Supporting Information

Facile Synthetic Routes to All Possible Enantiomeric Pairs of Conduritol Stereoisomers via Efficient Enzymatic Resolution of Conduritol B and C Derivatives

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(±)-1,2,3/4)-1,4-Di-*O*-benzoyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [2][22]

To a stirred solution of compound **1**[20] (2.60 g, 6.07 mmol), imidazole (1.67 g, 24.5 mmol), and triphenylphosphine (6.49 g, 24.5 mmol) in toluene (120 mL) at reflux, was added iodine (5.08 g, 20.0 mmol) portionwise. The mixture was stirred for 5.5 h, cooled to rt, decanted into excess aq. sodium thiosulfate and aq. $NaHCO_3$, and diluted with EtOAc. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The product mixture was subjected to column chromatography to give compound **2** (1.84 g, 77%). R_f 0.25 (EtOAc : Hex = 1 : 10); mp 120.5-122 °C; ^{1}H NMR ($CDCl_3$) δ 1.37, 1.43 (2s, 6H, C<u>Me</u>$_2$), 4.68 (dd, J = 3.1, 7.4 Hz, 1H, H-2 or H-3), 4.83 (dd, J = 4.0, 7.4 Hz, 1H, H-3 or H-2), 5.69 (app. t, J = 3.3 Hz, 1H, H-1 or H-4), 5.86 (dd, J = 2.1, 4.0 Hz, 1H, H-4 or H-1), 6.18-6.26 (m, 2H, H-5 & H-6), 7.43-8.14 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 25.05, 26.60 [C<u>Me</u>$_2$], 68.22, 70.27, 74.44, 76.47 [C-1 ~ C-4], 110.54 [<u>C</u>Me$_2$], 128.60-133.67 [C-5, C-6 & 2Ph], 166.04, 166.48 [2<u>C</u>OPh]; Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 70.11; H, 5.72.

(±)-(1,2,3/4)-2,3-*O*-Isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [3]

To a solution of compound **2** (9.75 g, 24.7 mmol) in MeOH (100 mL), was added sodium methoxide (300 mg, 5.5 mmol). After stirring under reflux for 3 h, the mixture was filtered through a short pad of silica gel and the filtrate was evaporated under reduced pressure. The crude product was subjected to column chromatography to give compound **3** (4.42 g, 96%) as a solid. R_f 0.12 (EtOAc : Hex = 1 : 2); mp 95-96 °C; ^{1}H NMR ($CDCl_3$) δ 1.39, 1.46 (2s, 6H, C<u>Me</u>$_2$), 2.37 (br. s, 1H, O<u>H</u>), 2.70 (d, J = 4.7 Hz, 1H, O<u>H</u>), 4.30-4.34 (m, 1H, H-2 or H-3), 4.44-4.47 (m,

2H, H-3 or H-2 & H-1 or H-4), 4.52 (br. s,1H, H-4 or H-1), 5.98-6.07 (m, 2H, H-5 & H-6); ^{13}C NMR ($CDCl_3$) δ 24.80, 26.72 [C$\underline{Me}_2$], 64.63, 68.47, 75.56, 79.42 [C-1 ~ C-4], 110.04 [$\underline{C}Me_2$], 132.16, 133.49 [C-5 & C-6]; Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.86; H, 7.55.

(±)-(1,2,3/4)-1,4-Di-*O*-acetyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [4]

To a solution of compound **3** (4.29 g, 23.0 mmol) in pyridine (80 mL) at 0 °C, was added acetic anhydride (4.4 mL, 46.1 mmol). After 30 min, the mixture was warmed up to rt and stirred overnight. The reaction mixture was treated with water and extracted with EtOAc. The organic layer was washed with 1 N HCl, aq. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, concentrated and chromatographed to give **4** (6.07 g, 97.5%) as an oil. R_f 0.39 (EtOAc : Hex = 1 : 4); ^{1}H NMR ($CDCl_3$) δ 1.34, 1.41 (2s, 6H, C$\underline{Me}_2$), 2.05, 2.15 (2s, 6H, 2COC$\underline{H}_3$), 4.45 (dd, J = 2.3, 7.2 Hz, 1H, H-2 or H-3), 4.67 (ddd, J = 0.85, 3.9, 7.2 Hz, 1H, H-3 or H-2), 5.25 (dd, J = 2.3, 4.6 Hz, 1H, H-1 or H-4), 5.50-5.53 (m, 1H, H-4 or H-1), 5.98 (ddd, J = 0.85, 2.5, 9.8 Hz, 1H, H-5 or H-6), 6.06 (ddd, J = 1.4, 4.6, 9.8 Hz, 1H, H-6 or H-5); ^{13}C NMR ($CDCl_3$) δ 20.74, 20.90 [2CO$\underline{C}H_3$], 24.48, 26.03 [C$\underline{Me}_2$], 67.46, 68.45, 73.99, 75.73 [C-1 ~ C-4], 109.69 [$\underline{C}Me_2$], 127.78, 131.75 [C-5 & C-6], 169.68, 170.25 [2$\underline{C}OCH_3$].

Lipase-catalyzed Resolution of Compound 4

To a solution of racemate **4** (6.65 g, 24.6 mmol) in 0.5 N sodium phosphate buffer (120 mL, pH 7.0), was added lipase (ca. 2.5 g) from *Candida rugosa* (Sigma) or *Pseudomonas cepacia*. (Amano). This suspension was vigorously stirred with its pH automatically adjusted to 7.0 with 0.5 N NaOH. After 3 h, conversion was ca 50%, and EtOAc (40 mL) was added. The suspension was filtered through Celite and the mixture was extracted 3 times with EtOAc. The combined extracts were washed with aq. $NaHCO_3$ and brine, dried ($MgSO_4$), concentrated and chromatographed to give **(+)-4** (3.26 g, 49%, 95% ee) as an oil, and **(-)-5** (2.70 g, 48%, 95% ee) whose optical purity could be improved to >99% ee after recrystallization from CH_2Cl_2-Hex. The optical purity of **(+)-4** could also be enhanced to >99% ee after repeated resolution. After acetylation of the monoacetate **(-)-5,** the optical purities (% ee) were determined by NMR analysis of the diacetates using europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] as the NMR shift agent. Compounds **(+)-4** and **(-)-5** were treated with NaOMe in MeOH to give compounds **(+)-3** and **(-)-3**, and their optical purities again could be improved to >99% ee by recrystallization from CH_2Cl_2-MeOH.

(+)-(1*S*,2*R*,3*S*,4*S*)-1,4-Di-*O*-acetyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(+)-4]

Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **4**; $[\alpha]_D^{20}$ +161.0 (*c* 4.60, $CHCl_3$) [lit.[19c] $[\alpha]_D^{20}$ +154.7 (*c* 1.106, $CHCl_3$)].

(–)-(1*R*,2*R*,3*R*,4*R*)-4-*O*-Acetyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(–)-5]

R_f 0.26 (EtOAc : Hex = 1 : 2); mp 63-64 °C; $[\alpha]_D^{20}$ –206.7 (*c* 4.23, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.37, 1.41 (2s, 6H, C$\underline{Me}_2$), 2.04 (s, 3H, CO$\underline{C}H_3$), 3.07 (br. s, 1H, O$\underline{H}$-1), 4.40-4.45 (m, 2H, H-1 & H-3), 4.59 (ddd, J = 1.0, 4.3, 7.3 Hz, 1H, H-2), 5.23 (dd, J = 2.8, 4.9 Hz, 1H, H-4), 5.97 (ddd, J = 1.4, 4.9, 9.8 Hz, 1H, H-5), 6.05 (ddd, J = 1.0, 2.5, 9.8 Hz, 1H, H-6); ^{13}C NMR ($CDCl_3$) δ 21.19 [CO$\underline{C}H_3$], 24.84, 26.43 [C$\underline{Me}_2$], 65.41, 68.66, 75.92, 76.02 [C-1 ~ C-4], 109.72 [$\underline{C}Me_2$], 126.65, 136.53 [C-5 & C-6], 170.26 [$\underline{C}OCH_3$]; Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.65; H, 7.20.

(+)-(1*S*,2*S*,3*R*,4*S*)- & (–)-(1*R*,2*R*,3*S*,4*R*)-2,3-*O*-Isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(+)-3 & (–)-3]

(+)-3: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **3**; mp 122-123 °C; $[\alpha]_D^{20}$ +88.6 (*c* 1.11, $CHCl_3$).

(–)-3: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **3**; mp 122-123 °C; $[\alpha]_D^{20}$ –88.5 (*c* 1.00, $CHCl_3$) [lit.[19c] $[\alpha]_D^{20}$ –157.2 (*c* 0.998, $CHCl_3$)].

(±)-(1,3/2,4)-1,4-Di-*O*-benzoyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [10]

Compound **9**[20] (6.98 g, 16.3 mmol) was treated by the same procedure as described for compound **2** to afford compound **10** (5.01 g, 78%). R_f 0.42 (EtOAc : Hex = 1 : 4); mp 193-194 °C; ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 6H, C$\underline{Me}_2$), 4.04 (dd, J = 2.4, 5.8 Hz, 2H, H-2 & H-3), 5.85-5.90 (m, 4H, H-1, H-4, H-5 & H-6), 7.26-8.11 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 27.36 (2C) [C$\underline{Me}_2$], 73.26 (2C), 78.03 (2C) [C-1 ~ C-4], 112.39 [$\underline{C}Me_2$], 128.81-133.76 [C-5, C-6 & 2Ph], 166.36 (2C) [2$\underline{C}$OPh]; Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 70.22; H, 5.84.

(±)-(1,3/2,4)-2,3-*O*-Isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [11]

Compound **10** (4.0 g, 12.4 mmol) was treated by the same procedure as described for compound **3** to afford compound **11** (1.84 g, 97.4%) as an oil. R_f 0.23 (EtOAc : Hex = 1 : 1); ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 6H, C$\underline{Me}_2$), 2.74 (br. s, 2H, 2O$\underline{H}$), 3.55 (dd, J = 2.3, 5.6 Hz, 2H, H-2 & H-3), 4.50 (dd, J = 2.3, 5.6 Hz, 2H, H-1 & H-4), 5.69 (s, 2H, H-5 & H-6); ^{13}C NMR ($CDCl_3$) δ 27.35 (2C) [C$\underline{Me}_2$], 71.08 (2C), 81.13 (2C) [C-1 ~ C-4], 111.71 [$\underline{C}Me_2$], 130.86 (2C) [C-5 & C-6].

(±)-(1,3/2,4)-1,4-Di-*O*-acetyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [12]

Compound **11** (3.25 g, 17.4 mmol) was treated by the same procedure as described for compound **4** to afford compound **12** (4.66 g, 98.8%) as a solid. R_f 0.5 (EtOAc : Hex = 1 : 2); mp 153-154 °C; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 6H, C<u>Me</u>$_2$), 2.13 (s, 6H, 2COC<u>H</u>$_3$), 3.79 (dd, J = 2.4, 5.9 Hz, 2H, H-2 & H-3), 5.54 (dd, J = 2.4, 5.9 Hz, 2H, H-1 & H-4), 5.70 (s, 2H, H-5 & H-6); ^{13}C NMR ($CDCl_3$) δ 21.41 (2C) [2CO<u>C</u>H$_3$], 27.24 (2C) [C<u>Me</u>$_2$], 72.70 (2C), 77.67 (2C) [C-1 ~ C-4], 112.22 [<u>C</u>Me$_2$], 128.87 (2C) [C-5 & C-6], 170.72 (2C) [2<u>C</u>OCH$_3$]; Anal. Calcd for $C_{13}H_{18}O_6$: C, 57,77; H, 6.71. Found: C, 57.39; H, 6.89.

Lipase-catalyzed Resolution of Compound 12

To a solution of the racemate **12** (2.71 g, 10.0 mmol) and Novozym 435 (immobilized lipase from *Candida Antarctica*, Novo Nordisk, 3.0 g) in *t*-BME (150 mL), was added *n*-BuOH (9.3 mL). The reaction mixture was stirred at 45 °C. After 30 min, the reaction mixture contained **(+)-12**, **(–)-13** and **(–)-11**. The monoacetate **(–)-13** was slowly converted to **(–)-11.** After 3 h, the enzyme was filtered off and the filtrate was concentrated and chromatographed to give the unreacted diacetate **(+)-12** (1.34 g, 49.5%, 98% ee) whose optical purity could be improved to >99% ee by recrystallization from EtOAc-pet. ether, and the diol **(–)-11** (906 mg, 48.5%, >99% ee) as an oil. After acetylation of the diol **(–)-11,** the optical purities (% ee) were determined by NMR analysis of the diacetates using europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] as the NMR shift agent. Compound **(+)-12** was treated with NaOMe in MeOH to give the diol **(+)-11**.

(+)-(1*S*,2*S*,3*S*,4*S*)-1,4-Di-*O*-acetyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(+)-12]

Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **12**; mp 94-95 °C; $[\alpha]_D^{20}$ +180.3 (*c* 1.27, $CHCl_3$).

(–)-(1*R*,2*R*,3*S*,4*R*)-1-*O*-Acetyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(–)-13]

R_f 0.26 (EtOAc : Hex = 1 : 2); $[\alpha]_D^{20}$ –94.4 (*c* 1.98, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 6H, C<u>Me</u>$_2$), 2.12 (s, 3H, COC<u>H</u>$_3$), 2.94 (br. s, 1H, O<u>H</u>-4), 3.62 (dd, J = 8.0, 9.8 Hz, 1H, H-2 or H-3), 3.71 (dd, J = 8.4, 9.8 Hz, 1H, H-3 or H-2), 4.48-4.51 (m, 1H, H-4), 5.51-5.56 (m, 1H, H-1), 5.64 (td, J = 2.0, 2.0, 10.2 Hz, 1H, H-5 or H-6), 5.74 (td, J = 1.8, 1.8, 10.2 Hz, 1H, H-6 or H-5); ^{13}C NMR ($CDCl_3$) δ 21.50 [CO<u>C</u>H$_3$], 27.25, 27.35 [C<u>Me</u>$_2$], 70.79, 73.24, 77.50, 81.22 [C-1 ~ C-4], 111.95 [<u>C</u>Me$_2$], 127.04, 132.72 [C-5 & C-6], 170.98 [<u>C</u>OCH$_3$].

(+)-(1*S*,2*R*,3*R*,4*S*)- & (–)-(1*R*,2*S*,3*S*,4*R*)-2,3-*O*-Isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(+)-11 & (–)-11]

(+)-11: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **11**; $[\alpha]_D^{20}$ +30.4 (*c* 3.98, $CHCl_3$).

(–)-11: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **11**; $[\alpha]_D^{20}$ –30.2 (*c* 2.40, $CHCl_3$).

(+)-(1*S*,2*R*,3*R*,4*S*)- & (–)-(1*R*,2*S*,3*S*,4*R*)-1-*O*-Benzoyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(+)-15 & (–)-15], (+)-(1*S*,2*S*,3*S*,4*S*)- & (–)-(1*R*,2*R*,3*R*,4*R*)-4-*O*-Benzoyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(+)-16 & (–)-16], and (+)-(1*S*,2*R*,3*S*,4*S*)- & (–)-(1*R*,2*S*,3*R*,4*R*)-1,4-Di-*O*-benzoyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(+)-2 & (–)-2]

To a solution of compound **(+)-3** (1.865 g, 10 mmol) in pyridine (50 mL) at 0 °C, was added BzCl (1.2 mL, 10.2 mmol) dropwise. After stirring for 5 h at 0-10 °C, the mixture was treated with water (3 mL) for 30 min, diluted with EtOAc, and washed with 1 N HCl, aq. $NaHCO_3$, and brine. The organic layer was separated, dried ($MgSO_4$), concentrated and chromatographed to afford **(+)-2** (448 mg, 11.3%), **(+)-15** (1.69 g, 58.3%), **(+)-16** (211 mg, 7.3%), and the starting material **(+)-3** (345 mg, 18.5%).

(+)-2: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **2**; mp 140-141 °C; $[\alpha]_D^{20}$ +175.3 (*c* 1.66, $CHCl_3$).

(+)-15: R_f 0.25 (EtOAc : Hex = 1 : 2); mp 128-129 °C; $[\alpha]_D^{20}$ +190.5 (*c* 2.07, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.34, 1.36 (2s, 6H, C<u>Me</u>$_2$), 2.77 (br. s, 1H, O<u>H</u>-4), 4.37 (dd, J = 4.3, 8.0 Hz, 1H, H-3), 4.53 (dd, J = 4.2, 8.0 Hz, 1H, H-2), 4.65 (br. s, 1H, H-4), 5.75 (app. t, J = 4.3 Hz, 1H, H-1), 6.06 (ddd, J = 1.4, 4.4, 9.4 Hz, 1H, H-6), 6.13 (dd, J = 2.8, 9.4 Hz, 1H, H-5), 7.37-8.04 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 24.90, 26.67 [C<u>Me</u>$_2$], 67.33, 69.71, 74.26, 79.85 [C-1 ~ C-4], 110.48 [<u>C</u>Me$_2$], 127.84-136.39 [C-5, C-6 & Ph], 166.39 [<u>C</u>OPh]; Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 65.79; H, 6.28.

(+)-16: R_f 0.32 (EtOAc : Hex = 1 : 2); mp 124-125 °C; $[\alpha]_D^{20}$ +205.6 (*c* 1.04, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.39, 1.45 (2s, 6H, C<u>Me</u>$_2$), 2.67 (br. s, 1H, O<u>H</u>-1), 4.50 (br. s, 1H, H-1), 4.61 (dd, J = 2.8, 7.3 Hz, 1H, H-3), 4.68 (dd, J = 4.4, 7.3 Hz, 1H, H-2), 5.53 (app. q, J = 2.7 Hz, 1H, H-4), 6.11 (m, 2H, H-5 & H-6), 7.41-8.00 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 24.97, 26.55 [C<u>Me</u>$_2$], 65.72, 68.98, 75.90, 75.96 [C-1 ~ C-4], 110.01 [<u>C</u>Me$_2$], 126.92-136.84 [C-5, C-6 & Ph], 1165.89 [<u>C</u>OPh]; Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 65.89; H, 6.42.

Similarly, compound **(–)-3** was converted to compounds **(–)-2**, **(–)-15**, **(–)-16**, and the starting material **(–)-3**.

(–)-2: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **2**; mp 140-141 °C; $[\alpha]_D^{20}$ –175.3 (*c* 1.62, $CHCl_3$).

(–)-15: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **(+)-15**; mp 128-129 °C; $[\alpha]_D^{20}$ –190.2 (*c* 2.15, $CHCl_3$).

(–)-16: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **(+)-16**; mp 124-125 °C; $[\alpha]_D^{20}$ –205.5 (*c* 1.05 , $CHCl_3$).

(+)-(4*S*,5*R*,6*S*)- & (–)-(4*R*,5*S*,6*R*)-4-Bezoyloxy-5,6-(isopropylidenedioxy)cyclohex-2-en-1-one [(+)-17 & (–)-17]

To a solution of compound **(+)-15** (581 mg, 2 mmol) and TEA (3 mL, 21.4 mmol) in DMSO (6 mL) at –15 °C, was

added sulfer trioxide-pyridine complex (1.136 g, 7 mmol) in DMSO (4 mL). After slowly warmed up to rt and stirred for 3 h, the mixture was poured into cooled brine, and extracted with EtOAc three times. The organic extracts were washed with 0.1 N HCl and brine, dried ($MgSO_4$) and concentrated to afford the enone **(+)-17** which was used for the next step without further purification.

(+)-17: R_f 0.41 (EtOAc : Hex = 1 : 2); ^{1}H NMR ($CDCl_3$) δ 1.38, 1.40 (2s, 6H, C<u>Me</u>$_2$), 4.44 (d, J = 4.7 Hz, 1H, H-6), 4.91 (dt, J = 2.2, 4.4, 4.4 Hz, 1H, H-5), 6.16 (td, J = 2.4, 2.4, 4.1 Hz, 1H, H-4), 6.22 (dd, J = 2.5, 10.4 Hz, 1H, H-2), 6.90 (td, J = 2.2, 2.2, 10.4, 9.4 Hz, 1H, H-3), 7.45-8.15 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 26.44, 27.78 [C<u>Me</u>$_2$], 67.74, 74.91, 75.82 [C-4 ~ C-6], 111.60 [<u>C</u>Me$_2$], 128.82-146.38 [C-2, C-3 & Ph], 166.14 [<u>C</u>OPh], 195.56 [C-1].

Similarly, compound **(–)-17** was prepared from compound **(–)-15**.

(–)-17: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **(+)-17**.

(–)-(1*S*,2*R*,3*R*,4*R*)- & (+)-(1*R*,2*S*,3*S*,4*S*)-1-*O*-Benzoyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(–)-18 & (+)-18]

To a solution of the crude enone **(+)-17** in MeOH-CH_2Cl_2 (1 : 5, 12 mL) at 0 °C, was added $NaBH_4$ (193 mg, 5 mmol). After stirring at rt for 2.5 h, the mixture was treated with water (2 mL), evaporated, and diluted with EtOAc. The organic layer was washed with water and brine, dried ($MgSO_4$), concentrated and chromatographed to afford compound **(–)-18** (433 mg, 74.5% from **(+)-15**).

(–)-18: R_f 0.24 (EtOAc : Hex = 1 : 2); mp 108-109 °C; $[\alpha]_D^{20}$ –42.6 (*c* 1.03, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.35, 1.42 (2s, 6H, C<u>Me</u>$_2$), 2.66 (br. s, 1H, O<u>H</u>-4), 4.10 (br. s, 1H, H-4), 4.60 (ddd, J = 1.6, 4.8, 7.4 Hz, 1H, H-3), 4.82 (ddd, J = 1.7, 3.7, 7.4 Hz, 1H, H-2), 5.33-5.36 (m, 1H, H-1), 5.76-5.81 (m, 1H, H-6), 5.83-5.88 (m, 1H, H-5), 7.44-8.14 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 25.17, 26.13 [C<u>Me</u>$_2$], 66.98, 69.95, 74.07, 75.65 [C-1 ~ C-4], 110.59 [<u>C</u>Me$_2$], 126.67-133.71 [C-5, C-6 & Ph], 166.62 [<u>C</u>OPh]; Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 65.87; H, 6.34.

Similarly, compound **(+)-18** was prepared from compound **(–)-15** via compound **(–)-17**.

(+)-18: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **(–)-18**; mp 108-109 °C; $[\alpha]_D^{20}$ +42.5 (*c* 0.74, $CHCl_3$).

(+)-(1*S*,2*S*,3*R*,4*S*)- & (–)-(1*R*,2*R*,3*S*,4*R*)-2,3-*O*-Isopropylidene-4-*O*-methoxymethylcyclohex-5-ene-1,2,3,4-tetrol [(+)-20 & (–)-20]

To a solution of compound **(+)-15** (900 mg, 3.10 mmol) in chloroform (12 mL), were added *N*,*N*-diisopropylethylamine (2.2 mL, 12.6 mmol) and chloromethyl methyl ether (0.71 mL, 9.35 mmol). After stirring at rt overnight, the reaction mixture was diluted with CH_2Cl_2. The organic layer was washed with aq. $NaHCO_3$ and brine, dried, and concentrated to dryness. The crude mixture was treated with 25 wt% sodium methoxide (in MeOH, 0.2 mL) in MeOH (12 mL). After refluxing for 3 h, the mixture was filtered through a short pad of silica gel and the filtrate was evaporated under reduced pressure. Column chromatography gave compound **(+)-20** (693 mg, 97.1%) as an oil.

(+)-20: R_f 0.22 (EtOAc : Hex = 1 : 2); $[\alpha]_D^{20}$ +111.3 (*c* 1.21, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.37, 1.41 (2s, 6H, C$\underline{Me}_2$), 2.99 (br. s, 1H, O$\underline{H}$-1), 3.36 (s, 3H, $CH_2OC\underline{H}_3$), 4.29 (app. t, J = 3.4 Hz, 1H, H-1 or H-4), 4.38-4.44 (m, 2H, H-4 or H-1 & H-2 or H-3), 4.51 (dd, J = 4.1, 7.5 Hz, 1H, H-3 or H-2), 4.65 (d, J = 6.7 Hz, 1H, $C\underline{H}_aH_bOCH_3$), 4.68 (d, J = 6.7 Hz, 1H, $CH_a\underline{H}_bOCH_3$), 5.97-6.03 (m, 2H, H-5 & H-6); ^{13}C NMR ($CDCl_3$) δ 24.77, 26.50 [C$\underline{Me}_2$], 55.68 [$CH_2O\underline{C}H_3$], 65.29, 71.37, 76.11, 77.45 [C-1 ~ C-4], 95.34 [$\underline{C}H_2OCH_3$], 109.48 [$\underline{C}Me_2$], 129.44, 134.65 [C-5 & C-6].

Similarly, compound **(–)-20** was prepared from **(–)-15**.

(–)-20: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **(+)-20**; $[\alpha]_D^{20}$ –111.5 (*c* 2.25, $CHCl_3$).

(–)-(1*R*,2*R*,3*R*,4*S*)- & (+)-(1*S*,2*S*,3*S*,4*R*)-1-*O*-Benzoyl-2,3-*O*-isopropylidene-4-*O*-methoxymethylcyclohex-5-ene-1,2,3,4-tetrol [(–)-21 & (+)-21]

Compound **(+)-20** (665 mg, 2.89 mmol) was treated by the same procedure as described for the Mitsunobu reaction of compound **15** to give compound **(–)-21** (938 mg, 97.1%) as an oil.

(–)-21: R_f 0.55 (EtOAc : Hex = 1 : 4); $[\alpha]_D^{20}$ –91.7 (*c* 4.37, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.39, 1.51 (2s, 6H, C$\underline{Me}_2$), 3.34 (s, 3H, $CH_2OC\underline{H}_3$), 4.26-4.31 (m, 2H, H-3 & H-4), 4.39-4.44 (m, 1H, H-2), 4.79 (d, J = 6.7 Hz, 1H, $C\underline{H}_aH_bOCH_3$), 4.90 (d, J = 6.7 Hz, 1H, $CH_a\underline{H}_bOCH_3$), 5.47-5.51 (m, 1H, H-1), 5.78 (td, J = 2.1, 2.1, 10.0 Hz, 1H, H-5), 5.91 (td, J = 2.2, 2.2, 10.0 Hz, 1H, H-6), 7.42-8.11 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 25.46, 27.59 [C$\underline{Me}_2$], 55.96 [$CH_2O\underline{C}H_3$], 73.27, 74.94, 76.41, 77.87 [C-1 ~ C-4], 96.21 [$\underline{C}H_2OCH_3$], 109.97 [$\underline{C}Me_2$], 127.95-133.60 [C-5, C-6 & Ph], 166.32 [$\underline{C}$OPh].

Similarly, compound **(+)-21** was prepared from compound **(–)-20**.

(+)-21: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **(–)-21**; $[\alpha]_D^{20}$ +91.3 (*c* 4.16, $CHCl_3$).

(1,2,3,4)-1,4-Di-*O*-benzoyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [25] and (±)-(1,2,3/4)-3,4-Di-*O*-benzoyl-1,2-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [26]

To a solution of the racemate **15** (mp 132-133 °C, 790 mg, 2.72 mmol), which was prepared from the racemate **3** by the same procedure as described for compound **(+)-15**, Ph_3P (1.80 g, 6.79 mmol), and benzoic acid (839 mg, 6.79 mmol) in toluene (25 mL), was added dropwise diethyl azodicarboxylate (1.1 mL, 6.79 mmol). After stirring at rt for 3 h, the mixture was filtered through silica gel (EtOAc-Hex = 1 : 4), concentrated and chromatographed to afford compounds **25** (91 mg, 8.5%) and **26** (785 mg, 73.1 %).

25: R_f 0.6 (EtOAc : Hex = 1 : 2); mp 201-202 °C; ^{1}H NMR ($CDCl_3$) δ 1.33, 1.44 (2s, 6H, C<u>Me</u>$_2$), 4.88 (app. t, J = 1.2 Hz, 2H, H-2 & H-3), 5.42 (dd, J = 2.4 Hz, 2H, H-1 & H-4), 5.96 (s, 2H, H-5 & H-6), 7.45-8.16 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 24.94, 25.93 [C<u>Me</u>$_2$], 69.78 (2C), 73.85 (2C) [C-1 ~ C-4], 110.68 [<u>C</u>Me$_2$], 127.58-133.48 [C-5, C-6 & Ph], 166.33 (2C) [2<u>C</u>OPh]; Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 69.83; H, 5.66.

26: R_f 0.61 (EtOAc : Hex = 1 : 2); mp 108-110 °C; ^{1}H NMR ($CDCl_3$) δ 1.36, 1.45 (2s, 6H, C<u>Me</u>$_2$), 4.71 (dd, J = 2.3, 8.4 Hz, 1H, H-2), 4.78-4.80 (m, 1H, H-1), 5.58 (dd, J = 2.3, 8.9 Hz, 1H, H-3), 5.83 (m, 2H, H-5 & H-6), 6.13 (br. d, J = 8.9 Hz, 1H, H-4), 7.33-8.06 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 27.18, 28.20 [C<u>Me</u>$_2$], 69.43, 72.84, 74.03, 74.91 [C-1 ~ C-4], 111.05 [<u>C</u>Me$_2$], 127.18-133.71 [C-5, C-6 & Ph], 166.42, 166.59 [2<u>C</u>OPh]; Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 69.79; H, 5.84.

(–)-(1*R*,2*S*,3*S*,4*R*)- & (+)-(1*S*,2*R*,3*R*,4*S*)-1,4-Di-*O*-benzoyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(–)-27 & (+)-27]

To a solution of compound **(+)-11** (295 mg, 1.58 mmol), Ph_3P (2.91 g, 11.0 mmol), and benzoic acid (1.35 g, 10.9 mmol) in toluene (20 mL), was added dropwise diethyl azodicarboxylate (1.9 mL, 11.7 mmol). After stirring at rt for 6 h, the mixture was filtered through silica gel (EtOAc-Hex = 1 : 2), concentrated and chromatographed to afford compound **(-)-27** (562 mg, 90%) as a solid.

(–)-27: R_f 0.59 (EtOAc : Hex = 1 : 2); mp 119-120 °C; $[\alpha]_D^{20}$ –452.3 (*c* 1.17, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 6H, C<u>Me</u>$_2$), 4.33 (d, J = 1.1 Hz, 2H, H-2 & H-3), 5.96 (d, J = 1.1 Hz, 2H, H-1 & H-4), 6.26 (m, 2H, H-5 & H-6), 7.43-8.07 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 27.10 (2C) [C<u>Me</u>$_2$], 66.73 (2C), 72.90 (2C) [C-1 ~ C-4], 111.54 [<u>C</u>Me$_2$], 126.29-133.63 [C-5, C-6 & Ph], 166.25 (2C) [2<u>C</u>OPh]; Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 69.74; H, 5.73.

Similarly, compound **(+)-27** was prepared from compound **(–)-11**.

(+)-27: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **(–)-27**; mp 119-120 °C; $[\alpha]_D^{20}$ +453.2 (*c* 1.24, $CHCl_3$).

(+)-(1*S*,2*S*,3*R*,4*S*)- & (–)-(1*R*,2*R*,3*S*,4*R*)-1-*O*-Benzoyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(+)-29 & (–)-29] and (+)-(1*S*,2*S*,3*S*,4*S*)- & (–)-(1*R*,2*R*,3*R*,4*R*)-1,4-Di-*O*-benzoyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(+)-10 & (–)-10]

To the solution of **(+)-11** (620 mg, 3.3 mmol) in pyridine (15 mL) at 0 °C, was added BzCl (0.41 mL, 3.50 mmol) dropwise. After stirring at 0-5 °C for 5 h, the mixture was treated with water (2 mL) for 20 min, diluted with EtOAc, and washed with 1 N HCl, aq. $NaHCO_3$, and brine. The organic layer was separated, dried ($MgSO_4$), concentrated and chromatographed to afford the dibenzoate **(+)-10** (184 mg, 14%), the monobenzoate **(+)-29** (590 mg, 61%), and the starting material **(+)-11** (58 mg, 9.4 %).

(+)-10: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **10**; mp 182-184 °C; $[\alpha]_D^{20}$ +208.2 (*c* 1.12, $CHCl_3$).

(+)-29: R_f 0.27 (EtOAc : Hex = 1 : 2); mp 123-124 °C; $[\alpha]_D^{20}$ +172.1 (*c* 1.71, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 6H, C<u>Me</u>$_2$), 3.46 (br. s, 1H, O<u>H</u>-4), 3.71 (dd, J = 8.3, 9.8 Hz, 1H, H-3), 3.88 (app. t, J = 9.2 Hz, 1H, H-2), 4.55 (br. d, J = 7.1Hz, 1H, H-4), 5.71-5.83 (m, 3H, H-1, H-5 & H-6), 7.41-8.09 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 27.31, 27.42 [C<u>Me</u>$_2$], 70.89, 73.74, 77.76, 81.34 [C-1 ~ C-4], 112.02 [<u>C</u>Me$_2$], 127.19, 128.77, 130.09, 130.25, 132.91, 133.69 [C-5, C-6 & Ph], 166.43 [<u>C</u>OPh]; Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.15. Found: C, 65.94; H, 6.54.

Similarly, compound **(–)-11** was converted to the dibenzoate **(–)-10**, the monobenzoate **(–)-29** and the starting material **(–)-11**.

(–)-10: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **10**; mp 182-184 °C; $[\alpha]_D^{20}$ –207.8 (*c* 1.13, $CHCl_3$).

(–)-29: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **(+)-29**; mp 123-124 °C; $[\alpha]_D^{20}$ –172.9 (*c* 1.41, $CHCl_3$).

(–)-(1*R*,2*S*,3*S*,4*S*)- & (+)-(1*S*,2*R*,3*R*,4*R*)-1,4-Di-*O*-benzoyl-2,3-*O*-isopropylidenecyclohex-5-ene-1,2,3,4-tetrol [(–)-30 & (+)-30]

Compound **(+)-29** (420 mg, 1.45 mmol) was treated by the same procedure as described for the Mitsunobu reaction of compound **15** to give compound **(–)-30** (560 mg, 98%) as an oil.

(–)-30: R_f 0.55 (EtOAc : Hex = 1 : 2); $[\alpha]_D^{20}$ –56.3 (*c* 3.29, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.43, 1.50 (2s, 6H, C<u>Me</u>$_2$), 3.86 (dd, J = 3.7, 10.0 Hz, 1H, H-2 or H-3), 4.39 (dd, J = 8.9, 10.0 Hz, 1H, H-3 & H-2), 5.79 (br. d, J = 9.1 Hz, 1H, H-4 or H-1), 5.93 (app. t, J = 4.3 Hz, 1H, H-1 or H-4), 6.00 (dd, J = 1.8, 10.0 Hz, 1H, H-5 or H-6), 6.13 (ddd, J = 1.8, 5.0, 10.0 Hz, 1H, H-6 or H-5), 7.44-8.13 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 27.02, 27.43 [C<u>Me</u>$_2$], 66.35,

73.74, 74.57, 75.74 [C-1 ~ C-4], 111.96 [$\underline{C}Me_2$], 126.58-133.74 [C-5, C-6 & Ph], 166.16, 166.31 [2$\underline{C}$OPh].

Similarly, compound **(+)-30** was prepared from **(–)-29**.

(+)-30: Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **(–)-30**; $[\alpha]_D^{20}$ +55.0 (*c* 3.10, $CHCl_3$).