Supplementary data

Crystal data for 3I*p*: $C_{26}H_{32}N_2O_5$, $M = 452.5$, orthorhombic, $a = 14.0720(1)$, $b = 14.2180(1)$, $c = 22.8890(3)$ Å, $U = 4579.4(1)$ Å^3, $T = 150(2)$ K, Mo-Kα radiation, $\lambda = 0.71073$ Å, space group $P2_12_12_1$ (no. 19), $Z = 8$, $F(000) = 1936$, $D_x = 1.313$ g cm^{-3}, $\mu = 0.091$ mm^{-1}, Nonius Kappa CCD diffractometer, $3.0^o < 2\theta < 55.0^o$, measured/independent reflections: 75191/10491, direct methods solution, full-matrix least squares refinement on F_o^2, anisotropic displacement parameters for non-hydrogen atoms; hydrogen atoms were located in a difference Fourier synthesis but were included in the final refinement at positions calculated from the geometry of the molecules using the riding model, with isotropic vibration parameters. There are two crystallographically independent dimer molecules which show no significant geometrical or stereochemically differences. Both molecules have helicity P at the N-C-C-N junction, with torsion angles $+117^0$ and $+108^0$ respectively. Final $R_1 = 0.046$ for 9171 data with $F_o > 4\sigma(F_o)$, 608 parameters, $\omega R_2 = 0.118$(all data), GoF = 1.07, $\Delta\rho_{min,max}$ = -0.30/0.50 e Å^{-3}. CCDC 746348. The absolute structure was not determined from this analysis but was assigned to correspond with the *known* absolute structure of *cis*-dihydrodiol **2B.**[1]

Crystal data for 2J: $C_{24}H_{28}N_2O_6$, $M = 440.5$, monoclinic, $a = 36.354(7)$, $b = 6.013(1)$, $c = 16.828(3)$ Å, $\beta = 117.07(1)^0$, $U = 3275.7(10)$ Å^3, $T = 150(2)$ K, Mo-Kα radiation, $\lambda = 0.71073$ Å, space group C2 (no. 5), $Z = 6$, $F(000) = 1404$, $D_x = 1.340$ g cm^{-3}, $\mu = 0.097$ mm^{-1}, Bruker SMART CCD diffractometer, ϕ/ω scans, $2.5^o < 2\theta < 46.5^o$, measured/independent reflections: 10583/4687, direct methods solution, full-matrix least squares refinement on F_o^2, anisotropic displacement parameters for non-hydrogen atoms; all hydrogen atoms were located in a difference Fourier synthesis but were included in the final refinement at positions calculated from the geometry of the molecules using the riding model, with isotropic vibration parameters. There are two crystallographically independent dimer molecules, one of which lies on the crystallographic 2-fold axis. Thus the asymmetric unit consists of 1.5 dimers. The independent molecules show no significant geometrical or stereochemical differences. All molecules have helicity P at the N-C-C-N junction, with torsion angles $+67.1^0$ and $+67.8^0$, respectively, for the two independent molecules. Final $R_1 = 0.031$ for 4218 data with $F_o > 4\sigma(F_o)$, 439 parameters, $\omega R_2 = 0.074$(all data), GoF = 0.99, $\Delta\rho_{min,max}$ = -0.16/0.12 e Å^{-3}. CCDC 746347. The absolute structure was not determined from this analysis but was assigned to correspond with the *known* absolute structure of *cis*-dihydrodiol **2B**.[1]**.**

Crystal data for 3J*p*: $C_{26}H_{32}N_2O_6$, $M = 468.5$, orthorhombic, $a = 14.1616(1)$, $b = 14.2969(1)$, $c = 22.8822(2)$ Å, $U = 4632.9(1)$ Å^3, $T = 150(2)$ K, Mo-Kα radiation, $\lambda = 0.71073$ Å, space group $P2_12_12_1$ (no. 19), $Z = 8$, $F(000) = 2000$, $D_x = 1.343$ g cm^{-3}, $\mu = 0.096$ mm^{-1}, Nonius Kappa CCD diffractometer, $3.0^o < 2\theta < 55.0^o$, measured/independent reflections: 66883/10614, direct methods solution, full-matrix least squares refinement on F_o^2, anisotropic displacement parameters for non-hydrogen atoms;

hydrogen atoms were located in a difference Fourier synthesis but were included in the final refinement at positions calculated from the geometry of the molecules using the riding model, with isotropic vibration parameters. There are two crystallographically independent dimer molecules which show no significant geometrical or stereochemically differences. Both molecules have helicity P at the N-C-C-N junction, with torsion angles $+112^0$ and $+107^0$ respectively. Final $R_1 = 0.055$ for 10001 data with $F_o > 4\sigma(F_o)$, 656 parameters, $\omega R_2 = 0.146$(all data), GoF = 1.16, $\Delta\rho_{min,max}$ = -0.81/0.49 e Å^{-3}, CCDC 746349. The absolute structure was not determined from this analysis but was assigned to correspond with the *known* absolute structure of *cis*-dihydrodiol **2B.**[1]

General method for the copper (I)-catalysed enantioselective allylic oxidation reaction of alkenes 10 or 12 with ligand 7F to yield benzoates 11 or 13

Ligand **7F** (0.06 mmol) and $Cu(OTf)_2$ (0.018 g, 0.05 mmol) were dissolved in acetone (4 ml) and the yellow solution stirred (1 h) at room temperature under nitrogen atmosphere. When phenylhydrazine (5.9 µl, 0.06 mmol) was added to the stirring reaction mixture, the colour of the solution changed to red. After 10 min, alkene **10** or **12** (5 mmol) was added, at the temperature listed in Table 4.1, followed by dropwise addition of *tert*-butyl peroxybenzoate (0.2 ml, 1.0 mmol). The progress of the reaction was monitored by TLC (10% EtOAc in hexane). When all of the oxidant had been consumed (starch and KI solution test), the solvent was removed under reduced pressure. The residue obtained was dissolved in dichloromethane (15 ml), washed, successively, with $NaHCO_3$ solution, brine, water, and then dried ($MgSO_4$). Purification of the crude product, left after removal of solvent, by PLC (10% EtOAc in hexane) gave allylic benzoate **11** or **13**.

(*S*)-2-Cyclohexenyl benzoate 11. 50% yield (from cyclohexene **10**); 79% *ee*. The enantiopurity was determined by chiral GC using a Supelco *β*-Dex 225 chiral column (120 min at 100 ºC, then 5 ºC/min to 200 ºC, t_R 133.468 min, t_S 133.127 min).

(*S*)-2-Cycloheptenyl benzoate 13. 53% yield (from cycloheptene **12**); 91% *ee*. The enantiopurity was determined by chiral stationary phase GC using a Supelco *β*-Dex 225 chiral column (210 min at 100 ºC, then 5 ºC/min to 200ºC, t_R 225.818 min, t_S 225.988 min).

General procedure (A) for the scandium-catalyzed enantioselective aminolysis of *meso*-epoxides

To a stirring solution of $Sc(OTf)_3$ (0.025 mg) and chiral bipyridine **9** (0.048 g, 12 mol %) in dichloromethane (2 ml) was added epoxide (0.5 mmol) and amine (0.5 mmol). When the reaction was complete (*ca.* 36 h, TLC), the solvent was evaporated and the product purified by PLC (25% EtOAc in hexane) to yield the corresponding 1,2-amino alcohol. The absolute configurations of amino alcohols were assigned by comparison of the reported optical rotation values with the literature values for amino alcohols of established absolute configurations.

General procedure (B) for the scandium-catalyzed enantioselective aminolysis of *meso*-epoxides

Asymmetric ring-opening reactions were carried out in water under an atmosphere of nitrogen. Chiral bipyridine **8** (2 mg, 1.2 mol %) was added to a stirred solution of scandium dodecyl sulfate [$Sc(DS)_3$] (4.2 mg) in deionised water (1M concentration with respect to substrates) and the solution stirred for 1 h at room temperature under nitrogen atmosphere. The amine (0.5 mmol) and the epoxide (0.5 mmol) were added to the solution and stirring continued for ~72 h at room temperature. The reaction mixture was then quenched with $NaHCO_3$ solution and the product extracted into ethyl acetate (3 x 15 ml). The combined organic extract was dried (Na_2SO_4), the solvent evaporated and the residue purified by PLC (25% EtOAc in hexane) to gave the corresponding amino alcohol.

(1*S*,2*S*)-1,2-Diphenyl-2-(phenylamino)ethanol 18

Employing procedures **A** and **B**, epoxide **16** (98 mg, 0.5 mmol) was treated with aniline (45µl, 0.5 mmol) to give amino alcohol **18** as a white solid; $[\alpha]_D$ -31 (*c* 0.74, CH_2Cl_2); [lit.[2] 91% *ee*, $[\alpha]_D$ –45.2 (*c* 0.52, CH_2Cl_2)]; mp 101-102 °C; δ_H (300 MHz, $CDCl_3$) 2.75 (1H, br s), 4.46 (1H, d, *J* 6.0, CH), 4.53 (1H, br s), 4.70 (1H, d, *J* 6.0, CH), 6.48-6.50 (2H, m, Ar*H*), 6.59-6.61 (1H, m, Ar*H*), 7.0-7.03 (2H, m, Ar*H*), 7.12-7.23 (10H, m, Ar*H*). The enantiopurity was determined by chiral stationary phase HPLC using a Chiralcel AD-H column, (*n*-hexane/*i*-PrOH 90:10, flow 1 ml/min, isocratic, λ=230 nm, $t_{S,S}$ 15.905 min, $t_{R,R}$ 18.487 min).

(1*S*,2*S*)-2-(*N*-Methyl-*N*-phenylamino)-1,2-diphenylethanol 20

Epoxide **16** (98 mg, 0.5 mmol) was treated with *N*-methyl aniline **19** (54µl, 0.5 mmol) (procedure **A**) to yield amino alcohol **20** as a white solid; $[\alpha]_D$ +119 (*c* 0.97, CH_2Cl_2); [lit.[2] 96% *ee*, $[\alpha]_D$ +171.7 (*c* 0.53, CH_2Cl_2)]; δ_H (300 MHz, $CDCl_3$) 2.69 (3H, s, CH_3), 3.95 (1H, br s), 4.86 (1H, d, *J* 10.0, CH), 5.27 (1H, d, *J* 10.0, CH), 6.88-6.90 (1H, m, Ar*H*), 6.95-7.01 (4H, m, Ar*H*), 7.11-7.28 (8H, m, Ar*H*), 7.38 (2H, d, *J* 7.6, Ar*H*). The enantiopurity was determined by chiral stationary phase HPLC using a Chiralcel OD column (*n*-hexane/*i*-PrOH 90:10, flow 0.8 ml/min, isocratic, λ= 251 nm, $t_{S,S}$ 20.1 min, $t_{R,R}$ 21.8 min).

(1*S*,2*S*)-1,2-Di(naphthalen-2-yl)-2-phenylamino-ethanol 22

Using procedures **A** and **B**, amino alcohol **22** was synthesised by the aminolysis of epoxide **21** (0.14 g, 0.5 mmol) with aniline **17** (45µl, 0.5 mmol) as a white solid; mp 146-148°C; $[\alpha]_D$ -123 (*c* 0.82, CH_2Cl_2); [lit.[2] 91% *ee*, $[\alpha]_D$ –133.8 (*c* 0.41, CH_2Cl_2)]; δ_H (300 MHz, $CDCl_3$) 2.90 (1H, br s), 4.76 (1H, d, *J* 6.0, CH), 5.04 (1H, d, *J* 5.8, CH), 6.52 (2H, d, *J* 8.7, Ar*H*), 6.59-6.61 (1H, m, Ar*H*), 6.98-7.03 (2H, m, Ar*H*), 7.28-7.32 (2H, m, Ar*H*), 7.37-7.43 (4H, m, Ar*H*), 7.66-7.76 (8H, m, Ar*H*). The other spectral data were also found to be identical to that reported in the literature.[1] The enantiopurity was determined by chiral stationary phase HPLC using a Chiralcel AD-H column, (*n*-hexane/*i*-PrOH 90:10, flow 1 ml/min, isocratic, λ= 230 nm, $t_{S,S}$ 30.596 min, $t_{R,R}$ 27.918 min).

General procedure for enantioselective allylation of aldehydes with allyltrichlorosilane

To a stirred mixture of the chiral bipyridine catalyst (10 mol %), diisopropylethylamine (0.35 ml, 2 mmol), tetra-*n*-butyl-ammonium iodide (0.18 g, 0.47 mmol) and aldehyde (0.4 mmol) in dichloromethane (5 ml), under nitrogen, was added allyltrichlorosilane (75 µl, 0.47 mmol) at the specified temperature. After stirring the reaction mixture, at the specified temperature and time, it was quenched with $NaHCO_3$ solution. The organic layer was separated and the aqueous layer extracted with dichloromethane (2 × 5 ml). The combined organic extract was washed with brine, dried (Na_2SO_4), and the solvent evaporated. The residue was purified by PLC (15% EtOAc in hexane).

(*R*)-(–)-1-Phenyl-but-3-en-1-ol [(*R*)-(–)-24]
From benzaldehyde **23** (*ca*. 20h, with incomplete conversion); Colourless oil, $[\alpha]_D$ +19 (*c* 1.0, $CHCl_3$); [lit.[3] (*S*) enantiomer: 84% *ee*, $[\alpha]_D$ -49 (*c* 1.5, $CHCl_3$)]; δ_H (300 MHz, $CDCl_3$,) 2.06 (1H, br s), 2.48-2.56 (2H, m), 4.77 (1H, dd, *J* = 7.7, 5.2 Hz,), 5.15-5.22 (2H, m), 5.79-5.89 (1H, m), 7.28-7.39 (5H, m). The enantiopurity was determined by chiral stationary phase HPLC using a Chiralcel OD-H column (*n*-hexane/*i*-PrOH 95:5, flow 1 ml/min, isocratic, λ=210 nm, t_S 10.067 min, t_R 10.733 min).

(*R*)-(–)-1-(4-Chloro-phenyl)-but-3-en-1-ol [(*R*)-(–)-26]
From *p*-chlorobenzaldehyde **25**; Colourless oil $[\alpha]_D$ +16 (*c* 1.5, $CHCl_3$); [lit.[4] (*S*) enantiomer: 89% *ee*, $[\alpha]_D$ -60 (*c* 1.5, $CHCl_3$)]; δ_H (300 MHz, $CDCl_3$,) 2.04 (1H, br s), 2.14 (2H, m), 4.73 (1H, m), 5.19 (2H, m), 5.76 (1H, m), 7.30 (4H, m, Ar). The enantiopurity was determined by chiral GC using a Chiral Beta dex 225 column (oven:100 °C hold 30 min ramp 2 °C/min to 170 °C hold 10 min, t_S 53.09 min, t_R 52.63 min).

(*R*)-(–)-1-(4-Methoxy-phenyl)-but-3-en-1-ol [(*R*)-(–)-28]

Obtained from *p*-anisaldehyde **27** (50 µl, 0.4 mmol) (*ca*. 20h, with incomplete conversion); Colourless oil; $[\alpha]_D$ +45 (*c* 0.96, $CHCl_3$); [lit.[3] (*S*) enantiomer: 87% *ee*, $[\alpha]_D$ -48 (*c* 1.0, $CHCl_3$)]; δ_H (300 MHz, $CDCl_3$) 2.01 (1H, br s), 2.49 (2H, t, *J* = 8.0), 3.80 (3H, s), 4.68 (1H, t, *J* = 6.5), 5.10-5.17 (2H, m), 5.74-5.84 (1H, m), 6.88 (2H, d, *J* = 8.7), 7.27 (2H, d, *J* = 8.7). The enantiopurity was determined by chiral stationary phase HPLC using a Chiralcel OD-H column, (*n*-hexane/*i*-PrOH 90:10, flow 0.75 ml/min, isocratic, λ=254 nm, t_S 6.919 min, t_R 7.857 min).

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Supplementary Material (ESI) for Organic & Biomolecular Chemistry