

Supplementary data

Experimental

General experimental methods have been previously described.¹ All non-aqueous reactions were performed under an atmosphere of nitrogen. Ether refers to diethyl ether and petrol refers to petroleum ether (b.p. 40-60 °C) unless otherwise stated. Analytical HPLC was conducted on a Dionex HPLC system with diode array detection; unless otherwise stated, the column oven was set at 24 °C. An Econosil columns (silica particle size: 10 µm) was used for analytical (4.6 × 250 mm) work, and a Chiracel OD column (4.6 × 250 mm) was used for chiral analytical HPLC; samples were calibrated against external standard samples dissolved in isopropanol. Microanalyses were carried out by staff of the Department of Chemistry using a Carlo Erba 1106 automatic analyser.

(1R*,3R*,4R*,6R*)-4,6-Diazidocyclohexane-1,3-diol³ 5

Diepoxide² **4** (200 mg, 3.57 mmol), sodium azide (2.32 g, 35.7 mmol) and ammonium chloride (1.9 g, 35.3 mmol) were dissolved in water (5 mL) and heated at reflux for 16 h. The reaction mixture was allowed to cool, then extracted with CH₂Cl₂ (3 × 50 mL), the combined organic extracts were dried (MgSO₄), filtered, evaporated under reduced pressure and recrystallised from CH₂Cl₂ to give the azide³ (489 mg, 96%) as colourless prisms, m.p. 97-98 °C (from CH₂Cl₂, lit.³ 96 °C); *R*_f 0.25 (7:3, petrol–EtOAc); (Found: C, 36.6; H, 5.20; N, 42.3; C₆H₁₀N₆O₂ requires C, 36.4; H, 5.10; N, 42.4%); $\nu_{\max}/\text{cm}^{-1}$ (thin film) 3368, 2923, and 2087; δ_{H} (300 MHz; *d*₄-MeOD) 3.71 (2H, q, *J* 5.8, 1-H and 3-H), 3.45 (2H, q, *J* 5.8, 4-H and 6-H), 1.80 (2H, t, *J* 5.8, 2-CH₂) and 1.73 (2H, t, *J* 5.8, 5-CH₂); δ_{C} (75 MHz; *d*₄-MeOD) 69.8, 63.4, 36.9 and 30.5; *m/z* (ES) 211 (100%, MNa⁺).

(1R,2R,4R,5R)-1,5-Diazido-2,4-bis-trimethylsilyloxy-cyclohexane

The diepoxide² **4** (168 mg, 3 mmol), (*S,S*)-*N-N'*-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexane-diaminochromium(III) chloride (84 mg, 0.12 mmol) and azidotrimethylsilane (1.2 mL, 9 mmol) were dissolved in ether (1 mL), after stirring for 48 h, azidotrimethylsilane (600 µL, 4.5 mmol) was added and the reaction mixture stirred for a further 16 h. The reaction

mixture was evaporated under reduced pressure to give a crude product, which was purified by flash chromatography eluting with 8:2 petrol–EtOAc + 1% Et₃N to give the *diazide* (662 mg, 70%) as a yellow oil; *R_f* 0.8 (8:2, petrol–EtOAc); $[\alpha]_D^{20} - 4.7$ (*c* 1.2 in CH₂Cl₂); $\nu_{\max}/\text{cm}^{-1}$ (thin film) 2958, 2903, 2496, 2102 and 1703; δ_{H} (500 MHz; CDCl₃) 3.70 (2H, q, *J* 5.7, 2-CH and 4-CH), 3.37 (2H, q, *J* 5.7, 1-CH and 5-CH), 1.72 (2H, t, *J* 5.7, 3-CH₂), 1.61 (2H, t, *J* 5.7, 5-CH₂) and 0.00 (18H, s, TMS); δ_{C} (75 MHz; CDCl₃) 69.7, 61.7, 36.9, 29.2 and 0.00; *m/z* (ES) 315 (100%, M–N₂⁺); (Found: M–N₂⁺ 315.1670; C₁₂H₂₇N₆O₂Si₂ requires *M–N₂*, 315.1673).

(1*R*,3*R*,4*R*,6*R*)-4,6-Diazidocyclohexane-1,3-diol *ent*-5

(1*R*,2*R*,4*R*,5*R*)-1,5-Diazido-2,4-bis-trimethylsilyloxy-cyclohexane (534 mg, 1.7 mmol) was dissolved in MeOH (2 mL), trifluoroacetic acid (2 μl) was added, and the reaction mixture stirred for 35 min. The reaction mixture was evaporated under reduced pressure to give a crude product, which was purified by flash chromatography eluting with 7:3 petrol–EtOAc to give the *diazide ent*-5 (327 mg, 97%) as colourless prisms, mp 97–98 °C (from MeOH–CH₂Cl₂, lit.³ 96 °C for the racemate); *R_f* 0.25 (7:3, petrol–EtOAc); $[\alpha]_D^{20} - 5.7$ (*c* 1.2 in CH₂Cl₂); (Found: C, 36.6; H, 5.20; N, 42.3%; C₁₄H₁₄N₂O requires C, 36.4; H, 5.10; N, 42.4%), spectroscopically identical to the racemate obtained previously.

The sample was shown to have >98% ee by chiral analytical HPLC (Chiracel OD column, 4.6 × 250 mm, detecting at 225 nm; 95:5 hexane–isopropanol; retention times 32 and 35 min).

(1*S*,3*S*,4*S*,6*R*)-4-Azido-7-oxabicyclo[4.1.0]heptan-3-ol **10**

Oxone (1.405 g, 2.286 mmol) dissolved in an aqueous solution of EDTA (4 mM, 2 mL) was added dropwise to a stirred solution of the alkene (353 mg, 2.54 mmol) dissolved in acetone (1.7 mL) and H₂O (1.7 mL) at 20 °C (Note: the temperature was regulated with a water bath). After 2 h, 20% w/v sodium sulfite (20 mL) was added cautiously and the reaction mixture extracted with CH₂Cl₂ (3 × 30 mL), dried (MgSO₄), filtered and evaporated under reduced pressure to give a 50:50 mixture of *syn* and *anti* epoxides, which were purified by HPLC (eluting with 5:95 isopropanol–hexane) to give the *title compound 10* (65.4 mg, 17%) as a

colourless oil, R_f 0.20 (9:1 petrol–EtOAc); $[\alpha]_D^{20} + 72.1$ (c 0.86 in CH_2Cl_2); $\nu_{\text{max}}/\text{cm}^{-1}$ (thin film) 3209, 2955, 2924 and 2131; δ_{H} (500 MHz; CDCl_3) 3.64 (1H, app. td, J 10.1 and 5.3, 3-H), 3.29 (1H, dt, J 10.5 and 4.8, 4-H), 3.26–3.24 (1H, m, 1-H), 3.15 (1H, d, J 4.8, 6-H), 2.60 (1H, ddd, 2J 14.8, and J 4.8 and 2.0, 5- H_a), 2.47 (1H, ddd, 2J 15.4, and J 5.3 and 3.7, 2- H_a), 2.29 (1H, s, OH), 1.95 (1H, dd, 2J 15.4 and J 10.1, 2- H_b) and 1.77 (1H, ddd, 2J 14.8, and J 10.5 and 2.0, 5- H_b); δ_{C} (75 MHz, CDCl_3) 68.5, 63.1, 53.8, 50.5, 32.6 and 29.8; m/z (EI) 155 (M^+) and 127 ($\text{M}^+ - \text{N}_2$).

The sample was shown to have 80% ee by conversion into its derivative **5** and chiral analytical HPLC.

Also obtained was (*1R,3S,4S,6S*)-4-Azido-7-oxabicyclo[4.1.0]heptan-3-ol **11**; (76 mg, 19%) as colourless plates, mp 58–61 °C (from IPA–hexane); R_f 0.20 (9:1 petrol–EtOAc); $[\alpha]_D^{20} + 44.8$ (c 0.85 in CH_2Cl_2); $\nu_{\text{max}}/\text{cm}^{-1}$ (thin film) 3210, 2955, 2924 and 2131; δ_{H} (500 MHz; CDCl_3) 3.59–3.56 (2H, m, 4-H and 3-H), 3.26 (1H, s, 6-H), 3.22 (1H, d, J 4.0, 1-H), 2.66 (1H, d, J 4.8, OH), 2.56 (1H, dd, 2J 16.1 and J 4.2, 5- H_a), 2.38 (1H, dd, 2J 15.8 and J 4.0, 2- H_a), 2.05 (1H, dd, 2J 15.8 and J 6.8, 2- H_b) and 1.96–1.90 (1H, m, 5- H_b); δ_{C} (75 MHz, CDCl_3) 68.9, 60.0, 52.1, 52.0, 30.1 and 28.3; m/z (EI) 155 (M^+) and 127 ($\text{M}^+ - \text{N}_2$).

(1R,3S,4S,6R)-4-Azido-7-oxabicyclo[4.1.0]heptan-3-O-trimethylsilane 12

Chlorotrimethylsilane (37 μL , 0.29 mmol) was added to a solution of the epoxide **10** (35.1 mg, 0.226 mmol) and DMAP (3 mg, 0.023 mmol) in Et_3N (1 mL). The reaction mixture was stirred for 15 min, then concentrated under reduced pressure to give a crude product, which was purified by flash chromatography eluting with 89:10:1 petrol–EtOAc– Et_3N to give the *silylated product* (49.5 mg, 96%) as a colourless oil; R_f 0.40 (9:1 petrol–EtOAc); $[\alpha]_D^{20} - 18.3$ (c 1.1 in CH_2Cl_2); $\nu_{\text{max}}/\text{cm}^{-1}$ (thin film) 2928, 2106 and 1751; δ_{H} (300 MHz; CDCl_3) 3.69 (1H, td, J 9.7 and 5.2, 3-H), 3.33–3.21 (2H, m, 6-H and 4-H), 3.09 (1H, app t, J 4.9, 1-H), 2.45 (1H, ddd, 2J 14.8, and J 5.4 and 2.5, 5- H_a), 2.35 (1H, ddd, 2J 15.7, and J 7.2 and 5.2, 2- H_b), 1.83–1.72 (2H, m, 5- H_b and 2- H_b) and 0.17 (9H, s, OTMS); δ_{C} (75 MHz, CDCl_3) 69.8, 62.1,

53.6, 50.3, 33.8, 29.8 and 0.0; m/z (ES) 245 (100%, MNH_4^+); (Found: MNH_4^+ 245.1428; $\text{C}_9\text{H}_{17}\text{N}_3\text{O}_2\text{Si}$ requires MH , 245.1428).

1. R. Hodgson, T. Majid and A. Nelson, *J. Chem. Perkin Trans. 1*, 2002, 1444.
2. J. Rudolph, K. L. Reddy, J. P. Chiang, and K. B. Sharpless, *J. Am. Chem. Soc.* 1997, **119**, 6189.
3. H. C. Kolb, M. G. Finn, and K. B. Sharpless, *Angew. Chem. Int. Ed.* 2001, **40**, 2004.

Figure S1: 500 MHz ^1H NMR spectra of the enantioselective ring-opening of the epoxide **4** as a function of time (see entry 2, Table 1; and Scheme 2)

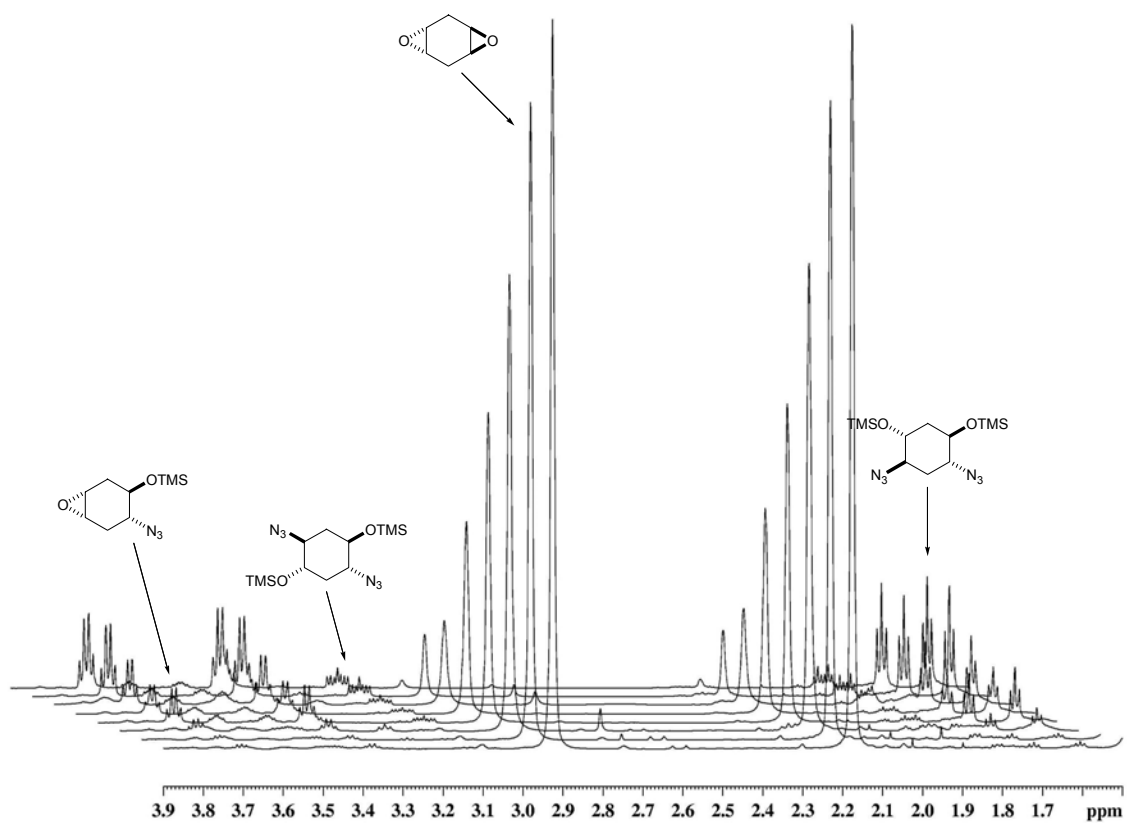


Figure S2: Stacked 500 MHz ^1H NMR spectra comparing the fate of the enantiomerically enriched epoxide **12** (which had 80% ee) in the ring-opening catalysed by (*R,R*)-**7** (bottom) and (*S,S*)-**7** (top) (see Table 2). In each case, the epoxide **4** has been completely consumed.

