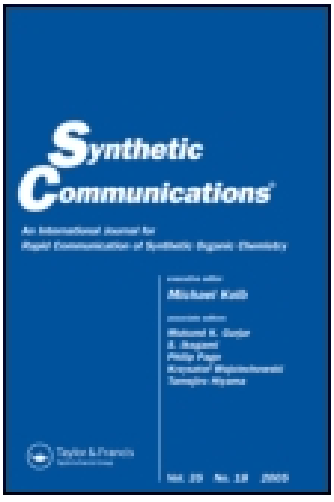

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Lipase-Catalyzed Esterification of a (±)-2,3-Di(Arylmethyl)-1,4-butanediol and Its Application to the Synthesis of (*S*,*S*)-(+)-Hinokinin

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Abstract: Racemic *trans*-2,3-di[(3,4-methylenedioxy)benzyl]-1,4-butanediol (dihydrocubebin) **6** was enantioselectively esterified using lipases as catalysts with vinyl acetate. Optically active (*S,S*)-1,4-butanediol **6** obtained was selectively oxygenated with a Fetizon reagent, affording (*S,S*)-(+)-hinokinin **9** in a high yield.

Keywords: Lipase, esterification, enantioselectivity, lignan, dihydrocubebin, hinokinin

Among various types of strategies for enantioselective transformations based on chemical and biological procedures, an enzymatic transformation is one of the most efficient and practical ones for preparing optically active compounds.[1] In a previous communication,[2] we reported a facile synthesis of optically active 1,4-diol derivatives (2,5-hexanediol, its monoacetate, and diacetate) by lipase-catalyzed esterification of a mixture of racemic and meso 1,4-diols with vinyl acetate. The chiral 2,5-hexanediol is a useful key compound for preparing several optically active 2,5-substituted five-membered heterocyclic compounds such as pyrrolidines[3] and phospholanes.[4] On the other hand, lipase-catalyzed esterification of 1,4-butanediols

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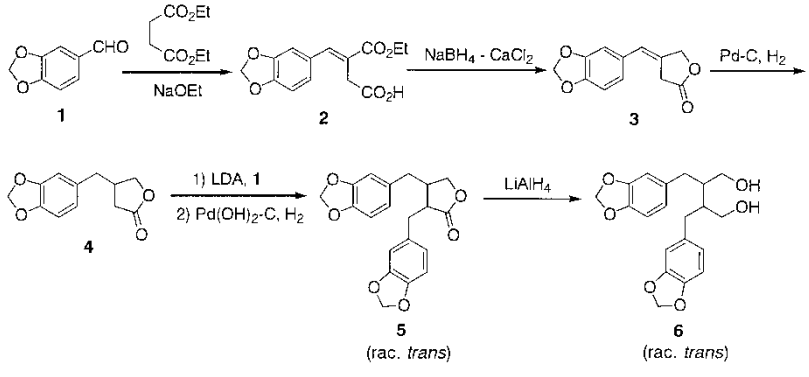
bearing 2,3-di(arylmethyl) groups has not been utilized for the synthesis of optically active, useful compounds, and only a few applications of lipase-catalyzed reactions to the synthesis of optically active lignans have appeared.[5] We report herein enantioselective esterification (optical resolution) of a racemic 1,4-butanediol, (±)-2,3-bis[3,4-(methylenedioxy) benzyl]-1,4-butanediol (dihydrocubebin) **6** using lipases, and its application to the enantioselective synthesis of a chiral lignan, (*S,S*)-2,3-bis[(3,4-methylenedioxy)benzyl]butyrolactone [(+)-hinokinin] **9**.

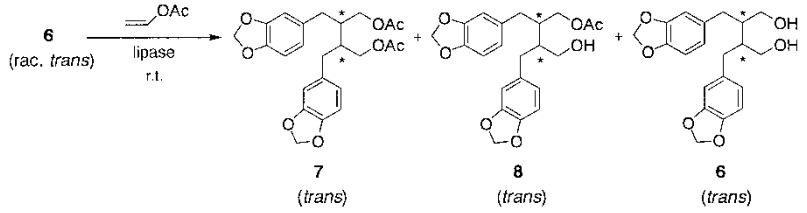
A substrate 1,4-diol, racemic 2,3-bis[3,4-(methylenedioxy)benzyl]-1,4-butanediol [(±)-dihydrocubebin] **6** was prepared from piperonal **1** by a route as shown in Scheme 1. Piperonal **1** was condensed with diethyl succinate in the presence of sodium ethoxide (Stobbe condensation[6]), yielding arylidenesuccinic acid monoester **2**. After conversion of the carboxylic group to the potassium salt, selective reduction of the ester group was carried out with calcium borohydride prepared *in situ* from calcium chloride and sodium borohydride,[7] yielding the corresponding β-arylidenebutyrolactone **3** (85%). Catalytic hydrogenation of **3** was carried out with Pd on carbon, affording the corresponding β-arylmethylbutyrolactone **4** (78%). The lactone **4** was allowed to react with piperonal **1** in the presence of LDA, and succeeding hydrogenolysis of an α-(α′-hydroxy)arylmethyl derivative thus obtained was carried out using a catalyst of $Pd(OH)_2$ on carbon, which yielded racemic *trans*-2,3-bis[(3,4-methylenedioxy)benzyl] butyrolactone ((±)-hinokinin) **5** in high overall yield (90%). The lactone **5** was reduced with lithium aluminum hydride, affording racemic 2,3-bis[3,4-(methylenedioxy)benzyl]-1,4-butanediol ((±)-dihydrocubebin) **6** (97%).

Lipase-catalyzed esterification of **6** was carried out with excess vinyl acetate (without solvent) at room temperature (rt) in the presence of various lipases (lipases MY-30, AY, OF, CCL, AH, QL, and PL). The results are summarized in Table 1. The products (diacetate **7**, monoacetate **8**, and diol **6**) were



Scheme 1.

Table 1. Lipase-catalyzed esterification of (±)-dihydrocubebin **6**[a]



Entry	Lipase	Time (h)	Diacetate **7**, C.Y. (%),[b] ee (%)[c]	Monoacetate **8**, C.Y. (%),[b] ee (%)[c]	Diol **6**, C.Y. (%),[b] ee (%)[c]
1	lipase MY-30	96	29, 64 (*R,R*)	53, 22 (*S,S*)	13, 98 (*S, S*)
2	lipase AY	48	47, 64 (*R,R*)	48, 49 (*S,S*)	3, 96 (*S, S*)
3	lipase OF	96	15, 11 (*S,S*)	65, 6 (*R,R*)	18, 12 (*S, S*)
4	lipase CCL	72	27, 62 (*R,R*)	54, 12 (*S,S*)	15, 94 (*S, S*)
5	lipase AH	15	23, 54 (*S,S*)	65, 23 (*R,R*)	7, >99 (*S, S*)
6	lipase QL	20	57, 33 (*S,S*)	40, 48 (*R,R*)	—
7	lipase PL	7	41, 36 (*S,S*)	52, 28 (*R,R*)	—

[a]All reactions were carried out by stirring a mixture of substrate **6** (1 mmol) and lipase (300 mg) in vinyl acetate (5 mL).

[b]Isolated yield by preparative TLC.

[c]Determined by HPLC analysis (CHIRALCEL OD-H) of diol **6** (after hydrolysis of **7** and **8**).

easily separated by silica-gel chromatography. The ee value and the absolute configuration of each product were determined by HPLC (CHIRALCEL OD-H) of the diol (after hydrolysis in case of the acetates) and by comparing the sign of the specific rotation of the diol with reported data,[8] respectively. Although all the lipases did not show high efficiency in enantioselectivity of the esterification of **6** in contrast to our previous results with 2,5-hexanediol,[2] lipases MY-30, AY, CCL, and AH (entries 1, 2, 4, and 5) gave relatively better results than others. Relative acetylation rates and the absolute configuration of the major enantiomers of diacetate **7**, monoacetate **8**, and diol **6** are depicted in Figure 1. Optically active diol (*S, S*)-**6** with high ee was isolated although the yield was not high [entry 1: 98% ee, 13% (26% theoretical) yield; entry 4: 94% ee, 15% (30% theoretical) yield].

Selective mono-oxygenation of diol (*S,S*)-**6** was easily carried out with Fetizon reagent[9] (silver carbonate-Celite), yielding (*S,S*)-(+)-hinokinin **9** in high yield (Scheme 2). The absolute configuration was determined by comparing the sign of the specific rotation with reported data [(*R,R*)-(−)-hinokinin].[10]

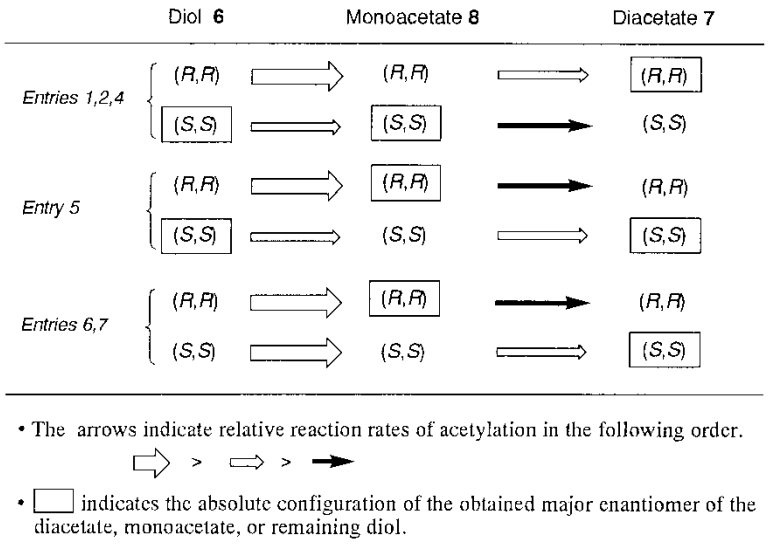
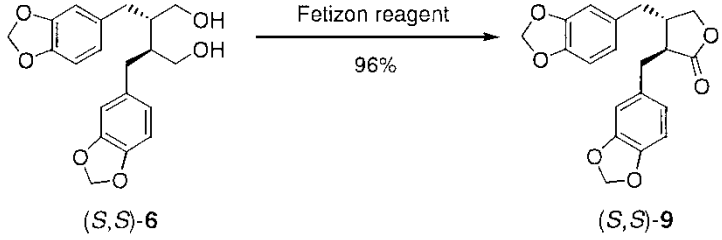


Figure 1. Relative acetylation rates and the absolute configuration of major enantiomers.

In summary, we have carried out lipase-catalyzed esterification of a 1,4-diol, racemic 2,3-bis[3,4-(methylenedioxy)benzyl]-1,4-butanediol [(±)-dihydrocubebin] with vinyl acetate, and found that this diol is a relatively difficult substrate for enantioselective esterification. However, a highly enantiomerically rich diol, (*S,S*)-dihydrocubebin, was able to be isolated. Oxygenation with Fetizon reagent gave (*S,S*)-(+)-hinokinin in high yield.

EXPERIMENTAL

Melting points (mp) were determined on a micro hot-stage apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-EX



Scheme 2.

270 spectrometer in $CDCl_3$ solution at 270 and 67.8 MHz, respectively. Chemical-shift values are expressed in ppm based on tetramethylsilane. IR spectra were measured on a JASCO IR-810 spectrometer. Optical rotations were measured on a JASCO DIP-140 digital polarimeter. Mass spectra were measured on JEOL-JMS-AX 505 W (GC-MS) and JEOL-JMS-SX 102 (FAB-MS) instruments. High-performance liquid chromatography (HPLC) was carried out with a Waters 600E equipped with a column CHIRALCEL OD-H (2-propanol/hexane). Column chromatographic isolation was conducted using silica gel (Kieselgel 60, 70–230 mesh, Merck). Kieselgel 60 F254 plates (Merck) were employed for preparative TLC. In general, all organic reagents were used as purchased. Lipases were supplied by Amano Pharmaceutical Co., Ltd. and Meito Sangyo Co., Ltd.; lipases (supported on Celite): MY-30 (*Candida rugosa*), AY (*Candida rugosa*), OF (*Candida rugosa*), CCL (*Candida rugosa*), AH (*Pseudomonas sp.*), QL (*Alcaligenes sp.*), and PL (*Alcaligenes sp.*). THF was distilled over sodium metal/benzophenone ketyl and used as peroxide-free.

(±)-3-[3,4-(Methyleledioxy)benzyl]butyrolactone 4

To a stirred and ice-cooled solution of (*E*)-4-[3,4-(methylenedioxy)phenyl]-3-ethoxycarbonyl-3-butenoic acid **2** (2.0 g, 7.2 mmol) in ethanol (15 mL) was added a solution of 2 M KOH (4 mL), and the mixture was stirred for 15 min and concentrated *in vacuo*. The residue was dissolved in ethanol (100 mL), stirred, and cooled in an ice bath. To the stirred solution were added calcium chloride (2.3 g, 21 mmol), sodium borohydride (1.06 g, 28 mmol), and a solution of KOH (170 mg, 3 mmol) in ethanol (15 mL), and the mixture was stirred at rt for 3 h. After ice-cooling, the reaction mixture was acidified to pH 1 with 6M HCl and stirred at rt for 0.5 h. After concentration, the residue was extracted with ether (200 mL) and the extract was washed successively with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/AcOEt = 9/1), affording (*E*)-3-[3,4-(methylenedioxy)benzylidene]-butyrolactone **3** (1.34 g, 85%) as crystals, mp 137–140°C. IR (nujol) cm^{-1}: 1740 (C═O). ^{1}H-NMR ($CDCl_3$) δ: 3.40 (s, 2H), 4.99 (s, 2H), 5.98 (s, 2H), 6.36 (s, 1H), 6.73 (d, $J = 8.9$ Hz, 1H), 6.74 (s, 1H), 6.82 (d, $J = 8.9$ Hz, 1H). ^{13}C-NMR ($CDCl_3$) δ: 33.1, 73.3, 101.3, 107.9, 108.6, 122.5, 123.8, 127.9, 129.8, 147.2, 148.0, 175.2. To a solution of **3** (218 mg, 1.0 mmol) was added 5% Pd on carbon (20 mg). The mixture was stirred at rt overnight under an atmosphere of hydrogen (1 atm). After filtration and concentration, the residue was subjected to bulb-to-bulb distillation under reduced pressure, affording **4** (171 mg, 78%) as a liquid [bp 270–300°C (bath temp.)/15 mmHg]. IR (neat) cm^{-1}: 1770 (C═O). ^{1}H-NMR ($CDCl_3$) δ: 2.24 (dd, $J = 6.9$, 17.5 Hz, 1H), 2.56 (dd, $J = 7.9$, 17.5 Hz, 1H), 2.68 (m, 2H), 2.80

(m, 1H), 3.98 (dd, $J = 5.9$, 9.2 Hz, 1H), 4.30 (dd, $J = 6.9$, 9.2 Hz, 1H), 5.91 (s, 2H), 6.59 (d, $J = 7.9$ Hz, 1H), 6.64 (s, 1H), 6.73 (d, $J = 7.9$ Hz, 1H). ^{13}C-NMR ($CDCl_3$) δ: 34.0, 37.2, 38.5, 72.5, 101.0, 108.4, 108.9, 121.6, 132.0, 146.3, 147.9, 176.9. Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.11; H, 5.49. Spectral data were well consistent with those reported previously.[5,11]

(±)-2,3-Bis[(3,4-methylenedioxy)benzyl]butyrolactone ((±)-Hinokinin) 5

To a stirred and cooled (−30°C) solution of lithium diisopropylamide (LDA), which was prepared from diisopropylamine (121 mg, 1.2 mmol) and *n*-butyllithium (1.7 M in hexane, 0.70 mL, 1.2 mmol) in THF (3 mL) under Ar, was added a solution of **4** (220 mg, 1.0 mmol) in THF (1 mL) and the mixture was stirred for 0.5 h. Then a solution of piperonal **1** (150 mg, 1.0 mmol) in THF (1 mL) was added at the same temperature, and the stirring was continued for 0.5 h. Saturated NH_4Cl solution (2 mL) was added and the mixture was stirred at rt for 0.5 h. The organic layer was extracted with ether (30 mL). The extract was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by preparative TLC (hexane/AcOEt = 1/1), affording a crude diastereomeric mixture of *trans*-2-{α-hydroxy-3,4-(methylenedioxy)benzyl-3-[3,4-(methylenedioxy)benzyl]-butyrolactone (358 mg, 97%) as an oil. Crude *trans*-2{α-hydroxy-3,4-(methylenedioxy)benzyl-3-[3,4-(methylenedioxy)benzyl]}-butyrolactone (370 mg, 1.0 mmol) was dissolved in a mixed solvent of acetic acid (15 mL) and THF (15 mL), and 20% $Pd(OH)_2$ on carbon (100 mg) was added. The mixture was stirred at rt overnight under an atmosphere of hydrogen (1 atm). After filtration and concentration, the residue was purified by preparative TLC (hexane/AcOEt = 1/1), affording **5** (320 mg, 90%) as a solid. Recrystallization from EtOH gave analytically pure **5** as prisms; mp 104–105°C. IR (nujol) cm^{-1}: 1760 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.50 (m, 4H), 2.83 (dd, $J = 6.9$, 14.2 Hz, 1H), 3.00 (dd, $J = 4.8$, 14.2 Hz, 1H), 3.85 (dd, $J = 7.0$, 9.2 Hz, 1H), 4.12 (dd, $J = 6.6$, 9.2 Hz, 1H), 5.94 (s, 4H), 6.45–6.75 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 34.8, 38.3, 41.3, 46.5, 71.1, 101.0, 108.2, 108.3, 108.8, 109.5, 121.5, 122.2, 131.4, 131.7, 146.3, 146.5, 147.9, 178.4. GC-MS (EI) m/z: 354 (M^+). Spectral data were consistent with those reported previously.[12]

(±)-2,3-Bis[3,4-(methylenedioxy)benzyl]-1,4-butanediol ((±)-Dihydro-cubebin) 6

To a stirred and ice-cooled solution of lithium aluminun hydride (520 mg, 13.6 mmol) in THF was added a solution of (±)-hinokinin **5** (2.4 g,

6.8 mmol) in THF (15 mL), and the stirring was continued at 0°C for 0.5 h and then at rt for 1 h. To the reaction mixture were added AcOEt (3 mL), dichloromethane (70 mL), and a solution of 5% NaOH (7 mL). After stirring for 1 h at rt, the mixture was filtered through Celite, and the filtrate was concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (hexane/AcOEt = 4/1∼1/2), affording **6** (2.34 g, 97%) as crystals; mp 103–105°C. IR (nujol) cm^{-1}: 3250 (OH). ^{1}H-NMR ($CDCl_3$) δ: 1.83 (br, 2H), 2.59 (dd, $J = 5.9$, 13.5 Hz, 2H), 2.72 (dd, $J = 8.6$, 13.5 Hz, 2H), 3.65 (m, 2H), 3.75 (br, 2H), 3.93 (s, 2H), 5.90 (s, 4H), 6.59 (d, $J = 7.7$ Hz, 2H), 6.63 (s, 2H), 6.75 (d, $J = 7.7$ Hz, 2H). ^{13}C-NMR ($CDCl_3$) δ: 35.8, 44.2, 59.9, 100.7, 108.0, 109.3, 121.8, 134.3, 145.6, 147.5. FAB-MS (NBA) m/z: 359 $(M + H)^+$. Anal. Calcd for $C_{20}H_{22}O_6$: C, 67.03; H, 6.19. Found: C, 67.02; H, 6.27.

Lipase-Catalyzed Esterification of (±)-2,3-Bis[3,4-(methylenedioxy)-benzyl]-1,4-butanediol 6

Typical Procedure

A mixture of **6** (358 mg, 1 mmol), lipase CCL (300 mg), and vinyl acetate (5 mL) was stirred at rt for 72 h. The lipase was removed by filtration though Celite, and the filtrate was concentrated *in vacuo*. The residue was subjected to preparative TLC separation (hexane/AcOEt = 2/1), affording the corresponding diacetate **7** (120 mg, 26.9%; 62% ee), monoacetate **8** (216 mg, 53.7%; 12% ee), and diol **6** (52 mg, 14.5%; 93.7% ee). The ee value of the product **6** was determined by HPLC (CHIRALCEL OD-H), and the ee values of the esters **7** and **8** were also measured after hydrolysis to the corresponding diol. The absolute configuration of each product was determined by comparing the sign of the specific rotation of the diol with the reported one.[8]

(*R*,*R*)-(+)-2,3-Bis[3,4-(methylenedioxy)benzyl]-1,4-butanediol diacetate **7**

A viscous liquid, 62% ee, $[\alpha]_D^{25}$ +1.95 ($c = 0.2$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 2.06 (s, 6H), 2.15 (m, 2H), 2.54 (dd, $J = 7.9$, 13.9 Hz, 2H), 2.67 (dd, $J = 6.7$, 13.9 Hz, 2H), 4.00 (dd, $J = 5.3$, 11.2 Hz, 2H), 5.92 (s, 4H), 6.52 (d, $J = 8.2$ Hz, 1H), 6.54 (s, 1H), 6.70 (s, $J = 8.2$ Hz, 1H). ^{13}C-NMR ($CDCl_3$) δ: 20.9, 34.9, 40.0, 64.2, 100.9, 108.1, 109.1, 121.8, 133.4, 145.7, 147.7, 170.9.

(*S*,*S*)-(−)-2,3-Bis[3,4-(methylenedioxy)benzyl]-1,4-butanediol monoacetate **8**

A viscous liquid, 12% ee, $[\alpha]_D^{25}$ −0.09 ($c = 0.56$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.92 (m, 1H), 2.00 (br, 1H), 2.04 (s, 3H), 2.16 (m, 1H), 2.49-2.74 (m, 4H),

3.59 (d, $J = 5.6$ Hz, 2H), 4.03 (dd, $J = 5.8$, 10.5 Hz, 1H), 4.12 (dd, $J = 7.0$ 10.5 Hz, 1H), 5.89 (s, 4H), 6.52–6.71 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 20.8, 34.5, 34.8, 39.8, 43.0, 61.9, 64.5, 100.7, 107.9, 109.1, 121.6, 122.0, 133.7, 134.0, 145.6, 145.7, 147.5, 171.0.

(*S*,*S*)-(+)-2,3-Bis[3,4-(methylenedioxy)benzyl]-1,4-butanediol **6**

93.7% ee, $[\alpha]_D^{24}$ +30.2 ($c = 0.5$, $CHCl_3$). [lit.,[8] (*R*,*R*)-(−)-dihydrocubebin, (*R*,*R*)-**6**: $[\alpha]_D^{17}$ −32.4 ($c = 3.3$, $CHCl_3$)].

(+)-Hinokinin (*S*,*S*)-9

To a solution of (*S*,*S*)-**6** (94% ee; 179 mg, 0.5 mmol) in toluene (6 mL) was added Fetizon reagent (0.9 g), which was prepared from $AgNO_3$, Na_2CO_3, and Celite according to a reported procedure. The mixture was stirred and heated under reflux for 3 h. After cooling to rt, the reaction mixture was filtered through Celite, and the filtrate was concentrated *in vacuo*. The residue was purified by preparative TLC (hexane/AcOEt = 1/1), affording (*S*,*S*)-**9** (170 mg, 96%); mp 104–105°C (EtOH); $[\alpha]_D^{24}$ +32.8 ($c = 1.88$, $CHCl_3$) [lit.,[10] (*R*,*R*)-(−)-hinokinin: $[\alpha]_D^{17}$-34.0 ($c = 0.98$, $CHCl_3$)]. IR (nujol) cm^{-1}: 1760 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.50 (m, 4H), 2.82 (dd, $J = 6.9$, 14.2 Hz, 1H), 2.98 (dd, $J = 5.0$, 14.0 Hz, 1H), 3.84 (dd, $J = 7.1$, 9.1 Hz, 1H), 4.10 (dd, $J = 6.7$, 9.4 Hz, 1H), 5.94 (s, 4H), 6.45–6.75 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 34.7, 38.2, 41.2, 46.3, 70.9, 100.8, 108.2, 108.3, 108.8, 109.5, 121.5, 122.2, 131.2, 131.5, 146.1, 146.3, 147.7, 178.3. GC-MS (EI) m/z: 354 (M^+). Spectral data were identical to those reported previously.[12]

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