diethyl ether. The filtrate was concentrated *in vacuo* and the residue chromatographed on silica (5% ethyl acetate in hexanes) to afford **2** in 94% yield (3.27 g, 18.8 mmol) as a colorless oil. $[\alpha]_D^{25}$ = +58.8 (*c* = 0.98, $CHCl_3$, 94.5% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.38-0.41 (m, 2H), 0.70-0.74 (m, 2H), 1.39-1.42 (m, 1H), 1.83 (s, 1H), 5.15 (d, 1H, *J* = 6.8 Hz), 5.29 (dd, 1H, *J* = 15.3, 8.8 Hz), 5.74 (dd, 1H, *J* = 15.3, 7.0 Hz), 7.25-7.38 (m, 5H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 7.29 (-$(CH_2)_2$- are overlapped), 13.90, 75.53, 126.57, 127.91, 128.89, 130.28, 136.98, and 143.90 ppm; IR (neat) 3450, 1605, 1550, 1495, 1450; HRMS-CI *m/z* 174.1052 [M^+; calcd for $C_{12}H_{14}O$: 174.1044].

(*S*)-1-Phenyl-hept-2-en-1-ol (1). The product was prepared by General Procedure A using 2.14 g (12.0 mmol) Cy_2BH, 1.4 mL (12.0 mmol) 1-hexyne, 6 mL (12.0 mmol, 2.0 M in toluene) Me_2Zn, 50.0 mg (0.2 mmol) (-)-MIB, and 1.0 mL (10.0 mmol) benzaldehyde. The crude product was purified by column chromatography (5% ethyl

acetate in hexanes) to give **1** as a colorless oil in 85% yield (1.62 g, 8.52 mmol). $[\alpha]_D^{20}$ = +38.3 (*c* = 1.01, $CHCl_3$, 95% ee); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.81 (t, *J* = 7.1 Hz, 3H), 1.16-1.32 (m, 4H), 1.94-1.99 (m, 2H), 2.02 (s, 1H), 5.27 (d, *J* = 6.7 Hz, 1H), 5.56 (dd, *J* = 15.8, 6.7 Hz, 1H), 5.66 (dt, *J* = 15.3, 6.6 Hz, 1H), 7.17-7.28 (m, 5H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 13.9, 22.2, 31.2, 31.8, 75.1, 126.1, 127.3, 128.4, 132.2, 132.7, 143.4 ppm; IR (neat) 3354, 3068, 3027, 2926, 1667, 1454 cm^{-1}; HRMS-CI *m/z* 190.1350 [M^+; calcd for $C_{13}H_{18}O$: 190.1358].

(*S*)-Cyclohexyl-1-phenyl-prop-2-en-1-ol (3). The product was prepared by General Procedure A using 997 mg (5.6 mmol) Cy_2BH, 600 mg (5.6 mmol) cyclohexylacetylene, 2.8 mL (5.6 mmol, 2.0 M in toluene) Me_2Zn, 22.5 mg (0.094 mmol) (-)-MIB, and 479 μL (4.7 mmol) benzaldehyde. The crude product was purified by column chromatography (10 % ethyl acetate in hexanes) to give **3** as a colorless oil in 85% yield (850 mg, 3.9 mmol). $[\alpha]_D^{20}$ = +21.3 (*c* = 1.04, $CHCl_3$, 95% ee); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.05-1.32 (m, 5H), 1.62-1.73 (m, 6H – overlapping OH), 1.98 (m, 1H), 5.15 (d, *J* = 6.7 Hz, 1H), 5.62 (dd, *J* = 15.5, 6.7 Hz, 1H), 5.73 (dd, *J* = 15.5, 6.4 Hz, 1H), 7.25-7.37 (m, 5H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ26.2, 26.7, 32.9, 40.5, 75.5, 126.4, 127.7, 128.7, 130.0, 138.7, 143.7 ppm; IR (neat) 3380, 3061, 3028, 2922, 2851, 1667, 1616 cm^{-1} ; HRMS-CI *m/z* 215.1430 [$(M-H)^+$; calcd for $C_{15}H_{19}O$: 215.1436].

(*S*)-4,4-Dimethyl-1-phenyl-pent-2-en-1-ol (4). The product was prepared by General Procedure A using 1.07 g (6.0 mmol) Cy_2BH, 739 μL (6.0 mmol) 2,2-dimethyl-3-butyne, 3.0 mL (6.0 mmol, 2.0 M in toluene) Me_2Zn, 24.0 mg (0.1 mmol) (-)-MIB, and 510 μL (5.0 mmol) benzaldehyde. The crude product was purified by column chromatography

(20% ethyl acetate in hexanes) to give **4** as a colorless oil in 86% yield (819 mg, 4.3 mmol). $[\alpha]_D^{20}$ = +40.6 (*c* = 1.00, $CHCl_3$, 96% ee); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.14 (s, 9H), 2.54 (s, 1H), 5.19 (d, *J* = 6.8 Hz, 1H), 5.65 (dd, *J* = 15.4, 6.9 Hz, 1H), 5.86 (d, *J* = 15.9 Hz, 1H), 7.34-7.45 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 30.0, 33.3, 75.7, 126.7, 127.8, 128.7, 128.9, 143.7, 144.1 ppm; IR (neat) 3346, 3086, 3063, 3029, 2959, 2902, 2866, 1494, 1476, 1453 cm^{-1}; HRMS-CI *m/z* 190.1356 [M^+; calcd for $C_{13}H_{18}O$: 190.1358].

(*S*)-3-Adamantyl-1-phenyl-prop-2-en-1-ol (5). The product was prepared according to general procedure A. Cy_2BH (11.0 mmol), 1.76g (11.0 mmol) of 1-adamantylacetylene in toluene (5.0 ml), 1.54 g (12.5 mmol) of Et_2Zn in hexanes (10 mL), 48 mg (2.0 mol%, 0.2 mmol) of (-)-MIB, and 1.01 mL (10 mmol) benzaldehyde. After column chromatography on silica (5% to 10% ethyl acetate in hexanes) the reaction afforded 77.3 % (2.2 g, 7.73 mmol) of **5** as a viscous oil. $[\alpha]_D^{20}$ +22.3 (*c* = 1.0, $CHCl_3$, 97 % ee); ^1H NMR (500 MHz, $CDCl_3$): δ 1.64-1.77 (m, 12H), 1.95 (s, 1H), 2.02 (s, 3H), 5.19 (d, 1H, *J* = 6.7 Hz), 5.55 (dd, 1H, *J* = 15.7, 6.9 Hz), 5.68 (d, 1H, *J* = 15.7 Hz), 7.28-7.42 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 28.84, 35.14 37.26, 42.55, 75.88, 126.62, 127.70, 127.81, 128.83, 143.99 144.16 ppm; IR (neat) 3450, 1605, 1500, 1450 cm^{-1}; HRMS-CI *m/z* 268.1816 [M^+; calcd for $C_{19}H_{24}O$: 268.1827].

(*S*)-7-Chloro-1-phenyl-hept-2-en-1-ol (6). The product was prepared according to general procedure A using Cy_2BH (12.0 mmol), 1.45 mL (12.0 mmol) of 6-chloro-1-hexyne, 1.72 g (14.0 mmol) of Et_2Zn in hexanes (5 mL), 48 mg (2.0 mol%, 0.2 mmol) of (-)-MIB and 1.01 mL (10 mmol) benzaldehyde. After column chromatography on silica

(5% ethyl acetate in hexanes), the reaction afforded 1.7 g of **6** as a colorless oil (76 % yield based on benzaldehyde). $[\alpha]_D^{20}$ = +13.9 (*c* 1.0, $CHCl_3$, 93.3% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.56-1.62 (m, 2H), 1.80-1.84 (m, 2H), 2.0 (s, 1H), 2.13 (m, 2H, *J* = 6.9 Hz), 3.56 (t, 2H, *J* = 6.3 Hz), 5.2 (d, 1H, *J* = 4.3 Hz), 5.73-5.78 (m, 2H, overlapping vinyl H's), 7.30-7.39 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 26.68, 31.79, 32.48, 45.31, 75.50, 126.57, 128.00, 128.94, 132.07, 133.36, 143.66 ppm; IR (neat) 3455, 1650, 1565, 1500, 1450 cm^{-1}; HRMS-CI *m/z* 224.0964 [M^+; calcd for $C_{13}H_{17}ClO$: 224.0967].

(*S,S*)-1,9-Diphenyl-nona-2,7-diene-1,9-diol (7). Inverse-addition Procedure: To a stirred solution of Cy_2BH (10.0 mmol) in toluene (10 mL), prepared according to Oppolzer's procedure (flask A),[1] was added 1.14 mL (5.0 mmol) of 1,7-heptadiyne dropwise at ambient temperature. In a separate flask (B) charged with 48 mg (2.0 mol%, 0.2 mmol) of (-)-MIB, was added Me_2Zn (7 mL, 14.0 mmol, 2.0 M in toluene) and diluted with 20 mL of toluene. The reaction was cooled to 0 °C and 1.01 mL (10 mmol) benzaldehyde was added. The contents of the flask (A) were taken up in a syringe and added to the flask (B), with the aid of a syringe pump, over 1 hour. The reaction was stirred at 0 °C for 2 hours and quenched with 2.0 mL of H_2O. After stirring for 1 hour, $MgSO_4$ was added and the content of the flask was filtered and thoroughly rinsed with ether. The filtrate was concentrated *in vacuo* and the residue chromatographed on silica (10%-20% ethyl acetate in hexanes) to afford **7** as a viscous oil in 65% yield (1.02 g, 3.25 mmol). $[\alpha]_D^{25}$ = -90 (*c* = 0.48, $CHCl_3$, 88% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.53-1.56 (m, 2H), 2.0 (s, 2H), 2.10 (m, 4H), 5.19 (d, 2H, *J* = 6.6 Hz), 5.66-5.78 (m, 4H,

overlapping vinyl H's), 7.29-7.39 (m, 10H) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 28.72, 32.08, 75.55, 126.57, 127.95, 128.91, 132.53, 133.11, 143.75 ppm; IR (neat) 3392, 1704, 1666, 1614, 1492, 1450 cm^{-1}; HRMS-ESI *m/z* 331.1665 [$(M+Na)^+$; calcd for $C_{21}H_{24}O_2Na$: 331.1675].

(*S*)-*N*-(1-Cyclopropyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide (9). A 25 mL round-bottom flask under N_2 atmosphere was charged with (*S*)-3-cyclopropyl-1-phenyl-2-en-1-ol, **2**, (174 mg, 1.0 mmol) and Cl_3CCN (120 μL, 1.2 mmol) followed by 10 mL of dry CH_2Cl_2. The reaction mixture was cooled to 0 °C with an ice bath. DBU (22.4 μL, 0.15 mmol) was added dropwise to the reaction mixture via a microsyringe. The reaction was allowed to stir at this temperature for 30 min then warmed to room temperature and stirred for an additional 3.5 hours. The solvent was removed *in vacuo* and the residue was chromatographed on silica (5% ethyl acetate in hexanes) to afford 296 mg (93% yield) of **9** as a viscous oil that solidified on standing over several days. m.p.: 66-68 °C; $[\alpha]_D^{25}$ = -32.2 (*c* = 0.64, $CHCl_3$, 89% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.46-0.47(m, 1H) , 0.53-0.57 (m, 1H), 0.65-0.72 (m, 2H), 1.4-1.6 (m, 1H), 4.08 (m, 1H), 6.22 (dd, 1H, *J*=14.7, 5.76 Hz), 6.68 (d, 1H, *J* = 15.8 Hz), 6.83 (d, 1H, *J* = 6.7 Hz), 7.29-7.42 (m, 5H) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 3.56, 3.71, 15.77, 57.80, 81.5, 126.99, 127.18, 128.4, 129.03, 132.17, 136.68, 161.6 ppm; IR (film) 3333, 1709, 1691.6, 1512, 1492, 1485 cm^{-1}; HRMS-CI *m/z* 317.0125 [M^+; calcd for $C_{14}H_{14}Cl_3NO$: 317.0140].

(*S*)-*N*-(1-Adamantyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide (12). General Procedure B. To a stirred solution of (*S*)-3-adamantyl-1-phenyl-prop-2-en-1-ol, **5**, (1.5

g, 5.3 mmol) in 150 mL of dry ether was added KH (60 mg, 1.5 mmol) in one portion under a stream of N_2. The reaction was stirred for 15 min until H_2 gas evolution ceased and a yellow to orange appearance was observed. The mixture was transferred via cannula to a flask containing Cl_3CCN (795 µL, 7.95 mmol) in 100 mL of dry ether at 0 °C over 10 min. After stirring for 1 h at ambient temperature, the reaction was quenched with 61 µL of MeOH, filtered, and thoroughly rinsed with ether. The filtrate was concentrated *in vacuo* and 50 mL of dry toluene was added. The reaction was refluxed for 1-2 hour under N_2 atmosphere. The toluene was removed *in vacuo* to afford 1.81 g of **12** (4.4 mmol, 83% yield) after a single recrystallization from hexanes-ethyl acetate. m.p.: 164-165 °C; $[\alpha]_D^{25}$ = -38.6 (*c* = 0.50, $CHCl_3$, 99% ee); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.6-1.79 (m, 12H), 2.07 (s, 3H), 4.27 (t, 1H), 6.21 (dd, 1H, J = 15.8, 7.7 Hz), 6.6 (d, 1H, J = 15.8 Hz), 6.79 (d, 1H, J = 9.2 Hz), 7.25-7.42 (m, 5H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 28.6, 37.24, 37.53, 39.19, 62.69, 81.6, 124.50, 126.94, 128.32, 129.02, 133.94, 136.85, 161.6 ppm; IR (KBr) 3423, 1706, 1509, 1449 cm^{-1}; HRMS-CI m/z 411.1010 [M^+; calcd for $C_{21}H_{24}Cl_3NO$: 411.0922].

(*S*)-N-(1-Butyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide (**8**). The product was prepared by General Procedure B using 95 mg (0.50 mmol) (*S*)-1-phenyl-hept-2-en-1-ol, 1, 60 µL (0.60 mmol) Cl_3CCN, and 4.0 mg (0.1 mmol) KH. The crude product was purified by crystallization from hexanes to give 8 as a white solid in 64% yield (107 mg, 0.32 mmol). m.p.: 64-66°C; $[\alpha]_D^{20}$ = -69.4 (c = 1.11, $CHCl_3$, 99% ee); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.93 (t, J = 7.0 Hz, 3H), 1.39 (m, 4H), 1.74 (m, 2H), 4.57 (m, 1H), 6.12 (dd, J = 16.5, 7.8 Hz, 1H), 6.59 (d, J = 15.8 Hz, 2H), 7.24-7.38 (m, 5H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 14.4, 22.9, 28.4, 35.1, 54.0, 81.1, 127.0, 128.4, 128.5, 129.1, 132.4, 136.8, 161.6

ppm; IR (KBr) 3368, 2952, 1692, 1513, 963, 816 cm^{-1}; HRMS-ESI m/z 356.0341 [$(M+Na)^+$; calcd for $C_{15}H_{18}C_{l3}NONa$: 356.0352].

(*S*)-*N*-(1-*tert*-Butyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide (11). The product was prepared by General Procedure B using 1.0 g (5.25 mmol) (*S*)-4,4-dimethyl-1-phenyl-pent-2-en-1-ol, **4**, 630 μL (6.3 mmol) Cl_3CCN, and 44 mg (1.1 mmol) KH. The crude product was purified by crystallization from hexanes to give **11** as a white solid in 90% yield (1.62 g, 4.8 mmol). m.p.: 96-98°C; $[\alpha]_D^{20}$ = -78.8 (*c* = 1.06, $CHCl_3$, 99.6% ee); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.07 (s, 9H), 4.44 (dd, *J* = 9.0, 7.4 Hz, 1H), 6.21 (dd, *J* = 15.8, 7.3 Hz, 1H), 6.63 (d, *J* = 15.8 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 7.29-7.42 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ26.6, 35.6, 62.1, 93.8, 125.2, 126.8, 128.2, 128.9, 133.6, 136.6, 161.3 ppm; IR (KBr) 3402, 3080, 3056, 3028, 2958, 2869, 1699, 1509, 1450 cm^{-1}; HRMS-CI *m/z* 333.0646 [M^+; calcd for $C_{15}H_{18}Cl_3NO$: 333.0454].

(*S*)-*N*-(1-Cyclohexyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide (10). The product was prepared by General Procedure B using 216 mg (1.0 mmol) (*S*)-cyclohexyl-1-phenyl-prop-2-en-1-ol, **3**, 120μL (1.2 mmol) Cl_3CCN, and 8.0 mg (0.2 mmol) KH. The crude product was purified by crystallization from hexanes to give **10** as a white solid in 96% yield (346 mg, 0.96 mmol). m.p.: 106-109°C; $[\alpha]_D^{20}$ = -14.5 (*c* = 1.27, $CHCl_3$, 99.9% ee); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.06-1.29 (m, 5H), 1.65-1.71 (m, 2H), 1.79-1.85 (m, 4H), 4.43 (m, 1H), 6.11 (dd, *J* = 15.8, 7.1 Hz, 1H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 7.25-7.38 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ26.2, 29.1, 29.8, 42.6, 58.6, 81.8, 126.76, 126.83, 128.2, 128.9, 132.9, 136.6, 161.4 ppm; IR (KBr)

3373, 2937, 2850, 1700, 1516, 1449, 1384, 1077, 965, 820, 747, 677 cm^{-1}; HRMS-ESI *m/z* 382.0519 [$(M+Na)^+$; calcd for $C_{17}H_{20}Cl_3NONa$: 382.0508].

(*S*)-*N*-(5-Chloro-1-styryl-pentyl)-2,2,2-trichloro-acetamide (13). The product was prepared according to procedure B using (*S*)-7-chloro-1-phenyl-hept-2-en-1-ol, **6**, (1.2 g, 5.58 mmol), Cl_3CCN (837 μL, 8.37 mmol) and KH (60 mg, 1.5 mmol) to afford 1.37 g (3.68 mmol, 66%) of viscous oil after column chromatography (5% ethyl acetate in hexanes). $[\alpha]_D^{25}$ = +36.8 (*c* = 1.13, $CHCl_3$, 93.3% ee); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.59-1.64 (m, 2H), 1.79-1.90 (m, 4H), 3.57-3.60 (m, 2H), 4.62 (m, 1H), 6.15 (dd, 1H, *J* = 15.9, 6.8 Hz), 6.65 (d, 2H, *J* = 16.0 Hz, NH and vinyl-H are overlapped), 7.29-7.43 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz): δ 23.42, 32.38, 34.42, 45.01, 53.75, 81.3, 126.98, 127.69, 128.56, 129.10, 132.83, 136.44, 161.63 ppm; IR (neat) 3329, 1767, 1693, 1514, 1448 cm^{-1}; HRMS-CI *m/z* 367.0058 [M^+; calcd for $C_{15}H_{17}Cl_4NO$: 367.0064].

(*S,S*)-2,2,2-Trichloro-*N*-[7-phenyl-1-styryl-5-(2,2,2-trichloro-acetylamino)-hept-6-enyl]-acetamide (14). The product was prepared according to procedure B using (*S,S*)-1,9-diphenyl-nona-2,7-diene-1,9-diol, **7**, (888 mg, 2.88 mmol) in dry THF (20 mL), Cl_3CCN (864 μL, 8.64 mmol) and KH (56 mg, 1.44 mmol) to afford 682 mg (1.14 mmol, 39.6% yield) of **14** after column chromatography (50 to 100% CH_2Cl_2 in hexanes). $[\alpha]_D^{20}$ = -23.8 (*c* = 0.63, $CHCl_3$, 93% ee); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.54-1.58 (m, 2H), 1.79-1.88 (m, 4H), 4.58-4.61 (m, 2H), 6.11 (dd, 2H, *J* = 15.9, 6.7 Hz), 6.60 (d, 2H, *J* = 15.9 Hz), 6.64(d, 2H, *J* = 7.7 Hz), 7.26-7.36 (m, 10H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 22.35, 34.78, 53.55, 81.5, 126.97, 127.68, 128.59, 129.09, 132.89, 136.35,

161.82 ppm; IR (neat) 3290, 1684, 1598, 1578, 1522, 1448 cm^{-1}; HRMS-ESI *m/z* 616.9882 [$(M+Na)^+$; calcd for $C_{25}H_{24}Cl_6NaN_2O_2$: 616.9866].

(*S*)-(1-Cyclopropyl-3-phenyl-allyl)-carbamic acid *tert*-butyl ester (16). To a 100 mL round-bottom flask charged with (*S*)-*N*-(1-cyclopropyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide, **9**, (318 mg, 1.0 mmol) was added absolute ethanol (20 mL) and 2N NaOH (10 mL). The reaction was stirred for 14 hours at ambient temperature. Excess $(Boc)_2O$ (436.5 mg, 2.0 mmol) was added directly into the reaction mixture. Disappearance of baseline material deemed the reaction complete. The reaction mixture was concentrated *in vacuo* and the residue was taken up in CH_2Cl_2 (30 mL) and washed with H_2O (30 mL). The aqueous layer was back extracted twice with CH_2Cl_2 (10 mL X 2). The combined organic layer was dried with $MgSO_4$ and concentrated *in vacuo*. The crude product was recrystallized with hexanes with a minimum amount of ethyl acetate to afford 223 mg (0.816 mmol, 81.6 % yield) of **16** as white needles. $[\alpha]_D^{25}$ = -3.38 (*c* = 0.33, $CHCl_3$, 99% ee); ^1H NMR (C_6D_6, 500 MHz, at 343 K): δ 0.09-0.18 (m, 1H), 0.27-0.34 (m, 3H), 0.63-0.72 (m, 1H), 1.47 (s, 9H), 3.87 (br, 1H), 4.37 (br, 1H), 6.01 (dd, 1H, *J* = 15.9, 5.8 Hz), 6.49 (d, 1H, *J* = 16.0 Hz), 7.02-7.21 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6, 500MHz, at 343 K to detect missing carbons because of restricted bond rotation): δ 2.99, 3.01, 16.36, 28.58, 56.48, 78.85, 126.85, 127.56, 128.70, 130.30, 130.51, 137.73, 155.32 ppm; IR (KBr) 3367, 1679, 1525, 1444 cm^{-1}; HRMS-ESI *m/z* 273.1724 [M^+; calcd for $C_{17}H_{23}NO_2$: 273.1729].

(*S*)-(1-Adamantyl-3-phenyl-allyl)-carbamic acid benzyl ester (17b). To a 50 mL round-bottom flask charged with (*S*)-*N*-(1-adamantyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide, **12**, (210 mg, 0.5 mmol) was added absolute ethanol (30 mL) and 2N NaOH (10 mL). The reaction was refluxed for 4 hours and monitored by TLC for the disappearance of starting material. The reaction mixture was concentrated *in vacuo* and the residue taken up in CH_2Cl_2 (10 mL) and saturated $NaHCO_3$ (10 mL). The biphasic mixture was cooled to 0 ^oC, and 107 μL Cbz-Cl (0.75mmol) was added dropwise. After 14 hours of stirring at room temperature, the organic layers were separated, and the aqueous layer was extracted twice with CH_2Cl_2 (10 mL X 2). The combined organic layer was dried with $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed (5% ethyl acetate in hexanes) on silica to afford 157 mg (0.39 mmol, 78 % yield) of **17b** as white foam. $[\alpha]_D^{25}$ = -5.15 (*c* = 0.86, $CHCl_3$, 99% ee); ^1H NMR (500 MHz, $CDCl_3$): δ 1.57-1.75 (m, 12H), 2.03 (s, 3H), 4.02 (br, 1H), 4.91 (br, 1H), 5.15 (s, 2H), 6.18 (dd, 1H, *J* = 15.8, 7.5 Hz), 6.53 (d, 1H, *J* = 15.7 Hz), 7.26-7.40 (m, 10H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 28.75, 37.02, 37.37, 39.21, 62.77, 67.27, 126.53, 127.91, 128.55, 128.84, 132.45, 137.01, 137.33, 156.3 ppm (Two 4^o carbons were not detected); IR (Kbr) 3330, 1697, 1530, 1448 cm^{-1}. HRMS-ESI *m/z* 424.2244 [$(M+Na)^+$; calcd for $C_{27}H_{31}NaNO_2$: 424.2255].

(*S*)-2-(2,2,2-Trichloro-acetylamino)-hexanoic acid (18). General Procedure C: To a stirred solution of 100 mg (0.3 mmol) *(S)-N*-(1-butyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide, **8**, in 1.0 mL carbon tetrachloride, 1.0 mL acetonitrile, and 1.5 mL water was added 260 mg (1.2 mmol) sodium periodate. Once all the sodium periodate had dissolved, 1.7 mg (0.008 mmol) ruthenium trichloride hydrate was added, and the

reaction mixture was stirred vigorously overnight at room temperature. It was then extracted with dichloromethane; the combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give a deep purple oil. The crude product was then redissolved in dichloromethane and stirred for 30 min with 28 μL (50 equiv with respect to the ruthenium catalyst) dimethylsulfoxide and 2 g silica gel. The solvent was removed *in vacuo* and the product, now pre-adsorbed to silica, was purified by column chromatography (0.25% acetic acid and 20-50% ethyl acetate in hexanes) to give **18** as a white solid in 75% yield (62 mg, 0.22 mmol). m.p.: 60-63°C; $[\alpha]_D^{29} = +35.2$ (*c* = 0.27, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.93 (t, *J* = 7.0 Hz, 3H), 1.34–1.43 (m, 4H), 1.81-1.89 (m, 1H), 2.01-2.08 (m, 1H), 4.63 (dt, *J* = 7.3, 5.4 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 13.5, 21.9, 26.8, 31.2, 53.5, 91.8, 161.4, 176.1 ppm; IR (KBr) 3420, 2930, 2371, 1707, 1519, 1384, 1246, 828 cm^{-1}; HRMS-ESI *m/z* 297.9819 [$(M+Na)^+$; calcd for $C_8H_{12}Cl_3NO_3Na$: 297.9780].

(*S*)-3,3-Dimethyl-2-(2,2,2-trichloro-acetylamino)-butyric acid (22). The product was prepared by General Procedure C using 100 mg (0.30 mmol) (*S*)-*N*-(1-*tert*-butyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide, **11**, 289 mg (1.35 mmol) $NaIO_4$, and 1.6 mg (0.008 mmol) $RuCl_3 \bullet 3H_2O$. The crude product was purified by column chromatography (0.5% acetic acid and 1% methanol in dichloromethane) to give **22** as a white solid in 92% yield (76 mg, 0.27 mmol). m.p.: 99-104°C; $[\alpha]_D^{29} = +11.1$ (*c* = 0.63, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.03 (s, 9H), 4.39 (d, *J* = 9.2 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 27.0, 36.2, 62.2, 80.0, 162.1, 175.0 ppm; IR (KBr) 3387, 3221, 2972, 1724, 1701, 1522, 1478, 1410, 1207, 1176, 1093, 837, 821 cm^{-1}; HRMS-CI *m/z* 275.9954 [MH^+; calcd for $C_8H_{13}Cl_3NO_3$: 275.9961].

(*S*)-Cyclohexyl-(2,2,2-trichloro-acetylamino)-acetic acid (21). The product was prepared by General Procedure C using 36 mg (0.10 mmol) (*S*)-*N*-(1-cyclohexyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide, **10**, 86 mg (0.40 mmol) $NaIO_4$, and 0.50 mg (0.003 mmol) $RuCl_3 \bullet 3H_2O$. The crude product was purified by column chromatography (0.25% acetic acid and 20-50% ethyl acetate in hexanes) to give **21** as a white solid in 83% yield (25 mg, 0.083 mmol). m.p.: 132-134°C; $[\alpha]_D^{29} = +24.7$ (*c* = 0.23, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.05-1.13 (m, 3H), 1.19-1.27 (m, 3H), 1.63 (d, *J* = 12.6 Hz, 2H), 1.75 (d, *J* = 12.4 Hz, 2H), 1.94 (m, 1H), 4.51 (dd, *J* = 8.5, 4.7 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 25.8, 27.8, 29.5, 41.0, 58.3, 161.8, 175.4 ppm; IR (KBr) 3420, 2929, 2855, 2365, 2345, 1725, 1691, 11536, 1450, 1420, 1384, 1237, 1123, 823, 658 cm^{-1}; HRMS-ESI *m/z* 323.9952 [$(M+Na)^+$; calcd for $C_{10}H_{14}Cl_3NO_3Na$: 323.9937].

(*S*)-Cyclopropyl-(2,2,2-trichloro-acetylamino)-acetic acid (19). The product was prepared according to procedure C using (*S*)-*N*-(1-cyclopropyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide, **9**, (318 mg, 1.0 mmol), $NaIO_4$ (941 mg, 4.4 mmol), and $RuCl_3 \bullet 3H_2O$ (4.1 mg, 0.02 mmol). After column chromatography on silica (15% to 50% ethyl acetate in hexanes and 0.25% glacial acetic acid) the reaction afforded 221mg (0.85 mmol, 85% yield) of **19** as a viscous oil that solidified on standing over several days. m.p.: 108-110 °C; $[\alpha]_D^{25} = -32.2$ (*c* = 0.50, $CHCl_3$, 89 %ee); ^1H NMR ($CDCl_3$, 500MHz): δ 0.60-0.78 (m, 4H), 1.26 (m, 1H), 4.09 (dd, 1H, *J* = 8.0), 7.20 (d, 1H, *J* = 6.7) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 3.79, 3.83, 13.99, 57.78, 92.42, 162.28, 176.21 ppm; IR (KBr) 3330, 1702, 1515, 1420 cm^{-1}; HRMS-CI *m/z* 259.9663 [MH^+; calcd for $C_7H_9Cl_3NO_3$: 259.9646].

(*S*)-6-Chloro-2-(2,2,2-trichloro-acetylamino)-hexanoic acid (25). The product was prepared according to procedure C using (*S*)-*N*-(5-chloro-1-styryl-pentyl)-2,2,2-trichloro-acetamide, **13**, (369 mg, 1.0 mmol), $NaIO_4$ (941 mg, 4.4 mmol), and $RuCl_3 \bullet 3H_2O$ (4.1 mg, 0.02 mmol). After column chromatography on silica (15% to 50% ethyl acetate in hexanes and 0.25% glacial acetic acid) the reaction afforded 252 mg (0.81 mmol, 81% yield) of **25** as a viscous oil. $[\alpha]_D^{25}$ = +36.8 (*c* = 0.50, $CHCl_3$, 93.3% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.58-1.62 (m, 2H), 1.84-1.91(m, 3H), 2.0-2.10 (m, 1H), 3.55-3.58 (t, *J* = 6.3 Hz, 2H), 4.63-4.67 (dt, 1H, *J* = 7.2 Hz), 6.8-7.3 (br, 1H, -CO_2H), 7.25 (d, 1H, *J* = 7.3 Hz) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 22.67, 31.38, 32.09, 44.70, 53.97, 92.42, 162.19, 175.96 ppm; IR (KBr) 3330, 1702, 1515, 1420 cm^{-1}; HRMS-CI *m/z* 309.9556 [MH^+; calcd for $C_8H_{12}Cl_4NO_3$: 309.9569].

(*S*)-*tert*-Butoxycarbonylamino-cyclopropyl-acetic acid (20).[2] The product was prepared according to procedure C using (*S*)-(1-cyclopropyl-3-phenyl-allyl)-carbamic acid *tert*-butyl ester, **16**, (273 mg, 1.0 mmol), $NaIO_4$ (941 mg, 4.4. mmol), and $RuCl_3 \bullet 3H_2O$ (4.1 mg, 0.02 mmol). After column chromatography on silica (15% to 50% ethyl acetate in hexanes and 0.25% of glacial acetic acid) the reaction afforded 146 mg (0.68 mmol, 68% yield) of **20** as a viscous oil that solidified on standing over several days. m.p.: 102-103 °C; $[\alpha]_D$25 = +41.9 (c = 0.72, $CHCl_3$, 99% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.46-0.48 (m, 1H), 0.56-0.67 (m, 3H), 1.13-1.15 (m, 1H), 1.48 (s, 9H), 3.78 (br, 1H), 5.10 (br, 1H) ppm; ^{13}C{^{1}H} NMR (CDCl3, 125 MHz): δ 3.36, 3.56, 13.94,

28.68, 30.09, 57.23, 156.0, 176.91 ppm; IR (KBr) 3368, 3107, 1733, 1710, 1689, 1636, 1515, 1478, 1416 cm^{-1}; HRMS-CI m/z 216.1243 [MH^+; calcd for $C_{10}H_{18}NO_4$: 216.1236].

(S)-1-Adamantyl-benzyloxycarbonylamino-acetic acid (23).[3] The product was prepared according to procedure C using (S)-(1-adamantyl-3-phenyl-allyl)-carbamic acid benzyl ester, **17b**, (80.3 mg, 0.2 mmol), $NaIO_4$ (188 mg, 0.88 mmol), and $RuCl_3 \bullet 3H_2O$ (0.8 mg, 0.004 mmol). After column chromatography on silica (15% to 50% ethyl acetate in hexanes and 0.25% glacial acetic acid) the reaction afforded 55 mg (0.16 mmol, 80% yield) of **23** as a white foam. $[\alpha]_D^{20}$ = +19.4 (c = 0.63, $CHCl_3$, 99% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.56-1.72 (m, 12H), 2.01 (s, 3H), 4.08 (d, 1H, J = 9.56 Hz), 5.11 (s, 2H), 5.31 (d, 1H, J = 9.50 Hz), 7.32-7.37 (m, 5H) ppm; 13C{1H} NMR (CDCl3, 125 MHz): δ 28.65, 36.71, 37.01, 38.95, 63.31, 67.65, 128.65, 128.96, 156.70, 175.97 ppm; HRMS-CI m/z 366.1668 [$(M+Na)^+$; calcd for $C_{20}H_{25}NaNO_4$: 366.1683].

(*R*)-1-Adamantyl-(2,2,2-trichloro-acetylamino)-acetic acid (24). The product was prepared according to procedure C using (*R*)-*N*-(1-adamantyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide, **12**, (411 mg, 1.0 mmol), $NaIO_4$ (941 mg, 4.4 mmol), and $RuCl_3 \bullet 3H_2O$ (4.1 mg, 0.02 mmol). After column chromatography on silica (10% to 50% ethyl acetate in hexanes and 0.25% of glacial acetic acid) the reaction afforded 202 mg (0.57 mmol, 57% yield) of **24** as white solid. m.p.: 144-146 °C; $[\alpha]_D^{25}$ = -31.3 (*c* = 0.55, $CHCl_3$, 99% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.60-1.80 (m, 12H), 2.08 (s, 3H), 4.35 (d, 1H, *J* = 9.2 Hz), 7.19 (d, 1H, *J* = 9.2 Hz) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 28.57, 36.87, 37.86, 38.98, 62.81, 81.3, 162.09, 174.20 ppm; IR (KBr) 3408, 3092, 1733,

1709, 1496, 1447, 1420 cm^{-1}; HRMS-CI *m/z* 376.0291[$(M+Na)^+$; calcd for $C_{14}H_{18}NaNO_3$: 376.0251].

(*S,S*)-*N,N'-bis*(2,2,2-Trichloro-acetyl)-diaminopimelic acid (26). The product was prepared according to procedure C using (*S,S*)-2,2,2-trichloro-*N*-[7-phenyl-1-styryl-5-(2,2,2-trichloro-acetylamino)-hept-6-enyl]-acetamide, **14**, (298 mg, 0.5 mmol), $NaIO_4$ (470 mg, 2.2 mmol) and $RuCl_3 \bullet 3H_2O$ (4.1 mg, 0.02 mmol). After column chromatography on silica (5% MeOH in CH_2Cl_2 and 0.25% glacial acetic acid) the reaction afforded 215 mg (0.44 mmol, 89% yield) of **26** as a viscous oil. $[\alpha]_D^{25}$ = -5.66 (*c* = 1.37, CH_3OH, 99% ee); ^1H NMR (CD_3OD, 500 MHz): δ 1.50-1.53 (m, 2H), 1.87-1.93 (m, 2H), 1.99-2.04 (m, 2H), 4.38-4.40 (m, 2H), 4.82 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR (CD_3OD, 125 MHz): δ 23.54, 31.45, 55.30, 82.23, 164.07, 173.86 ppm; IR (KBr) 3328, 1702, 1523, 1459, 1443 cm^{-1}; HRMS-CI *m/z* 500.8716 [$(M+Na)^+$; calcd for $C_{11}H_{12}NaN_2O_6$: 500.8726].

(*S*)-2-(2,2,2-Trichloro-acetylamino)-hexanoic acid methyl ester (27). General Procedure D: Ozone was passed through a stirred solution of 100 mg (0.3 mmol) (*S*)-*N*-(1-butyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide, **8**, in 10 mL dichloromethane and 1.0 mL of 2.5M methanolic sodium hydroxide at –78 °C. After 1h, the characteristic blue color of ozone persisted in the reaction mixture. At this point, oxygen was bubbled through the reaction mixture for 15 min. It was then diluted with dichloromethane and water, allowed to warm slowly to room temperature and extracted with dichloromethane. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The

crude product was then purified by column chromatography (20% ethyl acetate in hexanes) to give **27** as a colorless oil in 84% yield (73 mg, 0.25 mmol). $[\alpha]_D^{23}$ = -35.7 (*c* = 1.63, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 0.84 (t, *J* = 7.0 Hz, 3H), 1.19-1.31 (m, 4H), 1.69-1.74 (m, 1H), 1.88-1.93 (m, 1H), 3.74 (s, 3H), 4.51 (dt, *J* = 7.2, 5.4 Hz, 1H), 7.16 (d, *J* = 5.7 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 13.8, 22.2, 27.0, 31.7, 52.8, 53.9, 92.0, 161.4, 171.8 ppm; IR (neat) 3345, 2958, 1711, 1519, 1218, 827 cm^{-1}; HRMS-ESI *m/z* 311.9930 [$(M+Na)^+$; calcd for $C_9H_{14}Cl_3NO_3Na$: 311.9937].

(*S*)-3,3-Dimethyl-2-(2,2,2-trichloro-acetylamino)-butyric acid methyl ester (29). The product was prepared by General Procedure D using 100 mg (0.30 mmol) (*S*)-*N*-(1-*tert*-butyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide, **11**, 100 mg (2.5 mmol) NaOH in 1.0 mL MeOH, and a stream of ozone. The crude product was purified by column chromatography (20% ethyl acetate in hexanes) to give **29** as a colorless oil in 75% yield (65 mg, 0.22 mmol). $[\alpha]_D^{23}$ = -22.0 (*c* = 2.54, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 0.96 (s, 9H), 3,72 (s, 3H), 4.35 (d, *J* = 9.3 Hz, 1H), 7.14 (d, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 26.4, 35.7, 52.2, 61.8, 92.2, 161.5, 170.7 ppm; IR (neat) 3416, 3354, 2968, 2910, 2874, 2732, 1723, 1514, 1478, 1437, 1402, 1372, 1344, 1261, 1221, 1168, 1108, 1040, 1011, 993, 937, 897, 839, 820 cm^{-1}; HRMS-CI *m/z* 290.0115 [MH^+; calcd for $C_9H_{15}Cl_3NO_3$: 290.0118].

(*S*)-Cyclohexyl-(2,2,2-trichloro-acetylamino)-acetic acid methyl ester (28). The product was prepared by General Procedure D using 72 mg (0.20 mmol) (S)-*N*-(1-cyclohexyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide, **10**, 64 mg (1.6 mmol) NaOH in 0.64 mL MeOH, and a stream of ozone. The crude product was purified by column

chromatography (10% ethyl acetate in hexanes) to give **28** as a colorless oil in 78% yield (49 mg, 0.15 mmol). $[\alpha]_D^{23}$ = -61.4 (*c* = 1.52, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 0.98-1.09 (m, 3H), 1.14-1.23 (m, 2H), 1.52-1.62 (m, 2H), 1.66-1.73 (m, 3H), 1.85 (m, 1H), 3.73 (s, 3H), 4.44 (dd, *J* = 8.6, 5.0 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 26.1, 28.3, 29.7, 41.5, 52.8, 58.8, 92.3, 161.9, 171.5 ppm; IR (neat) 3408, 3342, 2929, 2855, 1745, 1715, 1514, 1449, 1346, 1299, 1269, 1215, 1176, 1146, 1021, 994, 904, 820, 765, 748, 705, 677 cm^{-1}; HRMS-ESI *m/z* 338.0090 $[(M+Na)^+$; calcd for $C_{11}H_{16}Cl_3NO_3Na$: 338.0093].

(S)-2-Benzyloxycarbonylamino-3,3-dimethyl-butyric acid methyl ester (30). The product was prepared by General Procedure D using 60 mg (0.19 mmol) (1-*tert*-butyl-3-phenyl-allyl)-carbamic acid benzyl ester, **17a**, 37 mg (0.93 mmol) NaOH in 0.40 mL MeOH, and a stream of ozone. The crude product was purified by column chromatography (5-20% ethyl acetate in hexanes) to give **30** as a colorless oil in 94% yield (49 mg, 0.18 mmol). $[\alpha]_D^{29}$ = 34.3 (*c* = 1.37, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 0.90 (s, 9H), 3.65 (s, 3H), 4.13 (d, *J* = 9.6 Hz, 1H), 5.28 (s, 2H), 5.29 (d, *J* = 9.0 Hz, 1H), 7.18-7.29 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 26.1, 34.4, 51.5, 61.5, 66.8, 127.88, 127.92, 128.25, 135.9, 155.8, 171.9 ppm; IR (neat) 3590, 3032, 2960, 2910, 2874, 1732, 1714, 1520, 1469, 1454, 1435 cm^{-1}; HRMS-CI *m/z* 302.1337 $[(M+Na)^+$; calcd for $C_{15}H_{21}NO_4Na$: 302.1368].

Conditions for the Determination of Enantiomeric Excess

Chiral HPLC analyses were performed using a Chiralcel OD-H column. The conditions for the resolution of the racemates are described below.

1-Phenyl-hept-2-en-1-ol (1): *S* = 6.38 min, *R* = 13.10 min (Hexane / 2-propanol: 95 / 5, 0.5 mL/min).

3-Cyclopropyl-1-phenyl-prop-2-en-1-ol (2): *R* = 12.6 min, *S* = 15.8 min (Hexanes/ 2-propanol: 95/ 5, 0.5 mL/ min)

Cyclohexyl-1-phenyl-prop-2-en-1-ol (3): *R* = 11.5 min, *S* = 14.9 min (Hexane / 2-propanol: 95 / 5, 0.8 mL/min).

4,4-Dimethyl-1-phenyl-pent-2-en-1-ol (4): *R* = 9.3 min, *S* = 11.8 min (Hexane / 2-propanol: 95 / 5, 0.8 mL/min).

3-Adamantyl-1-phenyl-prop-2-en-1-ol (5): *R* = 12.6 min, *S* = 15.8 min (Hexanes/ 2-propanol: 95/ 5, 0.5 mL/ min)

7-Chloro-1-phenyl-hept-2-en-1-ol (6): *R* = 16.9 min, *S* = 19.7 min (Hexanes/ 2-propanol: 90/ 10, 0.5 mL/ min)

1,9-Diphenyl-nona-2,7-diene-1,9-diol (7): *R* = 26.3 min, *S* = 28.9 min (Hexanes/ 2-propanol: 80/ 20, 0.5 mL/ min)

***N*-(1-Butyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide (8):** *R* = 13.5 min, *S* = 30.6 min (Hexane / 2-propanol: 95 / 5, 0.5 mL/min).
***N*-(1-Cyclopropyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide (9):** *R* = 15.5 min, *S* = 21.0 min (Hexanes/ 2-propanol: 95/ 5, 0.8 mL/ min)

***N*-(1-Cyclohexyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide (10):** *S* = 11.1 min, *R* = 13.5 min (Hexane / 2-propanol: 95 / 5, 0.8 mL/min).

***N*-(1-*tert*-Butyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide (11):** *R* = 13.7 min, *S* = 20.5 min (Hexane / 2-propanol: 95 / 5, 0.5 mL/min).

***N*-(1-Adamantyl-3-phenyl-allyl)-2,2,2-trichloro-acetamide (12):** *R* = 10.3 min, *S* = 12.6 min (Hexanes/ 2-propanol: 95/ 5, 0.5 mL/ min)

(1-Cyclopropyl-3-phenyl-allyl)-carbamic acid *tert*-butyl ester (16): *S* = 15.5 min, *R* = 24.9 min (Hexanes/ 2-propanol: 95/ 5, 0.5 mL/ min)

2-Benzyloxycarbonylamino-3,3-dimethyl-butyric acid methyl ester (17a): *S* = 18.1 min, *R* = 50.0 min (Hexane / 2-propanol: 95 / 5, 0.5 mL/min).

References

1) Oppolzer, W.; Radinov, R. N. *Helv. Chim. Acta* **1992**, *75*, 170-173.
2) Pauly, R.; Sasaki, N. A.; Potier , P. *Tetrahedron Lett.* **1994**, *35*, 237-240.
3) Clariana, J.; García-Granda, S.; Gotor, V.; Gutiérrez-Fernández, A.; Luna, A.; Moreno-Mañas, M.; Vallribera, A. *Tetrahedron: Asymmetry* **2000**, *11*, 4549-4557.