Angewandte Chemie

Eine Zeitschrift der Gesellschaft Deutscher Chemiker

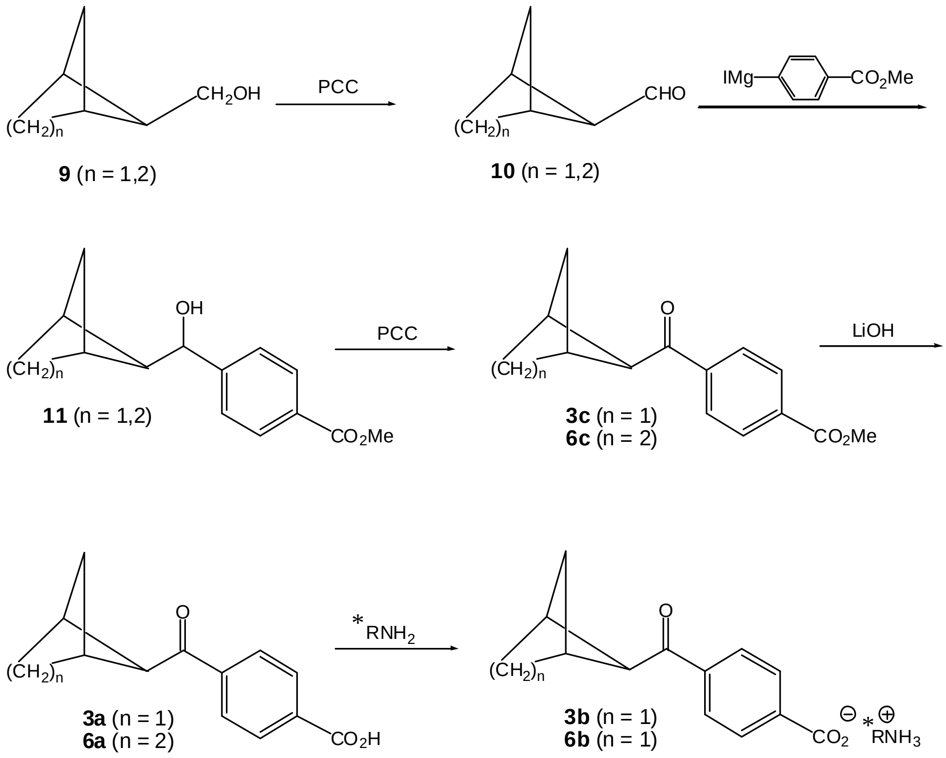
Supporting Information

69451 Weinheim, Germany

Orbital Overlap Control of 1,4-Hydroxybiradical Reactivity

Chao Yang, Wujiong Xia, John R. Scheffer,* Mark Botoshansky and Menahem Kaftory
Department of Chemistry, University of British Columbia, Vancouver, BC Canada V6T 1Z1,
Department of Chemistry, Technion, Haifa 32000, Israel
Email: scheffer@chem.ubc.ca

Synthetic Route:



Synthesis of Alcohol 11 (n = 1 and 2). Alcohol **9** (n = 2) (1.2 g, 0.01 mol), prepared by the procedure of Meinwald et al.[1] was dissolved in 100 mL of methylene chloride. To this solution, PCC (4.62 g, 0.02 mol) and Celite (10 g) ground homogeneously in a mortar were added. The mixture was stirred at room temperature overnight, filtered through a silica gel column and rinsed with diethyl ether. The solvent was then removed *in vacuo*, and the residue **10** (n = 2) was used for next step without purification (GC indicated a purity of approximately 98%). Aldehyde **10** (n = 1) was prepared in the same way starting from the known[2] alcohol **9** (n = 1).

To a solution of methyl *p*-iodobenzoate (3.1 g, 11.8 mmol) in 40 mL of anhydrous THF precooled to -40 ^{o}C was added dropwise isopropylmagnesium chloride (2 M, 5.9 mL). After addition, the mixture was stirred for 1 h at this temperature. To this solution, the aldehyde **10** (n = 2) dissolved in 10 mL of dry THF was added slowly. The solution was stirred at -40 ^{o}C for 4 h Saturated ammonium chloride solution (30 mL) was added quickly and the solution was extracted with diethyl ether (3 x 50 mL), and the combined organic layer washed with saturated brine solution (2 x 30 mL). The solvent was removed *in vacuo* after being dried over magnesium sulfate, and the residue was purified by silica gel chromatography (20% pet ether/diethyl ether) to give alcohol **11** (n = 2) as a white solid (800 mg, 30% yield), **mp** 121-122 °C. **^{1}H NMR** (400 MHz, CDCl$_3$): d 7.96 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.96 (d, *J* = 10.2 Hz, 1H), 3.87 (s, 3H), 2.62 (m, 1H), 2.57 (m, 2H), 2.03 (m, 1H), 1.30 (m, 4H), 1.04 (dd, *J* = 7.0 Hz, 1H). **^{13}C NMR** (100 MHz, CDCl$_3$): d 167.0 (+), 149.8 (+), 129.7 (-), 129.1 (+), 125.9 (-), 72.9 (-), 60.6 (-), 52.0 (-), 40.7 (-), 35.7 (+), 27.2 (+). **IR** (KBr) ?$_{max}$: 3016, 2962, 2906, 1702, 1607, 1288, 770, 711, 560 cm^{-1}. **LRMS** (EI): 246 [M$^+$], 228, 200, 169, 141, 115, 91, 77, 59. **Anal**. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.17; H, 7.40.

In exactly the same way, alcohol **11** (n = 1) was prepared as an oil in an overall yield of 59% from **9** (n = 1). **^{1}H NMR** (400 MHz, CDCl$_3$): d 7.96 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 5.06 (d, *J* = 9.6 Hz, 1H), 3.86 (s, 3H), 2.64 (d, *J* = 18 Hz, 1H), 2.59 (dd, *J* = 9.9, 3.4 Hz, 1H), 2.29 (dd, *J* = 9.6, 6.2 Hz, 1H), 2.17 (d, *J* = 18 Hz, 1H), 1.89 (dd, *J* = 6.2, 3.4 Hz, 1H), 1.79 (d, *J* = 2.0 Hz, 1H), 1.56 (dd, *J* = 9.9, 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, CDCl$_3$): d 167.0 (+), 149.4 (+), 129.7 (-), 128.9 (+), 125.5 (-), 70.7 (-), 68.6 (-), 52.1 (-), 48.0 (+), 46.3 (+), 35.4 (-), 34.8 (-). **IR** (neat) ?$_{max}$: 3422, 2971, 1723, 1611, 1283, 1115, 854, 772, 707 cm^{-1}. **LRMS** (EI): 232 [M$^+$], 214, 201, 178, 165, 131, 105, 77, 59. **HRMS** (EI) for $C_{14}H_{16}O_3$: Cacld. 232.1099; Found 232.1095.

Synthesis of Keto-esters 6c and 3c. To a solution of alcohol **11** (n = 2) (800 mg, 3.25 mmol) in 30 mL of anhydrous methylene chloride were added PCC (1.402 g, 6.50 mmol) and Celite (3 g). The mixture was stirred at room temperature overnight and diethyl ether (20 mL) was added. The solution was then filtered through a silica gel column and rinsed with diethyl ether. The solvent was removed *in vacuo* and the residue purified by column chromatography (10% pet ether/diethyl ether) to give keto-ester **6c** as a white solid (780 mg, 98% yield), **mp** 104-104.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): d 8.08 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H), 3.02 (d, *J* = 6.8 Hz, 1H), 2.92 (s, 2H), 2.15 (m, 1H), 1.88 (m, 2H), 1.79 (m, 2H), 1.04 (d, *J* = 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): d 199.4 (+), 166.2 (+), 140.0 (+), 129.7 (-), 128.0 (-), 60.0 (-), 52.3 (-), 43.6 (-), 36.5 (+), 27.3 (+). **IR** (KBr) ?$_{max}$: 2961, 2879, 1723, 1671, 1439, 1278, 1107, 768, 706, 541 cm^{-1}. **LRMS** (EI): 244 [M$^+$], 229, 215, 178, 163, 135, 115, 76, 53. **Anal**. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.90; H, 6.56.

An identical procedure starting from alcohol **11** (n = 1) afforded keto-ester **3c** in a yield of 84%, **mp** 63-64 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): d 8.07 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H), 3.49 (d, *J* = 6.8 Hz, 1H), 2.94 (s, 2H), 2.33 (dd, *J* = 9.8, 3.1 Hz, 1H), 1.89 (dd, *J* = 9.8, 2.2 Hz, 2H), 1.83 (dd, *J* = 6.8, 3.1 Hz, 1H), 1.81 (d, *J* = 2.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): d 199.0 (+), 166.2 (+), 139.8 (+), 133.7 (+), 129.7 (-), 128.1 (-), 67.4 (-), 52.3 (-), 47.6 (+), 46.8 (+), 37.7 (-). **IR** (KBr) ?$_{max}$: 3065, 2986, 1719, 1671, 1282, 1110, 822, 762, 696 cm^{-1}. **LRMS** (EI): 230 [M$^+$], 215, 199, 163, 135, 103, 76, 50. **Anal**. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.88; H, 6.22.

Synthesis of Keto-acids 6a and 3a. To a solution of keto-ester **6c** (780 mg, 3.20 mmol) in THF (20 mL) and H_2O (10 mL) was added LiOH (1.15 g, 48 mmol). The mixture was stirred at room temperature for 4 h and then diethyl ether (30 mL) was added. The organic layer was washed with water (3 x 20 mL) and the aqueous layers were combined and acidified with conc HCl. The solution was then extracted with diethyl ether (4 x 40 mL) and the combined organic layer was washed with water (3 x 20 mL) and dried over $MgSO_4$. Removal of solvent *in vacuo* gave a white solid, which was recrystallized from methanol to afford keto-acid **6a** as a colorless solid (725 mg, 99% yield), **mp** 194-196 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): d 8.18 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 3.03 (d, *J* = 6.8 Hz, 1H), 2.92 (brs, 2H), 2.16 (m, 1H), 1.82 (m, 3H), 1.58 (m, 1H), 1.03 (dd, *J* = 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): d 199.6 (+), 171.2 (+), 140.9 (+), 132.6 (+), 30.4 (-), 128.1 (-), 60.1 (-), 43.7 (-), 36.6 (+), 27.4 (+). **IR** (KBr)

?$_{max}$: 3069, 2967, 2872, 2552, 1673, 1291, 1217, 799, 705, 558 cm^{-1}. **LRMS** (ESI, infusion @ 10µL/min in MeOH –ve mode): 229.0 [M^+-1]. **Anal**. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.01; H, 6.09.

By the same procedure, keto-ester **3c** was converted into keto-acid **3a** in a yield of 93%, **mp** 195-197 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): d 8.15 (d, *J* = 8.6 Hz, 2H), 8.10 (d, *J* = 8.6 Hz, 2H), 3.67 (d, *J* = 6.8 Hz, 1H), 2.94 (s, 2H), 2.21 (dd, *J* = 9.8, 2.8 Hz, 1H), 1.96 (dd, *J* = 9.8, 1.9 Hz, 1H), 1.84 (dd, *J* = 6.8, 2.8 Hz, 1H), 1.83 (d, *J* = 1.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): d 199.0 (+), 166.7 (+), 140.6 (+), 134.9 (+), 130.5 (-), 128.9 (-), 68.1 (-), 47.9 (+), 47.1 (+), 38.1 (-). **IR** (KBr) ?$_{max}$: 3319, 3068, 2975, 2559, 1666, 1290, 806, 765, 692 cm^{-1}. **LRMS** (ESI, infusion @ 10µL/min in MeOH –ve mode): 215.1 [M^+-1]. **Anal**. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 71.99; H, 5.70.

Synthesis of (*S*)-(–)-1-Phenylethylammonium Salts 6b and 3b. To a solution of keto-acid **6a** (80 mg, 0.35 mmol) in diethyl ether (5 mL) was added one equivalent of optically pure (*S*)-(-)-a-Phenylethylamine. Upon addition, a precipitate formed immediately. The resulting suspension was suction filtered to give a quantitative yield of the salt, which was recrystallized from methanol, **mp** 172-175 °C. **^{1}H NMR** (400 MHz, CD_3OD): d 7.87 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.29 (m, 5H), 4.30 (m, 1H), 3.18 (m, 1H), 3.01 (d, *J* = 6.8 Hz, 1H), 2.74 (m, 2H), 2.00 (m, 1H), 1.82 (m, 2H), 1.67 (m, 2H), 1.49 (d, *J* = 6.8 Hz, 3H), 0.91 (dd, *J* = 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, CD_3OD): d 200.0 (+), 172.0 (+), 141.2 (+), 138.1 (+), 137.3 (+), 128.4 (-), 128.2 (-), 128.0 (-), 126.8 (-), 125.6 (-), 59.3 (-), 50.3 (-), 42.3 (-), 35.6 (+), 26.3 (+), 20.9 (-). **IR** (KBr) ?$_{max}$: 2955, 2215, 1672, 1582, 1219, 782, 698, 517 cm^{-1}. **LRMS** (ESI): 352 [M^++1], 285, 253, 243, 194, 154. **Anal**. Calcd for $C_{22}H_{25}NO_3$: C, 75.19; H, 7.17; N, 3.99. Found: C, 75.44; H, 7.21; N, 4.02. The (*R*)-(+)-1-phenylethylammonium of keto-acid **6a** was also prepared and gave identical analytical data.

An identical procedure starting with keto-acid **3a** afforded the (*S*)-(–)-1-phenylethylammonium salt **3b**, **mp** 146-149 °C (Methanol). **^{1}H NMR** (400 MHz, CD_3OD): d 7.90 (d, *J* = 8.6 Hz, 2H), 7.87 (m, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.28 (m, 3H), 4.32 (q, *J* = 6.8 Hz, 1H), 3.52 (d, *J* = 6.7 Hz, 1H), 3.20 (brs, 2H), 2.82 (s, 2H), 2.11 (dd, *J* = 9.8, 2.9 Hz, 1H), 1.86 (dd, *J* = 9.8, 1.9 Hz, 1H), 1.75 (dd, *J* = 6.7, 2.9 Hz, 1H), 1.74 (d,

J = 1.8 Hz, 1H), 1.50 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, CD_3OD): d 201.7 (+), 173.9 (+), 143.4 (+), 140.0 (+), 139.0 (+), 130.4 (-), 130.3 (-), 130.1 (-), 129.0 (-), 127.6 (-), 68.9 (-), 52.3 (-), 48.5 (+), 47.6 (+), 38.8 (-), 20.9 (-). **IR** (KBr) ?$_{max}$: 3320, 3034, 2971, 1667, 1620, 1236, 823, 767, 704 cm^{-1}. **LRMS** (ESI): 338 [M$^+$+1], 278, 243, 200, 178, 122. **Anal**. Calcd for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.54; H, 6.83; N, 4.12. The (*R*)-(+)-1-phenylethylammonium of keto-acid **3a** was also prepared and gave identical analytical data.

In addition to the above, the following salts were prepared and photolyzed in the solid state.

(*R*)-(-)-1-Cyclohexyl Ethylamonium Salt of Keto-Acid 6a. **Mp** 176-179 °C (Methanol). **^{1}H NMR** (400 MHz, CD_3OD): d 7.87 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 3.19 (m, 2H), 3.03 (m, 1H), 2.95 (m, 1H), 2.75 (d, J = 2.5 Hz, 1H), 2.01 (m, 1H), 1.82 (m, 1H), 1.68 (m, 6H), 1.41 (m, 2H), 1.18 (m, 3H), 1.11 (d, J = 6.8 Hz, 3H), 0.95 (m, 3H). **^{13}C NMR** (100 MHz, CD_3OD): d 202.0 (+), 173.2 (+), 143.4 (+), 139.2 (+), 130.3 (-), 128.8 (-), 61.2 (-), 53.4 (-), 44.3 (-), 42.7 (-), 37.4 (+), 31.3 (+), 28.8 (+), 28.2 (+), 27.0 (+), 24.8 (+), 16.0 (-). **IR** (KBr) ?$_{max}$: 2930, 2151, 1666, 1531, 1386, 816, 780, 519 cm^{-1}. **LRMS** (ESI): 358 [M$^+$+1], 352, 285, 255, 206. **Anal**. Calcd for $C_{22}H_{31}NO_3$: C, 73.91; H, 8.74; N, 3.92. Found: C, 74.03; H, 8.79; N, 3.96.

(*R*)-(-)-1-Amino-indan Salt of Keto-Acid 6a. **Mp** 188-191 °C (Methanol). **^{1}H NMR** (400 MHz, CD_3OD): d 7.86 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 7.6 Hz, 1H), 7.18 (m, 3H), 4.63 (m, 1H), 3.18 (m, 4H), 3.03 (m, 3H), 2.88 (m, 1H), 2.75 (d, J = 2.6 Hz, 2H), 2.46 (m, 1H), 1.99 (m, 2H), 1.93 (m, 2H), 1.67 (m, 2H), 0.92 (dd, J = 6.8 Hz, 1H). **^{13}C NMR** (100 MHz, CD_3OD): d 202.0 (+), 174.0 (+), 145.4 (+), 143.2 (+), 140.1 (+), 139.3 (+), 130.6 (-), 130.3 (-), 128.8 (-), 128.2 (-), 126.3 (-), 125.5 (-), 61.2 (-), 57.0 (-), 44.3 (-), 37.4 (+), 31.8 (+), 31.0 (+), 28.2 (+). **IR** (KBr) ?$_{max}$: 2995, 2639, 2218, 1666, 1582, 1537, 1395, 1219, 813, 762, 518 cm^{-1}. **LRMS** (ESI): 364 [M$^+$+1], 347, 331, 267, 134, 117. **Anal**. Calcd for $C_{23}H_{25}NO_3$: C, 76.01; H, 6.93; N, 3.85. Found: C, 75.91; H, 6.92; N, 3.89.

(1*S*,2*R*)-(-)-*cis*-1-Amino-2-indanol Salt of Keto-Acid 6a. **Mp** 179-184 °C (Methanol). **^{1}H NMR** (400 MHz, CD_3OD): d 7.91 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.37 (m, 1H), 7.22 (m, 3H), 4.62 (m, 1H), 4.47 (m, 1H), 3.11 (m, 4H), 2.94 (m, 1H), 2.28 (m, 2H), 1.85 (m, 5H), 0.94 (m, 1H). **^{13}C NMR** (100 MHz, CD$_3$OD): d 202.1 (+), 173.9 (+), 143.0 (+), 142.8 (+), 139.4 (+), 138.3 (+), 130.8 (-), 130.4 (-), 128.8 (-), 128.4 (-), 126.7 (-), 126.2 (-), 72.0 9-), 61.2 (-), 58.7 (-), 44.3 (-), 40.1 (+), 37.4 (+), 28.2 (+). **IR** (KBr) ?$_{max}$: 3440, 2969, 2876, 2065, 1669, 1586, 1386, 1221, 783, 522 cm^{-1}. **LRMS** (ESI): 380 [M$^+$+1], 363, 299, 287, 150, 133. **Anal**. Calcd for $C_{23}H_{25}NO_4$: C, 72.80; H, 6.64; N, 3.69. Found: C, 72.94; H, 6.74; N, 3.77.

(1*R*,2*R*)-(-)-2-Amino-1-phenyl-1,3-propanediol Salt of Keto-Acid 6a. **Mp** 149-152 °C (Methanol). **^{1}H NMR** (400 MHz, CD$_3$OD): d 7.82 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.20 (m, 5H), 4.57 (d, *J* = 8.8 Hz, 1H), 3.37 (m, 1H), 3.25 (m, 1H), 3.12 (m, 2H), 3.10 (m, 1H), 2.68 (m, 2H), 1.94 (m, 1H), 1.77 (m, 2H), 1.60 (m, 2H), 1.38 (m, 1H), 0.86 (dd, *J* = 6.8 Hz, 1H). **^{13}C NMR** (100 MHz, CD$_3$OD): d 202.0 (+), 174.0 (+), 143.0 (+), 142.1 (+), 139.3 (+), 130.3 (-), 129.6 (-), 128.9 (-), 128.2 (-), 127.5 (-), 72.3 (-), 72.2 (-), 61.4 (-), 60.4 (+), 44.9 (-), 37.5 (+), 28.2 (+). **IR** (KBr) ?$_{max}$: 3273, 2088, 1682, 1496, 1222, 1039, 820, 782, 545 cm^{-1}. **LRMS** (ESI): 398 [M$^+$+1], 381, 335, 190, 168, 150. **Anal**. Calcd for $C_{23}H_{27}NO_5$: C, 69.50; H, 6.85; N, 3.52. Found: C, 69.12; H, 6.91; N, 3.54.

(*R*)-(-)-1-Cyclohexyl Ethylamonium Salt of Keto-Acid 3a. **Mp** 152-154 °C (Methanol). **^{1}H NMR** (400 MHz, CD$_3$OD): d 7.93 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 3.55 (d, *J* = 6.8 Hz, 1H), 3.22 (brs, 2H), 2.99 (m, 1H), 2.85 (s, 2H), 2.14 (dd, *J* = 9.8, 2.8Hz, 1H), 1.89 (dd, *J* = 9.8, 1.8 Hz, 1H), 1.78 (dd, *J* = 9.8, 2.8Hz, 1H), 1.77 (d, *J* = 1.8 Hz, 1H), 1.74-1.64 (m, 5H), 1.41 (m, 1H), 1.20 (m, 2H), 1.15 (d, *J* = 6.7Hz, 3H), 1.09 (m, 1H), 0.99 (m, 2H). **^{13}C NMR** (100 MHz, CD$_3$OD): d 201.7 (+), 174.0 (+), 143.7 (+), 139.0 (+), 130.4 (-), 129.0 (-), 68.9 (-), 53.4 (-), 48.5 (+), 47.6 (+), 42.7 (-), 38.8 (-), 30.0 (+), 28.8 (+), 27.1 (+), 27.0 (+), 26.9 (+), 16.0 (-). **IR** (KBr) ?$_{max}$: 3320, 2975, 2604, 1669, 1537, 1237, 825, 780, 717 cm^{-1}. **LRMS** (ESI): 344 [M$^+$+1], 255, 206, 187, 169, 128. **Anal**. Calcd for $C_{21}H_{29}NO_3$: C, 73.44; H, 8.51; N, 4.08. Found: C, 73.32; H, 8.78; N, 4.08.

(*R*)-(-)-1-Amino-indan Salt of Keto-Acid 3a. **Mp** 166-168 °C (Methanol). **^{1}H NMR** (400 MHz, CD$_3$OD): d 7.88 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.21 (m, 3H), 4.63 (dd, *J* = 7.6, 5.4 Hz, 1H), 3.50 (d, *J* = 6.7 Hz, 1H), 3.17 (brs, 2H), 3.02 (m, 1H), 2.85 (m, 1H), 2.85 (s, 2H), 2.46 (m, 1H), 2.10 (dd, *J* = 9.8, 2.8Hz, 1H), 1.95 (m, 1H), 1.85 (dd, *J* = 9.8, 1.8 Hz, 1H), 1.74 (dd, *J* = 6.7, 2.8 Hz, 1H), 1.72 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR** (100 MHz, CD$_3$OD): d 201.7 (+), 173.9 (+), 145.4 (+), 143.4 (+), 140.1 (+), 139.0 (+), 130.6 (-), 130.4 (-), 129.0 (-), 128.2 (-), 126.3 (-), 125.5 (-), 68.9 (-), 56.9 (-), 48.5 (+), 47.6 (+), 38.8 (-), 31.8 (+), 31.0 (+). **IR** (KBr) ?$_{max}$: 3314, 2970, 2219, 1665, 1376, 1236, 828, 778, 763, 715 cm^{-1}. **LRMS** (ESI): 350 [M^{+}+1], 303, 267, 236, 188, 134, 117. **Anal.** Calcd for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.83; H, 6.74; N, 3.98.

(1*S*,2*R*)-(-)-*cis*-1-Amino-2-indanol Salt of Keto-Acid 3a. **Mp** 154-156 °C (Methanol). **^{1}H NMR** (400 MHz, CD$_3$OD): d 7.91 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.24 (m, 3H), 4.61 (q, *J* = 5.9 Hz, 1H), 4.46 (d, *J* = 5.9 Hz, 1H), 3.52 (d, *J* = 6.8 Hz, 1H), 3.20 (brs, 1H), 3.12 (dd, *J* = 16.3, 6.4 Hz, 1H), 2.92 (dd, *J* = 16.3, 5.0 Hz, 1H), 2.82 (s, 2H), 2.12 (dd, *J* = 9.8, 2.9 Hz, 1H), 1.86 (dd, *J* = 9.8, 1.7 Hz, 1H), 1.75 (dd, *J* = 6.8, 2.9 Hz, 1H), 1.74 (d, *J* = 1.7 Hz, 1H). **^{13}C NMR** (100 MHz, CD$_3$OD): d 201.7 (+), 173.9 (+), 143.3 (+), 142.8 (+), 139.1 (+), 138.2 (+), 130.8 (-), 130.4 (-), 129.0 (-), 128.4 (-), 126.6 (-), 126.2 (-), 72.0 (-), 68.9 (-), 58.6 (-), 48.5 (+), 47.6 (+), 40.1 (+), 38.8 (-). **IR** (KBr) ?$_{max}$: 3528, 3073, 2981, 2893, 1670, 1585, 1542, 1237, 828, 779, 740, 710 cm^{-1}. **LRMS** (ESI): 366 [M^{+}+1], 350, 343, 335, 321, 299, 172, 150, 133. **Anal.** Calcd for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.32; N, 3.76. Found: C, 72.13; H, 6.32; N, 3.76.

(1*R*,2*R*)-(-)-2-Amino-1-phenyl-1,3-propanediol Salt of Keto-Acid 3a. **Mp** 144-146 °C (Methanol). **^{1}H NMR** (400 MHz, CD$_3$OD): d 7.87 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.22 (m, 2H), 7.18 (m, 1H), 4.60 (d, *J* = 8.8Hz, 1H), 3.48 (d, *J* = 6.8 Hz, 1H), 3.39 (dd, *J* = 11.7, 3.6 Hz, 1H), 3.26 (dd, *J* = 11.7, 6.0 Hz, 1H), 3.16 (m, 1H), 3.13 (dd, *J* = 6.0, 3.6Hz, 1H), 2.08 (dd, *J* = 9.8, 2.9 Hz, 1H), 1.83 (dd, *J* = 9.8, 2.0 Hz, 1H), 1.72 (dd, *J* = 6.8, 2.9 Hz, 1H), 1.70 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, CD$_3$OD): d 201.7 (+), 173.9 (+), 143.3 (+), 142.1 (+), 142.1 (+), 139.1 (+), 130.4 (-), 129.8 (-), 129.6 (-), 129.0 (-), 127.9 (-), 72.3 (-), 68.9 (-), 60.3 (-), 59.9 (+), 48.5 (+), 47.6 (+), 38.8 (-). **IR** (KBr) ?$_{max}$: 3347, 3034, 2666, 1672, 1520, 1234, 1049, 825, 749, 703 cm^{-1}. **LRMS** (ESI): 384 [M^{+}+1], 335, 236, 190, 168, 150, 120. **Anal.** Calcd for $C_{22}H_{25}NO_5$: C, 68.91; H, 6.57; N, 3.65. Found: C, 69.00; H, 6.77; N, 3.63.

Irradiation of Keto-ester 6c in Acetonitrile. A solution of keto-ester **6c** (100 mg, 0.41 mmol) in aceonitrile (80 mL) was purged with N$_2$ for 15 min and irradiated with 450 W medium mercury pressure lamp under N$_2$ for 24 h. After irradiation, the solvent was removed *in vacuo* and the residue purified by column chromatography (10% pet ether/diethyl ether) to give photoproduct **8c** (66mg, 66%) and **7c** (30 mg, 30%) as colorless solids.

Photoproduct **8c**, **mp** 97-97.5 °C. **^{1}H NMR** (400 MHz, CDCl$_3$): d 8.10 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 5.77 (m, 1H), 5.69 (m, 1H), 3.93 (s, 3H), 3.25 (m, 1H), 3.10 (m, 1H), 2.98 (m, 1H), 2.35 (m, 2H), 2.19 (m, 1H), 1.46 (m, 1H). **^{13}C NMR** (100 MHz, CDCl$_3$): d 200.0 (+), 166.3 (+), 140.4 (+), 133.9 (-), 133.7 (+), 131.5 (-), 129.8 (-), 128.0 (-), 52.4 (-), 45.1 (+), 41.2 (-), 31.8 (+), 30.0 (-). **IR** (KBr) ?$_{max}$: 2953, 2927, 1727, 1279, 1108, 769, 711 cm^{-1}. **LRMS** (EI): 244 [M^{+}], 229, 179, 163, 147, 104, 76, 50. **Anal**. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.81; H, 6.57.

Photoproduct **7c**, **mp** 83-84 °C. **^{1}H NMR** (400 MHz, CDCl$_3$): d 8.02 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 3.50 (d, *J* = 6.6 Hz, 1H), 2.76 (s, 2H), 2.17 (s. 1H), 2.12 (d, *J* = 6.6 Hz, 1H), 1.76 (m, 2H), 1.66 (m, 2H). **^{13}C NMR** (100 MHz, CDCl$_3$): d 166.9 (+), 147.4 (+), 129.7 (-), 129.2 (+), 126.7 (-), 84.1 (+), 54.5 (-), 52.1 (-), 51.8 (-), 47.8 (-), 26.8 (+), 26.3 (+). **IR** (KBr) ?$_{max}$: 3447, 2910, 1698, 1287, 1011, 954, 867, 730 cm^{-1}. **LRMS** (EI): 244 [M^{+}], 229, 213, 178, 163, 104, 76. **Anal**. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.63; H, 6.81.

Irradiation of Keto-ester 3c in Acetonitrile. A solution of keto-ester **3c** (100 mg, 0.43 mmol) in aceonitrile (80 mL) was purged with N$_2$ for 15 min and irradiated with 450 W medium mercury pressure lamp under N$_2$ for 22 hrs. After irradiation, the solvent was removed *in vacuo* and the residue purified by column chromatography (12% pet ether/diethyl ether) to give photoproducts **5c** (23 mg, 23%) and **4c** (77 mg, 77%).

Photoproduct **5c,** oil. **^{1}H NMR** (400 MHz, CDCl$_3$): d 8.10 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 6.10 (d, *J* = 2.6 Hz, 1H), 6.04 (d, *J* = 2.6 Hz, 1H), 3.93 (s, 3H), 3.33 (m, 1H), 3.17 (d, *J* = 7.5 Hz, 2H), 2.83 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.17 (d, *J* = 13.8 Hz, 1H). **^{13}C NMR** (100 MHz, CDCl$_3$): d 199.1 (+), 166.2 (+), 140.2 (+), 140.0 (-), 135.9 (-), 133.8 (-), 129.8 (-), 128.0 (-), 52.4 (-), 43.5 (+), 39.2 (-), 37.1 (+). **IR** (neat)

?$_{max}$: 3050, 2953, 1723, 1676, 1437, 1284, 1110, 822, 759, 696 cm^{-1}. **LRMS** (EI): 230 [M$^+$], 215, 163, 135, 120, 104, 76, 50. **HRMS** (EI) for $C_{14}H_{14}O_3$: Cacld. 230.0942; Found 230.0944.

Photoproduct **4c**, oil. **^{1}H NMR** (400 MHz, $CDCl_3$): d 8.00 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 3.80 (s, 2H), 3.49 (d, *J* = 17.1 Hz, 1H), 2.49 (d, *J* = 17.1 Hz, 1H), 2.12 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): d 166.9 (+), 145.8 (+), 129.6 (-), 129.3 (+), 126.4 (-), 83.4 (+), 57.8 (-), 52.1 (-), 41.7 (-), 38.6 (+), 37.2 (-). **IR** (neat) ?$_{max}$: 3446, 2952, 1704, 1435, 1290, 1051, 954, 854, 780, 712 cm^{-1}. **LRMS** (EI): 230 [M$^+$], 212, 181, 163, 152, 115, 76, 51. **HRMS** (EI) for $C_{14}H_{14}O_3$: Cacld. 230.0942; Found 230.0934.

Irradiation of (*S*)-(–)-1-Phenylethylammonium Salts 6b and 3b in the Solid State. The salt crystals (2-5 mg) were crushed between two Pyrex microscope slides and sealed in a polyethylene bag under a positive pressure of nitrogen. The sample was irradiated from both sides with a 450W medium pressure mercury lamp. After irradiation, the salt crystals were suspended in an excess of ethereal diazomethane solution and allowed to stand until dissolution was complete. Ether and excess diazomethane were removed *in vacuo* and the residue was taken up in methylene chloride and passed through a short plug of silica gel to remove the chiral auxiliary. The residue was then submitted to HPLC analysis to give the enantiomeric excesses and GC analysis to give the conversions. The results are reported in Table 1 in the text.

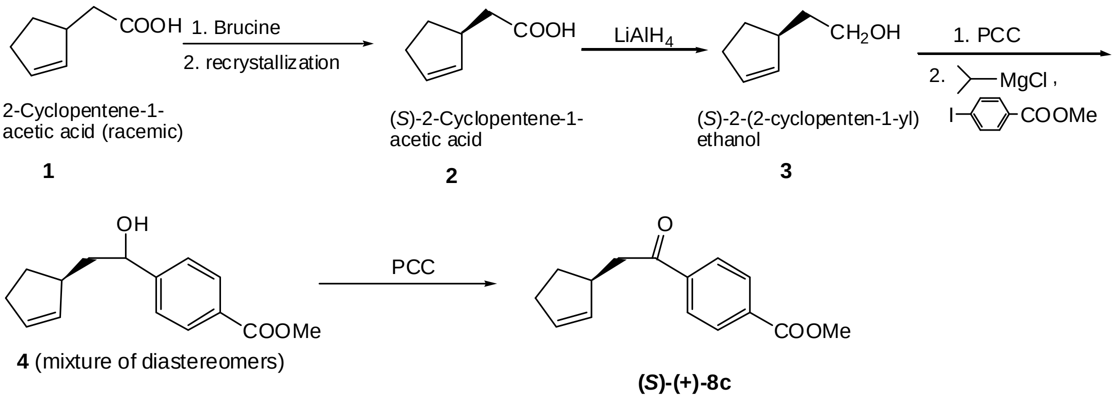
In addition, the other salts prepared above were photolyzed in the solid state, and the results are summarized in Table 3 below. Irradiation times for the 1-phenylethylammonium salts, as well as the salts listed in Table 3, varied from 3 to 76 h.

Table 3. Additional asymmetric studies of salts **3b** and **6b** in the solid state

	3b					**6b**				
amine	temp	conv. (%)[a]	ee (%)[b]	a[d]	CY: CL[e]	temp	conv. (%)[a]	ee (%)[c]	a[d]	CY: CL[e]
(*R*)-(+)-a-phenyl ethylamine	-20 °C	58	78	+	86:12	-20 °C	27	92	+	20:79
	20 °C	48	68	+	87:12	20 °C	74	77	+	22:75
	20 °C	50	67	+	87:11	20 °C	51	81	+	21:77
(*R*)-(-)-1-cyclohexylethylamine	-20 °C	38	20	-	88:11	20 °C	97	91	-	23:75
	20 °C	30	42	-	87:12	-20 °C	53	93	-	22:77
	20 °C	42	19	-	87:12	20 °C	31	92	-	21:77
(*R*)-(-)-1-aminoindan	20 °C	26	42	-	88:11	-20 °C	31	92	-	21:78
	20 °C	30	38	-	88:12	20 °C	53	88	-	21:78
	-20 °C	45	32	-	86:12	20 °C	81	75	-	22:76
(1*S*,2*R*)-(-)-*cis*-1-amino-2-indanol	-20 °C	51	48	+	85:13	-20 °C	48	72	+	21:77
	20 °C	45	23	+	86:12	20 °C	67	60	+	20:79
	20 °C	52	21	+	87:11	20 °C	91	53	+	22:76
(1*R*,2*R*)-(-)-2-amino-1-phenyl-1,3-propanediol	-20 °C	42	58	-	86:11	-20 °C	36	57	-	21:78
	20 °C	28	41	-	88:12	20 °C	73	55	-	21:77
	20 °C	31	38	-	88:12	20 °C	100	48	-	23:76

[a] Based on GC. [b] Analyzed on Chiral AS column with hexane:isopropanol = 99.7: 0.3 as the eluting solvent. [c] Analyzed on Chiral AS column with hexane:isopropanol = 99:1 as the eluting solvent. [d] Sign of rotation of major enantiomer at sodium D line. [e] Based on GC analysis.

Synthesis of (*S*)-(+)-8c from 2-cyclopentene-1-acetic acid



Resolution of 2-Cyclopentene-1-acetic Acid. The procedure was based on the literature report by Mislow et al.[3] Brucine (55.0 g) was added to a hot solution of 14.9 g of racemic 2-cyclopentene-1-acetic acid in 100 mL of acetone to which had been added 2.5 mL of water. The resulting precipitate was filtered and then recrystallized from acetone- water. After six recrystallizations, the solid reached the same melting point (147.5-148.5 ºC) as reported. The melting point remained unchanged on further recrystallization.

	1	2	3	4	5	6	7	8	9
mp(°C)	123.0-127.0	136.0-139.0	141.5-143,5	143.5-145.5	144.5-146.5	147.5-148.5	147.5-148.5	147.5-148.5	147.5-148.5

The diastereomerically pure salt was acidified with concentrated hydrochloric acid and extracted with diethyl ether. The ether extracts were washed with saturated sodium chloride solution and dried over sodium sulfate. The solvent was removed *in vacuo* and the residue (0.775 g), (*S*)-2-cyclopentene-1-acetic acid, was used directly in the next step.

Synthesis of (*S*)-2-(2-Cyclopenten-1-yl)ethanol (3). To a solution of (*S*)-2-cyclopentene-1-acetic acid (0.775g, 0.006 mol) in anhydrous diethyl ether was added 1.17 g, (0.03 mol) of $LiAlH_4$. The mixture was refluxed overnight. After cooling to room temperature, water was cautiously added to destroy excess $LiAlH_4$ and the solution was extracted with diethyl ether. The ether extracts were washed with dilute hydrochloric acid, saturated sodium chloride solution, dried over sodium sulfate and the solvent removed *in vacuo*. The residue was purified by silica gel column chromatography using pet ether/diethyl ether (4:1) as the eluting solvent to obtain (*S*)-2-(2-cyclopenten-1-yl)ethanol **3** (0.600g, 87%).

Synthesis of Alcohol 4. To (*S*)-2-(2-cyclopenten-1-yl)ethanol **3** (0.550g, 0.005 mol) dissolved in 100 mL of methylene chloride was added PCC (2.26 g, 0.01 mol) and Celite (5 g). The mixture was stirred at room temperature overnight, filtered on a silica gel column and rinsed with diethyl ether. The solvent was then removed *in vacuo*, and the residue used for the next step without purification.

To a solution of methyl *p*-iodobenzoate (1.31 g, 5.0 mmol) in 40 mL of anhydrous THF precooled to -40 °C was added dropwise isopropyl magnesium chloride (2 M, 2.5 mL). After addition, the mixture was stirred for one h at this temperature. To this solution, the aldehyde prepared above dissolved in anhydrous THF (10 mL) was added slowly. The solution was stirred at -40 °C for 4 h. Saturated ammonium chloride solution (30 mL) was added quickly and the solution was extracted with diethyl ether (3 x 50 mL), and the combined organic layer was washed with saturated brine solution (2 x 30 mL). The solvent was removed *in vacuo* after being dried over magnesium sulfate, and the residue was purified by column chromatography (10% pet ether/diethyl ether) to give alcohol **4** (532 mg, 43% yield).

Synthesis of (*S*)-(+)-8c. To a solution of alcohol **4** (500 mg, 2.03 mmol) in 40 mL of anhydrous methylene chloride were added PCC (916 mg, 4.06 mmol) and Celite (2 g). The mixture was stirred at room temperature overnight and diethyl ether (20 mL) was added. The solution was then filtered through a short silica gel column and rinsed with diethyl ether. The solvent was removed *in vacuo* and the residue purified by column chromatography (10% pet ether/diethyl ether) to afford compound **8c** (486 mg, 98% yield), $[\mathbf{a}]_D^{22}$ = +98.0° (c =0.45, MeOH), whose spectral properties were identical to those observed for compound **8c** prepared by photolysis of keto-ester **6c**.

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