

Enantioselective Organocatalytic Hydride Reduction

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Supporting Information

General Information. Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.¹ Non-aqueous reagents were transferred under nitrogen via syringe or cannula and purified according to the method of Grubbs.² Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel and Iatrobeads[®] according to the method of Still.³ Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Chromatograms were visualized by fluorescence quenching or by staining using either potassium permanganate or anisaldehyde stain.

¹H and ¹³C NMR spectra were recorded on a Varian Mercury 300 Spectrometer, and are internally referenced to residual solvent signals. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ¹³C NMR are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the Caltech Mass Spectroscopy facility by electron ionization, chemical ionization, or fast atom/ion bombardment techniques. Gas liquid chromatography (GLC) was performed on Hewlett-Packard 6850 and 6890 Series gas chromatographs equipped with a split-mode capillary injection system and flame ionization detectors using a Bodman ChiralDEX β -DM (30 m \times 0.25 mm), a Bodman ChiralDEX Γ -TA (30 m \times 0.25 mm) or a Hydrodex-B-TBDAC (50 m \times 0.25 mm) column as noted. High performance liquid chromatography (HPLC) was

¹ Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed., Pergamon Press, Oxford, 1988.

² Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

³ Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

performed on Hewlett-Packard 1100 Series chromatographs using a Chiralcel OD-H column (25 cm) and OD-H guard (5 cm). Optical rotations were measured on a Jasco P-1010 polarimeter, and $[\alpha]_D$ values are reported in $10^{-1} \text{ dg cm}^2 \text{ g}^{-1}$; concentration (c) is in g/100 ml.

Preparation of the starting materials

The following α,β -unsaturated aldehydes have already been described in the literature: (*E*)-3-phenylbut-2-enal,⁴ (*E*)-3-phenylpent-2-enal,⁵ (*E*)-methyl 3-formyl-2-methylacrylate⁶.

(*E*)-3-cyclohexylbut-2-en-1-ol: To a 0 °C solution of (*E*)-ethyl 3-cyclohexylbut-2-enoate⁷ (1 g, 5.09 mmol) in dry Et₂O (10 mL) was added a solution of lithium aluminum hydride (5.10 mL, 5.10 mmol, 1 M in Et₂O). After 5 minutes, the reaction mixture was neutralized by dropwise addition of THF solution followed by addition of a saturated solution of potassium sodium tartrate. The reaction mixture was stirred for 25 minutes, then diluted with Et₂O. The organic layer was separated and washed with water, dried over Na₂SO₄ and concentrated *in vacuo* to afford (*E*)-3-cyclohexylbut-2-en-1-ol as a colorless oil which was used directly in the following reaction.

(*E*)-3-cyclohexylbut-2-enal: To a solution of (*E*)-3-cyclohexylbut-2-enol (700 mg, 4.54 mmol) in dichloromethane (11 mL), cooled to 0 °C, was added Dess-Martin periodinane (2.11 g, 4.99 mmol). The resulting suspension was warmed to 23 °C and stirred for approximately 30 minutes until the reaction was judged to be complete by TLC. The reaction mixture was poured into 50 mL of saturated aqueous NaHCO₃ containing Na₂S₂O₃ (1 g). This mixture was stirred vigorously until both layers became clear. The aqueous layer was extracted with CH₂Cl₂ (2×) and the combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (25% EtOAc/hexanes) to afford the title compound as a colorless oil (350 mg, 51% yield) that was a 5.2:1 mixture of *E*:*Z* isomers. Major isomer: IR (film) 2929, 2854, 1729, 1674, 1640, 1450, 1383, 1198, 1164, 894, 850, 522 cm⁻¹; ¹H NMR (300

⁴ Gandhi, R. P.; Walia, J. S.; Mukherji, S. M. *J. Indian Chem. Soc.* **1957**, *34*, 509.

⁵ Schreiber, W. L.; Pittet, A. O.; Vock, M. H. *J. Agr. Food Chem.* **1974**, *22*, 269.

⁶ Ishida, A.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2077.

⁷ Appella, D.H.; Yasunori, M.; Shantini, R.; Ferreira, E.M.; Buchwald, S.M. *J. Am. Chem. Soc.* **1999**, *121*, 9473.

MHz, CDCl₃) δ 10.05 (d, 1H, $J = 7.9$ Hz CHO), 5.90 (dq, 1H, $J = 1.1, 7.9$ Hz, C=CH), 2.18 (d, 3H, $J = 1.3$ Hz, CH₃), 2.09–2.02 (m, 1H, CH₂CHCH₂), 1.87–1.70 (m, 5H), 1.40 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 191.9, 168.8, 125.8, 48.4, 31.4, 31.2, 26.3, 26.1, 26.0, 16.1; HRMS (EI⁺) exact mass calculated for [M]⁺ (C₁₀H₁₆O) requires m/z 152.1201, found m/z 152.1205.

(E)-ethyl 3-cyclohexylpent-2-enoate: To 90 mL of EtOH, cooled to 0 °C in an ice bath, was added sodium metal (1.64 g, 71.3 mmol). Once the metal had completely dissolved, triethyl phosphonoacetate (15.9 g, 14.1 mL, 71.3 mmol) was added via syringe. The resulting solution was warmed to room temperature and stirred for 10 minutes. Cyclohexyl ethyl ketone (9.44 g, 9.20 mL, 67.3 mmol) was added and the solution stirred for 15 h at room temperature. The reaction was quenched in 100 mL ice water slurry. The aqueous layer was extracted with 200 mL of Et₂O (3×). The combined organic layers were washed with 400 mL of brine, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The product was purified by flash chromatography (1% Et₂O/pentane) to provide a clear oil (2.5 g, 18% yield) that was a 3:1 mixture of *E*:*Z* isomers. Major isomer: IR (film) 2977, 2929, 2854, 2360, 2341, 1716, 1638, 1448, 1203, 1147, 1042, 862, 750 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.58 (s, 1H, C=CH), 4.15 (q, 2H, $J = 4.1$ Hz, OCH₂CH₃), 2.58 (q, 2H, $J = 7.4$ Hz, CH₂CH₃), 1.81–1.62 (m, 5H), 1.35–1.11 (m, 9H), 1.06 (t, 3H, $J = 2.2$ Hz, CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 171.3, 113.4, 59.6, 46.8, 32.3, 31.2, 26.9, 26.8, 26.6, 26.3, 25.3, 14.5, 13.8; HRMS (EI⁺) exact mass calculated for [M]⁺ (C₁₃H₂₂O₂) requires m/z 210.1620, found m/z 210.1628.

(E)-3-cyclohexylpent-2-enol: To a solution of (*E*)-ethyl 3-cyclohexylpent-2-enoate (2.3 g, 10.9 mmol) in Et₂O (22 mL), was added lithium aluminum hydride (1.0 M in Et₂O, 10.9 mL, 10.9 mmol) dropwise. After 5 minutes, the reaction mixture was slowly quenched with 1 mL of MeOH and poured into 100 mL of a saturated solution of potassium sodium tartrate. The aqueous layer was extracted with 100 mL Et₂O (3×). The combined organics were dried over Na₂SO₄, filtered and concentrated. The product was purified by flash chromatography (10% EtOAc/hexanes) to provide a clear oil (1.59 g, 87% yield) that was a 3:1 mixture of *E*:*Z* isomers. Major isomer: IR (film) 3421, 2929, 2854, 1732, 1684, 1635, 1449, 1235, 1164, 864, 749 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.33 (t, 1H, $J = 6.7$ Hz, CHCH₂OH), 4.17 (d, 2H, $J = 6.9$ Hz, CH₂OH), 2.07 (q, 2H, $J = 7.4$ Hz, CH₂CH₃), 1.99 to 1.63 (m, 6H), 1.48–1.08 (m, 6H), 0.97 (t,

3H, $J = 7.4$ Hz, CH_2CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 151.1, 121.2, 59.4, 44.8, 32.6, 31.6, 26.9, 26.7, 26.4, 23.1, 14.7; HRMS (EI^+) exact mass calculated for $[\text{M}]^+$ ($\text{C}_{11}\text{H}_{20}\text{O}$) requires m/z 168.1514, found m/z 168.1520.

(E)-3-cyclohexylpent-2-enal: To a solution of (*E*)-3-cyclohexylpent-2-enol (1.50 g, 8.91 mmol) in dichloromethane (45 mL), cooled to 0 °C, was added Dess-Martin periodinane (9.7 g, 22.9 mmol). The resulting suspension was warmed to room temperature and stirred for approximately 2 h until the reaction was judged to be complete by TLC. The reaction was poured into 100 mL of saturated aqueous NaHCO_3 containing $\text{Na}_2\text{S}_2\text{O}_3$ (3 g). This mixture was stirred vigorously until both layers became clear. The aqueous layer was extracted with CH_2Cl_2 (2 \times) and the combined organic layers were dried over MgSO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (5% Et_2O /pentane) to afford the title compound (1 g, 68% yield) as a colorless oil that was a 3:1 mixture of *E*:*Z* isomers. Major isomer: IR (film) 2927, 2746, 1668, 1622, 1450, 1189, 1124, 860 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 10.04 (d, 1H, $J = 8.24$ Hz, CHO), 5.83 (d, 1H, $J = 8.24$ Hz, $\text{C}=\text{CH}$), 2.61 (q, 2H, $J = 7.4$ Hz, CH_2CH_3), 2.07 (tt, 1H, $J = 2.6, 11.0$ Hz, CH_2CHCH_2), 1.88–1.71 (m, 5H), 1.41–1.15 (m, 8H); ^{13}C NMR (75 MHz, CDCl_3) δ 191.8, 175.2, 124.9, 46.2, 31.9, 26.5, 26.3, 26.0, 25.9, 24.2, 15.4; HRMS (EI^+) exact mass calculated for $[\text{M}]^+$ ($\text{C}_{11}\text{H}_{18}\text{O}$) requires m/z 166.1358, found m/z 166.1355.

(E)-ethyl 4-[tris-(1-methylethyl)silyloxy]-3-methylbut-2-enoate: To a suspension of sodium hydride (60% dispersion in mineral oil, 1.58 g, 62.6 mmol) in dry toluene (500 mL) at 0 °C, was added, dropwise, triethyl phosphonoacetate (12.4 mL, 62.6 mmol) under an atmosphere of argon. After 30 minutes, 1-[tris-(1-methylethyl)silyloxy]-pentanone (12 g, 52.2 mmol) was diluted into toluene (25 mL) and added to the reaction mixture, which was then allowed to warm to room temperature over a period of 2 h. The resulting mixture was washed with water, dried over MgSO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography (3% Et_2O /pentane) to afford (*E*)-ethyl 4-[tris-(1-methylethyl)silyloxy]-3-methylbut-2-enoate as a colorless oil (10.5 g, 67% yield). Major isomer: IR (film) 2945, 2868, 1716, 1663, 1223, 1154, 1114 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 6.07 (bs, 1H, CH), 4.21 (s, 2H, CH_2OTIPS), 4.17 (q, 2H, $J = 6.9$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 2.06 (s, 3H, CCH_3), 1.29 (t, 3H, $J = 7.8$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 1.09 (m, 21H, TIPS); ^{13}C NMR (75 MHz, CDCl_3) δ 167.0, 157.0, 113.2, 67.2, 59.4, 17.9, 15.3, 14.3,

11.9; HRMS (EI⁺) exact mass calculated for [M]⁺ (C₁₆H₃₂O₃Si) requires *m/z* 300.2121, found *m/z* 300.2125.

(E)-3-[tris-(1-methylethyl)silyloxy]but-2-en-1-ol: To a 0 °C solution of (*E*)-ethyl 4-[tris-(1-methylethyl)silyloxy]-3-methylbut-2-enoate (5 g, 17.6 mmol) in dry Et₂O was added a solution of lithium aluminum hydride (17.6 mL, 17.6 mmol, 1 M in Et₂O). After 30 minutes, the reaction mixture was neutralized by dropwise addition of THF followed by addition of a saturated solution of potassium sodium tartrate. The reaction mixture was stirred overnight and then diluted with Et₂O. The organic layer was separated and washed with water, dried over MgSO₄ and concentrated *in vacuo* to afford (*E*)-3-[tris-(1-methylethyl)silyloxy]but-2-en-1-ol as a colorless oil which was used directly into the next reaction.

(E)-3-[tris-(1-methylethyl)silyloxymethyl]but-2-enal: To a room temperature solution of (*E*)-3-[tris-(1-methylethyl)silyloxy]but-2-en-1-ol (crude from the previous step, assumed 17.6 mmol) in dichloromethane (100 mL) was added Dess-Martin periodinane (9.7 g, 22.9 mmol). The resulting suspension was stirred for 60 minutes, until the reaction was judged to be complete by TLC. The reaction mixture was diluted with Et₂O and a saturated aqueous solution of NaHCO₃ containing Na₂S₂O₃ was added. This mixture was stirred vigorously until both layers became clear. The aqueous layer was extracted with CH₂Cl₂ (2×) and the combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (5% Et₂O/pentane) to afford the title compound as a colorless oil (3.69 g, 82% yield). IR (film) 2944, 2867, 1681, 1464, 1384, 1123 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 10.09 (d, 1H, *J* = 8.3 Hz, CHO), 6.28 (dd, 1H, *J* = 1.5, 8.4 Hz, CH), 4.28 (d, 2H, *J* = 0.9 Hz, CH₂OTIPS), 2.09 (d, 3H, *J* = 0.6 Hz, CH₃C), 1.1 to 1.0 (m, 21H, TIPS); ¹³C NMR (75 MHz, CDCl₃) δ 191.2, 161.6, 124.1, 67.0, 18.0, 14.1, 11.9; HRMS (EI⁺) exact mass calculated for [M]⁺ (C₁₄H₂₈O₂Si) requires *m/z* 256.1859, found *m/z* 256.1862.

General procedure for the enantioselective hydrogenation of enals: A colorless solution of (*E*)-3-phenylbut-2-enal (140 mg, 1 mmol) dissolved in 5 mL of chloroform (0.2 M) was cooled to -30 °C in a dry ice/acetone bath. To this solution was added the trichloroacetic acid salt of

(*R*)-2-*tert*-butyl-3-methylimidazolidin-4-one (64 mg, 0.2 mmol) and Hantzsch ester (304 mg, 1.2 mmol). The resulting yellow suspension was stirred at $-30\text{ }^{\circ}\text{C}$ until the reaction was determined to be complete by TLC, by which time the mixture was a light yellow homogeneous solution.

Workup procedure A: The reaction mixture was then diluted with Et₂O and passed through a short pad of silica gel. The resulting solution was concentrated *in vacuo* and purified by flash chromatography (solvent noted) to provide the title compounds.

Workup procedure B: The cold reaction mixture was poured into a 10% HCl solution and diluted with Et₂O. The organic layer was washed 4 times with 10% HCl solution and once with a saturated aqueous solution of NaHCO₃. The resulting solution was dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by flash chromatography (solvent noted) to provide the title compounds.

(*S*)-3-phenylbutanal (Table 3, entry 1). Prepared according to the general procedure from (*E*)-3-phenylbut-2-enal (140 mg, 1 mmol) for 23 h, using workup procedure A to provide the title compound as a colorless oil (127 mg, 91% yield, 93% ee) after purification by flash chromatography on Iatrobeads[®] (20% Et₂O/pentane). The physical data were identical in all respects to those previously reported.⁸ The enantiomeric ratio was determined by GLC using a Bodman ChiralDex β -DM (30 m \times 0.25 mm) column (90 $^{\circ}\text{C}$ isotherm, 1 mL/min); (*R*) isomer t_r = 38.6 min and (*S*) isomer t_r = 39.5 min. $[\alpha]_D^{22} = +32.9^{\circ}$ ($c = 1.00$, EtOH).

(*S*)-3-phenylpentanal (Table 3, entry 3). Prepared according to the general procedure from (*E*)-3-phenylpent-2-enal (160 mg, 1 mmol) for 16 h, using workup procedure A to provide the title compound as a colorless oil (119 mg, 74% yield, 94% ee) after purification by flash chromatography on Iatrobeads[®] (10% Et₂O/pentane). The physical data were identical in all respects to those previously reported.⁹ The enantiomeric ratio was determined by GLC using a Bodman ChiralDex β -DM (30 m \times 0.25 mm) column (95 $^{\circ}\text{C}$ isotherm, 1 mL/min); (*R*) isomer t_r = 42.8 min and (*S*) isomer t_r = 43.9 min. $[\alpha]_D^{22} = +20.1^{\circ}$ ($c = 1.00$, EtOH)

⁸ Bull, S. D.; Davies, S. G.; Nicholson, R. L.; Sanganee, H. J.; Smith, A. D. *Org. Biomol. Chem.* **2003**, *1*, 2886.

⁹ Berlan, J.; Besace, Y.; Pourcelot, G.; Cresson, P. *Tetrahedron* **1986**, *42*, 4757. (reported a rotation of $+2.1^{\circ}$ for a product that was 15% ee)

(S)-3-cyclohexylbutanal (Table 3, entry 5). Prepared according to the general procedure from (*E*)-3-cyclohexylbut-2-enal (154 mg, 1 mmol) for 22 h, using workup procedure A to provide the title compound as a colorless oil (45.1 mg, 91% yield, 96% ee) after purification by flash chromatography on silica gel (10% Et₂O/hexane). The physical data were identical in all respects to those previously reported.¹⁰ The enantiomeric ratio was determined by GLC using a Bodman Chiraldex β-DM (30 m × 0.25 mm) column (80 °C isotherm, 1 mL/min); (*R*) isomer *t_r* = 70.6 min and (*S*) isomer *t_r* = 71.3 min. $[\alpha]_D^{22} = +8.3^\circ$ (c = 1.00, EtOH).

(S)-3-cyclohexylpentanal (Table 3, entry 6). Prepared according to the general procedure from (*E*)-3-cyclohexylpent-2-enal (250 mg, 1.50 mmol) for 24 h, using workup procedure A to provide the title compound as a colorless oil (240.8 mg, 95% yield, 91% ee) after purification by flash chromatography on silica gel (10% Et₂O/pentane). The enantiomeric ratio was determined by GLC using a Hydrodex-B-TBDAC (50 m × 0.25 mm) column (90 °C isotherm, 1 mL/min); (*R*) isomer *t_r* = 35.2 min and (*S*) isomer *t_r* = 37.9 min. IR (film) 2927, 2854, 1732, 1708, 1449, 1412, 1381, 1286, 1164, 954, 892 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 9.79 (t, 1H, *J* = 2.4.3 Hz, CHO), 2.44, (ddd, 1H, *J* = 2.1, 5.8, 16.4 Hz, CH), 2.28 (ddd, 1H, *J* = 2.7, 7.2, 16.2 Hz, CH), 1.82 to 1.61 (m, 5H), 1.47 to 0.99 (m, 12H); ¹³C NMR (75 MHz, CDCl₃) 203.9, 45.7, 40.3, 39.9, 30.4, 29.2, 26.74, 26.69, 26.67, 24.3, 11.8; HRMS (EI⁺) exact mass calculated for [M]⁺ (C₁₁H₂₀O) requires *m/z* 168.1514, found *m/z* 168.1522; $[\alpha]_D^{22} = +6.2^\circ$ (c = 1.03, CHCl₃).

(S)-methyl 2-methyl-4-oxobutanoate (Table 3, entry 7). Prepared according to the general procedure from (*E*)-methyl 3-formyl-2-methylacrylate (100 mg, 0.781 mmol) for 26 h to provide the title compound (83% yield, 91% ee). Yield was determined via ¹H NMR by comparison with an internal standard (BnOMe). The physical data were identical in all respects to those previously reported.¹¹ The enantiomeric ratio was determined by GLC using a Bodman Chiraldex Γ-TA (30 m × 0.25 mm) column (100 °C isotherm, 1 mL/min); (*S*) isomer *t_r* = 6.7 min and (*R*) isomer *t_r* = 7.7 min. $[\alpha]_D^{22} = +1.4^\circ$ (c = 1.15, CHCl₃).

¹⁰ Tanaka, K.; Fu, G.C.. *J. Org. Chem.* **2001**, *66*, 8177. (reported a rotation of +7.4° for a product that was 74% ee)

¹¹ Kollar, L.; Consiglio, K.; Pino, P. *J. Organomet. Chem.* **1987**, *330*, 305. (reported a rotation of +0.58° for a product that was 10% ee)

(S)-3-[tris-(1-methylethyl)silyloxymethyl]butanal (Table 3, entry 8). Prepared according to the general procedure from (*E*)-3-[tris-(1-methylethyl)silyloxymethyl]but-2-enal (245 mg, 1 mmol) for 72 h, using workup procedure A to provide the title compound as a colorless oil (190 mg, 74% yield, 90% ee) after purification by flash chromatography on Iatrobeads® (10% Et₂O/pentane). The enantiomeric ratio was determined by HPLC (the aldehyde was reduced and protected using BzCl) on Chiralcel® OD-H (0.46 mm × 25 cm) isocratic 5% EtOH/Hexanes, 1 mL/min, 25 °C); (*S*) isomer $t_r = 19.2$ min and (*R*) isomer $t_r = 22.2$ min. IR (film) 2944, 2867, 2716, 1728, 1464, 1385, 1101 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 9.80 (t, 1H $J = 2.4$ Hz, CHO), 3.66 (dd, 1H, $J = 5.1, 9.9$ Hz, TIPSOCH), 3.47 (dd, 1H, $J = 6.9, 9.6$ Hz, TIPSOCH), 2.58 (m, 1H, CHCHO), 2.28 (m, 2H, MeCHCH), 1.06 (m, 21H, TIPSO), 0.97 (d, $J = 6.9$ Hz, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 202.7, 68.0, 48.2, 31.6, 17.9, 16.7, 11.9; HRMS (EI⁺) exact mass calculated for [M-H]⁺ (C₁₄H₂₉O₂Si) requires m/z 257.1930 found m/z 257.1937; $[\alpha]_D^{22} = -2.7^\circ$ (c = 1.07, CHCl₃).

(S)-3,4,4-trimethylpentanal (Table 3, entry 9). Prepared according to the general procedure, at room temperature, from (*E*)-3,4,4-trimethylpent-2-enal (70 mg, 0.56 mmol) for 5 minutes to provide the title compound (95% yield, 97% ee). Yield was determined using ¹H NMR by comparison with an internal standard (BnOMe). The physical data were identical in all respects to those previously reported.¹² The enantiomeric ratio was determined by GLC using a Bodman Chiraldex β-DM (30 m × 0.25 mm) column (60 °C isotherm, 1 mL/min); (*R*) isomer $t_r = 19.29$ min and (*S*) isomer $t_r = 20.32$ min. $[\alpha]_D^{22} = +29.3^\circ$ (c = 1.00, CHCl₃).

¹² Berlan, J.; Besace, Y.; Pourcelot, G.; Cresson, P. *Tetrahedron* **1986**, *42*, 4757. (reported a rotation of +3.4° for a product that was 16% ee)