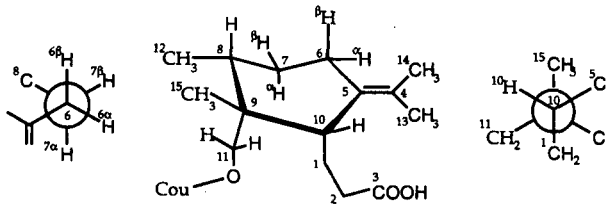

Figure 3. Revised configuration of galbanic acid.

The carboxylic group was also confirmed by the long range C-H correlation peaks between the carbonyl carbon 3 at 180.02 ppm and the methylene protons at C-2.

With this carbon fragment information and the C-H HETCOR experiment, the phase sensitive NOESY experiment was done for stereochemical analysis. The expanded partial NOESY spectrum of **1** is shown in Figure 2. Based on the fact that the carbons at C-4, C-5, C-6, C-10, C-13, and C-14 are in the same plane, we may easily predict the NOE cross peaks between protons at C-13 and C-10 or C-1.

Figure 2 shows clearly the NOE cross peak between the protons at C-10 and C-13 which says that the previous chemical shift assignments of methyl protons at C-13 and C-14 are reversed.[5] On the other hand, the methyl protons at C-14 show the NOE peak with the α-proton at C-6. Thus, the NOE results of the methyl protons at C-13 and C-14 not only can correct the previous chemical shift assignments of these protons, but can support the pseudo-equatorial position of the protons at C-10 and H-6α.

With these fixed two positions and the coupling constants (J) 13.7, 13.0, 13.0 and 4.7 Hz in *dddd* splitting pattern of H-7α, we can arrange the stereochemistry of H-6β and H-8 to have anti-parallel axial positions with respect to H-7α, respectively. The further streochemical arrangements in C-8 and C-9 are supported by the NOE peaks between the H-7α and one proton at C-11, and between the protons at C-12 and the other proton at C-11. Thus, the two methyl groups, which were assigned as α and β previously, at C-8 and C-9 should have α and β positions in the twisted boat conformation, respectively. The revised configuration of **1** is shown in Figure 3 with partial conformations. The final assignments of chemical shifts of the α and β protons at C-6 and C-7, which belong to equatorial or axial protons of cyclohexane depending on position, are valid for relationship, $\delta H_a < \delta H_e$.

In summary, we have shown that unambiguous structural analysis of galbanic acid (**1**) was done by using modern 2D NMR techniques including the 2D INADEQUATE experiment. It is also evident that the stereochemistry at C-8 and C-9 determined previously should be revised.

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Enantioselective Synthesis of the C20-C25 Portion of the Cytotoxic Natural Product, Amphidinolide B1

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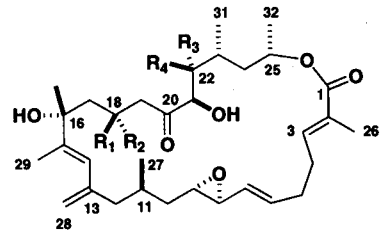
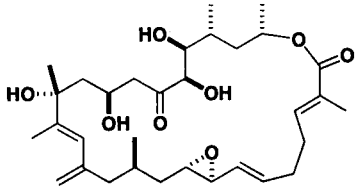
Amphidinolides A-Q have recently been isolated from dinoflagellates, genus *Amphidinium*, symbiotic with the Okinawan marine flatworms and generally exhibited potent toxicities against cancer tumor cell lines.[1,2] Although the chemical structures of them were elucidated mainly on the basis of extensive spectroscopic studies including 2D NMR experiments, their configurations still remain unclear except for amphidinolides B, J, and L. The relative stereochemical relationship of amphidinolide B group (**1**), the most representative and important group of amphidinolides family, was unambiguously solved by single crystal X-ray diffraction method[3a] and the absolute configuration of amphidinolide B1 (**1a**) was established on the basis of enantiospecific synthesis of a degradation product.[3b] The absolute configurations of amphidinolide J and L were determined similarly.[4a,4b]

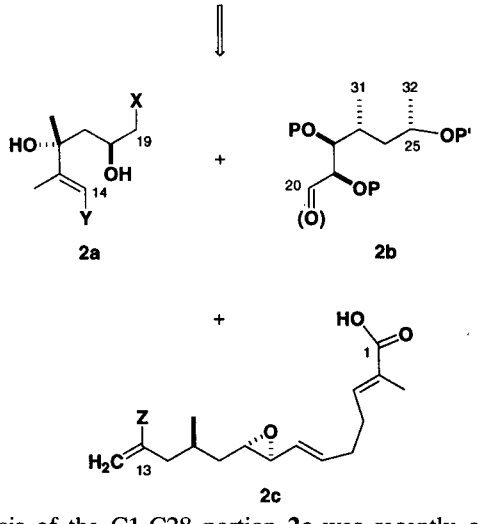
In our program toward the total synthesis of amphidinolide B1 (**1a**), the target molecule was initially divided into three components **2a**, **2b**, and **2c** and enantioselective



1a : Amphidinolide B1 (R_1=R_4=OH, R_2=R_3=H)
1b : Amphidinolide B2 (R_2=R_4=OH, R_1=R_3=H)
1c : Amphidinolide B3 (R_1=R_3=OH, R_2=R_4=H)



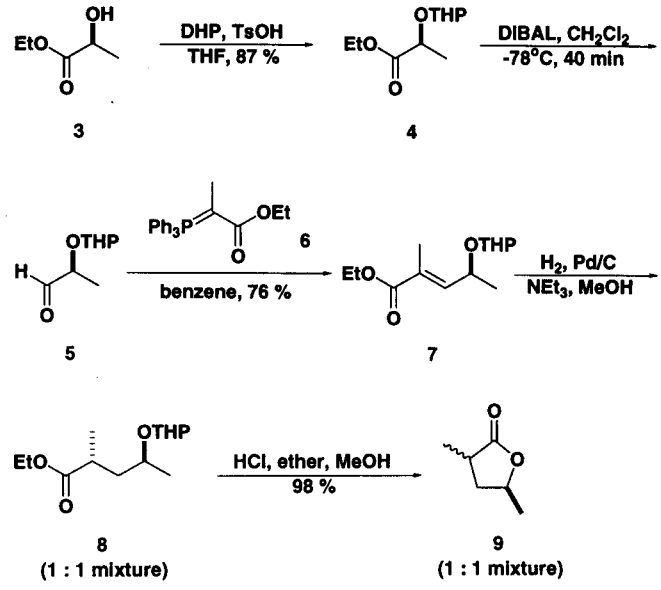
Amphidinolide B1(1a)



2a 2b 2c

synthesis of the C1-C28 portion **2c** was recently completed in our lab.[5] Now we report herein the enantioselective synthesis of the other segment **2b**, a C20-C25 portion.

First, ethyl (S)-(-)-lactate **3** was treated with 2,3-dihydro-2H-pyran and a catalytic amount of p-TsOH in THF at rt for 2 h to provide the THP protected ether **4** in 87% isolation yield (Scheme 1). DIBAL reduction of the ester **4** in methylene chloride at −78 °C for 40 min and olefination of the crude aldehyde **5** with the stabilized Wittig reagent, (carbethoxyethylene)triphenylphosphorane[7] **6** in benzene at 70 °C for 6 h provided the conjugate ester **7** in 76% overall yield. Hydrogenation of the ester **7** in the presence of a catalytic amount of triethylamine in methanol at rt for 5 h produced the crude ester **8** and the acidic hydrolysis of **8** in a mixture of ether and methanol at rt for 10 min resulted in the deprotection of the THP group and the spontaneous cyclization to give the butyrolactone **9** as an 1:1 mixture of isomers in 98% yield. Use of a catalytic amount of triethylamine as a base turned out to be essential in this hydrogenation reaction. Without triethylamine, the THP protecting group was often eliminated before hydrogenation of the double bond and the hydrogenation reaction then slowed down.

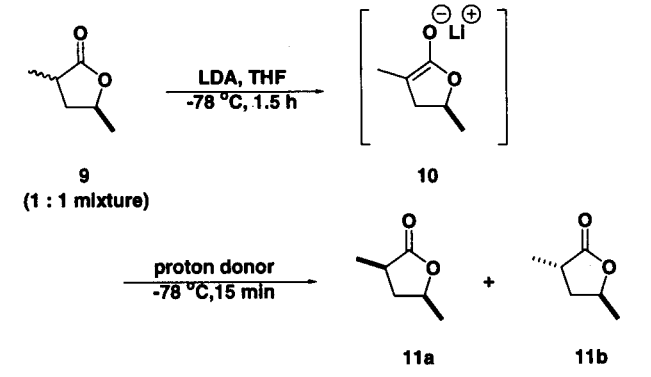


Scheme 1. Synthesis of Lactol 9.

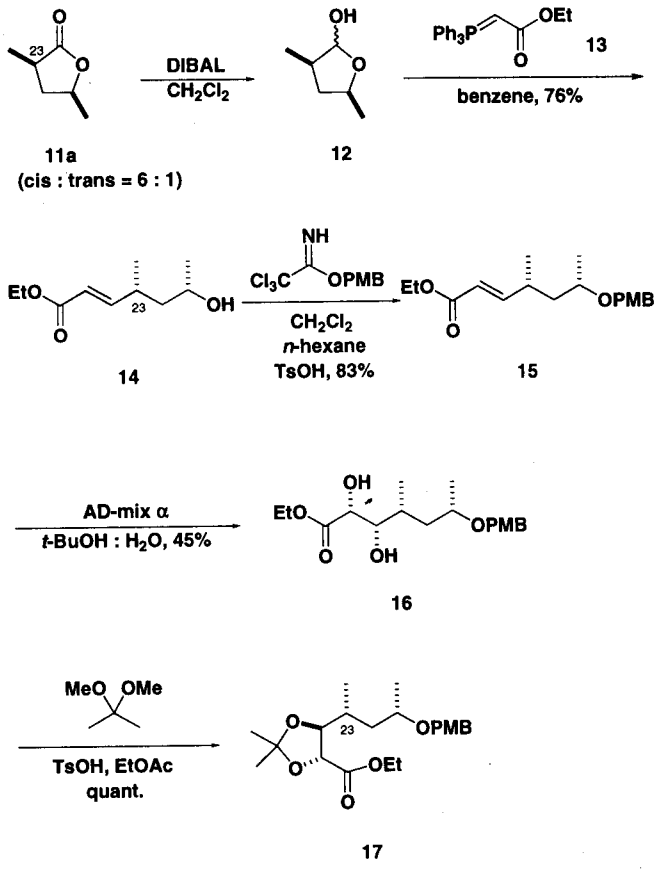
In order to prepare the *cis*-(2*R*,4*S*)-dimethylbutyrolactone **11a**, the diastereomeric lactones **9** were treated with LDA in THF at −78 °C for 1.5 h and the resulting enolate **10** was quenched with several proton sources (Table 1). The prediction was based on the fact that kinetic protonation would occur from the less hindered face to provide the *cis*-isomer **11a** rather than the *trans*-isomer **11b**. As shown in Table 1, the best diastereoselectivity (6:1) was realized with *p*-toluenesulfonic acid in 78% yield.

The crude diastereomeric mixture **11a/11b** was treated with DIBAL in methylene chloride at −78 °C for 40 min (Scheme 2) and the crude lactol **12** was subsequently converted to conjugate ester **14** by reaction with the stabilized Wittig reagent, (carbethoxymethylene)triphenylphosphorane **13** in benzene at 80 °C for 6 h in 76% overall yield. The hydroxyl group in **14** was protected as its PMB ether[8] in 83%

Table 1. Kinetic Protonation.



Proton Donor	11a : 11b
H_2O in THF	3:1
CF_3CO_2H	3:1
AcOH	3:1
TsOH	3:1



Scheme 2. Synthesis of C20-C25 Segment (**17**).

yield (*p*-methoxybenzyl 2,2,2-trichloroacetimidate, *p*-toluenesulfonic acid, *n*-hexane-CH_2Cl_2 at rt for 12 h) and the product **15** was treated with Sharpless AD-mix α in aqueous *t*-butanol at 0 °C for 24 h to give the diol **16** in 45% yield.[9]

Diol **16** was then treated with 2,2-dimethoxypropane and *p*-toluenesulfonic acid in ethyl acetate at 40 °C for 40 min to complete the synthesis of the C20-C25 segment **17** of amphidinolide B1 (**1a**). However, the final product turned out to be a 6 : 1 mixture of the desired fragment **17** and its inseparable C23 diastereomer, which was originated in the kinetic protonation reaction of the enolate **10** (Table 1).

In summary, enantioselective synthesis of the C20-C25 fragment **17** of amphidinolide B1 (**1a**), was efficiently completed in 9.3% overall yield *via* an 11 step sequence starting from ethyl (S)-(-)-lactate **3**.

Experimental Section

Ethyl (S)-2-[(2-tetrahydropyranyl)oxy]propionate (4). To a stirred solution of ethyl-(S)-(-)-lactate (10 g, 85.7 mmol, 1 eq.) in dry THF (50 mL) was added 2,3-dihydro-2H-pyran (7.8 g, 93.1 mmol, 1.1 eq.) at −5 °C. After a solution of *p*-toluene sulfonic acid (161 mg, 0.8 mmol, 0.01 eq.) in THF (3 mL) was added at −5 °C, the reaction mixture was slowly warmed to room temperature and stirred for 2 hr. The mixture was quenched with a small amount of triethylamine (425 mg, 4.23 mmol, 0.05 eq.). Solvents were evaporated on a rotavap and the crude residue was diluted with water and ether. The aqueous layer was extracted with ether (x3) and washed with water (x1) and brine (x1), dried over anhydrous $MgSO_4$, filtered on a sintered glass funnel, and finally concentrated *in vacuo*. The residue was chromatographed on silica gel (EtOAc : *n*-hexane, 1 : 3, 1% TEA) to provide 14.3 g (87%) of the desired product: R_f=0.54 (*n*-hexane-ethyl acetate=3 : 1); $[\alpha]_D^{24.7}$ −63.14 (*c* 0.252, $CHCl_3$); FT-IR (neat, cm^{-1}) 2942, 2874 (aliphathic), 1748 cm^{-1} (ester); ^1H NMR (200 MHz, $CDCl_3$) δ 4.71 (m, 1H), 4.41, 4.18 (q, q, 3H), 3.88 (m, 1H), 3.49 (m, 1H), 1.47-1.98 (m (br), 6H), 1.41 (d, d, 3H), 1.27 (t, t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.53, 98.17, 72.34, 69.81, 62.18, 60.53, 30.05, 25.05, 18.79, 13.81; GC-Ms [m/z (relative intensity)] 202.93 (0.01), 129.05 (6.36), 101.11 (19.57), 85.20 (100.00), 45.40 (11.08); Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.40; H, 8.95.

(S)-2-[(2-tetrahydropyranyl)oxy]propionaldehyde (5). To a solution of lactate (7.45 g, 36.9 mmol, 1 eq.) in dichloromethane (100 mL) at −78 °C was added dropwise 1.5 M diisobutylaluminium hydride in toluene (29.5 mL, 44.0 mmol, 1.2 eq.). The reaction mixture was stirred at −78 °C for 40 min, carefully quenched with methanol, and then warmed to room temperature. The precipitates were filtered on a pad of celite and the filtrate was concentrated *in vacuo*. The residue was diluted with excess dichloromethane, and washed with brine (x1). The combined organic layers were dried over anhydrous $MgSO_4$, filtered on a sintered glass funnel, and evaporated on a rotavap to give aldehyde. The crude aldehyde was used without further purification: R_f=0.60 (*n*-hexane : ethyl acetate, 3 : 1); ^1H NMR (200 MHz, $CDCl_3$) δ 9.68 (d, 1H), 4.69 & 4.39 (m, 2H), 3.91 (m, 1H), 3.51 (m, 1H), 1.48-1.97 (br, 4H), 1.42 (d, 3H).

Ethyl (S)-2-methyl-4-[(2-tetrahydropyranyl)oxy]-(2*E*)-pentenoate (7). A mixture of the crude aldehyde (36.9 mmol, max., 1 eq.) and (carbethoxyethylidene)triphenylphosporane in benzene (70 mL) was heated at reflux (70 °C) for 6 hr. The reaction mixture was cooled to room temperature and the solvent was concentrated *in vacuo*. The residue was diluted with distilled *n*-hexane at room temperature to recrystallize the triphenylphosphine oxide. The precipitates was filtered on a pad of celite and the filtrate was evaporated on a rotavap. The residue was purified by silica gel chromatography (EtOAc : *n*-hexane=1 : 5, 1% TEA) to provide 6.75 g (76%, 2 step overall yield from ethyl lactate) of the desired product. R_f=0.60 (*n*-hexane-ethyl acetate, 3 : 1); $[\alpha]_D^{24}$ −35.02 (c 0.331, $CHCl_3$); FT-IR (neat) 2975, 2943, 2872, 1714, 1249 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.78 & 6.56 (d, d, *J*=8.46, 9.08 Hz, 1H), 4.45-4.79 (m, 2H), 4.20 (q, 2H), 3.88 (m, 1H), 3.49 (m, 1H), 1.89 (s, 3H), 1.47-1.9 (br, 6H), 1.28 (m, 6H); GC-Ms [m/z (relative intensity)] 227.84 (0.02), 157.99 (8.12), 141.05 (59.55), 113.11 (89.72), 85.20 (100.00); Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15. Found: C, 64.31; H, 9.47.

(2R,4S)- & (2S,4S)-Dimethylbutyrolactone (9). A mixture of α,β-unsaturated ester (5.65 g, 23.0 mmol), 10% Pd/C, and absolute methanol (30 mL) was stirred vigorously under *ca.* 60 psi of H_2 for 5 hr at room temperature. The reaction mixture was filtered through a pad of celite, and the filtrate was transferred to a round bottomed flask. Hydrochloric acid in diethyl ether, prepared by reaction of acetyl chloride and methanol at room temperature, was added dropewise so that the pH of the solution is ad-

justed to around 3. After stirring at room temperature for 10 min, the mixture was concentrated *in vacuo* to give 2.6 g (98%) of lactones: $[\alpha]_D^{24}$ −18.9 (*c* 0.343, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 4.33-4.77 (m, 1H), 2.42-2.82, 1.93-2.17 (m, 2H), 1.39 (d, d, 3H), 1.27 (d, d, 3H); GC-Ms [m/z (relative intensity)] 115.11 (0.53), 114.09 (3.82), 99.12 (22.98), 71.26 (23.61), 70.27 (85.96), 55.36 (100.00), 45.41 (18.23), 42.45 (75.51); Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.09; H, 8.82.

(2R,4S)-Dimethylbutyrolactone (11a). To a stirred solution of diisopropylamine (132.8 mg, 1.3 mmol, 2 eq.) in dry THF (6 mL) was added *n*-BuLi (2.2 M in hex., 0.6 mL, 1.3 mol, 2 eq.) at 0 °C. The reaction mixture was stirred at 0 °C for 20 min and cooled −78 °C. A solution of 2, 4-dimethyl butyrolactone (65.8 mg, 0.7 mmol, 1 eq.) in THF (1 mL) was added dropwise at −78 °C. After stirring for *ca.* 1.5 h, a solution of *p*-toluene sulfonic acid THF (5 mL) was carefully added at −78 °C, and then the reaction mixture was slowly warmed to room temperature. Solvent was evaporated on a rotavap and the residue was diluted with excess ethyl acetate. The organic layer was washed with a small amount of water (x1) and saturated $NaHCO_3$ solution (x1). The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give the desired (2R,4S)-dimethyl butyrolactone (51.4 mg, 78%) as a 6 : 1 mixture of diastereomers: $[\alpha]_D^{26}$ −6.875 (c 0.312, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 4.33-4.77 (m, 1H), 2.42-2.82, 1.93-2.17 (m, 2H), 1.39 (d, 3H), 1.27 (d, 3H).

(2R,4S)-2,4-Dimethylbutyrolactol (12). To a solution of lactone (495 mg, 4.3 mmol, 1 eq.) in dichloromethane (25 mL) at −78 °C was added dropwise 1.5 M diisobutylaluminium hydride/toluene (3.4 mL, 5.1 mmol, 1.2 eq.). After the reaction mixture was stirred at −78 °C for 40 min, the reacton mixture was carefully quenched with methanol, and the resultant mixture was then allowed to room temperature. The precipitates was filtered on a pad of celite and filtrate was concentrated *in vacuo*. The residue was diluted with excess dichloromethane, and washed with brine (x1). The combined organic layers were dried over anhydrous $MgSO_4$, filtered on a sintered glass funnel, and evaporated on a rotavap to give the desired lactol. This crude lactol was used without further purification.

GC-Ms [m/z (relative intensity)] 115.06 (0.55), 99.14 (1.54), 70.28 (74.10), 55.34 (100.00), 45.40 (18.19), 42.44 (34.23).

Ethyl (4R,6S)-6-hydroxy-4-methyl-2-heptenoate (14). A mixture of the crude lactol (4.3 mmol, max., 1 eq.) and (carbethoxymethylene) triphenylphosporane in benzene (10 mL) was heated at reflux (80 °C) for 6 hr. The reaction mixture was cooled to room temperature and the solvent was concentrated *in vacuo*. The residue was diluted with distilled *n*-hexane at room temperature to recrystallize the triphenylphosphine oxide. The precipitates was filtered on a pad of celite and the filtrate was evaporated on a rotavap. The residue was purified by silica gel chromatography (EtOAc : *n*-hexane=1 : 3, 1% TEA) to provide 349 mg (76%, 2 step overall yield from **11a/11b**) of the desired product: R_f=0.26 (*n*-hexane-ethyl acetate, 3 : 1); $[\alpha]_D^{26.7}$ −2.88 (*c* 0.158, $CHCl_3$); FT-IR (neat) 3433 (br, OH), 2966, 2930, 2876, 1720, 1651, 1460 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.73 (dd, 1H), 5.76-5.84 (dd, 1H), 4.17 (q, 2H), 3.86 (m, 1H), 2.51 (m, 1H), 1.60 (m, 2H), 1.26 (t, 3H), 1.20 (d, 3H), 1.08 (d, 3H); ^{13}C NMR (50 MHz) δ 167.30, 154.78, 119.98, 66.07, 60.65, 45.78, 33.85, 24.33, 19.56, 14.68; GC-Ms [m/z (relative intensity)] 185.96 (0.27), 142.03 (25.37), 126.05 (15.26), 111.07 (26.90), 99.12 (37.14), 95.16 (57.95), 70.28 (100.00), 55.35 (57.39), 45.41 (75.33), 43.42 (60.73); Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.47; H, 9.84.

Ethyl (4R,6S)-6-*p*-methoxybenzyloxy-4-methyl-2-heptenoate (15). To a soluttion of alcohol (746.4 mg, 4.0 mmol, 1 eq.) in methylene chloride (10 mL) and *n*-hexane (20 mL) was added *p*-methoxybenzyl-2,2,2-trichloro acetimidate (1.67 mL, 8.0 mmol, 2 eq.) and *p*-toluenesulfonic acid (38 mg, 0.2 mmol, 0.05 eq.) at room temperature. After stirring for *ca.* 12 h, excess of *n*-hexane was added and the white solid was filtered with *n*-hexane. The filtrate was diluted with ethylacetate and transfered to a separatory funnel. The organic layer was washed with water (x1) and brine. The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel (EtOAc : *n*-hexane=1 : 5, 1% TEA) to provide 1.0 g of the desired product (83%): R_f=0.53 (*n*-hexane-ethyl acetate, 3 : 1); $[\alpha]_D^{26.7}$ +18.32 (*c* 0.1, $CHCl_3$); FT-IR (neat) 2967, 2932, 2970, 2837, 1719, 1612, 1461 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.28 (m, 2H), 6.89 (m, 2H), 4.42 (dd, 2H), 4.18 (q, 2H), 3.80 (s, 3H), 3.51 (m, 1H), 2.52 (m, 1H), 1.73 (m, 1H), 1.27 (t, 3H), 1.18 (d, 3H), 1.02 (d, 3H); ^{13}C NMR (75 MHz) δ 167.33, 159.63, 154.95, 131.41, 129.85, 129.73, 119.82, 114.28, 72.62, 71.96, 70.45, 60.60, 55.74, 43.67, 33.67, 20.21, 19.60, 14.74; GC-Ms [m/z (relative intensity)] 305.83 (0.05), 287.82 (0.072), 257.84 (0.72), 184.96 (3.95), 149.98 (3.42), 137.02 (19.47), 121.08 (100.00), 55.37 (2.43), 45.38 (0.52), 43.39 (3.28); Anal. Calcd for $C_{10}H_{18}O_3$: C, 70.56; H, 8.55. Found: C, 70.69; H, 8.37

Ethyl (2R,3S,4R,6S)-2,3-dihydroxy-6-*p*-methoxybenzyloxy-4-methyl-2-heptenoate (16). To a solution of (4R,6S)-ethyl-4-methyl-6-*p*-methoxybenzyloxy-2-heptenoate (41 mg, 0.13 mmol, 1 eq.) in *t*-BuOH (2 mL) and H_2O (2 mL) was added AD-mix-α (187 mg, 1.4 g/mmol) at 0 °C. The reaction mixture was stirred for *ca* 24 h at that temperature and then quenched with saturated aqueous $Na_2S_2O_7$ solution. After stirring for 30 min at 0 °C, the mixture was slowly warmed to room temperature and transferred to a separatory funnel. The mixture was extracted with ether (x3), washed with brine, dried over $MgSO_4$, filtered, evaporated *in vacuo* to give crude product. The crude was purified by silica gel chromatography (EtOAc : *n*-hexane=1 : 3, 1% TEA) to provide 20.5 mg (45%) of the desired product: R_f=0.08 (*n*-hexane-ethyl acetate, 3 : 1); $[\alpha]_D^{26.7}$ +21.67 (*c* 0.204, $CHCl_3$); FT-IR (neat) 3510, 3055, 2970, 1756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.29 (m, 2H), 6.89 (m, 2H), 4.47 (dd, 2H), 4.26 (m, 3H), 3.81 (s, 3H), 3.63 (m, 2H), 1.67-2.11 (m, 2H), 1.28 (t, 3H), 1.20 (d, 3H), 0.97 (d, 3H); ^{13}C NMR (75 MHz) δ 173.90, 159.21, 130.69, 129.37, 113.66, 76.01, 71.92, 71.42, 69.62, 61.40, 54.91, 40.57, 32.71, 19.58, 14.74, 13.68; GC-Ms [m/z (relative intensity)] 338.88 (0.12), 280.95 (1.25), 173.10 (1.84), 121.24 (100.00), 73.34 (10.93); Anal. Calcd for $C_{10}H_{18}O_3$: C, 63.51; H, 8.29. Found: C, 63.57; H, 8.24.

Isopropylidene acetal of Ethyl (2R,3S,4R,6S)-2,3-dihydroxy-6-*p*-methoxybenzyloxy-4-methyl-2-heptenoate (17). 2,2-Dimethoxypropane (184 mg, 1.77 mmol, 5 eq.) and *p*-toluenesulfonic acid (0.05 eq.) were added to a solution of ethyl 6-*p*-methoxybenzyloxy 4,6-dimethyl-2,3-dihydroxy hexanoate (120.2 mg, 0.35 mmol, 1 eq.) in dry ethyl acetate (5 mL) at room temperature. The reaction mixture was warmed to 40 °C and stirred at that temperature for 40 min. Catalytic amount of triethylamine was introduced to quench the reaction at 40 °C and the mixture was cooled to rt and stirred for additional 40 min. Saturated sodium bicarbonate solution was added and the mixture was diluted with excess ethyl acetate. The organic layer was washed with water (x1) and aqueous $NaHCO_3$ solution (x1), dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (25% ethyl acetate in *n*-hexane, 1% NEt_3) to afford the product quantitatively as a colorless oil: R_f=0.45 (*n*-hexane-ethyl acetate, 3 : 1); $[\alpha]_D^{26.7}$ +0.307 (*c* 0.15, $CHCl_3$); FT-IR (neat) 3055 (aromatic), 2985, 2934, 2857 (alipathic), 1751 (ester), 1267, 741 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.29 (d, 2H, *J*=8.6 Hz), 6.89 (d, 2H, *J* =8.6 Hz), 4.47 (dd, 2H), 4.26 (m, 2H), 4.12 (m, 1H), 3.80 (s, 3H), 3.63 (m, 1H), 2.12 (m, 1H), 1.76 (m, 1H), 1.44 (s, 6H), 1.30 (m, 5H), 0.91 (d, 3H, *J*=6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.53, 159.09, 150.63, 129.06, 113.51, 110.53, 82.96, 76.60, 71.26, 69.55, 60.76, 54.72, 40.71, 31.24, 26.45, 25.16, 19.47, 13.55, 13.19; GC-Ms [m/z (relative intensity)] 382.64 (0.00), 379.77 (0.01), 364.94 (0.21), 303.93 (0.43), 185.97 (15.03), 136.44 (29.69), 121.24 (100.00), 43.43 (10.70); Anal. Calcd for $C_{21}H_{32}O_6$: C, 66.29; H, 8.48. Found: C, 66.19; H, 8.63.

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