Experimental Section

General Aspects: ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker AC 200 or AC 250 (^{1}H: 200 or 250 MHz; ^{13}C: 50 or 63 MHz) spectrometer, with $CDCl_3$ as reference standard. IR spectra were determined on a Perkin-Elmer 1600 series FTIR spectrophotometer. Mass spectra were carried out on a Finnigan MAT8200, exact mass on a Finnigan MAT90. HPLC analyses were run on a Kontron 322 equipment, furnished with a spectrophotometer UVIKON 720 micro and a polarimetric detector CHIRALYSER 1.6 from IBZ Messtechnik. The specific rotation $[\alpha]^{20}_{D}$ was determined on a Perkin-Elmer 241 MC polarimeter.

General Procedure for the Manganese-Catalyzed Epoxidation of the Allylic Alcohols 2: A solution of 100 μmol (10 mol%) of the particular Mn(salen*)Cl catalyst **1** and 200 μmol (20 mol%) of 4-pyridine *N*-oxide (PPNO) in 10 mL CH_2Cl_2 was stirred for 3 min at RT (ca. 20 °C). After addition of 1.00 mmol of the appropriate alcohol **2**, the mixture was stirred for another 2 min and 132 mg (600 μmol) of PhI=O was administered in small portions during 2 min. The resulting suspension was stirred for ca. 14 h until a clear, brown solution was obtained. After removal of the solvent (20 °C, 400 mbar), the residue was transferred onto a short column of silica gel (ca. 10 g) and eluted first with 100 mL of petroleum ether to remove iodobenzene, afterwards with 200 mL of a petroleum ether / diethyl ether mixture (1:1) to recover the oxidation products. After removal of the solvent (30 °C, 10 mbar), the resulting colorless oil was analyzed by ^{1}H-NMR spectroscopy and chiral HPLC; the mass balance was determined by the weight of the crude product and the products detected by NMR spectroscopy. The quantitative data are summarized in Table 1 (see main text), and the HPLC data are given in Table S1.

Table S1. HPLC Data for the Allylic Alcohols **2** and the Epoxides **3**

compound	column	*n*-hexane : ^{i}PrOH	flow [mL/min]	retention time[a] [min]
2a	OD-H	90 : 10	0.5	11.2 [*S*(+)] / 17.2 [*R*(-)]
threo (*cis*)-**3a**	OD-H	90 : 10	0.5	15.4 [2*S*(+)] / 17.9 [2*R*(-)]
erythro (*cis*)-**3a**	OD-H	95 : 5	0.5	16.8 [2*S*(-)] / 17.5 [2*R*(+)]
threo (*trans*)-**3a**	OD-H	90 : 10	0.5	20.2 [2*R*(-)] / 27.6 [2*S*(+)]
2b	OB-H	80 : 20	0.5	12.2 [*R*(-)] / 19.2 [*S*(+)]
cis-**3b**	OB-H	80 : 20	0.5	25.4 [1*S*(-)] / 40.1 [1*R*(+)]
trans-**3b**	OB-H	80 : 20	0.5	17.0 [1*S*(-)] / 22.5 [1*R*(+)]
2c	OD-H	95 : 5	0.5	16.2 [*S*(-)] / 17.2 [*R*(+)]
cis-**3c**	OD-H	90 : 10	0.5	19.5 [2*S*(-)] / 20.7 [2*R*(+)]
trans-**3c**	OD-H	90 : 10	0.5	17.5 [2*R*(-)] / 18.6 [2*S*(+)]
2d	OD	99.5 : 0.5	0.8	23.8 (+) / 25.9 (-)
cis-**3d**	OD	95 : 5	0.8	18.0 (-) / 19.7 (+)
trans-**3d**	OD	95 : 5	0.8	15.4 (-) / 16.6 (+)
2e	AS	90 : 10	1.0	5.7 [*R*(+)] / 6.6 [*S*(-)]
threo-**3e**	AS	90 : 10	1.0	7.4 [2*R*(+)] / 9.8 [2*S*(-)]
erythro-**3e**	AS	90 : 10	1.0	5.6 [2*S*(-)] / 6.5 [2*R*(+)]
2f	OD	90 : 10	1.0	5.4 (+) / 6.2 (-)
threo-**3f**	AS	90 : 10	1.0	7.3 (+) / 10.3 (-)
erythro-**3f**	OD	90 : 10	1.0	5.5 (-) / 6.2 (+)

a) The absolute configuration and/or sign of the optical rotation is given in brackets.

*Spectral and Analytical Data for the Allylic Alcohols **2**, the Epoxides **3** and the Enones **4***

(Z)-4-Phenyl-3-buten-2-ol (2a):[16]

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31(d, *J* = 6.4 Hz, 3 H, 1-H), 1.74 (br.s, 1 H, OH), 4.73 (m, 1 H, 2-H), 5.64 (dd, *J* = 11.6 Hz, 2.7 Hz, 1 H, 3-H), 6.45 (d, *J* = 11.6 Hz, 1 H, 4-H), 7.18-7.27 (m, 5 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.6, 64.1, 127.2, 128.3, 128.7, 130.0, 135.6, 136.6.

***threo*-(2α,3α)-α-Methyl-3-phenyloxiranemethanol (3a):**

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 (d, *J* = 6.1 Hz, 3 H, 1-H), 2.22 (br.s, 1 H, OH), 3.15 (dd, *J* = 8.4 Hz, 4.3 Hz , 1 H, 3-H), 3.29 (dq, *J* = 8.4 Hz, 6.2 Hz, 1 H, 2-H), 4.20 (d, *J* = 4.3 Hz, 1 H, 4-H), 7.29-7.33 (m, 5 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.3, 57.4, 63.2, 66.1, 125.9, 127.8, 128.3, 134.8.

***erythro*-(2α,3α)-α-Methyl-3-phenyloxiranemethanol (3a):**

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.36 (d, *J* = 5.1 Hz, 3 H, 1-H), 2.22 (br.s, 1 H, OH), 3.10 (dd, *J* = 3.4 Hz, 6.8 Hz, 1 H, 3-H), 3.23-3.35 (m, 1 H, 2-H), 4.17 (d, *J* = 3.4 Hz, 1 H, 4-H), 7.29-7.33 (m, 5 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.7, 47.4, 62.0, 64.4, 126.2, 127.8, 128.3, 143.8.

For the diastereomeric mixture:

IR (KBr): ν = 3301 cm^{-1}, 2973, 1497, 1452, 1368, 1311, 1082, 876.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. **Found:** C, 73.16; H, 7.35.

(Z)-4-Phenyl-3-buten-2-one (4a):[17]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.15 (s, 3 H, 1-H), 6.30 (d, *J* = 12.7 Hz, 1 H, 3-H), 7.02 (d, *J* = 12.7 Hz, 1 H, 4-H), 7.40-7.89 (m, 5 H, H_{Ar}).

2-Indenol (2b):[18]

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.59 (br.s, 1 H, OH), 5.11 (br.s, 1 H, 1-H), 6.33 (dd, *J* = 5.8 Hz, 1.9 Hz, 1 H, H_{Ar}), 6.66 (d, *J* = 5.8 Hz, 1 H, H_{Ar}), 7.10-7.24 (m, 3 H, H_{Ar}), 7.44 (d, *J* = 6.4 Hz, 1 H, H_{Ar}).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.6, 121.4, 123.4, 126.1, 128.5, 132.7, 137.7, 142.3, 145.4.

***cis*-1a,6a-Dihydro-6H-indeno[1,2-b]oxiren-2-ol (3b):**[19]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.12 (d, *J* = 11.8 Hz, 1 H, OH), 4.06 (dd, *J* = 2.9 Hz, 2.8 Hz, 1 H, 2-H), 4.20 (d, *J* = 2.8 Hz, 1 H, 3-H), 5.12 (dd, *J* = 11.8 Hz, 2.9 Hz, 1 H, 1-H), 7.27 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1 H, 6-H), 7.34 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1 H, 7-H), 7.41 (d, *J* = 7.5 Hz, 1 H, 8-H), 7.43 (d, *J* = 7.5 Hz, 1 H, 5-H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 56.8, 57.4, 73.5, 124.9, 126.5, 128.1, 129.4, 139.7, 143.7.

***trans*-1a,6a-Dihydro-6H-indeno[1,2-b]oxiren-2-ol (3b):**[19]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.92 (d, *J* = 8.1 Hz, 1 H, OH), 4.21 (d, *J* = 2.5 Hz, 1 H, 3-H), 4.30 (m, 1 H, 2-H), 5.03 (d, *J* = 8.1 Hz, 1 H, 1-H), 7.32 (d, *J* = 7.3 Hz, 1 H, 6-H), 7.35 (d, *J* = 7.5 Hz, 1 H, 7-H), 7.50 (d, *J* = 7.5 Hz, 1 H, 8-H), 7.54 (d, *J* = 7.3 Hz, 1 H, 5-H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 57.7, 62.8, 77.7, 125.1, 126.3, 128.5, 129.1, 140.8, 146.4.

2-Indenone (4b):[20]

^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.82 (d, *J* = 6.1 Hz, 1 H, 2-H), 6.99 (d, *J* = 7.0 Hz, 1 H, H_{Ar}), 7.13-7.37 (m, 3 H, H_{Ar}), 7.50 (dd, *J* = 6.1 Hz, 0.9 Hz, 1 H, H_{Ar}).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 122.2, 122.6, 127.1, 129.1, 130.3, 133.6, 144.6, 149.8, 198.4.

1,1-Dimethyl-1,2-dihydronaphthalen-2-ol (2c):[8b]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.37, 1.55 (2×s, 6 H, 9-H, 9'-H), 4.14 (br.s, 1 H, 2-H), 6.22 (dd, *J* = 9.6 Hz, 4.6 Hz, 1 H, 3-H), 6.66 (d, *J* = 9.6 Hz, 1 H, 4-H), 7.22-7.45 (m, 3 H, H_{Ar}), 7.52 (dd , *J* = 6.9 Hz, 2.1 Hz, 1 H, H_{Ar}).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.7, 27.0, 39.2, 74.1, 125.1, 126.5, 127.2, 128.3, 128.7, 129.1, 131.4, 142.9.

***cis*-1a,2,3,7b-Tetrahydro-3,3-dimethylnaphth[1,2-b]oxiren-2-ol (3c):**

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.34, 1.38 (2×s, 6 H, 9-H, 9'-H), 2.12 (d, *J* = 9.2 Hz, 1 H, OH), 3.84 (dd, *J* = 4.6 Hz, 2.8 Hz, 1 H, 3-H), 3.90-4.01 (m, 2 H, 2-H, 4-H), 7.34-7.48 (m, 4 H, H_{Ar}).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 26.6, 27.2, 40.0, 54.2, 57.3, 73.4, 126.2, 126.3, 129.4, 130.2.

***trans*-1a,2,3,7b-Tetrahydro-3,3-dimethylnaphth[1,2-b]oxiren-2-ol (3c):**

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31, 1.42 (2×s, 6 H, 9-H, 9'-H), 1.52 (d, *J* = 8.2 Hz, 1 H, OH), 3.78 (dd, *J* = 3.8 Hz, 2.8 Hz, 1 H, 3-H), 3.90-4.01 (m, 2 H, 2-H, 4-H), 7.34-7.48 (m, 4 H, H_{Ar}).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 26.1, 30.9, 39.3, 52.3, 56.6, 66.2, 126.3, 126.5, 129.5, 130.3.

For the diastereomeric mixture:

IR (KBr): ν = 3422 cm^{-1}, 2969, 1719, 1491, 1384, 1361, 1040, 994, 902.

HRMS (EI) Calcd. for $C_{12}H_{14}O_2$ 190.0994, found 190.0994.

1,1-Dimethyl-1,2-dihydronaphthalen-2-one (4c):[8a]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.35, (s, 6 H, 9-H), 6.05 (d, J = 9.9 Hz, 1 H, H_{Ar}), 6.95-7.85 (m, 5 H, H_{Ar}).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.7, 47.4, 124.5, 126.2, 126.6, 128.6, 129.5, 130.0, 144.7, 147.7, 204.5.

1,1,2-Trimethyl-1,2-dihydronaphthalen-2-ol (2d):[9]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.34, 1.35, 1.41 (3×s, 9 H, 9-H, 9'-H, 10-H), 2.12 (s, 1 H, OH), 5.91, 6.46 (2×d, *J* = 9.6 Hz, 2 H, 3-H, 4-H), 7.07-7.46 (m, 4 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.3, 22.5, 22.8, 42.4, 74.8, 124.6, 126.3, 126.8, 128.0, 131.3, 136.1, 144.3.

***cis*-1a,2,3,7b-Tetrahydro-2,3,3-trimethylnaphth[1,2-b]oxiren-2-ol (3d):**

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.16, 1.35, 1.39 (3×s, 9 H, 9-H, 9'-H, 10-H), 2.20 (s, 1 H, OH), 3.58 (d, *J* = 4.4 Hz, 1 H), 3.96 (d, *J* = 4.3 Hz, 1 H), 7.18-7.29 (m, 4 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.2, 24.7, 42.6, 54.6, 62.2, 62.3, 73.1, 126.0, 126.8, 129.3, 130.1, 130.2, 146.0.

***trans*-1a,2,3,7b-Tetrahydro-2,3,3-trimethylnaphth[1,2-b]oxiren-2-ol (3d):**

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.28, 1.44, 1.55 (3×s, 9 H, 9-H, 9'-H, 10-H), 1.63 (s, 1 H, OH), 3.58 (d, *J* = 4.4 Hz, 1 H), 3.92 (d, *J* = 4.1 Hz, 1 H), 7.18-7.29 (m, 4 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.2, 28.2, 42.2, 54.6, 62.2, 62.3, 72.4, 126.2, 128.1, 129.6, 130.2, 130.7, 145.7.

For the diastereomeric mixture:

IR (KBr): ν = 3485 cm^{-1}, 2969, 1491, 1383, 1336, 1161, 1105, 1031, 900.

HRMS (EI) Calcd. for $C_{13}H_{16}O_2$ 204.1150, found 204.1155.

(*E*)-4-Phenyl-3-penten-2-ol (2e):[21]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.35 (d, *J* = 6.4 Hz, 3 H, 1-H), 1.65 (br.s, 1 H, OH), 2.10 (d, *J* = 1.4 Hz, 3 H, 5-H), 4.67 (dq, *J* = 8.6 Hz, 6.4 Hz, 1 H, 2-H), 5.72 (dd, *J* = 8.3 Hz, 1.5 Hz, 1 H, 3-H), 7.28-7.30 (m, 5 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0, 23.5, 65.2, 125.7, 127.2, 128.2, 131.9, 136.1, 142.8.

***threo*-(2α,3β)-α,3-Dimethyl-3-phenyloxiranemethanol (3e):**

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31 (d, *J* = 6.4 Hz, 3 H, 1-H), 1.70 (br.s, 3 H, 5-H), 2.47 (br.s, 1 H, OH), 2.87 (d, *J* = 7.6 Hz, 1 H, 3-H), 3.93 (m, 1 H, 2-H), 7.27-7.31 (m, 5 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.8, 19.3, 61.4, 66.8, 70.5, 125.0, 127.5, 128.3, 142.0.

***erythro*-(2α,3β)-α,3-Dimethyl-3-phenyloxiranemethanol (3e):**

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.42 (d, *J* = 6.4 Hz, 3 H, H-1), 1.77 (s, 3 H, H-5), 1.94 (br.s, 1 H, OH), 2.77 (d, *J* = 7.6 Hz, 1 H, H-3), 3.79-3.93 (m, 1 H, H-2), 7.27-7.31 (m, 5 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.0, 20.9, 65.8, 66.3, 69.2, 125.1, 127.4, 128.4, 142.2.

For the diastereomeric mixture:

IR (neat): ν = 3415 cm^{-1}, 2971, 1496, 1447, 1424, 1381, 1050, 875.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. **Found:** C, 73.68; H, 7.65.

(*E*)-4-Phenyl-3-penten-2-one (4e):[22]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, 1-H), 2.54 (d, *J* = 1.2 Hz, 3 H, 5-H), 6.51 (d, *J* = 1.1 Hz, 1 H, 3-H), 7.36-7.50 (m, 5 H, H_{Ar}).

(*Z*)-4-Phenyl-3-penten-2-ol (2f):[21]

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.35 (d, *J* = 6.1 Hz, 3 H, 1-H), 1.42 (br.s, 1 H, OH), 2.00 (d, *J* = 1.5 Hz, 3 H, 5-H), 4.24 (dq, *J* = 9.2 Hz, 6.4 Hz, 1 H, 2-H), 5.46 (dd, *J* = 9.5 Hz, 1.5 Hz, 1 H, 3-H), 7.13-7.21 (m, 5 H, H_{Ar}).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 23.7, 25.6, 65.4, 127.0, 127.7, 128.2, 131.2, 138.5, 141.2.

***threo*-(2α,3α)-α,3-Dimethyl-3-phenyloxiranemethanol (3f):**

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.06 (m, 3 H, 1-H), 1.66 (s, 3 H, 5-H), 1.99 (br.s, 1 H, OH), 3.01 (m, 2 H, 2-H, 3-H), 7.29-7.34 (m, 5 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.3, 24.7, 63.4, 67.1, 69.3, 126.2, 127.5, 128.3, 139.0.

***erythro*-(2α,3α)-α,3-Dimethyl-3-phenyloxiranemethanol (3f):**

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.06 (m, 3 H, 1-H), 1.68 (s, 3 H, 5-H), 1.99 (br.s, 1 H, OH), 3.01, (m, 2 H, 2-H, 3-H), 7.29-7.34 (m, 5 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.7, 24.5, 63.1, 66.1, 68.0, 125.9, 127.5, 128.4, 139.1.

For the diastereomeric mixture:

IR (KBr): ν = 3414 cm^{-1}, 2974, 2927, 1447, 1383, 1093, 1036, 878.

HRMS [CI (NH_3)] Calcd. for $C_{11}H_{14}O_2$ 196.1338 $(M + NH_4)^+$, found 196.1334.

(*Z*)-4-Phenyl-3-penten-2-one (4f):[23]

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.80 (s, 3 H, 1-H), 2.19 (d, *J* = 1.2 Hz, 3 H, 5-H), 6.13 (d, *J* = 1.2 Hz, 1 H, 3-H), 7.18-7.22 (m, 2 H, H_{Ar}), 7.34-7.37 (m, 3 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.3, 30.1, 125.1, 127.1, 128.3, 128.4, 140.9, 152.9, 200.3.

Determination of the Absolute Configuration of the Allylic Alcohol ***2a***

(*S*)-4-Phenyl-2-butanol:[13] A suspension of 37.5 mg (253 μmol) of (+)-4-phenyl-3-buten-2-ol (**2a**, 53% *ee*) and of 20 mg palladium on charcoal in 7 mL of EtOAc was stirred under a hydrogen-gas atmosphere for 15 h at RT. Filtration of the reaction mixture through Cellite and removal of the solvent (30 °C, 10 mbar) yielded 38.0 mg (quant.) of a colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.15 (d, *J* = 6.1 Hz, 3 H, CH_3), 1.64-1.76 (m, 2 H, 4-H), 2.03 (d, *J* = 12.9 Hz, 1 H, OH), 2.51-2.83 (m, 2 H, 3-H), 3.76 (sext, *J* = 6.2 Hz, 1 H, 2-H), 7.07-7.24 (m, 5 H, H_{Ar}).

$[\alpha]_D^{20}$ = + 15.6 ° (Lit.[24] + 16.7 °)

Determination of the Absolute Configuration of the Allylic Alcohol ***2c***

(*S*)-1,1-Dimethyl-1,2-dihydronaphthalen-2-ol Acetate:[25] A mixture of 122 mg (700 µmol) of 1,1-dimethyl-1,2-dihydronaphthalen-2-ol (*rac*-**2c**) and 70 mg of the enzyme CHIRAZYME® L-1 (BSL, *Burkholderia sp.*) was suspended in 15 mL of MTBE. After addition of 380 µl (3.50 mmol) of isopropenyl acetate, the mixture was stirred for ca. 24 h at RT. The enzyme was removed by filtration and the extent of conversion was determined to be 49% by HPLC analysis. After removal of the solvent (30 °C, 10 mbar), the crude product was purified by silica-gel chromatography on elution with a 5:1 mixture of petroleum ether and diethyl ether to yield 72.0 mg (97%) of (*S*)-1,1-dimethyl-1,2-dihydronaphthalen-2-ol acetate (92% *ee*) and 62.5 mg (quant.) of (*R*)-1,1-dimethyl-1,2-dihydronaphthalen-2-ol (**2c**, 88% *ee*).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.21, 1.38 (2×s, 6 H, 9-H, 9'-H), 2.00 (s, 3 H, OAc), 5.21 (d, *J* = 4.9 Hz, 1 H, 2-H), 5.99 (dd, *J* = 9.6 Hz, 5.0 Hz, 1 H, 3-H), 6.60 (d, *J* = 9.2 Hz, 1 H, 4-H), 7.09-7.39 (m, 4 H, H_{Ar}).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.0, 22.1, 27.4, 37.6, 75.2, 124.3, 124.6, 126.5, 127.4, 128.5, 130.7, 131.2, 142.6, 170.9.

HPLC (OD-H, 95:5 hexane/isopropanol, flow 0.5 mL/min, λ = 220 nm): t_R [*S(-)*] = 10.0 min, t_R [*R(+)*] = 10.5 min.

$[\alpha]_D^{20}$ = - 511 ° ($CHCl_3$, c = 2)

Benzoate of (*R*)-1,1-Dimethyl-1,2-dihydronaphthalen-2-ol: To a solution of 34.4 mg (197 µmol) of (*R*)-1,1-dimethyl-1,2-dihydronaphthalen-2-ol (**2c**, 76% *ee*) and ca. 2 mg of *para*-dimethylaminopyridine (DMAP) in 2 mL pyridine was added 36.0 µl (296 µmol) of benzoyl chloride. After stirring for 15 h at RT, 1 mL toluene was added and the solvent was removed (30 °C, 10 mbar). The resulting solid was extracted with Et_2O (5× 3 mL) and after removal of the solvent (30 °C, 10 mbar), the crude product was purified by silica-gel chromatography on elution with a 20:1 mixture of petroleum ether and diethyl ether to yield 45.8 mg (83%) of the benzoate (75% *ee*) as a colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.31, 1.48 (2×s, 6 H, 9-H, 9'-H), 5.49 (d, *J* = 5.0 Hz, 1 H, 2-H), 6.11 (dd, *J* = 9.6, 4.6 Hz, 1 H, 3-H), 6.63 (d, *J* = 9.8 Hz, 1 H, 4-H), 7.12-7.56 (m, 7 H, H_{Ar}), 7.96 (d, *J* = 6.9 Hz, 2 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.2, 27.0, 37.8, 76.1, 124.5, 125.0, 126.7, 127.6, 128.5, 128.7, 129.8, 130.5, 130.9, 131.5, 133.1, 142.9, 166.5.

HPLC (OD-H, 95:5 hexane/isopropanol, flow 0.5 mL/min, λ = 220 nm): t_R [*S(-)*] = 10.6 min, t_R [*R(+)*] = 11.1 min.

IR (neat): ν = 3062 cm^{-1}, 2971, 1714, 1602, 1450, 1270, 1109, 937.

HRMS (EI) Calcd. for $C_{19}H_{18}O_2$ 278.1307, found 278.1308.

Determination of the Absolute Configuration of the Allylic Alcohol ***2e***

(*S*)-(*E*)-2-Benzyloxy-4-phenylpent-3-ene: To a solution of 50.0 mg (308 µmol) of (-)-(*E*)-4-phenyl-3-penten-2-ol (**2e**, 21% *ee*) in 2 mL DMF was added 15.4 mg (385 µmol) of 60% NaH, 73.2 µl (616 µmol) of benzyl bromide, and a small amount (ca. 1.3 mg) of tetra-*n*-butyl ammonium iodide at 0 °C. The resulting mixture was stirred for 2.5 h at RT and then diluted with 15 mL of EtOAc. The mixture was washed with water (3× 5 mL) and the organic phase was dried over $MgSO_4$. After removal of the solvent (30 °C, 10 mbar), the crude product was purified by silica-gel chromatography on elution with a 30:1 mixture of petroleum ether and diethyl ether to yield 59.0 mg (76%) of a colorless powder.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.36 (d, *J* = 6.2 Hz, 3 H, 1-H), 2.05 (d, *J* = 1.2 Hz, 3 H, 5-H), 4.37-4.66 (m, 3 H, 2-H, Ph-CH_2), 5.81 (dq, *J* = 8.8, 1.2 Hz, 1 H, 3-H), 7.26-7.32 (m, 10 H, H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.1, 21.4, 70.0, 71.5, 125.7, 127.2, 127.4, 127.8, 128.2, 128.3, 130.6, 137.0, 138.9, 142.9.

(*S*)-2-Benzyloxypropanal:[26] Through a solution of 59.0 mg (234 µmol) of (*S*)-(*E*)-2-benzyloxy-4-phenylpent-3-ene in 3 mL of CH_2Cl_2 and 0.02 mL of MeOH was allowed to pass a gentle stream of ozone gas at -78 °C for 3 h. After warming up to RT, 0.1 mL of Me_2S was added and the resulting mixture was stirred at RT for 24 h. After removal of the solvent (30 °C, 10 mbar), the residual oil was dissolved in 50 mL of CH_2Cl_2 and extracted with water (2× 30 mL). The organic phase was dried over $MgSO_4$ and after removal of the solvent

(30 °C, 10 mbar), the crude product was purified by silica-gel chromatography on elution with a 9:1 mixture of petroleum ether and diethyl ether to yield 21.3 mg (55%) of a colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.33 (d, *J* = 7.0 Hz, 3 H, CH_3), 3.90 (dq, *J* = 6.9 Hz, 1.8 Hz, 1 H, C*H*-CH_3), 4.63 (dd, *J* = 11.7 Hz, 14.9 Hz, 2 H, Ph-CH_2), 7.32-7.39 (m, 5 H, H_{Ar}), 9.67 (d, *J* = 1.7 Hz, 1 H, CH=O).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.9, 72.0, 79.4, 128.3, 128.4, 128.9, 137.7, 204.3.

$[\alpha]_D^{20}$ = ca. - 40 ° (Lit.[14] - 38.5 °)

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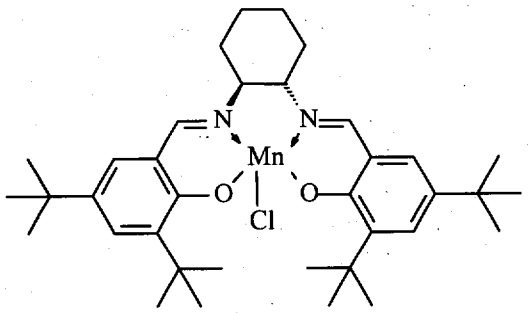
Structure Matrix

(not for the main text)



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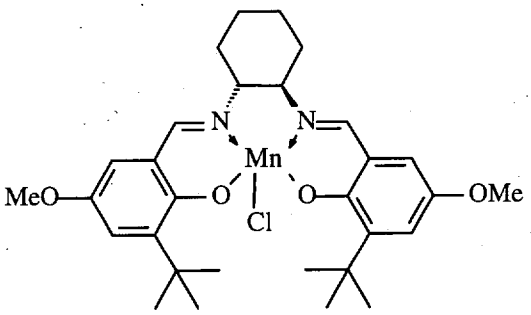

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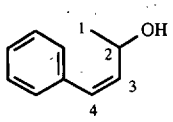

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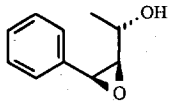

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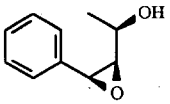

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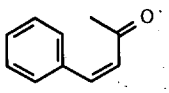

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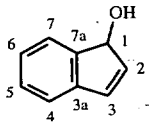

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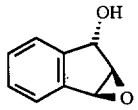

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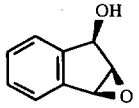

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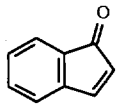

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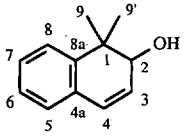

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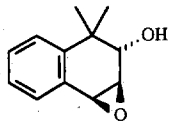

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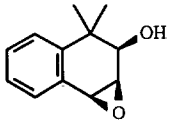

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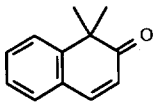

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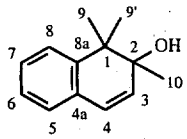

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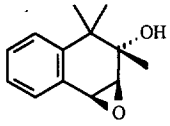

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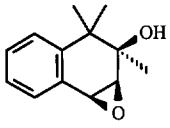

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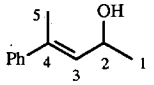

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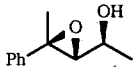

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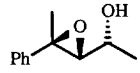

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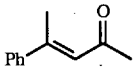

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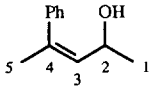

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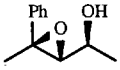

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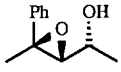

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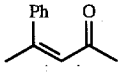

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