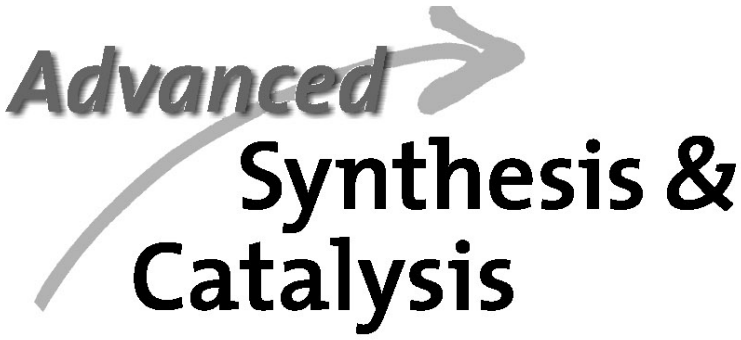

Supporting Information

Biocatalytic Asymmetric Dihydroxylation of Conjugated Mono- and Poly-Alkenes to Yield Enantiopure Cyclic *cis*-Diols

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Supporting Information

^{1}H NMR spectra were recorded at 300MHz (Bruker Avance DPX-300) and at 500MHz (Bruker Avance DRX-500) in $CDCl_3$ solvent. Chemical shifts (δ) are reported in ppm relative to $SiMe_4$. Mass spectra were recorded at 70eV on a VG Autospec Mass Spectrometer. Accurate molecular weights were determined by the peak matching method with perfluorokerosene as standard. Elemental microanalyses were obtained on a Perkin-Elmer 2400 CHN microanalyser. Optical rotation ($[\alpha]_D$) measurements were carried out with a Perkin-Elmer 214 polarimeter. Flash column chromatography and PLC were preformed on Merck Kieselgel type (250-400 mesh) and PF $_{254/366}$ respectively. Circular dichroism (CD) spectra were recorded using a JASCO J-720 model in acetonitrile solvent. Melting points are uncorrected.

Commercially available (Aldrich Chemical Co) compounds included substrates **1a-1g**, **14a-f** and products **3a**, **3e**, **5**, and **12**. Substrates **9, 14h-i** were synthesised according to the literature methods[34,-36] and substrate **14g** was prepared by a similar route.[35]

5-(1'-Ethylpropylidene)-1,3-cyclopentadiene 14g: Oil (4.98 g, 84%, yield); HRMS: *m/z* $(M)^+$ = 134.1102, calcd. for $C_{10}H_{14}$: 134.1096.^{1}H NMR; d = 1.22 (6H, t, *J* 7.5, 2x CH_2CH_3), 2.62 (4H, q, *J* 7.5, 2xCH_2CH_3), 6.51-6.57 (4H, m, 1-H, 2-H, 3-H, 4-H); ^{13}C NMR (125MHz): d =14.59, 26.90, 120.38, 130.46, 132.07, 161.08; MS: *m/z* (%) = 134 (100, M^+), 119 (29), 105 (66).

Biotransformation of substituted styrenes 1a-g by *P. putida* UV4 (TDO) and *P. putida* NCIMB 8859 (NDO): Biotransformations of substrates **1a-1g** were carried out using whole cells of *P. putida* UV4 (TDO) and *P. putida* NCIMB 8859 (NDO) employing procedures similar to those reported earlier.[13, 29,37] The aqueous medium, containing the mixture of bioproducts, was repeatedly extracted with EtOAc. The extract was dried ($MgSO_4$), concentrated under reduced pressure, and the crude mixture of bioproducts separated by multielution PLC. The alkene 1,2-diol metabolite was generally less polar (high R_f) than the corresponding arene *cis*-dihydrodiol (low R_f).

Styrene 1a (with **TDO**)

***cis*-(1*S*, 2*R*)-1,2-Dihydroxy-3-vinylcyclohexa-3,5-diene 2a:** Recrystallized from $CHCl_3$ (125 mg, 32% yield), mp 53-54 °C; high R_f (20% ethyl acetate hexane); (lit.[20] 54-55 °C); $[a]_D^{20}$: + 113 (*c* 0.49, MeOH) (lit.[20] +115); CD: ?/nm 235 (? e -8,60), 282 (?e 3.246); > 98% ee (from MEPBA boronates).

(1*R*)-1-Phenyl-1,2-dihydroxyethane 3a: (12 mg, 3% yield); $[a]_D^{20}$: -60 (*c* 0.85, $CHCl_3$); 88% ee (from MTPA esters).

Styrene 1a, (with **NDO)**

(1*R*)-1-phenyl-1,2-dihydroxyethane 3a: (240 mg, 60% yield); 80% ee (from MTPA esters).

3-Fluorostyrene 1b (with **TDO)**

(1*R*)-1-(3'-Fluorophenyl)-1,2-dihydroxyethane 3b: Recrystallized from MeOH (56 mg, 22% yield), mp 62-63 °C; R_f 0.30 (15% EtOAc in hexane); $[a]_D^{20}$: -33 (*c* 0.64, $CHCl_3$); anal. calcd. for $C_8H_9FO_2$: C, 61.5, H, 5.8; found: C, 61.7, H, 6.1; ^{1}H NMR: d = 3.63 (1H, dd, $J_{2a,2b}$ = 11.3 Hz, $J_{2a,1}$ = 8.0 Hz, 2-H_A), 3.77 (1H, dd, $J_{2b,2a}$ = 11.3 Hz, $J_{2b,1}$ = 3.4 Hz, 2-H_B), 4.82 (1H, dd, $J_{1,2a}$ = 8.0 Hz, $J_{1,2b}$ = 3.4 Hz, 1-H), 6.99-7.41 (4H, m, ArH); MS: *m/z* (%) = 156 (55, M^+), 138 (100); 62% ee (from MTPA esters).

***cis*-(1*S*, 2*R*)-1,2-Dihydroxy-5-fluoro-3-vinylcyclohexa-3,5-diene 2b:** Recrystallized from Et_2O/ hexane (700 mg, 27% yield), mp 43-44 °C; R_f 0.22 (15% EtOAc in hexane); $[a]_D^{20}$: +28° (*c* 0.5, MeOH); anal. calcd. for $C_8H_9FO_2$: C, 61.5, H, 5.8;

found: C, 61.1, H, 5.9; ^{1}H NMR: d = 4.42 (1H, d, $J_{2,1}$ = 5.8 Hz, 2-H), 4.56 (1H, m, 1-H), 5.33 (1H, d, J_{cis} = 11.0 Hz, CH=CH_2), 5.65 (1H, d, J_{trans} = 17.6 Hz, CH=CH_2), 5.91 (2H, m, 4-H, 6-H), 6.42 (1H, dd, J_{cis} = 11.0 Hz, J_{trans} = 17.6 Hz, CH=CH_2); MS: *m/z* (%) = 156 (32, M^+), 138 (60), 97 (100); > 98% ee, (from MEPBA boronates).

3-Fluorostyrene 1b (with **NDO)**

(1*R*)-3b: (36 mg, 14% yield); 62% ee (from MTPA esters).

3-Chlorostyrene 1c (with **TDO)**

(1*R*)-1-(3'-Chlorophenyl)-1,2-dihydroxyethane 3c: Recrystallized from $CHCl_3$/hexane (78 mg, 14% yield), mp 102-104 °C; R_f 0.24 (20% EtOAc in hexane); $[a]_D^{20}$: -11.0 (*c* 0.94, EtOH) (lit.[14] +24.1 for 1*S* -**3c**); 42% ee (from MTPA esters).

***cis*-(1*S*, 2*R*)-1,2-Dihydroxy-5-chloro-3-vinylcyclohexa-3,5-diene 2c:** Oil (11 mg, 2% yield); R_f 0.16 (20% EtOAc in hexane); $[a]_D^{20}$: +56 (*c* 0.81, EtOH); HRMS: *m*/*z* $(M)^+$ = 172.0287, calcd. for $C_8H_9ClO_2$: 172.0291; ^{1}H NMR: d = 4.38 (1H, d, $J_{2,1}$ = 5.9 Hz, 2-H), 4.49 (1H, m, 1-H), 5.31 (1H, d, J_{cis} = 10.8 Hz, CH=CH_2), 5.59 (1H, d, J_{trans} = 17.6 Hz, CH=CH_2), 5.89 (2H, m, 4-H, 6-H), 6.37 (1H, dd, J_{cis} = 10.8 Hz, J_{trans} = 17.6 Hz, C*H*=CH_2); MS: *m/z* (%) = 172 (38, M^+), 154 (69), 91 (100). >98% ee (from MEPBA boronates).

3-Chlorostyrene 1c (with **NDO)**

(1*R*)-3c: (100 mg, 18% yield); 56% ee (from MTPA esters).

3-Methylstyrene 1d (with **TDO)**

(1*R*)-1-(3'-Methylphenyl)-1,2-dihydroxyethane 3d: Recrystallized from $CHCl_3$/hexane (26 mg, 8% yield), mp 111-112 °C; R_f 0.38 (15% EtOAc in hexane); $[a]_D^{20}$: -62 (*c* 0.58, $CHCl_3$); anal. calcd. for $C_9H_{12}O_2$: C, 71.0; H, 8.0; found: C, 71.0, H, 8.3; ^{1}H NMR: d = 2.32 (3H, s, CH_3), 3.58 (1H, dd, $J_{2a,2b}$ = 11.0 Hz, $J_{2a,1}$ = 8.0 Hz, 2-H_A), 3.64 (1H, dd, $J_{2b,2a}$ = 10.9 Hz, $J_{2b,1}$ = 4.2 Hz, 2-H_B), 4.73 (1H, dd, $J_{1,2a}$ = 8.0Hz., $J_{1,2b}$ = 4.0 Hz, 1-H), 7.08-7.21 (4H, m, ArH); MS: *m/z* (%) = 152 (100, M^+), 134 (100); 48% ee (from MTPA esters).

***cis*-(1*S*, 2*R*)-1,2-Dihydroxy-5-methyl-3-vinylcyclohexa-3,5-diene 2d: (**71 mg, 22% yield), mp 34-36 °C; R_f 0.30 (15% EtOAc in hexane); $[a]_D^{20}$: +60 (*c* 0.48, MeOH); anal. calcd. for $C_9H_{12}O_2$: C, 71.0, H, 8.0, found: C, 71.4, H, 8.1; ^{1}H NMR: d = 2.01

(3H, s, Me), 4.40 (1H, d, $J_{2,1}$ = 5.6 Hz, 2-H), 4.53 (1H, m, 1-H), 5.30 (1H, d, J_{cis} = 11.0 Hz, CH=CH_2), 5.63 (1H, d, J_{trans} = 16.8 Hz, CH=CH_2), 5.88 (2H, m, 4-H, 6-H), 6.44 (1H, dd, J_{cis} = 11.0 Hz, J_{trans} = 16.8 Hz, C*H*=CH_2); MS: *m/z* (%) = 152 (28, M^+), 134 (42), 91(100); >98% ee (from MEPBA boronates).

3-Methylstyrene 1d (with **NDO)**

(1*R*)-3d: (40mg, 12% yield); 56 % ee (from MTPA esters).

***a*-Methylstyrene 1e (**with **TDO)**

***cis*-(1*S*, 2*R*)-1,2-Dihydroxy-isopropenylcyclohexa-3,5-diene 2e:** Recrystallized from $CHCl_3$/hexane (62 mg, 24% yield), mp. 78-80 °C; $[a]_D^{20}$: +87 (*c* 0.86, MeOH); anal. calcd. for $C_9H_{12}O_2$: C, 71.0; H, 8.0, found: C, 71.2, H, 7.9; ^{1}H NMR: d = 1.95 (3 H, s, CH_3), 4.40 (1H, d, $J_{2,1}$ = 5.6 Hz, 2-H), 4.51 (1H, m, 1-H), 5.14 (1H, br s, C=CH_2), 5.37 (1H, br s, C=CH_2), 5.86 (1H, d, $J_{4,5}$ = 7.1 Hz, 4-H), 6.05 (2H, m, 5-H, 6H); MS: *m/z* (%) = 152 (68, M^+), 134 (42), 91(100); CD: ?/nm 218 (? e -9.487), 281 (?e 2.377); >98% ee (from MEPBA boronates).

***a*-Methylstyrene 1e (**with **NDO)**

1-Hydroxy-2-phenylprop-2-ene 4: Oil (8 mg, 12% yield); R_f 0.63 (5% MeOH in $CHCl_3$); ^{1}H NMR: d = 4.53 (2H, s, -CH_2OH), 5.34 (1H, d, $J_{3a,3b}$ = 1.2 Hz, 3-H_A), 5.47 (1H, d, $J_{3b,3a}$ = 1.1 Hz, 3-H_B), 7.21-7.42 (5H, m, ArH).[38]

(1*R*)-1,2-Dihydroxy-2-phenylpropane 3e: (17 mg, 20% yield), R_f 0.30 (5% MeOH in $CHCl_3$); $[a]_D^{20}$: -1.9 (*c* 0.42, EtOH) (lit.[39] -4.3); 46 % ee (from MTPA esters).

***cis*-ß-Methylstyrene 1f (**with **TDO)**

***cis*-(1*S*, 2*R*)-1,2-Dihydroxy-3-(*cis*-1'-propenyl)cyclohexa-3 5-diene 2f:**

Recrystallized from Et_2O/hexane (108 mg, 42% yield), mp 112-115 °C; $[a]_D^{20}$: + 128 (*c* 0.36, MeOH); anal. calcd. for $C_9H_{12}O_2$: C, 71.0, H 8.0, found: C, 71.4, H, 8.1; ^{1}H NMR: d = 1.78 (3H, d, $J_{Me,2'}$ = 7.3 Hz, CH_3), 4.38 (1H, d, $J_{2,1}$ = 5.9 Hz, 2-H), 4.48 (1H, m, 1-H), 5.80 (1H, d, $J_{4,5}$ = 7.3 Hz, 4-H), 5.83 (1H, m, 2'-H), 6.01 (2H, m, 5-H, 6-H), 6.20 (1H, d, $J_{1',2'}$ = 10.7 Hz, 1'-H); MS: *m/z* (%) = 152 (56, M^+), 134 (48),

91(100);); CD: ?/nm 217.5 (? *e* -5.546), 280 (? *e* 1.446); >98% ee (from MEPBA boronates).

***cis*-ß-Methylstyrene 1f (**with **NDO)**

***erythro*-(1*R*, 2*S*)-1,2-Dihydroxy-1-phenyl propane**, **3f:** Recrystallized from hexane (20 mg, 15% yield), mp. 91-92 °C (lit.[40] 89-90 °C); $[a]_D^{20}$: -33 (*c* 0.78, $CHCl_3$) (lit.[40] -35); HRMS: *m/z* $(M)^+$ = 152.0834, calcd. for $C_9H_{10}O_2$: 152. 0837; ^{1}H NMR: d = 1.01 (3H, d, $J_{Me,2}$ = 6.2 Hz, CH_3), 3.96 (1H, m, 2-H), 4.62 (1H, d, $J_{1,2}$ = 4.0 Hz, 1-H), 7.16-7.32 (5H, m, ArH); MS: *m/z* (%) = 152 (64, M^+), 134, (74), 108(100); 82% ee (from MTPA esters).

***trans*-ß-Methylstyrene 1g (**with **TDO)**

***cis*-(1*S*, 2*R*)-1 2-Dihydroxy-3-(*trans*-1'-propenyl)cyclohexa-3,5-diene 2g:**

Recrystallized from $CHCl_3$/EtO_2 (95 mg, 37% yield); mp 93-95 °C; $[a]_D^{20}$: +78 (*c* 0.93, MeOH); anal. calcd. for $C_9H_{12}O_2$: C, 71.0, H, 8.0, found: C, 71.1, H, 8.2; ^{1}H NMR: d = 1.86 (3H, d, $J_{Me,2'}$ = 5.9 Hz, CH_3), 4.31 (1H, d, $J_{2,1}$ = 5.7 Hz, 2-H), 4.47 (1H, m, 1-H), 5.76 (1H, d, $J_{4,5}$ = 6.6 Hz, 4-H), 5.80 (1H, m, 2'-H), 6.08 (2H, m, 5-H, 6-H), 6.11 (1 H, d, $J_{1,2'}$ = 16.9 Hz, 1'-H); MS: *m/z* (%) = 152 (72, M^+), 134 (54), 91(100); CD: ?/nm 235 (? e -8.596), 282 (? e 3.257); >98% ee (from MEPBA boronates).

***trans*-ß-Methylstyrene 1g (**with **NDO)**

***trans*-Cinnamic acid 5:** (65 mg, 52% yield); identical to an authentic sample.

Biotransformation of 2-methyl-1*H*-indene 9 by *P. putida* UV4 (TDO) and *P. putida* NCIMB 8859 (NDO)

2-Methyl-1*H*-indene 9 (with **TDO)**

(*R*)-2-Methyl-1*H*-inden-1-ol 11: (5 mg, 1% yield), R_f 0.6 (50% EtOAc in hexane); $[a]_D^{20}$: -101 (*c* 0.25, $CHCl_3$); HRMS: *m/z* $(M)^+$ = 146.0733, calcd. for $C_{10}H_{10}O$: 146.0732; ^{1}H NMR: d = 1.51 (1H, d, $J_{OH,1}$ = 8.4 Hz, OH), 2.07 (3H, s, CH_3), 4.85 (1H, d, $J_{1,OH}$ = 8.4 Hz, 1-H), 6.34 (1H, s, 3-H),7.44-7.46 (4H, m, Ar-H);); MS: *m/z*

(%) = 146 (100, M^+), 131 (91); CD: ?/nm 289.2 (? e -1.06), 227.1 (? e 1.24), 207.8 (? e -1.01); >98% ee (from MTPA esters).

(*R*/*S*)-2-methyl-1-indanone 12: (325 mg, 57% yield), R_f 0.7 (50% EtOAc in hexane); $[a]_D^{20}$: 0 (*c* 0.25, $CHCl_3$) (lit.[41] +42); ^{1}H NMR: d = 1.30 (3H, d, $J_{Me,2}$ = 7.3 Hz, CH_3), 2.60-2.72 (2H, m, 3-H), 3.36 (1H, m, 2-H), 7.37-7.80 (4H, m, Ar-H); MS: *m/z* (%) = 146 (75, M^+), 131 (100).

(1*S*,2*R*)-1,2-Dihydroxy-2-methylindan 10: (170 mg, 26% yield), mp 93-94 ^{o}C; R_f 0.3 (50% EtOAc in hexane); $[a]_D^{20}$: -23 (*c* 0.57, $CHCl_3$); anal. calcd. for $C_{10}H_{12}O_2$: C, 73.2, H, 7.4, found: C, 72.8 H, 7.2; ^{1}H NMR: d = 1.43 (3H, s, CH_3), 2.95 (2H, ddd, $J_{3,OH}$ = 12.0 Hz, $J_{3,3'}$ = 16.0 Hz, $J_{3',1}$ = 5.3 Hz, 3-H, 3'-H), 4.64 (1H, d, $J_{1,3'}$ = 5.3 Hz, 1-H), 7.18-7.37 (4H, m, Ar-H);); MS: *m/z* (%) = 164 (43, M^+), 104 (100); CD: ?/nm 289.2 (? e -1.06), 227.1 (? e 1.24), 207.8 (? e -1.01); >98 % ee (from di-MTPA esters).

2-Methyl-1*H*-indene 9 (with **NDO)**

(*S*)-2-Methyl 1*H*-inden-1-ol 11: Oil (15 mg, 67% yield); R_f 0.6 (50% EtOAc in hexane); $[a]_D^{20}$: +107 (*c* 0.37, $CHCl_3$); >98% ee (from MTPA esters).

2-Hydroxymethyl-1*H*-indene 13: Oil (10 mg, 5% yield), R_f 0.4 (50% EtOAc in hexane);: HRMS: *m/z* $(M)^+$ = M^+ 146.0726, calcd. for $C_{10}H_{10}O$: 146.0732; ^{1}H NMR: d = 1.70 (1H, br s, OH), 3.41 (2H, s, 1-H, 1-H'), 4.57 (2H, br s, CH_2OH), 6.74 (1H, s, 3-H), 7.14 -7.43 (4H, m, Ar-H); MS: *m/z* (%) = 146 (47, M^+), 115 (100).

Biotransformation of conjugated dienes 14a-d and trienes 14e-i by *P. putida* UV4 (TDO) and *P. putida* NCIMB 8859 (NDO)

Cyclopentadiene 14a (with **TDO)**

(1*R*,2*S*)-1,2-Dihydroxycyclopent-3-ene 15a: Oil (3.2 g, 32% yield); $[a]_D^{20}$: +13 (*c* 0.4, $CHCl_3$) (lit.[32] + 26, 38% ee); ^{1}H NMR: d = 2.34 (1H, m, 5-H), 2.59 (1H, m, 5-H'), 4.30 (1H, m, 1-H), 4.57 (1H, m, 2-H), 5.78 (1H, m, 3-H), 5.92 (1H, m, 4-H); ^{13}C NMR (125MHz): d = 39.23, 70.57, 75.69, 131.39, 132.89; MS: *m/z* (%) = 100 (2, M^+), 82 (80), 39 (100); 20 % ee (from MEPBA boronates).

Cyclohexa-1,3-diene 14b (with **TDO)**

The mixture of bioproducts, (1*R*,2*S*)-1,2-dihydroxycyclohex-3-ene **15b** and *cis*-1,2-dihydroxycyclohexa-3,5-diene **16**, could not be separated by chromatographic methods. *cis*-Dihydrodiol **16** (10% yield) was isolated (PLC) as a 4-phenyl-1,2,4-triazoline-3,5-dione cyclodduct and identified by comparison with an authentic sample.

(1*R*,2*S*)-1,2-Dihydroxycyclohex-3-ene 15b: (25 mg, 12% yield), $[a]_D^{20}$: + 107 (*c* 0.5, $CHCl_3$) (lit.[32] + 39, 37% ee.); ^{1}H NMR: d = 1.76 (2H, m, H-5/H-5'), 2.08 (1H, m, 6-H), 2.19 (1H, m, 6'-H), 3.83 (1H, m, 1-H), 4.13 (1H, m, 2-H), 5.74 (1H, m, 4-H), 5.93 (1H, m, 3-H);); ^{13}C NMR (125MHz): d = 23.52, 25.92, 66.53, 68.86, 126.99, 131.43; MS: *m/z* (%) = 114(6, M^+), 86 (37), 70(100); > 98% ee (from di-MTPA esters).

Cyclohexa-1,3-diene 14b (with **NDO)**

(1*R*,2*S*)-1,2-Dihydroxycyclohex-3-ene 15b: (8 mg, 8% yield); > 98% ee (from di-MTPA esters).

1,3-Cycloheptadiene 14c (with **TDO)**

(1*R*,2*S*)-1,2-Dihydroxycyclohept-3-ene 15c: (550 mg, 20% yield), $[a]_D^{20}$: +59 (*c* 0.6, $CHCl_3$) (lit.[32] +12.9, 21% ee); ^{1}H NMR: d = 1.51 (1H, m, 7-H), 1.62 (1H, m,7'-H), 1.77 (1H, m, 6-H), 2.05 (2H, m, 5-H and 6'-H), 2.20 (1H, m, 5'-H), 3.93 (1H, d, $J_{1,2}$ = 5.9 Hz, 1-H), 4.31 (1H, m, 2-H), 5.34 (1H, m,4-H), 5.90 (1H, m, 3-H); MS: *m/z* (%) = 128 (4, M^+), 110(60), 81(90), 55(100); > 98% ee (from di-MTPA esters).

1,3-Cycloheptadiene 14c (with **NDO)**

(1*R*,2*S*)-1,2-Dihydroxycyclohept-3-ene 15c: (480 mg, 24% yield); > 98% ee (from di-MTPA esters).

1,3-Cyclooctadiene 14d (with **TDO)**

(1*R*,2*S*)-1,2-Dihydroxycyclooct-3-ene 15d: (1.1 g, 4%); $[a]_D^{20}$: -19 (*c* 0.7, $CHCl_3$) (lit.[32] +1.4, 21% ee); ^{1}H NMR: d = 1.25-1.90 (6H, m, 8-H, 8'-H, 7-H, 7'-H, 6-H, 6'-

H), 2.11-2.32 (2H, m, 5-H, 5-H'), 3.96(1H, m, 1-H), 4.64 (1H, ddd, $J_{2,1}$ = 3.10 Hz, $J_{2,3}$ = 7.4 Hz, $J_{2,4}$ = 1.56 Hz, 2-H), 5.25 (1H, ddd, $J_{3,2}$ = 7.4 Hz, $J_{3,4}$ = 10.9 Hz, $J_{3,1}$ = 1.1 Hz, 3-H), 5.82(1H, m, 4-H); MS: *m/z* (%) = 142(10, M^+), 124(55), 81(85), 57(100); > 98% ee (from di-MTPA esters).

1,3-Cyclooctadiene 14d (with **NDO)**

(1*R*,2*S*)-1,2-Dihydroxycyclooct-3-ene 15d: (8 mg, 4%); > 98% ee (from di-MTPA esters).

Cycloheptatriene 14e (with **TDO)**

(1*R*,2*S*)-1,2-Dihydroxycyclohepta-3,5-diene 15e: (60 mg, 29% yield); $[a]_D^{20}$: + 21 (*c* 0.5, $CHCl_3$) (lit.[32] + 6.4, 24% ee); ^{1}H NMR: d = 2.46 (1H, m, 7-H), 2.58 (1H, m, 7'-H), 4.05 (1H, m, 1-H), 4.38 (1H, m, 2-H), 5.67-5.93 (4H, m, 3-H, 4-H, 5-H, 6-H); ^{13}C NMR (125MHz): d = 33.82, 73.03, 125.31, 125.62, 129.98, 130.86; MS: *m/z* (%) = 126 (3, M^+), 108 (22), 79 (100); > 98% ee (from di-MTPA esters). *cis*-Diol **15e** could only be separated, form the isomeric bioproduct, *cis*-1,2-dihydroxycyclohepta-3,6-diene **15e',** as the 4-phenyl-1,2,4-triazoline-3,5-dione cycloadduct. The experimental data recorded for diol **15e** was, thus, collected from: (i) the isomeric mixture of diols (ii) the di-MTPA ester of the cycloadduct and (iii) an enantiopure sample of diol **15e** obtained using NDO.

***cis*-1,2-Dihydroxycyclohepta-3,6-diene 15e':** (30 mg, 15% yield); ^{1}H NMR: d = 2.85 (1H, dt, $J_{5,5'}$ = 20.7 Hz, $J_{5,4}$ = 5.7 Hz, 5-H), 2.93 (1H, m, 5'-H), 4.42 (2H, d, $J_{2,3}$ = 2.8 Hz, H-1/H-2), 5.75 (2H, dd, $J_{3,2}$ = 2.8 Hz, $J_{3,4}$ = 11.6 Hz, 3-H), 5.83 (2H, ddd, $J_{4,3}$ = 11.6 Hz, $J_{4,5}$ = 5.7 Hz, $J_{4,5'}$ = 3.7 Hz, 4-H, 6-H); MS: *m/z* (%) = 126 (4, M^+), 108 (21), 79 (100).

Cycloheptatriene 14e (with **NDO)**

(1*R*,2*S*)-1,2-Dihydroxycyclohepta-3,5-diene 15e: (48 mg, 24% yield); > 98% ee (from di-MTPA esters).

5-(1'-Methylethylidene)-1,3-cyclopentadiene 14f (with **TDO)**

(1*R*,2*S*)-5-(1'-Methylethylidene)-3-cyclopentene-1,2-diol 15f: (250 mg, 19% yield); $[a]_D^{20}$: + 103 (*c* 1.0, $CHCl_3$) (lit.[32] + 27.7; 30% ee); ^{1}H NMR: d = 1.81, 1.92 (3H each, s, 2xCH_3), 4.64 (1H, d, $J_{3,4}$ = 6.0 Hz, 2-H), 4.69 (1H, d, $J_{4,3}$ = 6.0 Hz, 1-H), 5.88 (1H, d, $J_{4,3}$ = 5.8 Hz, 4-H), 6.48 (1H, dd, $J_{3,4}$ = 5.8 Hz, $J_{3,2}$ = 1.5 Hz, 3-H); ^{13}C NMR (125MHz): d = 20.95, 21.00, 69.86, 75.24, 130.10, 132.17, 133.81, 139.13; MS: *m/z* (%) = 140 (64, M^+), 122 (42), 79 (100); > 98% ee (from di-MTPA esters).

5-(1'-Methylethylidene)-1,3-cyclopentadiene 14f (with **NDO)**

(1*R*,2*S*)-5-(1'-Methylethylidene)-3-cyclopentene-1,2-diol 15f: (14 mg, 7% yield); > 98% ee (from di-MTPA esters).

5-(1'-Ethylpropylidene)-1,3-cyclopentadiene 14g (with **TDO**)

(1*R*,2*S*)-5-(1'-Ethylpropylidene)-3-cyclopentene-1,2-diol 15g: Recrystallized from EtOAc/hexane (88 mg, 7% yield), mp 55-57 ºC; $[a]_D^{20}$: + 139 (*c* 0.5, $CHCl_3$); HRMS: *m/z* $(M)^+$ = 168.1151, calcd. for $C_{10}H_{16}O_2$: 168.1150; ^{1}H NMR: d = 1.01 (3H, t, $J_{5,6}$ = 7.7 Hz, CH_2CH_3), 1.07 (3H, t, $J_{8,7}$ = 7.6 Hz, CH_2CH_3), 2.13-2.23 (2H, m, CH_2CH_3), 2.29-2.35 (2H, m, CH_2CH_3), 4.65-4.70 (2H, m, 1-H, 2-H), 5.90 (1H, dd, $J_{3,4}$ = 6.0 Hz, $J_{3,2}$ = 2.0 Hz, 3-H), 6.48 (1H, d, $J_{4,3}$ = 6.0 Hz, 4-H); ^{13}C NMR (125MHz): d = 13.47, 13.59, 24.72, 25.25, 69.62, 75.15, 131.96, 134.28, 138.43, 141.89; MS: *m/z* (%) = 168 (57, M^+), 150 (72), 139 (64), 135 (59), 121 (100); > 98% ee (from di-MTPA esters).

1*R*,2*S*)-5-(1'-Methylethylidene)-3-cyclopentene-1,2-(1'*S*)-dicamphanate 17: Diol **15f** (25 mg, 0.18 mmol) was reacted with (-)-(1*S*)-camphanic chloride (87 mg, 0.4 mmol) in dry pyridine solution (0.3 cm^3). After stirring the reaction mixture at room temperature (12 h), pyridine was removed under reduced pressure. The residue obtained was purified by PLC (40% EtOAc in hexane; R_f 0.4) to give the dicamphanate **17** as white needles from $CHCl_3$/hexane (75 mg, 84%), mp 182-183 ºC; $[a]_D^{20}$: + 163 (*c* 0.43, $CHCl_3$); anal. calcd. for $C_{28}H_{36}O_8$: C, 67.2, H, 7.3, found: C, 66.8, H 7.0; ^{1}H NMR: d = 0.93, 0.97, 1.02, 1.06, 1.09, 1.094 (3H each, s, 6xCH_3), 1.81 and 1.87 (3H each, s, $C(CH_3)_2$), 1.70-2.45 (8H, m, 2 x camphanic-H), 5.86 (1H, d, $J_{3,4}$ = 5.8 Hz, 3-H), 6.01 (2H, s, 1-H, 2-H), 6.63 (1H, d, $J_{4,3}$ = 5.8 Hz, 4-H).

Crystal data for 17: $C_{28}H_{36}O_8$, M_r = 500.6, orthorhombic, a = 6.2750(5), b = 17.6613(16), c = 23.480(2) Å, U = 2602.2(4) Å^3, T = 293 K, *Mo-Ka* radiation, l = 0.71069 Å, space group $P2_12_12_1$, Z = 4, $F(000)$ = 1072, D_x = 1.278 g cm^{-3}, m = 0.093 mm^{-1}, 0.35 x 0.20 x 0.04 mm, Bruker CCD area detector diffractometer, f and w scan, $2.9 < 2\theta < 57.1^o$, measured/independent reflections: 29559/5959, direct methods solution, full matrix least squares refinement on F_o^2, anisotropic displacement parameters for non-hydrogen atoms, hydrogens located in difference Fourier but included at positions determined by the geometry of the molecule using the riding model, with isotropic vibration parameters, $R1$ = 0.047 for 3009 data with $F_o > 4\sigma(F_o)$, 334 parameters, $wR2$ = 0.126 (all data), GoF = 0.85, $Dr_{min,max}$ = -0.20/0.20 e Å^{-3}. Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 260441. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: (internat.) + 44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

5-Cyclopentyliden-1,3-cyclopentadiene, 14h (with **TDO)**

(**1*R*,2*S*)-5-Cyclopentyliden-3-cyclopentene-1,2-diol 15h:** Recrystallized from EtOAc/ hexane (60 mg, 5% yield), mp 58-60 ºC; $[a]_D^{20}$: +122 (*c* 0.2, $CHCl_3$); HRMS: *m/z* $(M)^+$ = 166.0999, calcd. for $C_{10}H_{14}O_2$: 166.0994; ^{1}H NMR: d = 1.67-1.74 (4H, m, 2x3'-H, 2x4'-H), 2.34-2.42 (4H, m, 2x2'-H, 2x5'-H) 4.57 (1H, d, $J_{2,1}$ = 5.85 Hz, 2-H), 4.70 (1H, d, $J_{1,2}$ = 5.8 Hz, 1-H), 5.88 (1H, d, $J_{4,3}$ = 5.1 Hz, 4-H), 6.35 (1H, dd, $J_{3,2}$ = 1.5 Hz, $J_{3,4}$ = 5.1 Hz, 3-H); ^{13}C NMR (125MHz): d = 26.30, 26.55, 30.64, 31.21, 70.91, 75.20, 133.17, 133.41, 135.14, 141.41; MS: *m/z* (%) = 166 (66, M^+), 148 (71), 148 (100), 120 (71), 105 (70); > 98% ee (from di-MTPA esters).

5-Cyclohexyliden-1,3-cyclopentadiene 14i (with **TDO)**

(1*R*,2*S*)-5-Cyclohexyliden-3-cyclopentene-1,2-diol 15i: (61 mg, 5% yield); $[a]_D^{20}$: +114 (*c* 0.5, $CHCl_3$); HRMS: *m/z* $(M)^+$ = 180.1155, calcd. for $C_{11}H_{16}O_2$: 180.1150; ^{1}H NMR: d = 1.60 (6H, m, 2x3'-H, 2x4'-H, 2x5'-H), 2.25-2.27 (2H, m, 2x6'-H), 2.33-2.43 (2H, m, 2x2'-H), 4.68 (1H, d, $J_{2,1}$ = 6.1 Hz, 2-H), 4.70 (1H, d, $J_{1,2}$ = 6.1 Hz, 1-H), 5.89 (1H, d, $J_{4,3}$ = 6.0 Hz, 4-H), 6.51 (1H, dd, $J_{3,4}$ = 6.0 Hz, $J_{3,2}$ = 1.4 Hz, 3-H); ^{13}C

NMR (125MHz): d = 26.11, 27.98, 29.21, 31.51, 31.65, 69.22, 75.04, 131.52, 134.06, 136.30, 138.44; MS: *m/z* (%) = 180 (37, M^+), 162 (100), 133 (42), 107 (46), 91 (84); > 98% ee (from di-MTPA esters).

Application of *cis*-(1*R*,2*S*)-5-(1'-methylethylidene)-3-cyclopentene-1,2-diol 15f in the synthesis of (2*S*,3*S*,4*S*,5*S*)-2,3:4,5-*bis*-(*iso*-propylidenedioxy) cyclopentanone 21

(i)(3a*R*,6a*S*)-2,2-Dimethyl-4-(1-methylethylidene)-4,6a-dihydro-3a*H*-cyclopenta[*d*][1,3]dioxole 18: A suspension of *cis*-(1*R*,2*S*)-5-(1'-methylethylidene)-3-cyclopentene-1,2-diol **15f** (1.5 g, 10.7 mmol) in 2,2'-dimethoxypropane (25 cm^3) containing a trace of *p*-toluenesulfonic acid was stirred at room temperature (3 h).The reaction mixture was evaporated, the residue extracted (Et_2O), the extract washed (aq. $NaHCO_3$ solution), dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified (PLC) to give acetonide **18** as oil (1.83 g, 95% yield); $[a]_D^{20}$: +219 (*c* 1.1, $CHCl_3$); HRMS: *m/z* $(M)^+$ = 180.1150, calcd. for $C_{11}H_{16}O_2$: 180.1150; ^{1}H NMR: d = 1.40, 1.41 (3H each, s, 2xCH_3), 1.83, 1.93 (3H each, s, C(CH_3)$_2$), 5.06 (1H, d, $J_{6a,3a}$ = 6.1 Hz, 6a-H), 5.11 (1H, d, $J_{3a,6a}$ = 6.1 Hz, 3a-H), 5.93 (1H, d, $J_{4,5}$ = 5.7 Hz, 4-H), 6.43 (1H, d, $J_{5,4}$ = 5.7 Hz, 5-H); ^{13}C NMR (125MHz): d = 20.93, 21.40, 25.58, 27.36, 77.80, 83.25, 110.20, 130.94, 131.76, 132.75, 137.02; MS: *m/z* (%) = 180 (76,M^+), 165 (74), 123 (100), 121 (64), 107 (71).

(3a*S*,4*R*,5*R*,6a*R*)-2,2-dimethyl-6-(1-methylethylidene)perhydrocyclopenta[*d*][1,3]dioxole-4,5-diol 19: To a stirred solution of acetonide **18** (1 g, 5.56 mmol) in CH_2Cl_2 (100 cm^3) was added osmium tetroxide (catalytic amount) and *N*-methylmorpholine-*N*-oxide (650 mg, 5.56 mmol). After stirring the reaction mixture (18 h) a saturated aq. solution of Na_2SO_3 (5 cm^3) was added and the stirring continued (0.5 h). The CH_2Cl_2 layer was separated, dried (Na_2SO_4), and the solvent distilled off. The residual crude product was purified by flash column chromatography (4% MeOH in $CHCl_3$) to yield acetonide diol **19**, (370 mg, 31% yield); it crystallized from EtOAc/ hexane, mp 102-103 ºC; $[a]_D^{20}$: + 85 (*c* 0.5, $CHCl_3$); anal. calcd. for $C_{11}H_{18}O_4$: C, 61.7, H, 8.5, found: C, 61.7, H 8.7; ^{1}H NMR: d = 1.36, 1.47 (3H each, s, 2xCH_3), 1.89, 1.91 (3H each, s, C(CH_3)$_2$), 4.09 (1H, d, $J_{3a,6a}$ = 5.9 Hz, 3a-H), 4.49 (1H, d, $J_{6a,3a}$ = 5.9 Hz, 6a-H), 4.72 (1H, d, $J_{4,5}$ =

5.0 Hz, 4-H), 5.12 (1H, d, $J_{5,4}$ = 5.0 Hz, 5-H); ^{13}C NMR (125MHz): d = 20.93, 21.65, 25.58, 27.70, 72.76, 78.00, 78.23, 84.39, 112.21, 131.75, 141.44; MS: *m/z* (%) = 214 (34, M^+), 199 (42), 156 (47), 138 (58).

(3a*R*,3b*R*,6a*R*,7a*R*)-2,2,5,5-tetramethyl-7-(1-methylethylidene)perhydro [1,3]dioxolo[4',5':3,4]cyclopenta[*d*][1,3]dioxole 20: Treatment of acetonide diol **19** (300 mg, 1.4 mmol) in a similar manner to diol **15f** gave the *bis*-acetonide **20** (340 mg, 96% yield) which crystallized from hexane, mp 73-74 ºC; $[a]_D^{20}$: +65 (*c* 1.2, $CHCl_3$); HRMS: *m/z* $(M)^+$ = 254.1521 calcd. for $C_{14}H_{22}O_4$: requires 254.1515; ^{1}H NMR: d = 1.33, 1.38 (6H each, s, 2xC(CH_3)$_2$), 1.87 (6H, s, C(CH_3)$_2$), 4.52 (2H, d, $J_{3a,7a}$ = 5.6 Hz, 3a-H, 3b-H), 5.20 (2H, m, $J_{7a,3a}$ = 5.6 Hz, 6a-H, 7a-H); ^{13}C NMR (125MHz): d = 21.51, 25.35, 27.15, 80.41, 83.60, 110.81, 133.34, 140.35; MS: *m/z* (%) = 254 (15, M^+), 239 (46), 181 (40), 137 (100).

(2*S*,3*S*,4*S*,5*S*)-2,3:4,5-*bis*-(*iso*-Propylidenedioxy)cyclopentanone 21: A slow stream of ozone enriched O_2 was bubbled through a cooled (-78 °C) CH_2Cl_2 solution (20 cm^3) of *bis*-acetonide **20** (250 mg, 1 mmol) until the blue colour disappeared (0.5 h). Triphenylphosphine (1.0 g, 4 mmol) was then added to the reaction mixture and it was stirred at room temperature (0.5 h). The crude product was purified by flash column chromatography (25% Et_2O in hexane) to give ketone **21** (200 mg, 89% yield); it crystallized from Et_2O/hexane, mp 74-75 ºC; $[a]_D^{20}$: + 141 (*c* 1.0, $CHCl_3$) (lit.[33] + 124); HRMS: *m/z* $(M)^+$ = 228.0990, calcd. for $C_{11}H_{16}O_5$: 228.0998; ^{1}H NMR: d = 1.36, 1.41 (6H each, s, 2xC(CH_3)$_2$), 4.59 (2H, d, $J_{3a,7a}$ = 5.0 Hz, 2x3a-H), 4.68 (2H, d, $J_{7a,3a}$ = 5.0 Hz, 2x7a-H).