Supporting Information.

1-(3, 4-Dihydronaphthalen-1-yl)-propan-1-ol (14). To a solution of the tetralone tosyl hydrazone[7] (0.80 g, 2.54 mmol) in TMEDA (12 mL) was added *n*-BuLi (5.5 mL of a 1.6 M solution in hexanes, 8.9 mmol) dropwise via syringe at -78 ºC under N_2. The resulting yellow solution was slowly warmed to 0 ºC over 20 min, then to room temperature. As the solution warmed, gas evolution was observed and the solution gradually turned dark brown. After 3 h, gas evolution had ceased and the solution was recooled to -78 ºC. Propionaldehyde (0.55 mL, 7.63 mmol, used as received from Acros) was added in 2 mL of hexanes. The mixture was stirred at -78 ºC for 15 min and was then transferred to a 0 ºC bath and allowed to warm to room temperature, stirring overnight. The reaction mixture was diluted with water (25 mL) and extracted with ether (3 x 50 mL). The combined ether layers were washed successively with 10% HCl (50 mL), and water (3 x 50 mL), dried ($MgSO_4$) and filtered. After removal of solvent (aspirator), the residue was purified by flash chromatography on silica gel (15 x 3.5 cm), 4:1 hexane/ether eluent to give 0.26 g of a pale yellow oil; analytical tlc on silica gel 60 F254, 1:1 hexane/ether, Rf= 0.37. Molecular ion calcd for $C_{13}H_{16}O$: 188.12010; found m/e= 188.1208, error= 4 ppm; base peak= 131 amu; IR (neat, cm^{-1}) 3367, O-H; 400 MHz NMR ($CDCl_3$, ppm) δ 7.41 (1H, d, J= 7.3 Hz) 7.2-7.1 (3H, m) 6.15 (1H, t, J= 4.6 Hz) 4.6-4.5 (1H, m) 2.72 (2H, t, J= 8.1 Hz) 2.3-2.2 (2H, m) 1.9-1.8 (1H, m) 1.8-1.6 (1H, m) 1.65 (1H, d, J= 3.7 Hz) 0.97 (3H, t, J= 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 139.2, 137.1, 133.5, 128.0, 127.0, 126.5, 125.1, 123.2, 73.7, 29.1, 28.5, 23.0, 10.5.

1-(2-Methyl-3, 4-dihydro-naphthalen-1-yl)-ethanol (15). To a solution of the tetralone tosylhydrazone[7] (0.81 g, 2.47 mmol) in TMEDA (12 mL) was added *n*-BuLi (5.5 mL of a 1.6

M solution in hexanes, 8.6 mmol) dropwise *via* syringe at -78 ºC under N_2. The resulting yellow solution was slowly warmed to 0 ºC over 35 min, then to room temperature. As the solution warmed, gas evolution was observed and the solution gradually turned dark brown. After 50 min, gas evolution had ceased and the solution was recooled to -78 ºC. Acetaldehyde (0.42 mL, 7.4 mmol, distilled) was added in 1.5 mL of hexanes. The mixture was stirred at -78 ºC for 20 min, and then was transferred to a 0 ºC bath and allowed to warm to room temperature, stirring overnight. The reaction mixture was diluted with water (25 mL) and extracted with ether (3 x 50 mL). The combined ether layers were washed successively with 10% HCl (50 mL) and water (3 x 50 mL), dried ($MgSO_4$), and filtered. After removal of solvent (aspirator), the residue was purified by flash chromatography on silica gel (15 x 4 cm), 9:1 hexane/dichloromethane eluent to give 0.25 g of a pale yellow oil; analytical tlc on silica gel 60 F254, 1:1 hexane/ether, Rf= 0.36. Molecular ion calcd for $C_{13}H_{16}O$: 188.12010; found m/e= 188.1196, error= 0 ppm; base peak= 155 amu; IR (neat, cm^{-1}) 3346, O-H; 400 MHz NMR ($CDCl_3$, ppm) δ 7.73 (1H, d, J= 8.1 Hz) 7.2-7.1 (3H, m) 5.24 (1H, qd, J= 6.6, 2.6 Hz) 2.67 (2H, t, J= 7.7 Hz) 2.2-2.1 (2H, m) 2.01 (3H, s) 1.67 (1H, d, J= 2.6 Hz) 1.54 (3H, d, J= 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.4, 135.4, 133.8, 132.8, 127.3, 125.9, 125.8, 124.4, 67.0, 31.5, 28.6, 21.8, 20.1.

General Procedure for Kinetic Resolutions: Analytical Scale KR of 1-(3,4-dihydronaphthalen-1-yl)-ethanol (13). 1-(3,4-Dihydronaphthalen-1-yl)-ethanol **13**[5] (21 mg, 0.12 mmol) was added to a solution of phosphine **7**[2b] (1.97 mg, 0.006 mmol) in 1.2 mL toluene. The solution was cooled to -40 ºC in a Cryocool apparatus and *iso*-butyric anhydride (50 mL, 0.3 mmol, Acros) was added via syringe. The reaction was stirred for 72 h, followed by

quenching with *iso*-propylamine (120 mL, 1.4 mmol, Aldrich). After stirring for 15 min at -40 ºC the mixture was warmed to RT and evaporated under reduced pressure. Careful integration of the ^{1}H-NMR spectrum (CD_3COCD_3) showed that 51% conversion to the ester had occurred, and that 5 mole% of catalyst had been used (catalyst loading was alternatively determined by adding a phosphine solution in toluene of known molar concentration). After evaporation of acetone, the residue was chromatographed on a 15 x 1.2 cm EM silica gel 60 column in dichloromethane/hexanes 6:1 (9 mL fraction size). Fractions 3-4 contained product, fractions 5-6 were blank, and fractions 7-14 contained unreacted alcohol. The ester fractions were concentrated and 5% NaOH/MeOH (1 mL) was added to saponify the ester prior to assay. The solution was warmed gently for 5 min and then left at RT for 2 h. Methanol was evaporated, and the residue was filtered through an 8 x 1.2 cm pad of EM silica gel 60 in dichloromethane. After solvent removal (aspirator), HPLC assay was carried out on a CHIRALCEL OD analytical column, 10% *iso*-propanol/hexanes, 1 mL/min flow rate. Retention times of enantiomers: 7.0 min (*S*) (minor), 9.0 min (*R*) (major), 86.7% ee. The unreacted alcohol fractions from chromatography were assayed in the same way: 96.1% ee, (*S*) (configurations assigned according to aromatization [6] followed by comparison with the known 1-naphthyl-ethanol).[2b]

Assay for Enantiomer Excess:

(*E*)-4-(4-Chlorophenyl)-but-3-en-2-ol (3a):[4] HPLC analysis: CHIRALPAK AD, flow rate 1 mL/min, 5% isopropanol/hexanes. Retention times 27.7 min (*S*) according to (-) sign of optical rotation,[4] 27.3 min (*R*).

(*E*)-3-Methyl-4-phenyl–but-3-en-2-ol (3b):[8] HPLC analysis: CHIRALCEL OD, flow rate 1

mL/min, 3% isopropanol/hexanes. Retention times 13.7 min, (*R*) according to comparison of literature data,[1d,9] 16.0 min (*S*).

5-Phenyl-pent-1-en-3-ol (6a):[10] HPLC analysis: CHIRALPAK AD, flow rate 1 mL/min, 0.2% isopropanol/hexanes. Retention times 32.5 min (*R*), 34.8 min (*S*).

2-Methyl-5-phenyl-pent-1-en-3-ol (6b):[11] HPLC analysis: CHIRALCEL OD, flow rate 1 mL/min, 4% isopropanol/hexanes. Retention times 14.2 min (*S*) , 19.0 min (*R*).

3-Phenyl-but-3-en-2-ol (6c):[12] HPLC analysis: CHIRALCEL OD, flow rate 1 mL/min, 5% isopropanol/hexanes. Retention times 8.2 min (*S*) , 10.7 min (*R*).

1-Cyclohexa-1,5-dienyl-ethanol (12): HPLC analysis: CHIRALCEL OB, flow rate 1 mL/min, 0.1% isopropanol/hexanes. Retention times 11.3 min (*S*) (configurations assigned according to aromatization[6] followed by comparison with the known 1-phenyl-ethanol), [2b] 13.9 min (*R*).

1-(3,4-Dihydronaphthalen-1-yl)-propan-1-ol (14): HPLC analysis: CHIRALPAK AD, flow rate 1 mL/min, 3% isopropanol/hexanes. Retention times 13.7 min (*S*), 15.1 min (*R*).

1-(2-Methyl-3,4-dihydro-naphthalen-1-yl)-ethanol (15): HPLC analysis: CHIRALCEL OD, flow rate 1 mL/min, 10% isopropanol/hexanes. Retention times 6.3 min (*S*) , 12.1 min (*R*).

1-(2-Methyl-1-cyclopentenyl)-ethanol (16):[13] HPLC analysis: CHIRALPAK AS, flow rate 1 mL/min, 0.2% isopropanol/hexanes. Retention times 9.1 min (*S*) , 10.3 min (*R*).

1-Cyclopentenyl-1-propanol (17):[14] GLC analysis: SUPELCO BETA-DEX 120, 95 ºC, 2 mL/min carrier gas flow. Retention times: 18.4 min (*S*), 19.1 min (*R*).

Table 2. Kinetic Resolution Data for Table 1. [a]

Alcohol	**Time (h)**	**Conversion**	**ee**[b]	**ee'**[c]	**Enantio-selectivity s**
3a	12	55.1	77.7	63.3	10
3b	27	45.1	67.3	82.0	21
6a	41	47.9	41.7	45.4	4
6b	19	48.1	66.4	71.7	12
6c	19	38.1	45.7	74.3	11
12	7	53.0	90.0	81.4	34[d]
13	72	52.6	96.1	86.7	55
14	128	34	48.9	94.8	61
15	25	40.3	64.2	95.3	82[d]
16	46	67.2	99.9	48.8	25[d]
17	46	37.7	56.4	93.5	52

(a) -40 °C in toluene; *iso*-butyric anhydride and *ca.* 5 mol % **7**. (b) ee of unreacted alcohol (c) product ee (alcohol obtained by ester saponification). (d) heptane solution.

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