Supporting Information

Experimental Section

Column chromatographic separations were performed by using Merck SiO_2 60Å (0.035-0.070 mm) silica gel with ethyl acetate/heptane (E/H) mixtures as eluents. TLC analyses were made on Merck SiO_2 60 F254 pre-coated glass plates and the spots were visualized by charring with a solution of phosphomolybdic acid (25g), $Ce(SO_4)_2 \cdot 4 H_2O$ (10g), conc. H_2SO_4 (60 ml) in H_2O (940 ml). NMR spectra were recorded in $CDCl_3$ at 21°C ((^1H)400 MHz, $CHCl_3$ δ 7.27 and (^{13}C) 100 MHz, $CHCl_3$ δ 77.2). GLC analyses were performed with DBwax (J&W Scientific) capillary column (30m; 0.25 mm i.d., 0.25 μm stationary phase). IR spectra were recorded on a Perkin-Elmer 298 spectrometer. GC-MS were obtained using a JEOL SX-102 instrument at 70 eV. Chiral HPLC analyses were performed with a (R,R)-WHELK 01 column (MERCK), using an hexane/isopropanol (80:20 + 0.25% acetic acid) mixture as eluent. Melting points are given uncorrected.

All reactions were carried out in oven-dried glassware sealed with a screw cap. All air- and moisture-sensitive reagents were transferred by dried, argon-flushed syringes. Heptane was distilled from sodium. Toluene was distilled from P_2O_5 and stored over 4Å molecular sieves. Me_3Al (2.0 M in toluene; Aldrich) and Me_2Zn (2.0 M in toluene; Aldrich) were used as delivered. Trans,trans-2,4-hexadien-1-ol was purchased form Aldrich and diluted with toluene to give a 1.0 M solution. All the other chemicals were used as purchased. Na_2SO_4 was used as drying agent.

The structures of the various cycloadducts were established by 1H, 13C NMR and COSY, HETCOR and NOESY experiments. No definitive assignment of stereochemistry for the compounds **3b** and **4b** could be made from the NOSEY experiment

General procedure for alane IMDA reactions (**Procedure A**).The 2,6 di-tertbutylphenol **5** (1 eq, 1.0 mmol) was added to a solution of Me_3Al (1 eq, 1.0mmol) in dry toluene (30 ml**)** at room temperature. After 10 min the dienophile **2a-c** or sorbic alcohol **1** (1 eq, 1.0 mmol) was added and after another 10 min was the diene **1** (1 eq, 1.0 mmol) added. The flask was sealed after 10 minutes from the gas evolution deceased and the resulting mixture was stirred at 160^{o}C for 60h and then cooled to ambient temperature, whereafter quenched by dilution with ethyl acetate and slow addition of H_2O, and stirred for 15 min. The gelatinous aqueous phase was extracted with ethyl acetate (3x10 ml), and the combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was column chromatographed (SiO_2, E/H 1:4) to give the products.

General procedure for alanate IMDA reactions (**Procedure B**). Dienophile **2a-c** or sorbic alcohol **1** (1 equiv, 1.0 mmol) was added to a solution of Me_3Al (1 equiv, 1.0 mmol) in dry toluene (10 ml) at room temperature. After 10 min diene **1** (1 equiv, 1.0 mmol) was added and after another 5 min the same dienophile (2 equiv, 2.0 mmol) was

added to the previous mixture. The flask was sealed and the resulting mixture was stirred at 152^{o}C for 72 h and then cooled to ambient temperature, whereafter quenched by dilution with ethyl acetate and slow addition of H_2O, and stirred for 15 min. The gelatinous aqueous phase extracted with ethyl acetate (3x10 ml), and the combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was column chromatographed (SiO_2, E/H 1:4) to give the products.

General procedure for alanate IMDA reactions employing a chiral ligand. (R)-Binol (1 equiv, 0.2 mmol) was added to a solution of Me_3Al (1 equiv, 0.2 mmol) in dry toluene (6 ml) at room temperature. After 10 min, dienophile **2c** (1 equiv, 0.1) was added and after another 10 min diene **1** (1 equiv, 0.2mmol) was added to the previous mixture. The flask was then sealed and the solution stirred at 160 ^{o}C for 60h and then cooled to ambient temperature, whereafter quenched by dilution with ethyl acetate and slow addition of H_2O, and stirred for 15 min. The gelatinous aqueous phase was extracted with ethyl acetate (3x10ml), and the combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was column chromatographed (SiO_2, E/H 1:4) to give the products.

General procedure for zinc-tethering reactions. Diene **1** (1 equiv, 1.0 mmol) was added to a solution of Me_2Zn (1 equiv, 1.0 mmol) in dry toluene **(**10 ml) at room temperature. After 5 min dienophile **2c** (1 equiv, 1.0 mmol) was added to the previous mixture. The flask was sealed and the solution stirred at 160 ^{o}C for 160h and then cooled to ambient temperature, whereafter quenched according to the usual work up and stirred for 15 min. The gelatinous aqueous phase was extracted with ethyl acetate (3x10 ml) and the combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, E/H 1:4) to give the products.

1,2-dihydroxymethyl-5-methyl-3-cyclohexene (±)-3a and (±)-4a. Diene **1** and dienophile **2a** were subjected to the general procedures (A or B) and gave **3a** and **4a**. **3a** (oil): IR (Film) 3350 cm^{-1} (OH), 1650 cm^{-1} (C=C); ^{1}H NMR δ 5.62 (m, 1H, H-4); 5.54 (m, 1H, H-3); 3.63 (m, 4H, H-1´and H-1", H-2´and H-2"); 2.53 (m, 1H, H-2); 2.24 (m, 1H, H-5); 2.06 (m, 1H, H-1); 1.52 (m, 1H, H-6); 1.02 (m, 1H,H-6´); 0.98 (d, 3H, J_{Me-5}= 7 Hz, Me-5´); ^{13}C NMR δ 136.1 (C-4); 126.2 (C-3); 65.6 (C-1´); 62.6 (C-2´); 39.3 (C-2); 38.4 (C-1); 31.7 (C-6); 30.5 (C-5); 21.8 (C-5´); MS (CI-CH_4) 157 (M^+ +1), 139 (M^+ -18) 121 (M^+-36); HRMS (CI-CH_4) calcd for $C_9H_{17}O_2$ (*M*+H): 157.1229, found 157.1261 and **4a** (oil): IR (Film) 3360 cm^{-1} (OH), 1655 cm^{-1} (C=C); ^{1}H NMR δ 5.72 (ddd, 1H, J_{4-3}= 10.10 Hz, J_{4-5}= 3.6 Hz, J_{4-2}= 2.4 Hz, H-4); 5.42 (ddd, 1H, J_{3-4}= 10 Hz, J_{3-2}= 3.11 Hz, J_{3-5}= 1.95 Hz, H-3); 3.58 (m, 4H, H-1´and H-1", H-2´and H-2"); 2.24 (m, 1H, H-5); 2.15 (m, 1H, H-2); 1.84 (m, 1H, H-1); 1.60 (ddd, 1H, $J_{6'-1}$= 13.2 Hz, $J_{6'-5}$= 9 Hz, $J_{6'-6}$= 5.4 Hz, H-6'); 1.37 (ddd, 1H, J_{6-5}= 13.2 Hz, $J_{6-6'}$= 5.4 Hz, J_{6-1}= 3.5Hz, H-6); 0.99 (d, 3H, J_{Me-5}= 7 Hz, Me-5´); ^{13}C NMR δ 135.3 (C-4); 125.9 (C-3); 67.1, 66.8 (C-1´and C-2´); 42.1 (C-2); 36.4 (C-1); 31.3 (C-6); 28 (C-5); 21.4 (C-5´); MS (EI+) 138 (M^+ -18),120 (M^+ -36); HRMS (CI-CH_4) calcd for $C_9H_{17}O_2$ (*M*+H): 157.1229, found 157.1255.

1-(1-hydroxyethyl)-2-hydroxymethyl-5-methyl-3-cyclohexene (±)-3b and (±)-4b. Diene **1** and dienophile **2b** were subjected to the procedures (A or B) and gave **3b** and **4b**. **3b** (oil): IR (Film) 3360 cm^{-1} (OH), 1645 cm^{-1} (C=C); ^{1}H NMR δ 5.53 (m, 2H, H-3 and H-4); 3.75 (m, 1H, H-1´); 3.58 (m, 2H, H-2´and H-2"); 2.70 (m, 1H, H-2); 2.18 (m, 1H, H-5); 1.75 (m, 1H, H-1); 1.58 (dd, 1H, H-6); 1.30 (d, 3H, $J_{Me\text{-}1´}$= 6.6 Hz, Me-1´); 1.03 (dd, 1H, H-6´); 0.98 (d, 3H, $J_{Me\text{-}5}$= 7 Hz, Me-5´); ^{13}C NMR δ 135.4 (C-4); 126.6 (C-3); 69.7 (C-1´); 62.3 (C-2´); 45.2 (C-2); 40.1 (C-1); 32.5, 32.1 (C-5 and C-6); 21.8 (C-1´); 21.4 (C-5´); HRMS (CI-CH_4) calcd for $C_{10}H_{19}O_2$ (*M*+H): 171.1385, found 171.1397 and **4b** (oil): IR (Film) 3355 cm^{-1}(OH), 1655 cm^{-1} (C=C);^{1}H NMR δ 5.70 (m, 1H, H-4); 5.43 (m, 1H, H-3); 3.75 (dd, 1H, H-1´); 3.63 (dd, 1H, H-2´); 3.44 (m, 1H, H-2"); 2.48 (m, 1H, H-2); 2.14 (m, 1H, H-5); 1.67 (m, 1H, H-1); 1.56 (m, 1H, H-6); 1.33 (m,1H ,H-6´); 1.23 (d, 3H, $J_{Me\text{-}1´}$= 6.7 Hz, Me-1´); 0.98 (d, 3H, $J_{Me\text{-}5}$= 7 Hz, Me-5´); ^{13}C NMR δ 135.6 (C-4); 126.1(C-3); 69.3 (C-1´); 66.3 (C-2´); 41.0 (C-2); 40.1 (C-1); 30.1 (C-6); 27.2 (C-5); 21.9 (CH_3-1´); 21.6 (C-5´); HRMS (CI-CH_4) calcd for $C_{10}H_{19}O_2$ (*M*+H): 171.1385, found 171.1363.

1,2-dihydroxymethyl-5-methyl-6-phenyl-3-cyclohexene (±)-3c and (±)-4c. Diene **1** and dienophile **2c** were subjected to the general procedures (A, B, chiral ligand or zinc-tethering) and gave **3c** and **4c**. **3c** (white solid): IR (KBr) 3260 cm^{-1} (OH), 3020 cm^{-1} (Aryl-H); ^{1}H NMR δ 7.25 (m, 5H, Ph-H); 5.69 (m, 2H, H-3 and H-4); 3.75 (m, 1H, H-2´); 3.64 (m, 1H, H-2"); 3.39 (m, 2H, H-1´and H-1"); 2.64 (m, 1H, H-2); 2.33 (m, 3H, H-1, H-5 and H-6); 0.79 (d, 3H, $J_{Me\text{-}5}$= 6.6 Hz, Me-5´); ^{13}C NMR δ 143.4, 128.7, 128.3, 126.7 (Ph-C); 135.2 (C-4); 126.2 (C-3); 63.4 (C-1´); 63.02 (C-2´); 47.0 (C-6); 43.1 (C-5); 41 (C-2); 39.1 (C-1); 20 (C-5´); MS (EI+): 232 (M^+), 184 (M^+ -48); HRMS (CI-CH_4) calcd for $C_{15}H_{21}O_2$ (*M*+H): 233.1542, found 233.1506; m.p.=124-124.6°C. and **4c** (white solid): IR (KBr): 3350 cm^{-1} (OH), 3035 cm^{-1} (Aryl-H); ^{1}H NMR δ 7.28 (5H, Ph-H); 6.00 (m, 1H, H-4); 5.55 (m, 1H, H-3); 3.80 (m, 1H, H-2´); 3.68 (m, 2H, H-2"and H-1´); 3.46 (m, 1H, H-1"); 2.97 (dd, 1H, $J_{6\text{-}1}$= 5.8 Hz, $J_{6\text{-}5}$= 3.6 Hz, H-6); 2.56 (m, 1H, H-2); 2.28 (m, 2H, H-1 and H-5); 0.78 (d, 3H, $J_{Me\text{-}5}$= 6.7 Hz, Me-5´); ^{13}C NMR δ 142.5, 129.1, 128.4, 126.4 (Ph-C); 136.1 (C-4); 126.3 (C-3); 66.7 (C-2´); 64.7 (C-1´); 45.8 (C-6); 43.4 (C-2); 36.7 (C-1); 36.0 (C-5); 16.7 (C-5´); MS (EI+): 232 (M^+), 214 (M^+ -18), 183 (M^+ -49); HRMS (CI-CH_4) calcd for $C_{15}H_{21}O_2$ (*M*+H): 233.1542, found 233.1538; m.p.= 76.5-77.1°C.

Employing (+)-Binol as the third alcohol resulted in optically active (+)-**3c**; $[\alpha]_D$ = +15,2° (c 0.25, $CHCl_3$), 70% ee according to chiral-column HPLC analysis.

(±)-1,2-(1´,2´-diacetyl)-methyl-5-methyl-6-phenyl-3-cyclohexene:

Compound **3c** was acetylated to determinate its stereochemical structure: acetylation was carried out by adding the alcohol (40 mg, 0.17 mmol, 1eq) to a solution of acetic anhydride (2 eq), pyridine (2 eq) in dry (4-Å molecular sieves) dichloromethane. After being stirred at room temperature for 24 h, the solution was washed with HCl (0.1 M), saturated aqueous $NaHCO_3$, and water, dried and concentrated in vacuo. Column chromatography (E/H 1:6) of the crude product gave an oil (43mg; 79%): ^{1}H NMR δ 7.25 (m, 5H, Ph-H); 5.75 (m, 2H, H-3 and H-4); 4.24 (dd, 1H, J_{vic}=11 Hz, J_{gem}= 6 Hz,

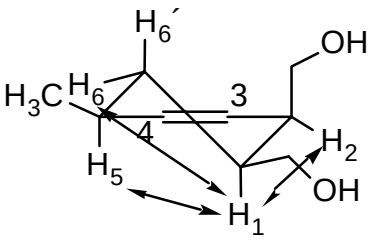
H-2´); 4.08 (dd, 1H, J_{vic}= 11 Hz, J_{gem}= 5.5 Hz, H-2"); 3.75 (m, 2H, H-1´and H-1"); 2.74 (m, 1H, H-2); 2.51 (m, 1H, H-1); 2.37 (m, 2H, H-5 and H-6); 2.06 (s, 3H, CO$\underline{CH_3}$); 1.95 (s, 3H, CO$\underline{CH_3}$); 0.82 (d, 3H, $J_{Me\text{-}5}$= 6.5 Hz,Me-5´); ^{13}C NMR δ 171.3, 170.9 (C=O); 142.7, 128.8, 128.2, 126.9 (Ph-C); 135.4 (C-4); 125.8 (C-3); 65, 64.7 (C-1´and C-2´); 47.4 (C-6); 40 (C-2); 39 (C-1); 36.1 (C-5); 21.2, 21 (CH_3-ac); 19.9 (C-5´).

1,2-dihydroxymethyl-5-methyl-6-(1-propenyl)-3-cyclohexene (±)-3d and (±)-4d. Diene **1** was subjected to the general procedures (A or B) and gave **3d** and **4d**. **3d** (white solid): IR (KBr): 3350 cm^{-1} (OH), 1655 cm^{-1} (C=C); ^{1}H NMR δ 5.55 (m, 3H, H-3 and H-4 and H-7´); 5.20 (ddq, 1H, $J_{6'\text{-}7'}$= 15.1 Hz, $J_{6'\text{-}6}$= 9.2 Hz, $J_{6'\text{-}Me}$= 1.6 Hz, H-6´); 3.74 (m, 2H, H-1´and H-1"); 3.58 (m, 2H, H-2´and H-2"); 2.52 (m, 1H, H-2); 1.89 (m, 2H, H-1 and H-5); 1.78 (m, 1H, H-6); 1.71 (dd, 3H, $J_{Me\text{-}7'}$= 6.4 Hz, $J_{Me\text{-}6'}$= 1.6 Hz, Me-8´); 0.92 (d, 3H, $J_{Me\text{-}5}$= 7 Hz, Me-5´); ^{13}C NMR δ 134.8 (C-7´); 133.6 (C-6´); 126.9, 126.2 (C-3 and C-4); 64 (C-1´); 63 (C-2´); 43.9 (C-6); 42.16 (C-1); 40.6 (C-2); 36.8 (C-5); 19.9 (C-5´); 18.1 (C-8´); MS (CI-CH_4) 197 (M^++1), 179 (M^+-18); m.p.=70.7-71.2 °C; HRMS (CI-CH_4) calcd for $C_{12}H_{21}O_2$ (*M*+H): 197.1542, found 197.1569 and **4d** (oil): IR (Film) 3350 cm^{-1} (OH), 1660 cm^{-1} (C=C); ^{1}H NMR δ 5.86 (ddd, 1H, $J_{4\text{-}5}$= 5.3 Hz, $J_{4,3}$= 7.7 Hz, $J_{4,2}$= 2.3 Hz, H-4); 5.48 (m, 3H, H-3 and H-6´and H-7´); 3.77 (dd, 1H, J_{vic}= 11.3 Hz, J_{gem}= 3.3 Hz, H-1´); 3.67 (dd, 1H,J_{vic}= 10.8 Hz, J_{gem}= 4 Hz, H-2´); 3.53 (2dd, 2H, J_{gem}= 6.1 Hz, J_{vic}= 11.3 Hz, H-1"and H-2"); 2.26 (m, 2H, H-2 and H-6); 2.15 (m, 1H, H-5); 1.69 (d, 3H, $J_{Me\text{-}7'}$= 5 Hz, Me-8´); 1.65 (m, 1H, H-1); 0.91 (d, 3H, $J_{Me\text{-}5}$= 7 Hz, Me-5´); ^{13}C NMR δ 135.7 (C-4); 133.7 (C-3); 126.4 (C-6´and C-7´); 66.5 (C-2´); 65.15 (C-1´); 43.53 (C-2); 42.69 (C-6); 38.3 (C-1); 35.4 (C-5); 18.2 (C-8´); 16 (C-5´); MS (EI+): 196 (M^+), 147 (M^+ -49); HRMS (CI-CH_4) calcd for $C_{12}H_{21}O_2$ (*M*+H): 197.1542, found 197.1541

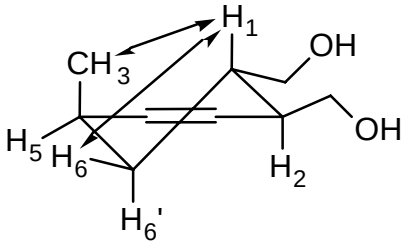
Structure determination of the IMDA cycloadducts

The stereochemistry of each compound was established by COSY, HETCOR and NOESY studies (the strong NOE effects are shown by arrows). No definitive assignment of the stereochemistry for the compounds **3b** and **4b** could be made from the NOSEY experiment.

1,2-dihydroxymethyl-5-methyl-3-cyclohexene (±)-3a and (±)-4a

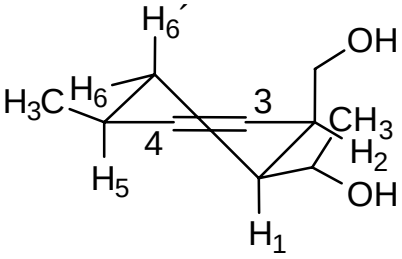


3a

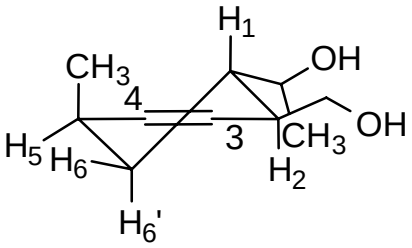


4a

1-(1-hydrohyethyl)-2-hydroxymethyl-5-methyl-3-cyclohexene (±)-3b and (±)-4b



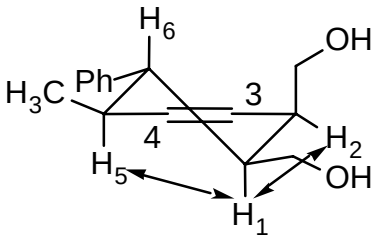
3b



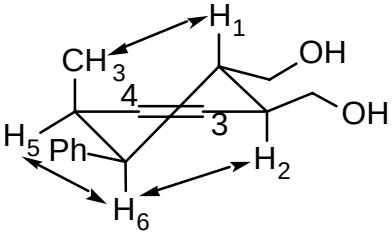
4b

Assignment of the stereochemistry based on TLC peformance compared with the other diastereomeric pairs.

1,2-dihydroxymethyl-5-methyl-6-phenyl-3-cyclohexene (±)-3c and (±)-4c



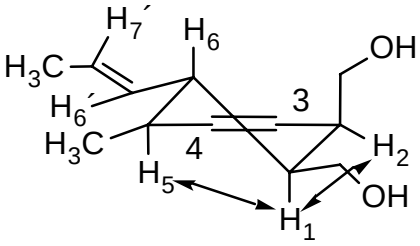
3c



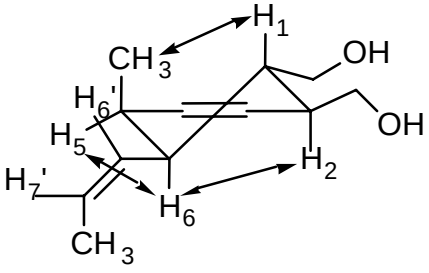
4c

The stereochemistry of compound **3c** was determined from its diacetylated derivate.

1,2-dihydroxymethyl-5-methyl-6-(1-propenyl)-3-cyclohexene (±)-3d and (±)-4d



3d



4d