Reductive Cross-Aldol Reaction Using Bromoaldehyde and an Aldehyde Mediated by Germanium(II): One-Pot, Large-Scale Protocol

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Supporting Information

General. IR spectra were recorded as thin films or as solids in KBr pellets on a HORIBA FT-720 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained with TMS as internal standard. Techniques of HMBC or HMQC were employed to assign signals. Mass spectra were recorded on a JEOL JMS-DS303 spectrometer. Column chromatography was performed on silica gel. Bulb-to-bulb distillation (Kugelrohr) was accomplished in a Sibata GTO-250RS at the oven temperature and pressure indicated. Yields were determined by ^1H NMR using internal standards.

Materials. THF, Et_2O , hexane were distilled from sodium with benzophenone. DMF was predried by MS3A and distilled. Dichloromethane, dehydrated purchased from Wako Pure Chemical Ind. Ltd. (stabilized with 2-methyl-2-butene) was used without purification. Methanol was dried over MS3A. Zn, SmI_2 , CrCl_2 , and SnCl_2 were commercially available. GeCl_2 -dioxane was prepared by known method.¹ The aldehydes **2a-e** and heptanal **7** were commercially available. The bromoaldehydes **1a** and **1b** were prepared by known procedure.^{2,3} The bromoaldehyde **1c** was prepared according to the known procedure.⁴ To a stirred solution of 3-phenylpropanal (120 mmol) and DMSO (125 mmol) in dry acetonitrile (100 mL) was slowly added Me_3SiBr (130 mmol) for 15 min. The reaction temperature was kept at 20 °C by external cooling for 45 min. Volatiles were directly removed under reduced pressure at rt. The distillation (73-76 °C/0.2mmHg) gave the product **1c** (22.8 g, 89%).⁵ The brominated bis aldehyde **5** was prepared as shown below.

4-(2-Formylphenyl)butanal

A solution of the 6,7-dihydro-5H-benzocycloheptene (benzosuberene)⁶ (5.7 g, 39.5 mmol) in CH_2Cl_2 (140mL) and MeOH (17 mL) was cooled to $-78\text{ }^\circ\text{C}$, and O_3 was bubbled until the reaction mixture was light blue (excess O_3). The resulting mixture was stirred for 15 min at room

temperature after Me₂S (5 mL, 68 mmol) was added. Then the solution was washed with aqueous NaHCO₃ (saturated; 100 mL, 20 mL x 2), and aqueous FeSO₄·7H₂O (0.04 M; 100 mL), and the organic layer was dried over MgSO₄. The solvent was evaporated under reduced pressure and the residue was purified by distillation to give a pure product, containing a trace amount of acid (4.2 g, 23.7 mmol, 60%): bp: 113 °C / 0.8 mmHg; IR: (neat) 1697 (2'-CHO), 1720 (C₁HO) cm⁻¹; ¹H NMR: (400 MHz, CDCl₃) 10.22 (s, 1H, 2'-CHO), 9.79 (t, *J* = 1.5 Hz, 1H, 1-H), 7.83-7.81 (m, 1H, 3'-H), 7.54-7.50 (m, 1H, 5'-H), 7.43-7.39 (m, 1H, 4'-H), 7.29-7.27 (m, 1H, 6'-H), 3.07 (t, *J* = 7.8 Hz, 2H, 4-H₂), 2.53 (td, *J* = 7.3, 1.5 Hz, 2H, 2-H₂), 1.95 (tt, *J* = 7.8, 7.3 Hz, 2H, 3-H₂); ¹³C NMR: (67.9 MHz, CDCl₃) 201.97 (d, C-1), 192.54 (d, 2'-CHO), 143.82 (s, C-1'), 133.68 (d, C-5'), 133.58 (d, ²*J*_{CH}, C-2'), 133.09 (t, C-3'), 131.01 (d, C-6'), 126.72 (d, C-4'), 43.23 (td, C-2), 31.87 (t, C-4), 24.01 (t, C-3); MS: (EI, 70 eV) *m/z* 176 (M⁺, 10), 158 (M⁺ - H₂O, 38), 133 (M⁺ - CH₂CH₂CHO, 100), 129 (M⁺ - H₂O - CHO, 78), 104 (Ph - CO, 60), 91 (PhCH₂, 55); HRMS: (EI, 70 eV) calcd for C₁₁H₁₂O₂ 176.0837 (M⁺) found for *m/z* 176.0833. Anal. Calcd for C₁₁H₁₂O₂: C, 74.98; H, 6.86. Found C, 75.08; H, 6.81.

2-Bromo-4-(2-formylphenyl)butanal (5)

To the solution of 4-(2-formylphenyl)butanal (6.0 mmol) and DMSO (6.7 mmol) in MeCN (12mL) was slowly added Me₃SiBr (6.7 mmol). The reaction was slightly exothermic and was kept room temperature by water bath. The resulting mixture was stirred for 70 min, and then quenched by water (50mL), extracted with Et₂O, and the organic layer was dried over MgSO₄. The solvent was evaporated under reduced pressure, and the crude product was quickly used in the subsequent reaction: IR: (neat) 1697 (2'-CHO), 1724 (C₁HO) cm⁻¹; ¹H NMR: (600 MHz, CDCl₃) 10.18 (s, 1H, 2'-CHO), 9.48 (d, *J* = 2.4 Hz, 1H, 1-H), 7.84-7.81 (m, 1H, 3'-H), 7.56-7.52 (m, 1H, 5'-H), 7.47-7.44 (m, 1H, 4'-H), 7.34-7.32 (m, 1H, 6'-H), 4.27 (ddd, *J* = 8.3, 5.9, 2.4 Hz, 1H, 2-H), 3.30-3.24 (ddd, *J* = 13.2, 9.5, 5.6 Hz, 1H, 4-H^A), 3.19-3.12 (ddd, *J* = 13.2, 9.5, 6.3 Hz, 1H, 4-H^B), 2.42-2.34 (ddddd, *J* = 14.7, 9.5, 6.3, 5.9 Hz, 1H, 3-H^A), 2.24-2.17 (ddddd, *J* = 14.7, 9.5, 8.3, 5.6 Hz, 1H, 3-H^B); ¹³C NMR: (150 MHz, CDCl₃) 192.88 (-, 2'-CHO), 192.32 (-, C-1), 142.18 (+, C-1'), 134.42 (-, C-3'), 133.91 (-, C-4'), 133.80 (+, C-2'), 131.38 (-, C-6'), 127.30 (-, C-5'), 54.61 (-, C-2), 33.03 (+, C-3), 30.39 (+, C-4); MS: (CI, 70 eV) *m/z* 257 (M⁺ + 3, 74), 255 (M⁺ + 1, 81), 239 (M⁺ + 3 - H₂O, 20), 237 (M⁺ + 1 - H₂O, 18), 221 (M⁺ + 3 - 2H₂O, 18), 219 (M⁺ + 1 - 2H₂O, 29), 207 (M⁺ - CHO - H₂O, 87), 175 (M⁺ - HBr + 1, 68), 159 (100), 147 (M⁺ - CHO - Br + 1, 25), 129 (M⁺ - CHO - Br - H₂O + 1, 52); HRMS: (CI, 70 eV) calcd for C₁₁H₁₂⁸¹BrO₂ 257.0021 (M⁺ + 3) found for *m/z* 256.9991, calcd for C₁₁H₁₂⁷⁹BrO₂ 255.0021 (M⁺ + 1) found for *m/z* 254.9950.

Reaction of Bromoheptanal (1a) with Benzaldehyde (2a) in the presence of Zn (Table 1, entry 1). To a stirred solution of 2-bromoheptanal **1a** (1 mmol) and benzaldehyde **2a** (1 mmol) in dry THF (2 mL) was added Zn power (1 mmol) at room temperature. The reaction was stirred

at 68 °C for 2 h. H₂O (10 mL) was added to the reaction mixture. The resulting mixture was extracted with Et₂O, and organic layer was dried over MgSO₄. The complicated mixture was observed by ¹H NMR with recovering of benzaldehyde **2a** (47%). The bromoaldehyde **1a** was totally consumed.

Reaction of Bromoheptanal (1a) with Benzaldehyde (2a) in the presence of SmI₂ (Table 1, entry 2). To a stirred solution of SmI₂ (0.1 M in THF, 20 mL) was slowly added mixture of 2-bromoheptanal **1a** (1 mmol) and benzaldehyde **2a** (1 mmol) in dry THF (2 mL) at –78 °C for 10 min. The reaction was stirred at –78 °C for 2 h. Aqueous NaHCO₃ (saturated; 20 mL) was added to the reaction mixture. The resulting mixture was extracted with Et₂O, and organic layer was dried over MgSO₄. The complicated mixture was observed by ¹H NMR with recovering of benzaldehyde **2a** (25%). The bromoaldehyde **1a** was totally consumed.

Reaction of Bromoheptanal (1a) with Benzaldehyde (2a) in the presence of CrCl₂ (Table 1, entry 3). To a stirred suspension of CrCl₂ (1.46 mmol) and benzaldehyde **2a** (0.5 mmol) in dry THF (2 mL) was added 2-bromoheptanal **1a** (0.47 mmol) at room temperature. The reaction was stirred at room temperature for 14 h. H₂O (10 mL) was added to the reaction mixture. The resulting mixture was extracted with Et₂O, and organic layer was dried over MgSO₄. The complicated mixture was observed by ¹H NMR with recovering of benzaldehyde **2a** (14%). The bromoaldehyde **1a** was totally consumed.

Reaction of Bromoheptanal (1a) with Benzaldehyde (2a) in the presence of SnCl₂ (Table 1, entry 4). To a stirred solution of SnCl₂ (0.68 mmol) and benzaldehyde **2a** (0.67 mmol) in dry THF (2 mL) was added 2-bromoheptanal **1a** (0.68 mmol) at room temperature. The reaction was stirred at room temperature for 2 h. Aqueous NH₄F (15%, 10 mL) was added to the reaction mixture. The resulting mixture was extracted with Et₂O, and organic layer was dried over MgSO₄. The recovery of bromoaldehyde **1a** (65%) and benzaldehyde **2a** (49%) were found by ¹H NMR without any other products.

Reaction of Bromoheptanal (1a) with Benzaldehyde (2a) in the presence of GeCl₂-dioxane (Table 1, entry 5). To a stirred solution of GeCl₂-dioxane (0.6 mmol) and benzaldehyde **2a** (0.6 mmol) in dry THF (2 mL) was added 2-bromoheptanal **1a** (0.6 mmol) at room temperature. The reaction was stirred at room temperature for 2 h. H₂O (10 mL) was added to the reaction mixture. The resulting mixture was extracted with Et₂O, and organic layer was dried over MgSO₄. The aldol product **3** was observed by ¹H NMR in 60% yield (*syn:anti* = 64:36)⁷ with recovering of benzaldehyde **2a** (23%). A small amount of heptanal which derived from reduction of **1a** was observed (14%).

General Procedure for Reductive Aldol Reaction Using GeCl₂-dioxane with MeOH-quenching (Tables 2 and 3). To a stirred suspension of Bu₄NBr (0.006 mmol), GeCl₂-dioxane complex (0.6 mmol) and aldehyde **2** (0.6 mmol) in solvent (2 mL) was added bromoaldehyde **1** (0.6 mmol) under nitrogen. The reaction mixture was stirred under the reaction conditions noted in the text. Methanol (8 mL) was added and the resulting solution was stirred for additional 1 h at

room temperature. Then aqueous NaHCO_3 (saturated; 5 mL) was added to the reaction mixture. The resulting mixture was extracted with Et_2O /hexane (4/1), and organic layer was dried over MgSO_4 . The procedures of further purification for new compounds are shown in the Product Data section.

Product Data. The spectral data of **4aa** was in an excellent agreement with the reported data.⁷ Spectral data for the products, **4ab**, **4ac**, **4ba**, **4ca**, **4cd**, **4ce**, **4cb**, **4cc**, and **6** are shown below. The experiments for the isolation of the products were employed in about fivefold scale.

Determination of Stereochemistry of the Products. The relative stereoconfiguration of the products **4** was determined based on the coupling constant between hydrogens on chiral centers. The products exist as intramolecularly hydrogen bonded structures with the six-membered ring in chair conformation.⁸ The substituents on the ring tend to locate in equatorial position except one of the two MeO groups of acetal moiety because of anomeric effect.⁹ The relative stereoconfiguration of **6** was determined by X-ray structural analysis.

(6*R,7*S**)-7-Dimethoxymethyl-6-dodecanol (syn-4ab).**

According to the general procedure, this compound was prepared from **1a**, **2b**, GeCl_2 -dioxane, and Bu_4NBr in Et_2O to give the product as a colorless liquid after column chromatography (hexane/ethyl acetate, 95/5) on silica gel (BW-300): IR: (neat) 3521 (OH) cm^{-1} ; ^1H NMR: (270 MHz, CDCl_3) *syn* (major) 4.33 (d, $J = 5.1$ Hz, 1H, 7- $\text{CH}(\text{OMe})_2$), 3.89-3.79 (m, 1H, 6-H), 3.44 (s, 3H, OMe^A), 3.37 (s, 3H, OMe^B), 2.97 (d, $J = 4.9$ Hz, 1H, OH, D_2O -exchangeable), 1.75-1.65 (m, 1H, 7-H), 1.58-1.17 (m, 16H, 2- H_2 , 3- H_2 , 4- H_2 , 5- H_2 , 8- H_2 , 9- H_2 , 10- H_2 , and 11- H_2), 0.97-0.81 (m, 6H, 1- H_3 , and 12- H_3); ^1H NMR: (600 MHz, CDCl_3 , small amount of D_2O) 4.33 (d, $J = 5.1$ Hz, 1H, 7- $\text{CH}(\text{OMe})_2$), 3.83 (ddd, $J = 9.0, 4.2, 1.9$ Hz, 1H, 6-H), 3.44 (s, 3H, OMe^A), 3.37 (s, 3H, OMe^B), 1.70 (tdd, $J = 7.3, 5.1, 1.9$ Hz, 1H, 7-H), 1.54-1.23 (m, 16H, 2- H_2 , 3- H_2 , 4- H_2 , 5- H_2 , 8- H_2 , 9- H_2 , 10- H_2 , and 11- H_2), 0.95-0.87 (m, 6H, 1- H_3 , and 12- H_3); ^{13}C NMR: (67.9 MHz, CDCl_3) 108.10 (d, 13- $\text{CH}(\text{OMe})_2$), 70.60 (d, C-6), 55.90 (q, OMe^A), 53.78 (q, OMe^B), 45.06 (d, C-7), 33.51 (t, C-5), 32.08 (t, C-10), 31.80 (t, C-3), 27.96 (t, C-9), 26.17 (t, C-4), 24.58 (t, C-8), 22.57 (t, C-2), 22.44 (t, C-11), 13.95 (q), 13.93 (q); MS: (CI, 70 eV) m/z 243 ($\text{M}^+ - \text{H}_2\text{O} + 1$, 4), 229 ($\text{M}^+ - \text{OMe}$, 9), 211 ($\text{M}^+ - \text{H}_2\text{O} - \text{OMe}$, 12), 197 ($\text{M}^+ - (\text{OMe})_2 + 1$, 13), 129 ($\text{M}^+ - \text{C}_5\text{H}_{11}\text{CHOH} - \text{OMe} + 1$, 100), 115 ($\text{M}^+ - \text{C}_5\text{H}_{11} - \text{CH}(\text{OMe})_2 + 1$, 28), 89 ($\text{CHCH}(\text{OMe})_2 + 1$, 14); HRMS: (CI, 70 eV) calcd for $\text{C}_{15}\text{H}_{31}\text{O}_2$ 243.2264 ($\text{M}^+ - \text{H}_2\text{O} + \text{H}$) found for m/z 243.2326. Anal. Calcd for $\text{C}_{15}\text{H}_{32}\text{O}_3$ (260.41): C, 69.18; H, 12.39. Found C, 69.14; H, 12.12.

(6*S,7*S**)-7-Dimethoxymethyl-6-dodecanol (*anti*-4ab).**

This compound was a minor product in the reaction of **1a** with **2b** and was not purely isolated. The selected signals in the crude mixture were shown below: ^1H NMR: (270 MHz, CDCl_3) 4.41 (d, $J = 4.4$ Hz, 1H, 7- $\text{CH}(\text{OMe})_2$), 3.65 (ddd, $J = 8.6, 6.0, 2.9$ Hz, 1H, 6-H), 3.43 (s, 3H, OMe^A), 3.40 (s, 3H, OMe^B), 3.33 (d, $J = 4.6$ Hz, 1H, OH, D_2O -exchangeable), 1.68-1.64 (m, 1H, 7-H); Irradiation at 7-H caused disappearance of spin-spin coupling ($J = 6.0$ Hz) at 6-H; ^{13}C NMR: (67.9 MHz, CDCl_3) 107.86 (d, 13- $\text{CH}(\text{OMe})_2$), 71.21 (d, C-6), 55.78 (q, OMe^A), 54.33 (q, OMe^B), 44.99 (d, C-7).

(1*R,2*S**)-1-Cyclohexyl-2-dimethoxymethyl-1-heptanol (*syn*-4ac).**

According to the general procedure, this compound was prepared from **1a**, **2c**, GeCl_2 -dioxane, and Bu_4NBr in Et_2O to give the product as a colorless liquid after flash column chromatography [hexane/ethyl acetate, 99/1 and then 95/5] on silica gel (Fuji Silysia BW-300). The *syn* isomer was eluted later than the *anti* isomer: IR: (neat) 3544 (OH) cm^{-1} ; ^1H NMR: (600 MHz, CDCl_3) 4.35 (d, $J = 3.5$ Hz, 1H, 2- $\text{CH}(\text{OMe})_2$), 3.62 (d, $J = 9.4$ Hz, 1H, 1-H), 3.45 (s, 3H, OMe^A), 3.39 (s, 3H, OMe^B), 2.86 (brs, 1H, OH, D_2O -exchangeable), 2.14-2.06 (m, 1H, 6'- H^A), 1.78-1.69 (m, 3H, 2-H, 3'- H^A , and 5'- H^A), 1.67-1.62 (m, 1H, 4'- H^A), 1.60-1.55 (m, 1H, 2'- H^A), 1.47-1.09 (m, 12H, 3- H_2 , 4- H_2 , 5- H_2 , 6- H_2 , 1'-H, 3'- H^B , 4'- H^B , and 5'- H^B), 0.90 (t, 3H, $J = 7.1$ Hz, 3H, 7- H_3), 0.98-0.83 (m, 2H, 2'- H^B and 6'- H^B); ^{13}C NMR: (67.9 MHz, CDCl_3) 109.07 (d, 2- $\text{CH}(\text{OMe})_2$), 74.46 (d, C-1), 56.68 (q, OMe^A), 55.52 (q, OMe^B), 41.74 (d, C-2), 40.08 (d, C-1'), 32.35 (t, C-5), 30.03 (dd, C-6'), 29.28 (t, C-2'), 28.19 (t, C-4), 26.49 (t, C-4'), 26.09 (t, C-3'), 25.96 (t, C-5'), 23.24 (t, C-3), 22.60 (t, C-6), 14.10 (q, C-7); MS: (CI, 70 eV) m/z 255 ($\text{M}^+ - \text{H}_2\text{O} + 1$, 3), 241 ($\text{M}^+ - \text{MeOH} + 1$, 2), 223 ($\text{M}^+ - \text{H}_2\text{O} - \text{MeOH} + 1$, 16), 209 ($\text{M}^+ - \text{MeOH} - \text{OMe}$, 7), 129 (100), 113 ($\text{C}_6\text{H}_{11}\text{CHOH}$, 7), 95 ($\text{C}_6\text{H}_{10}=\text{CH}$, 3), 75 ($\text{CH}(\text{OMe})_2$, 3); HRMS: (CI, 70 eV) calcd for

$C_{16}H_{31}O_2$ 255.2245 ($M^+ - H_2O + 1$) found for m/z 255.2331. Anal. Calcd for $C_{16}H_{32}O_3$: C, 70.54; H, 11.84. Found C, 70.25; H, 11.55.

(1*R, 2*R**)-1-Cyclohexyl-2-dimethoxymethyl-1-heptanol (*anti*-4ac).**

This compound was a minor product in the reaction of **1a** with **2c** and was not purely isolated. The selected signals in the crude mixture were shown below: 1H NMR: (270 MHz, $CDCl_3$) 4.41 (d, $J = 3.9$ Hz, 1H, 2- $CH(OMe)_2$), 3.43 (s, 3H, OMe), 3.41 (s, 3H, OMe), 3.30-3.20 (brs, 1H, OH, D_2O -exchangeable); 1H NMR: (270 MHz, C_6D_6 with small amount of D_2O) 4.31 (d, $J = 4.4$ Hz, 1H, 2- $CH(OMe)_2$), 3.57 (dd, $J = 5.9, 5.9$ Hz, 1H, 1-H); ^{13}C NMR: (67.9 MHz, $CDCl_3$) 107.90 (2- $CH(OMe)_2$), 75.29 (C-1), 56.16 (OMe), 54.73 (OMe).

(1*R, 2*R**)-2-Dimethoxymethyl-3-methyl-1-phenyl-1-butanol (*syn*-4ba).**

According to the general procedure, this compound was prepared from **1b**, **2a**, $GeCl_2$ -dioxane, and Bu_4NBr in Et_2O to give the product as a colorless liquid after flash column chromatography (hexane/ethyl acetate, 95/5) on silica gel (BW-300). Further purification was performed by distillation under reduced pressure: bp: 120 $^{\circ}C$ / 0.1 mmHg; IR: (neat) 3467 (OH) cm^{-1} ; 1H NMR: (270 MHz, $CDCl_3$) 7.37-7.19 (m, 5H, Ar), 5.29 (brs, 1H, 1-H), 4.43 (d, $J = 3.4$ Hz, 1H, 2- $CH(OMe)_2$), 3.49 (s, 3H, OMe^A), 3.43 (s, 3H, OMe^B), 3.29 (d, $J = 2.4$ Hz, 1H, OH, D_2O -exchangeable), 2.01-1.89 (m, 1H, 3-H), 1.83 (ddd, $J = 3.3, 3.3, 3.3$ Hz, 1H, 2-H), 1.00 (d, $J = 7.1$ Hz, 3H, 3- CH_3), 0.77 (d, $J = 7.1$ Hz, 3H, 4- H_3); 1H NMR: (270 MHz, $CDCl_3$, small amount of D_2O) 7.37-7.19 (m, 5H, Ar), 5.29 (d, $J = 2.4$ Hz 1H, 1-H), 4.43 (d, $J = 3.4$ Hz, 1H, 2- $CH(OMe)_2$), 3.49 (s, 3H, OMe^A), 3.43 (s, 3H, OMe^B), 2.01-1.89 (m, 1H, 3-H), 1.83 (ddd, $J = 3.5, 3.5, 3.5$ Hz, 1H, 2-H), 1.00 (d, $J = 7.1$ Hz, 3H, 3- CH_3), 0.77 (d, $J = 7.1$ Hz, 3H, 4- H_3); ^{13}C NMR: (67.9 MHz, $CDCl_3$) 143.80 (s, *i*-Ph), 127.75 (d, *m*-Ph), 126.26 (d, *p*-Ph), 125.66 (d, *o*-Ph), 107.03 (d, 2- $CH(OMe)_2$), 72.11 (d, C-1), 55.57 (q, OMe^A), 54.99 (q, OMe^B), 52.25 (d, C-2), 24.33 (d, C-3), 23.11 (q, C-4), 20.53 (q, 3- CH_3); MS: (CI, 70 eV) m/z 121 ($PhCH(OH)CH + 1, 15$), 107 ($PhCHOH, 25$), 101 ($((CH_3)_2CHCHCHOMe + 1, 100$), 75 ($CH(OMe)_2, 28$). Anal. Calcd for $C_{14}H_{22}O_3$ (238.32): C, 70.56; H, 9.30. Found C, 70.49; H, 8.87.

(1*R,2*S**)-2-Dimethoxymethyl-3-methyl-1-phenyl-1-butanol (*anti*-4ba).**

This compound was a minor product in the reaction of **1b** with **2a** and was not purely isolated. The selected signals in the crude mixture were shown below: ^1H NMR: (270 MHz, CDCl_3) 4.93 (dd, $J = 7.8, 3.2$ Hz, 1H, 1-H), 4.41 (d, $J = 3.4$ Hz, 1H, 2- $\text{CH}(\text{OMe})_2$), 4.06 (d, $J = 3.2$ Hz, 1H, OH, D_2O -exchangeable), 3.43 (s, 3H, OMe^A), 3.42 (s, 3H, OMe^B), 0.95 (d, $J = 7.1$ Hz, 3H, 3- CH_3), 0.86 (d, $J = 6.8$ Hz, 3H, 4- H_3); ^{13}C NMR: (67.9 MHz, CDCl_3) 107.00 (d, 2- $\text{CH}(\text{OMe})_2$), 73.41 (d, C-1).

(1*R,2*R**)-2-Benzyl-3,3-dimethoxy-1-phenyl-1-propanol (*syn*-4ca).**

According to the general procedure, this compound was prepared from **1c**, **2a**, GeCl_2 -dioxane, and Bu_4NBr in Et_2O to give the product as a colorless liquid after flash column chromatography [hexane/ethyl acetate, 97/3 and then 95/5] on silica gel (Fuji Silysia BW-300). The *syn* isomer was eluted earlier than the *anti* isomer: IR: (neat) 3521 (OH) cm^{-1} ; ^1H NMR: (400 MHz, CDCl_3) 7.42-7.31 (m, 4H, 1- $\text{Ph}(o)$ and 1- $\text{Ph}(m)$), 7.26-7.16 (m, 3H, 1- $\text{Ph}(p)$ and 2- $\text{CH}_2\text{Ph}(m)$), 7.15-7.09 (m, 1H, 2- $\text{CH}_2\text{Ph}(p)$), 7.00-6.95 (m, 2H, 2- $\text{CH}_2\text{Ph}(o)$), 5.31 (brs, 1H, 1-H), 4.12 (d, $J = 2.3$ Hz, 1H, 3-H), 3.61 (d, $J = 2.2$ Hz, 1H, OH, D_2O -exchangeable), 3.44 (s, 3H, OMe^A), 3.30 (s, 3H, OMe^B), 2.74 (dd, $J = 14.1, 10.1$ Hz, 1H, 2- CH^APh), 2.60 (dd, $J = 14.1, 4.5$ Hz, 1H, 2- CH^BPh), 2.25-2.19 (m, 1H, 2-H); ^1H NMR: (270 MHz, CDCl_3 , small amount of D_2O) 5.31 (d, $J = 1.7$ Hz, 1H, 1-H); ^{13}C NMR: (100 MHz, CDCl_3) 142.73 (s, 1- $\text{Ph}(i)$), 140.47 (s, 2- $\text{CH}_2\text{Ph}(i)$), 128.76 (d, 2- $\text{CH}_2\text{Ph}(o)$), 128.22 (d, 2- $\text{CH}_2\text{Ph}(m)$), 127.97 (d, 1- $\text{Ph}(m)$), 126.64 (d, 1- $\text{Ph}(p)$), 125.77 (d, 1- $\text{Ph}(o)$), 125.75 (d, 2- $\text{CH}_2\text{Ph}(p)$), 107.30 (d, C-3), 71.08 (d, C-1), 56.88 (q, OMe^A), 55.31 (q, OMe^B), 50.05 (d, C-2), 29.35 (t, 2- CH_2Ph); MS: (EI, 70 eV) m/z 286 (M^+ , 0.03), 254 ($\text{M}^+ - \text{MeOH}$, 0.4), 236 ($\text{M}^+ - \text{H}_2\text{O} - \text{MeOH}$, 0.04), 179 ($\text{M}^+ - \text{C}_6\text{H}_5\text{CHOH}$, 1), 163 ($\text{M}^+ - \text{PhCH}_2 - \text{MeOH}$, 35), 148 (100), 147 ($\text{M}^+ - \text{PhCHOH} - \text{MeOH}$, 39), 117 (PhCH_2CHCH , 15), 107 (PhCHOH , 13), 91 (PhCH_2 , 16), 75 ($\text{CH}(\text{OMe})_2$, 66); HRMS: (EI, 70 eV) calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3$

286.1569 (M^+) found for m/z 286.1557. Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74. Found C, 75.41; H, 7.64.

(1*R,2*S**)-2-Benzyl-3,3-dimethoxy-1-phenyl-1-propanol (*anti*-4ca).**

This compound was a minor product in the reaction of **1c** with **2a** and was not purely isolated. The selected signals in the crude mixture were shown below: 1H NMR: (270 MHz, $CDCl_3$) 4.78 (dd, $J = 6.6, 4.4$ Hz, 1H, 1-H), 4.22 (d, $J = 4.4$ Hz, 1H, OH, D_2O -exchangeable), 4.08 (d, $J = 2.7$ Hz, 1H, 3-H), 3.38 (s, 3H, OMe), 3.36 (s, 3H, OMe); 1H NMR: (270 MHz, $CDCl_3$ with small amount of D_2O) 4.78 (d, $J = 6.6$ Hz, 1H, 1-H); ^{13}C NMR: (67.9 MHz, $CDCl_3$) 143.06 (*i*-Ph), 140.09 (*i*-Ph), 106.99 (C-3), 73.04 (C-1), 56.64 (OMe), 55.73 (OMe), 49.40 (C-2), 31.84 (2- CH_2Ph).

(1*R,2*R**)-2-Benzyl-3,3-dimethoxy-1-*p*-methylphenyl-1-propanol (*syn*-4cd).**

According to the general procedure, this compound was prepared from **1c**, **2d**, $GeCl_2$ -dioxane, and Bu_4NBr in Et_2O to give the product as a colorless liquid after flash column chromatography [hexane/ethyl acetate, 97/3 and then 95/5] on silica gel (Fuji Silysia BW-300). The *syn* isomer was eluted earlier than the *anti* isomer: IR: (neat) 3521 (OH) cm^{-1} ; 1H NMR: (600 MHz, $CDCl_3$) 7.29-7.26 (m, 2H, 2'-Hx2), 7.22-7.19 (m, 2H, 2- $CH_2Ph(m)$), 7.17-7.11 (m, 3H, 3'-Hx2 and 2- $CH_2Ph(p)$), 7.02-6.99 (m, 2H, 2- $CH_2Ph(o)$), 5.28-5.25 (brs, 1H, 1-H), 4.11 (d, $J = 4.1$ Hz, 1H, 3-H), 3.57-3.55 (brs, 1H, OH, D_2O -exchangeable), 3.44 (s, 3H, OMe^A), 3.30 (s, 3H, OMe^B), 2.74 (dd, $J = 14.4, 10.1$ Hz, 1H, 2- CH^APh), 2.60 (dd, $J = 14.4, 4.6$ Hz, 1H, 2- CH^BPh), 2.34 (s, 3H, 4'- CH_3), 2.25-2.20 (m, 1H, 2-H); 1H NMR: (600 MHz, $CDCl_3$, small amount of D_2O) 5.27-5.25 (brs, $^3J_{1-H,2-H} < 2$ Hz, 1H, 1-H); ^{13}C NMR: (150 MHz, $CDCl_3$) 140.57 (s, 2- $CH_2Ph(i)$), 139.67 (s, C-1'), 136.11 (s, C-4'), 128.82 (d, 2- $CH_2Ph(o)$), 128.69 (d, C-3'), 128.24 (d, 2- $CH_2Ph(m)$), 125.75 (d, 2- $CH_2Ph(p)$), 125.72 (d, C-2'), 107.31 (d, C-3), 71.08 (d, C-1), 56.85 (q, OMe^A), 55.23 (q, OMe^B), 49.99 (d, C-2), 29.49 (t, 2- CH_2Ph), 21.01 (q, 4'- CH_3); MS: (EI, 70 eV) m/z 300 (M^+ , 0.08), 268 ($M^+ - MeOH$, 0.4), 177 ($M^+ - PhCH_2 - MeOH$, 34), 148 (100), 147 ($M^+ - PhCHOH - MeOH$, 24), 117 ($PhCH_2CHCH$, 15), 91 ($PhCH_2$, 20), 75 ($CH(OMe)_2$, 44); HRMS:

(EI, 70 eV) calcd for C₁₉H₂₄O₃ 300.1725 (M⁺) found for m/z 300.1729. Anal. Calcd for C₁₉H₂₄O₃: C, 75.97; H, 8.05. Found C, 76.55; H, 8.03.

(1*R,2*S**)-2-Benzyl-3,3-dimethoxy-1-*p*-methylphenyl-1-propanol (*anti*-4cd).**

This compound was a minor product in the reaction of **1c** with **2d** and was not purely isolated. The selected signals in the crude mixture were shown below: ¹H NMR: (270 MHz, CDCl₃) 4.75 (dd, *J* = 6.7, 4.6 Hz, 1H, 1-H), 4.15 (d, *J* = 4.6 Hz, 1H, OH, D₂O-exchangeable), 4.09 (d, *J* = 2.9 Hz, 1H, 3-H), 3.38 (s, 3H, OMe), 3.35 (s, 3H, OMe), 2.35 (s, 3H, 4'-CH₃); ¹H NMR: (600 MHz, CDCl₃ with small amount of D₂O) 4.74 (d, *J* = 6.7 Hz, 1H, 1-H); ¹³C NMR: (67.9 MHz, CDCl₃) 140.33, 140.14, 136.62, 107.14 (C-3), 73.04 (C-1), 56.68 (OMe), 55.78 (OMe), 49.50 (C-2), 32.02 (2-CH₂Ph).

(1*R,2*R**)-2-Benzyl-3,3-dimethoxy-1-(4'-nitrophenyl)-1-propanol (*syn*-4ce).**

According to the general procedure, this compound was prepared from **1c**, **2e**, GeCl₂-dioxane, and Bu₄NBr in Et₂O to give the product as a colorless liquid after flash column chromatography [hexane/ethyl acetate, 97/3 to 80/20] on silica gel (Fuji Silysia BW-300). The *syn* isomer was eluted earlier than the *anti* isomer: IR: (neat) 3514 (OH) cm⁻¹; ¹H NMR: (270 MHz, CDCl₃) 8.24-8.17 (m, 2H, 3'-Hx2), 7.60-7.53 (m, 2H, 2'-Hx2), 7.25-7.10 (m, 3H, 2-CH₂Ph(*m*) and 2-CH₂Ph(*p*)), 6.98-6.91 (m, 2H, 2-CH₂Ph(*o*)), 5.48-5.45 (brs, 1H, 1-H), 4.16 (d, *J* = 2.7 Hz, 1H, 3-H), 3.75 (d, *J* = 1.5 Hz, 1H, OH, D₂O-exchangeable), 3.52 (s, 3H, OMe^A), 3.38 (s, 3H, OMe^B), 2.76 (dd, *J* = 14.4, 10.6 Hz, 1H, 2-CH^APh), 2.48 (dd, *J* = 14.4, 4.4 Hz, 1H, 2-CH^BPh), 2.25-2.16 (m, 1H, 2-H); ¹H NMR: (600 MHz, CDCl₃, small amount of D₂O) 5.46-5.45 (brs, ³*J*_{1-H,2-H} < 1.5 Hz, 1H, 1-H); ¹³C NMR: (67 MHz, CDCl₃) 150.66 (s, C-1'), 146.49 (s, C-4'), 139.40 (s, 2-CH₂Ph(*i*)), 128.52 (d, 2-CH₂Ph(*o*)), 128.15 (d, 2-CH₂Ph(*m*)), 126.44 (d, C-2'), 125.83 (d, 2-CH₂Ph(*p*)), 122.98 (d, C-3'), 107.12 (d, C-3), 70.38 (d, C-1), 57.24 (q, OMe^A), 55.91 (q, OMe^B), 50.05 (d, C-2), 29.13 (t, 2-CH₂Ph); MS: (EI, 70 eV) m/z 331 (M⁺, 0.5), 299 (M⁺ - MeOH, 3), 282 (M⁺ - MeO - H₂O, 0.4), 208 (M⁺ - C₆H₄NO₂, 16), 148 (46), 147 (M⁺ - NO₂C₆H₄CHOH - MeOH, 84), 133 (NO₂C₆H₄, 6), 117 (PhCH₂CHCH, 14), 91 (PhCH₂, 22), 75 (CH(OMe)₂, 100); HRMS:

(EI, 70 eV) calcd for $C_{18}H_{21}NO_5$ 331.1420 (M^+) found for m/z 331.1422. Anal. Calcd for $C_{18}H_{21}NO_5$: C, 65.24; H, 6.39; N, 4.23. Found C, 65.27; H, 6.42; N, 4.15.

(1*R,2*S**)-2-Benzyl-3,3-dimethoxy-1-(4'-nitrophenyl)-1-propanol (*anti*-4ce).**

This compound was a minor product in the reaction of **1c** with **2e** and was not purely isolated. The selected signals in the crude mixture were shown below: 1H NMR: (600 MHz, $CDCl_3$) 4.87 (dd, $J = 6.1, 5.0$ Hz, 1H, 1-H), 4.38 (d, $J = 5.0$ Hz, 1H, OH, D_2O -exchangeable), 4.07 (d, $J = 2.8$ Hz, 1H, 3-H), 3.40 (s, 3H, OMe), 3.35 (s, 3H, OMe), 2.55 (dd, $J = 13.9, 8.0$ Hz, 1H, 2- CH^A Ph), 2.34-2.30 (m, 1H, 2-H); 1H NMR: (600 MHz, $CDCl_3$ with small amount of D_2O) 4.86 (d, $J = 6.1$ Hz, 1H, 1-H); ^{13}C NMR: (67.9 MHz, $CDCl_3$) 151.12, 146.97, 139.40, 106.94 (C-3), 72.58 (C-1), 56.93 (OMe), 55.88 (OMe), 49.56 (C-2), 32.11 (2- CH_2 Ph).

(2*R,3*S**)-2-Benzyl-1,1-dimethoxy-3-octanol (*syn*-4cb).**

According to the general procedure, this compound was prepared from **1c**, **2b**, $GeCl_2$ -dioxane, and Bu_4NBr in Et_2O to give the product as a colorless liquid after flash column chromatography [hexane/ethyl acetate, 90/10 and then 80/20] on silica gel (Fuji Silysia BW-300). The product was isolated as a mixture of diastereomers: IR: (neat) 3545 (OH) cm^{-1} ; 1H NMR: (600 MHz, $CDCl_3$) 7.30-7.26 (m, 2H, *m*-Ph), 7.22-7.17 (m, 3H, *o*-Ph and *p*-Ph), 4.18 (d, $J = 4.3$ Hz, 1H, 1-H), 3.97-3.93 (m, 1H, 3-H), 3.43 (s, 3H, OMe^A), 3.28 (s, 3H, OMe^B), 3.00 (d, $J = 3.7$ Hz, 1H, OH, D_2O -exchangeable), 2.78 (dd, $J = 14.5, 8.7$ Hz, 1H, 2- CH^A Ph), 2.73 (dd, $J = 14.5, 6.5$ Hz, 1H, 2- CH^B Ph), 2.06-2.01 (m, 1H, 2-H), 1.57-1.39 (m, 3H, 4- H_2 and 5- H^A), 1.35-1.24 (m, 5H, 5- H^B , 6- H_2 and 7- H_2), 0.89 (t, $J = 7.0$ Hz, 3H, 8- H_3); 1H NMR: (600 MHz, $CDCl_3$, small amount of D_2O) 3.94 (ddd, $J = 1.5, 4.5, 8.6$ Hz, 1H, 3-H). Irradiation at 2-H caused disappearance of spin-spin coupling ($J = 1.5$ Hz) at 3-H. ^{13}C NMR: (100 MHz, $CDCl_3$) 140.75 (s, *i*-Ph), 128.87 (d, *o*-Ph), 128.29 (d, *m*-Ph), 125.80 (d, *p*-Ph), 107.60 (d, C-1), 69.74 (d, C-3), 56.36 (q, OMe^A), 54.46 (q, OMe^B), 47.00 (d, C-2), 33.69 (t, C-4), 31.76 (t, C-6), 30.66 (t, 2- CH_2 Ph), 25.99 (t, C-5), 22.53 (t, C-7), 13.95 (q, C-8); MS: (EI, 70 eV) m/z 280 (M^+ , 0.06), 248 ($M^+ - MeOH$, 0.3), 230 ($M^+ -$

H₂O - MeOH, 0.2), 157 (M⁺ - PhCH₂ - MeOH, 3), 148 (39), 147 (M⁺ - *n*-C₅H₁₁CHOH - MeOH, 39), 117 (PhCH₂CHCH, 13), 91 (PhCH₂, 17), 75 (CH(OMe)₂, 100), 71 (*n*-C₅H₁₁, 4); HRMS: (EI, 70 eV) calcd for C₁₇H₂₈O₃ 280.2034 (M⁺) found for m/z 280.2036. Anal. Calcd for C₁₇H₂₈O₃ 280.4024: C, 72.82; H, 10.06. Found C, 72.53; H, 9.82.

(2*R,3*R**)-2-Benzyl-1,1-dimethoxy-3-octanol (*anti*-4cb).**

This compound was a minor product in the reaction of **1c** with **2b** and was not purely isolated. The selected signals in the crude mixture were shown below: ¹H NMR: (270 MHz, CDCl₃) 4.30 (d, *J* = 3.2, 1H, 1-H), 3.70-3.59 (m, 1H, 3-H), 3.43 (s, 3H, OMe), 3.36 (s, 3H, OMe); ¹H NMR: (600 MHz, CDCl₃ with small amount of D₂O) 3.63 (td, *J* = 5.8, 5.8 Hz, 1H, 3-H). Irradiation at 2-H caused disappearance of spin-spin coupling (*J* = 5.8 Hz) at 3-H. ¹³C NMR: (67.9 MHz, CDCl₃) 140.52 (*i*-Ph), 107.45 (C-1), 70.67 (C-3), 56.30 (OMe), 55.34 (OMe).

(1*R,2*S**)-2-Benzyl-1-cyclohexyl-3,3-dimethoxy-1-propanol (*syn*-4cc).**

According to the general procedure, this compound was prepared from **1c**, **2c**, GeCl₂-dioxane, and Bu₄NBr in Et₂O to give the product as a colorless liquid after flash column chromatography [hexane/ethyl acetate, 95/5] on silica gel (Fuji Silysia BW-300). The product was isolated as a mixture of diastereomers: IR: (neat) 3537 (OH) cm⁻¹; ¹H NMR: (600 MHz, CDCl₃) 7.30-7.25 (m, 2H, *m*-Ph), 7.21-7.17 (m, 3H, *o*-Ph and *p*-Ph), 4.09 (d, *J* = 3.0 Hz, 1H, 3-H), 3.75 (d, *J* = 9.5 Hz, 1H, 1-H), 3.41 (s, 3H, OMe^A), 3.25 (s, 3H, OMe^B), 3.09-3.07 (brs, 1H, OH, D₂O-exchangeable), 2.83 (dd, *J* = 14.3, 4.5 Hz, 1H, 2-CH^APh), 2.74 (dd, *J* = 14.3, 10.1 Hz, 1H, 2-CH^BPh), 2.20-2.10 (m, 2H, 2-H and 6'-H^A), 1.78-1.57 (m, 4H, 2'-H^A, 3'-H^A, 4'-H^A and 5'-H^A), 1.52-1.44 (m, 1H, 1'-H), 1.28-1.08 (m, 3H, 3'-H^B, 4'-H^B and 5'-H^B), 1.04-0.85 (m, 2H, 2'-H^B and 6'-H^B). Irradiation at 1'-H caused disappearance of spin-spin coupling (*J* = 9.5 Hz) at 1-H. ¹³C NMR: (67.9 MHz, CDCl₃) 140.92 (s, *i*-Ph), 128.88 (d, *o*-Ph), 128.23 (d, *m*-Ph), 125.72 (d, *p*-Ph), 108.06 (d, C-3), 73.65 (d, C-1), 56.75 (q, OMe^A), 55.60 (q, OMe^B), 43.58 (d, C-2), 39.85 (d, C-1'), 30.05 (dd, C-6'), 29.63 (t, 2-CH₂Ph), 29.03 (t, C-2'), 26.39 (t, C-4'), 26.00 (t, C-3'), 25.86 (t, C-5'); MS: (EI,

70 eV) m/z 292 (M^+ , 0.04), 260 ($M^+ - \text{MeOH}$, 0.3), 242 ($M^+ - \text{H}_2\text{O} - \text{MeOH}$, 0.1), 148 (51), 147 ($M^+ - \text{C}_6\text{H}_{11}\text{CHOH} - \text{MeOH}$, 15), 117 (PhCH_2CHCH , 19), 91 (PhCH_2 , 20), 75 ($\text{CH}(\text{OMe})_2$, 100); HRMS: (EI, 70 eV) calcd for $\text{C}_{18}\text{H}_{28}\text{O}_3$ 292.2038 (M^+) found for m/z 292.2044. Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_3$ C, 73.93; H, 9.65. Found C, 73.81; H, 9.48.

(1*R,2*R**)-2-Benzyl-1-cyclohexyl-3,3-dimethoxy-1-propanol (*anti*-4cc).**

This compound was a minor product in the reaction of **1c** with **2c** and was not purely isolated. The selected signals in the crude mixture were shown below: ^1H NMR: (600 MHz, CDCl_3) 4.31 (d, $J = 3.0$ Hz, 1H, 3-H), 3.44 (s, 3H, OMe), 3.39 (s, 3H, OMe); ^1H NMR: (600 MHz, C_6D_6 with small amount of D_2O) 4.19 (d, $J = 3.1$ Hz, 1H, 3-H), 3.54 (dd, $J = 6.0, 6.0$ Hz, 1H, 1-H), 3.05 (s, 3H, OMe), 2.94 (s, 3H, OMe); ^{13}C NMR: (67.9 MHz, CDCl_3) 140.52 (s, *i*-Ph), 128.98, 128.17, 107.54 (d, C-3), 74.63 (d, C-1), 56.46 (OMe), 41.06, 31.73, 28.02, 26.29.

(1*R,2*R**)-2-Dimethoxymethyl-1,2,3,4-tetrahydro-1-naphthol (*syn*-6).**

To a stirred solution of bis-aldehyde **5** (0.44 g, used without purification), Bu_4NBr (0.01 mmol), MS4A (0.8 g) in Et_2O (12 mL) was added GeCl_2 -dioxane (1.1 mmol) at room temperature. After the mixture was stirred for 2 h, at room temperature, methanol (20 mL) was added and the resulting solution was stirred for additional 1 h at room temperature. Then aqueous NaHCO_3 (saturated; 50 mL) was added, and the mixture was extracted with Et_2O /hexane (4/1) and the organic layer was dried over MgSO_4 . The solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography (hexane/ethyl acetate, 95/5) on silica gel (Fuji Silysia BW-300). The *syn* isomer was eluted later than *anti* isomer. Further purification was performed by recrystallization (hexane) to give the product as a white solid. X-ray analysis was performed and determined a stereochemistry of the compound: mp: 81 °C; IR: (neat) 3413 (OH) cm^{-1} ; ^1H NMR: (600 MHz, CDCl_3) 7.34-7.31 (m, 1H, 8'-H), 7.22-7.15 (m, 2H, 6'-H, 7'-H), 7.12-7.09 (m, 1H, 5'-H), 4.81 (brs, 1H, 1-H), 4.50 (d, $J = 7.7$ Hz, 1H, 2- $\text{CH}(\text{OMe})_2$), 3.42 (s, 3H, OMe^A), 3.39 (s, 3H, OMe^B), 2.89 (ddd, $J = 17.1, 5.4, 2.9$ Hz, 1H, 4- H^A), 2.76 (ddd, $J = 17.1, 11.2, 6.6$ Hz, 1H, 4- H^B), 2.58-2.51 (brs, 1H, OH, D_2O -exchangeable), 2.04-1.98 (m, 1H, 2-H),

1.92-1.80 (m, 2H, 3-H₂); ¹H NMR: (600 MHz, CDCl₃, small amount of D₂O) 4.79 (d, *J* = 2.9 Hz, 1H, 1-H); ¹³C NMR: (150 MHz, CDCl₃) 137.97 (s, C-8a), 136.60 (s, C-4a), 129.77 (d, C-8), 128.81 (d, C-5), 127.79 (d, C-6), 126.02 (d, C-7), 105.58 (d, 2-CH(OMe)₂), 67.58 (d, C-1), 54.04 (q, OMe^A), 53.54 (q, OMe^B), 41.80 (d, C-2), 28.55 (t, C-4), 18.64 (t, C-3); MS: (EI, 70 eV) *m/z* 204 (M⁺ - H₂O, 1), 190 (M⁺ - MeOH, 1), 173 (M⁺ - H₂O - OMe, 3), 130 (M⁺ - C(OMe)₂ - H₂O, 61), 129 (M⁺ - CH(OMe)₂ - H₂O, 23), 75 (CH(OMe)₂, 100), 71 (M⁺ - CH(OMe)₂ - C₆H₄, 20); HRMS: (EI, 70 eV) calcd for C₁₃H₁₆O₂ 204.1150 (M⁺ - H₂O) found for *m/z* 204.1153. Anal. Calcd for C₁₃H₁₈O₃: C, 70.24; H, 8.16. Found C, 70.06; H, 8.36.

(1*R,2*S**)-2-Dimethoxymethyl-1,2,3,4-tetrahydro-1-naphthol (*anti*-6).**

This compound was a minor product in the reaction of **1c** with **2b** and was not purely isolated. The selected signals in the crude mixture were shown below: ¹H NMR: (270 MHz, CDCl₃) 7.60-7.53 (m, 1H, Ar), 7.25-7.11 (m, 2H, Ar), 7.08-7.02 (m, 1H, Ar), 4.75 (d, *J* = 8.8 Hz, 1H, 1-H), 4.40 (d, *J* = 6.8 Hz, 1H, 2-CH(OMe)₂), 3.93 (brs, 1H, OH, D₂O-exchangeable) 3.48 (s, 3H, OMe^A), 3.40 (s, 3H, OMe^B), 2.92-2.68 (m, 2H, 4-H₂), 2.13-1.90 (m, 2H, 2-H and 3-H^A), 1.62-1.43 (m, 1H, 3-H^B); ¹³C NMR: (67 MHz, CDCl₃) 137.94 (s), 136.01 (s), 127.99 (d), 127.33 (d), 126.75 (d), 126.09 (d), 108.01 (d, 2-CH(OMe)₂), 69.71 (d, C-1), 55.42 (q, OMe^A), 52.66 (q, OMe^B), 44.08 (d, C-2), 28.43 (t, C-4), 22.57 (t, C-3); MS: (EI, 70 eV) *m/z* 204 (M⁺ - H₂O, 2), 190 (M⁺ - MeOH, 27), 158 (M⁺ - 2MeOH, 34), 130 (M⁺ - C(OMe)₂ - H₂O, 60), 129 (M⁺ - CH(OMe)₂ - H₂O, 42), 75 (CH(OMe)₂, 100), 71 (M⁺ - CH(OMe)₂ - C₆H₄, 42); HRMS: (EI, 70 eV) calcd for C₁₃H₁₆O₂ 204.1150 (M⁺ - H₂O) found for *m/z* 204.1136.

A Trial for Intramolecular Reductive Cross-Aldol Reaction of **5 Using SmI₂.** To a stirred solution of SmI₂ (0.1 M in THF, 12 mL) was slowly added bominated bis-aldehyde **5** (0.77 mmol) in dry THF (5 mL) at -78 °C for 10 min. The reaction was stirred at -78 °C for 2 h. A mixture of THF:H₂O (1:1, 20 mL) was added to the reaction mixture. The resulting mixture was extracted with Et₂O/hexane (4/1), and organic layer was dried over MgSO₄. The complicated mixture was observed by ¹H and ¹³C NMR. The starting material **5** was totally consumed.

One-Pot Cross-Aldol Reaction for Synthesis of **4aa (Scheme 2).** To a stirred solution of heptanal **7** (110 mmol) and DMSO (121 mmol) in dry acetonitrile (100 mL) was slowly added Me₃SiBr (132 mmol) for 10 min.⁴ The reaction temperature was kept at 20 °C by external cooling for 50min. Volatiles were removed under reduced pressure at rt. To the resultant bromoheptanal was added dry Et₂O (150 mL), MS4A (10 g) benzaldehyde **2a** (110 mmol), and Bu₄NBr (1 mmol). GeCl₂-dioxane was added with keeping at 20 °C by external cooling. The reaction mixture was stirred for 2 h at room temperature. Methanol (600 mL) was added and the resulting solution was stirred for additional 1 h at room temperature. The mixture was slowly poured into 1 L of saturated NaHCO₃aq. The resulting mixture was extracted with Et₂O/hexane

(4/1), and organic layer was dried over MgSO_4 . The organic layer was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (BW-300, 41mm ϕ x 45 cm). The solvents (1000 mL of hexane and 500 mL of hexane/EtOAc = 95/5) eluted the dimethyl acetal of benzaldehyde. The following solvents (500 mL of hexane/EtOAc = 95/5, 1000 mL of hexane/EtOAc = 90/10, and 500 mL of hexane/EtOAc = 80/20) afforded the product **4aa** (17.3 g, 65%, *syn:anti* = 83:17).

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X-ray Structure Report for *syn-6*

Experimental

Data Collection

A colorless block crystal of $C_{13}H_{18}O_3$ having approximate dimensions of 0.50 x 0.50 x 0.40 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K α radiation.

Indexing was performed from 2 oscillations which were exposed for 3.0 minutes. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

$$\begin{aligned} a &= 7.872(1) \text{ \AA} \\ b &= 7.923(1) \text{ \AA} & \beta &= 98.156(9)^\circ \\ c &= 9.822(1) \text{ \AA} \\ V &= 606.4(2) \text{ \AA}^3 \end{aligned}$$

For $Z = 2$ and F.W. = 222.28, the calculated density is 1.22 g/cm³. Based on the systematic absences of:

$$0k0: k \neq 2n$$

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$$P2_1 (\#4)$$

The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ to a maximum 2θ value of 54.9° . A total of 44 images, corresponding to 220.0° oscillation angles, were collected with 2 different goniometer settings. Exposure time was 1.00 minutes per degree. The camera radius

was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. Data were processed by the PROCESS-AUTO program package.

Data Reduction

Of the 5068 reflections which were collected, 1480 were unique ($R_{\text{int}} = 0.026$).

The linear absorption coefficient, μ , for Mo-K α radiation is 0.9 cm⁻¹. A symmetry-related absorption correction using the program ABSCOR¹ was applied which resulted in transmission factors ranging from 0.55 to 0.97. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods² and expanded using Fourier techniques³. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement⁴ was based on 1459 observed reflections ($I > 0.00\sigma(I)$, $2\theta < 54.91$) and 215 variable parameters and converged (largest parameter shift was 0.68 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma (F_o^2 - F_c^2) / \Sigma F_o^2 = 0.113$$

$$R_w = [(\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2)]^{1/2} = 0.126$$

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.052 \quad \text{for } I > 2.0\sigma(I) \text{ data}$$

The standard deviation of an observation of unit weight⁵ was 2.16. The weighting scheme was based on counting statistics and included a factor ($p = 0.050$) to downweight the intense reflections. Plots of $\Sigma w (F_o^2 - F_c^2)^2$ versus F_o^2 reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.29 and -0.20 e⁻/Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁶. Anomalous dispersion effects were included in Fcalc⁷; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁸. The values for the mass attenuation coefficients are those of Creagh and Hubbel⁹. All calculations were performed using the *teXsan*¹⁰ crystallographic software package of Molecular Structure Corporation.

References

(1) ABSCOR: Higashi T. (1995). Program for Absorption Correction, Rigaku Corporation, Tokyo, Japan.

(2) SHELXS-97: Sheldrick, G.M. (1997). Program for the Solution of Crystal Structures. University of Goettingen, Germany.

(3) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(4) Least-Squares:

$$\begin{aligned} \text{Function minimized: } & \sum w(F_o^2 - F_c^2)^2 \text{ where} \\ w = & 1/[\sigma^2(F_o^2)] = [\sigma_c^2(F_o^2) + (p \\ & (\text{Max}(F_o^2, 0) + 2F_c^2)/3)^2]^{-1} \\ \sigma_c(F_o^2) = & \text{e.s.d. based on counting statistics} \\ p = & \text{p-factor} \end{aligned}$$

(5) Standard deviation of an observation of unit weight:

$$\begin{aligned} & [\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2} \\ \text{where: } & N_o = \text{number of observations} \\ & N_v = \text{number of variables} \end{aligned}$$

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(10) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1999).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	C ₁₃ H ₁₈ O ₃
Formula Weight	222.28
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.50 X 0.50 X 0.40 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit	
Cell Determination (2 θ range)	6040 (4.2 - 54.8°)
Indexing Images	2 oscillations at 3.0 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 7.872(1) Å b = 7.923(1) Å c = 9.822(1) Å β = 98.156(9)° V = 606.4(2) Å ³
Space Group	P2 ₁ (#4)
Z value	2
D _{calc}	1.217 g/cm ³
F ₀₀₀	240.00
μ (MoK α)	0.85 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID Imaging Plate
Radiation	MoK α (λ = 0.71069 Å) graphite monochromated
Temperature	23.0 °C
Voltage, Current	50 kV, 40 mA
Collimator Size	0.8 mm
Detector Aperture	270.0 mm x 256.0 mm
Data Images	44 exposures at 1.0 minutes per degree

Oscillation Range ($\phi=0.0^\circ, \chi=45.0^\circ$)	ω 130.0 – 190.0 $^\circ$ with 5.0 $^\circ$ step
Oscillation Range ($\phi=180.0^\circ, \chi=45.0^\circ$)	ω 0.0 – 160.0 $^\circ$ with 5.0 $^\circ$ step
Camera Radius	127.40 mm
Pixel Size	0.100 mm
$2\theta_{\max}$	54.9 $^\circ$
No. of Reflections Measured	Total: 5068
	Unique: 1480 ($R_{\text{int}} = 0.026$)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.5450 – 0.9666)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXS-97)
Refinement	Full-matrix least-squares
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$1/\sigma^2(F_o^2)$
p-factor	0.0500
Anomalous Dispersion	All non-hydrogen atoms
No. of Observations ($I > 0.00\sigma(I)$, $2\theta < 54.91^\circ$)	1459
No. Variables	215
Reflection/Parameter Ratio	6.79
Residuals: R; R_w	0.113 ; 0.126
Residuals: R_1	0.052
No. of Reflections to calc R_1	1376
Goodness of Fit Indicator	2.16
Max Shift/Error in Final Cycle	0.683
Maximum peak in Final Diff. Map	0.29 e $^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	-0.20 e $^-/\text{\AA}^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
O(1)	0.0729(2)	0.8711	0.3531(1)	4.33(2)
O(2)	0.1680(2)	0.6294	0.6338(1)	4.44(2)
O(3)	0.4180(2)	0.5374(2)	0.5622(1)	4.69(3)
C(1)	0.0117(2)	0.6996(3)	0.3583(1)	3.54(3)
C(2)	0.1686(2)	0.5867(3)	0.3950(1)	3.60(3)
C(3)	0.2740(2)	0.6428(2)	0.5296(2)	3.67(3)
C(4)	0.2399(3)	0.6964(4)	0.7639(2)	5.49(5)
C(5)	0.5780(3)	0.6211(4)	0.5762(3)	5.63(5)
C(6)	0.2709(2)	0.5846(3)	0.2738(2)	4.35(3)
C(7)	0.1666(3)	0.4973(4)	0.1511(2)	5.15(4)
C(8)	-0.0161(2)	0.5570(3)	0.1234(2)	4.06(3)
C(9)	-0.1184(3)	0.5138(3)	-0.0003(2)	4.93(4)
C(10)	-0.2874(3)	0.5605(3)	-0.0266(2)	5.51(4)
C(11)	-0.3611(2)	0.6555(3)	0.0700(2)	5.31(4)
C(12)	-0.2621(2)	0.6986(3)	0.1930(2)	4.33(3)
C(13)	-0.0907(2)	0.6501(3)	0.2209(1)	3.72(3)
H(1)	-0.059(2)	0.687(3)	0.423(2)	3.2(3)
H(2)	-0.010(3)	0.937(3)	0.349(2)	4.8(4)
H(3)	0.131(2)	0.478(3)	0.403(2)	2.6(3)
H(4)	0.316(2)	0.757(3)	0.526(2)	3.1(3)
H(5)	0.282(4)	0.811(5)	0.751(3)	6.6(6)
H(6)	0.333(3)	0.632(4)	0.808(3)	6.1(5)
H(7)	0.145(4)	0.690(4)	0.825(3)	6.9(6)
H(8)	0.596(3)	0.670(4)	0.495(3)	7.3(7)
H(9)	0.655(5)	0.541(5)	0.600(4)	8.6(8)
H(10)	0.581(4)	0.706(5)	0.644(3)	7.7
H(11)	0.381(3)	0.528(3)	0.292(2)	5.0(5)
H(12)	0.302(3)	0.701(3)	0.248(2)	4.0(4)
H(13)	0.168(3)	0.376(5)	0.165(3)	6.4(6)
H(14)	0.212(3)	0.512(5)	0.067(3)	7.3(7)
H(15)	-0.073(3)	0.441(4)	-0.069(3)	6.7(6)
H(16)	-0.350(3)	0.515(3)	-0.111(2)	5.6(5)
H(17)	-0.487(3)	0.700(4)	0.053(2)	6.1(5)
H(18)	-0.316(3)	0.762(3)	0.254(2)	4.6(4)

$$B_{eq} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa*bb*)\cos \gamma + 2U_{13}(aa*cc*)\cos \beta + 2U_{23}(bb*cc*)\cos \alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O(1)	0.0457(6)	0.0443(6)	0.0728(7)	0.0025(5)	0.0030(5)	-0.0048(5)
O(2)	0.0583(6)	0.0634(8)	0.0465(5)	-0.0113(6)	0.0060(4)	-0.0060(5)
O(3)	0.0576(6)	0.0434(6)	0.0741(7)	0.0071(5)	-0.0014(5)	0.0060(5)
C(1)	0.0407(6)	0.0509(7)	0.0445(6)	-0.0035(6)	0.0110(5)	-0.0043(6)
C(2)	0.0482(7)	0.0410(7)	0.0482(6)	-0.0027(6)	0.0086(5)	-0.0004(6)
C(3)	0.0460(7)	0.0383(7)	0.0549(7)	-0.0031(6)	0.0062(5)	0.0011(6)
C(4)	0.074(1)	0.076(1)	0.0571(9)	0.001(1)	0.0022(8)	-0.0175(9)
C(5)	0.0487(9)	0.074(1)	0.089(1)	0.0072(8)	0.0011(9)	0.006(1)
C(6)	0.0506(8)	0.0593(10)	0.0583(8)	0.0078(8)	0.0178(6)	0.0004(7)
C(7)	0.0681(10)	0.074(1)	0.0565(9)	0.0112(9)	0.0177(7)	-0.0112(8)
C(8)	0.0631(8)	0.0492(9)	0.0438(6)	-0.0057(7)	0.0136(5)	-0.0007(6)
C(9)	0.085(1)	0.062(1)	0.0415(7)	-0.0094(9)	0.0112(7)	-0.0063(7)
C(10)	0.082(1)	0.078(1)	0.0443(8)	-0.018(1)	-0.0070(7)	0.0031(8)
C(11)	0.0573(9)	0.084(1)	0.0565(8)	-0.0058(10)	-0.0043(6)	0.0054(8)
C(12)	0.0499(7)	0.063(1)	0.0513(7)	-0.0042(8)	0.0067(6)	-0.0011(8)
C(13)	0.0509(7)	0.0478(8)	0.0433(6)	-0.0080(7)	0.0094(5)	0.0005(6)

The general temperature factor expression:

$$\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
O(1)	C(1)	1.445(3)	O(2)	C(3)	1.414(3)
O(2)	C(4)	1.424(3)	O(3)	C(3)	1.408(3)
O(3)	C(5)	1.413(4)	C(1)	C(2)	1.526(3)
C(1)	C(13)	1.522(3)	C(2)	C(3)	1.524(3)
C(2)	C(6)	1.529(3)	C(6)	C(7)	1.524(4)
C(7)	C(8)	1.502(4)	C(8)	C(9)	1.402(4)
C(8)	C(13)	1.401(3)	C(9)	C(10)	1.370(5)
C(10)	C(11)	1.400(5)	C(11)	C(12)	1.384(4)
C(12)	C(13)	1.392(4)			

Table 4. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
O(1)	H(2)	0.83(4)	C(1)	H(1)	0.91(3)
C(2)	H(3)	0.92(3)	C(3)	H(4)	0.96(3)
C(4)	H(5)	0.98(5)	C(4)	H(6)	0.95(4)
C(4)	H(7)	1.02(4)	C(5)	H(8)	0.91(5)
C(5)	H(9)	0.89(6)	C(5)	H(10)	0.95(6)
C(6)	H(11)	0.97(3)	C(6)	H(12)	1.00(4)
C(7)	H(13)	0.97(5)	C(7)	H(14)	0.95(5)
C(9)	H(15)	0.99(4)	C(10)	H(16)	0.97(4)
C(11)	H(17)	1.05(4)	C(12)	H(18)	0.93(4)

Table 5. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(3)	O(2)	C(4)	114.9(2)	C(3)	O(3)	C(5)	114.9(2)
O(1)	C(1)	C(2)	107.3(2)	O(1)	C(1)	C(13)	110.4(2)
C(2)	C(1)	C(13)	111.6(2)	C(1)	C(2)	C(3)	110.9(2)
C(1)	C(2)	C(6)	108.7(2)	C(3)	C(2)	C(6)	113.3(2)
O(2)	C(3)	O(3)	109.2(2)	O(2)	C(3)	C(2)	107.6(2)
O(3)	C(3)	C(2)	110.3(2)	C(2)	C(6)	C(7)	109.6(2)
C(6)	C(7)	C(8)	113.3(2)	C(7)	C(8)	C(9)	119.8(2)
C(7)	C(8)	C(13)	121.7(2)	C(9)	C(8)	C(13)	118.4(2)
C(8)	C(9)	C(10)	121.4(3)	C(9)	C(10)	C(11)	120.1(2)
C(10)	C(11)	C(12)	119.2(3)	C(11)	C(12)	C(13)	120.9(3)
C(1)	C(13)	C(8)	121.4(2)	C(1)	C(13)	C(12)	118.7(2)
C(8)	C(13)	C(12)	119.9(2)				

Table 6. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	O(1)	H(2)	109(2)	O(1)	C(1)	H(1)	111(1)
C(2)	C(1)	H(1)	108(1)	C(13)	C(1)	H(1)	107(1)
C(1)	C(2)	H(3)	108(1)	C(3)	C(2)	H(3)	109(1)

C(6)	C(2)	H(3)	105(1)	O(2)	C(3)	H(4)	109(1)
O(3)	C(3)	H(4)	107(1)	C(2)	C(3)	H(4)	112(1)
O(2)	C(4)	H(5)	109(2)	O(2)	C(4)	H(6)	113(2)
O(2)	C(4)	H(7)	106(2)	H(5)	C(4)	H(6)	107(3)
H(5)	C(4)	H(7)	113(4)	H(6)	C(4)	H(7)	106(3)
O(3)	C(5)	H(8)	111(2)	O(3)	C(5)	H(9)	104(3)
O(3)	C(5)	H(10)	109(2)	H(8)	C(5)	H(9)	110(4)
H(8)	C(5)	H(10)	108(4)	H(9)	C(5)	H(10)	112(4)
C(2)	C(6)	H(11)	114(1)	C(2)	C(6)	H(12)	111(1)
C(7)	C(6)	H(11)	107(2)	C(7)	C(6)	H(12)	110(1)
H(11)	C(6)	H(12)	103(2)	C(6)	C(7)	H(13)	109(2)
C(6)	C(7)	H(14)	114(2)	C(8)	C(7)	H(13)	109(2)
C(8)	C(7)	H(14)	105(2)	H(13)	C(7)	H(14)	104(4)
C(8)	C(9)	H(15)	120(2)	C(10)	C(9)	H(15)	117(2)
C(9)	C(10)	H(16)	115(1)	C(11)	C(10)	H(16)	124(1)
C(10)	C(11)	H(17)	123(1)	C(12)	C(11)	H(17)	117(2)
C(11)	C(12)	H(18)	116(1)	C(13)	C(12)	H(18)	122(1)

Table 7. Torsion Angles($^{\circ}$)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(1)	C(1)	C(2)	C(3)	56.4(2)	O(1)	C(1)	C(2)	C(6)	-68.8(2)
O(1)	C(1)	C(13)	C(8)	98.3(3)	O(1)	C(1)	C(13)	C(12)	-82.0(3)
O(2)	C(3)	O(3)	C(5)	-120.6(2)	O(2)	C(3)	C(2)	C(1)	60.9(2)
O(2)	C(3)	C(2)	C(6)	-176.5(2)	O(3)	C(3)	O(2)	C(4)	67.6(3)
O(3)	C(3)	C(2)	C(1)	179.9(2)	O(3)	C(3)	C(2)	C(6)	-57.5(3)
C(1)	C(2)	C(6)	C(7)	-66.5(3)	C(1)	C(13)	C(8)	C(7)	1.8(4)
C(1)	C(13)	C(8)	C(9)	179.2(2)	C(1)	C(13)	C(12)	C(11)	-179.5(3)
C(2)	C(1)	C(13)	C(8)	-20.9(3)	C(2)	C(1)	C(13)	C(12)	158.9(2)
C(2)	C(3)	O(2)	C(4)	-172.8(2)	C(2)	C(3)	O(3)	C(5)	121.4(2)
C(2)	C(6)	C(7)	C(8)	46.8(3)	C(3)	C(2)	C(1)	C(13)	177.5(2)
C(3)	C(2)	C(6)	C(7)	169.7(2)	C(6)	C(2)	C(1)	C(13)	52.2(3)
C(6)	C(7)	C(8)	C(9)	167.6(2)	C(6)	C(7)	C(8)	C(13)	-15.0(4)
C(7)	C(8)	C(9)	C(10)	177.4(3)	C(7)	C(8)	C(13)	C(12)	-178.0(3)
C(8)	C(9)	C(10)	C(11)	0.9(5)	C(8)	C(13)	C(12)	C(11)	0.3(4)
C(9)	C(8)	C(13)	C(12)	-0.6(4)	C(9)	C(10)	C(11)	C(12)	-1.2(5)
C(10)	C(9)	C(8)	C(13)	-0.1(4)	C(10)	C(11)	C(12)	C(13)	0.6(5)

Table 8. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	atom	atom	distance
O(1)	O(2) ¹⁾	2.805(2)	O(1)	C(5) ²⁾	3.378(4)
O(3)	C(5) ³⁾	3.569(4)			

Symmetry operations

(1)	$-X, Y+1/2, -Z+1$	(2)	$-X+1, Y+1/2, -Z+1$
(3)	$-X+1, Y-1/2, -Z+1$		