Supporting Information:

NMR spectra were recorded on a Bruker DPX 400. Column chromatography was conducted on silica gel 60 (mesh size 40-63 μm). Enantiomeric excesses were determined by HPLC analysis using a Thermo Quest (TSP) GC-LC-MS equipped with an appropriate optically active column, as described in the footnotes of the corresponding Tables. GC-MS spectra were determined on a phenomenex Zebron ZB-5 capillary column (5% phenylmethylsiloxane). Optical rotations were measured with Bellingham & Stanley P20 polarimeter or with an Autopol IV automatic polarimeter.

Synthesis of (±)-6-acetoxy-3-methoxycyclohex-2-en-1-one (3)

2.45 g (0.02 mol) of 3-methoxycyclohex-2-en-1-one **(2)** was dissolved in 75 mL of cyclohexane (or benzene), 17.3 g (0.08 mol) of $Mn(OAc)_3$ was added and refluxed under Dean-Stark trap for 48 hours. The reaction mixture was first filtered through celite, then concentrated and purified by column chromatography (1:2 Hexane:EtOAc) to afford 3.11 g of 6-acetoxy-3-methoxycyclohex-2-en-1-one **(3)** in 87 % yield (2.54 g, 71 % yield in case of benzene).

General Procedure for Enzymatic Kinetic Resolution

To a stirred solution of (±)-6-acetoxy-3-methoxycyclohex-2-en-1-one **(3)** (180 mg, 0.97 mmol) in DMSO (2 mL) and phosphate buffer (pH 7.0, 60 mL) enzyme (PLE 200μl, Amano PS, CCL and PPL 6 mg) was added in one portion and the reaction mixture was stirred at rt. Conversion was monitored by TLC and LC-MS up to 50 % conversion. After filtration, the filtrate was extracted with DCM, dried over $MgSO_4$, concentrated and purified by column chromatography (1:2 Hexane:EtOAc) to afford (*R*)-6-acetoxy-3-methoxycyclohex-2-en-1-one **(*R*)-3** and (*S*)-6-hydroxy-3-methoxycyclohex-2-en-1-one **(*S*)-4** in 41-54 % and 37-47 % yields.

(*R*)-3: viscous oil, $[\alpha]_D^{25}$= -143° (c= 0.4, $CHCl_3$) [**(*S*)-3** $[\alpha]_D^{25}$= +141° (c= 0.4, $CHCl_3$)]; R_t(*R*)= 20.4 min. [R_t(*S*)= 17.3 min.], 96% ee (Chiralpak AD column, UV detection at 254 nm, eluent: hexane/2-propanol = 9:1, flow 0.80 mL min^{-1} 20ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01-2.14 (m, 2H), 2.09 (s, 3H), 2.41-2.45 (m, 1H), 2.55-2.62 (m, 1H), 3.65 (s, 3H), 5.18 (dd, *J*= 5.1, 12.5 Hz, 1H), 5.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 26.7, 27.7, 56.7, 72.6, 101.4, 170.5, 178.0, 193.5. Anal. Calc. ($C_9H_{12}O_4$, 184.07 g/mol); calc. C, 58.69, H, 6.57; found C, 58.66, H, 6.51.

(*S*)-4: viscous oil, $[\alpha]_D^{25}$= +78° (c= 0.5, $CHCl_3$) [**(*R*)-4** $[\alpha]_D^{25}$= -77° (c= 0.5, $CHCl_3$)]; R_t(*S*)= 22.9 min. [R_t(*R*)= 25.7 min.], >98% ee (Chiralpak AD column, UV detection at 254 nm, eluent: hexane/2-propanol = 9:1, flow 0.80 mL min^{-1} 20ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12-2.17 (m, 1H), 2.36-2.38 (m, 1H), 2.45-2.51 (m, 1H), 2.61-2.67 (m, 1H), 3.74 (s, 3H), 4.01 (dd, *J*= 5.4, 12.9 Hz, 1H), 5.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 27.4, 56.9, 73.1, 102.1, 179.1, 195.6. Anal. Calc. ($C_7H_{10}O_3$, 142.06 g/mol); calc. C, 59.14, H, 7.09; found; C, 59.21, H, 7.21.

General Procedure for Reductions

To a suspension of LAH (31.1 mg, 0.82 mmol), in anhydrous ether (30 mL) was added acetoxy enone **(*R*)-3** and *rac*-**3** (50.4 mg, 0.27 mmol) or hydroxy enone **(*S*)-4** (38.36 mg, 0.27 mmol) at rt over 15 min. The mixture was refluxed for 30 min. (monitored by TLC), cooled to rt and quenched with 30 mL of 10% H_2SO_4 (or 2N HCl), the mixture was stirred for an additional 2 hours at rt. Organic layers were separated and washed with sat. $NaHCO_3$ solution, brine, and dried over $MgSO_4$. After evaporation of the solvent column chromatography (1:1 Hexane:EtOAc) was performed to obtain 4-hydroxy-cyclohex-2-en-1-one in 79-86 % yields ((***S*)-1** 79%, (***R*)-1** 81% and *rac*-**1** 86%).

(*R*)-1: viscous oil, $[\alpha]_D^{25}$= +110° (c= 0.2, $CHCl_3$) [**(*S*)-1** $[\alpha]_D^{25}$= -105° (c= 0.2, $CHCl_3$)]; 96-98% ee (Chiralcel OB column, UV detection at 254 nm, eluent: hexane/2-propanol = 2:1, flow 0.50 mL min^{-1} 20ºC); [Lit. $[\alpha]_D^{25}$= -110° (c= 0.9, $CHCl_3$)[1], $[\alpha]_D^{25}$= -95° (c= 0.06, $CHCl_3$)[2], $[\alpha]_D^{25}$= -78° (c= 0.5, $CHCl_3$)[3] for (***S***)-isomer],[$[\alpha]_D^{25}$= +92° (c= 0.96, $CHCl_3$)[4] for (***R***)-isomer]; ^{1}H-NMR (400 MHz, $CDCl_3$): 1.75-2.05 (m, 1H), 2.15-2.54 (m, 3H), 3.71 (br.s, 1H), 4.42-4.57 (m, 1H), 5.84 (d, *J*= 10.1 Hz, 1H), 6.87 (d, *J*= 10.1 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 32.0, 35.1, 65.7, 129.1, 154.1, 200.1; MS(*m/z*): 112[M^+], 95, 91, 79.

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