Solvolysis of (4,5)-*anti*-4-Aryl-5-tosyloxy-2(*E*)-hexenoate Derivatives

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The solvolysis reaction of (4,5)-*anti*-4-aryl-5-tosyloxy-2(*E*)-hexenoates 4a—k gave (4,5)-*anti*-4-aryl-5-hydroxy-2(*E*)-hexenoates 2a—k and (4,5)-*anti*-5-aryl-4-hydroxy-2(*E*)-hexenoates 5a—k along with the complete inversion. This 1,2-aryl migration was induced by treatment with heating in water-saturated nitromethane. On the basis of the substituent effect on the aromatic ring, this 1,2-aryl migration is thought to proceed *via* the σ-bridged phenonium ion. The product selectivity between 2a—k and 5a—k was found to be subtly governed by the substituent and substitution pattern in the aromatic ring of the substrates 4a—k.

Key words solvolysis; 1,2-aryl migration; phenonium ion

We previously reported that solvolysis of 4-aryl-5-tosyloxy-2(*E*)-pentenoate **A** in water-saturated $MeNO_2$ gave 1,2-aryl migration product **C** along with complete inversion in good yield.[1,2] In the case of this reaction, an intermolecular attack of the nucleophile (H_2O) to the σ-bridged phenonium ion **B** proceeded selectively at the C(4)-position to provide the 4-hydroxy-5-aryl-2(*E*)-pentenoate **C**. If the (4,5)-*anti*-4-aryl-5-tosyloxy-2(*E*)-hexenoate **D** is subjected to solvolysis in the presence of a nucleophile, 1,2-aryl migration followed by intermolecular nucleophilic substitution along with inversion at the C(4)-position should occur to afford the (4,5)-*anti*-5-aryl-4-substituted-2(*E*)-hexenoate derivatives **E**. However, this type of reaction has not been reported so far. In this paper, we wish to report both the possibility of the above-mentioned reaction and its stereochemical course based on the substituent effect in the aromatic ring.

Synthesis of Substrates In our previous paper, we reported that the reaction of (4,5)-*trans*-epoxy-2(*E*)-hexenoate **1** with aromatic nucleophiles having electron-donating group in the presence of $BF_3 \cdot Et_2O$ gave the (4,5)-*anti*-5-hydroxy-4-aryl-2(*E*)-hexenoate **2** and (2,5)-*anti*-5-hydroxy-2-aryl-3(*E*)-hexenoate **3**.[3—5] This reaction was carried out using other nine kinds of aromatic compounds. The reaction of **1** and anisole gave **2a**[4] (53%) and **2b** (3%). The reaction of **1** and *m*-methoxytoluene gave **2c** (51%) and **2d** (28%). Moreover, the reaction of **1** and *o*-methoxytoluene, 1,2-dimethoxybenzene, *p*-methoxytoluene, 2,5-dimethoxytoluene, 2,5-dimethylanisole, *m*-xylene, 1,2,3,4-tetramethylbenzene provided **2e** (70%), **2f** (90%), **2g** (51%), **2h** (63%), **2i** (84%), **2j** (55%), and **2k** (94%), respectively, as shown in Chart 2. The yields of **2a**, **2f** and **2g** were improved in comparison to the reported data.[4] The substitution pattern in the aromatic ring of the products was determined by a nuclear Overhauser effect (NOE) experiment as shown in Chart 2.

1,2-Aryl Migration Under Solvolysis Condition At first, 1,2-aryl migration along with the intermolecular nucleophilic substitution at the C(4)-position using **4a** and **6a** was examined. The substrate **2a** was treated with TsCl in pyridine to give the corresponding tosylate **4a**, which was subjected to solvolysis in water-saturated $MeNO_2$ to provide **2a** (10%) and **5a** (70%). Meanwhile, the corresponding mesylate **6a** was exposed to the same reaction condition to give **2a** (12%) and **5a** (42%). It was apparent that 1,2-migration ability of the aromatic group of the tosylate **4a** is higher than that of the mesylate **6a** (Chart 3).

Consequently, the residual ten kinds of the (4,5)-*anti*-5-hydroxy-4-aryl-2(*E*)-hexenoates **2b**—**k** were converted into the corresponding tosylates **4b**—**k** in good yield as shown in Chart 2. The reaction product **2a** was identical with the synthesized **2a**. Structure elucidation of **5a** was carried out as follows. Acetylation of **5a** gave the corresponding acetate **8a** whose NMR spectrum showed the presence of an acetoxyl group at the C_4-position, because the signal due to C_4-H was a triple doublet at δ 5.46 with three coupling constants (J=7, 6, 2 Hz). Moreover, the chemical shift (δ 5.46) due to C_4-H of **8a** appeared to the lower field in comparison to that (δ 5.16, dq, J=7, 9 Hz) due to C_5-H of an acetate **7a** derived from **2a**. The 4,5-*anti*-configuration of **5a** was determined using the same type compound **5c** as **5a** at late in this text. To investigate the solvent effect, usage of the residual ni-

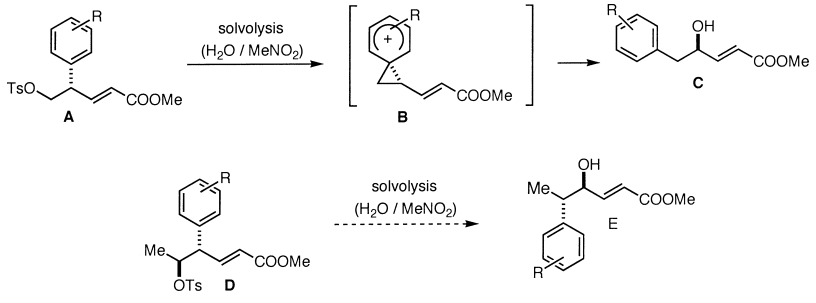

Chart 1

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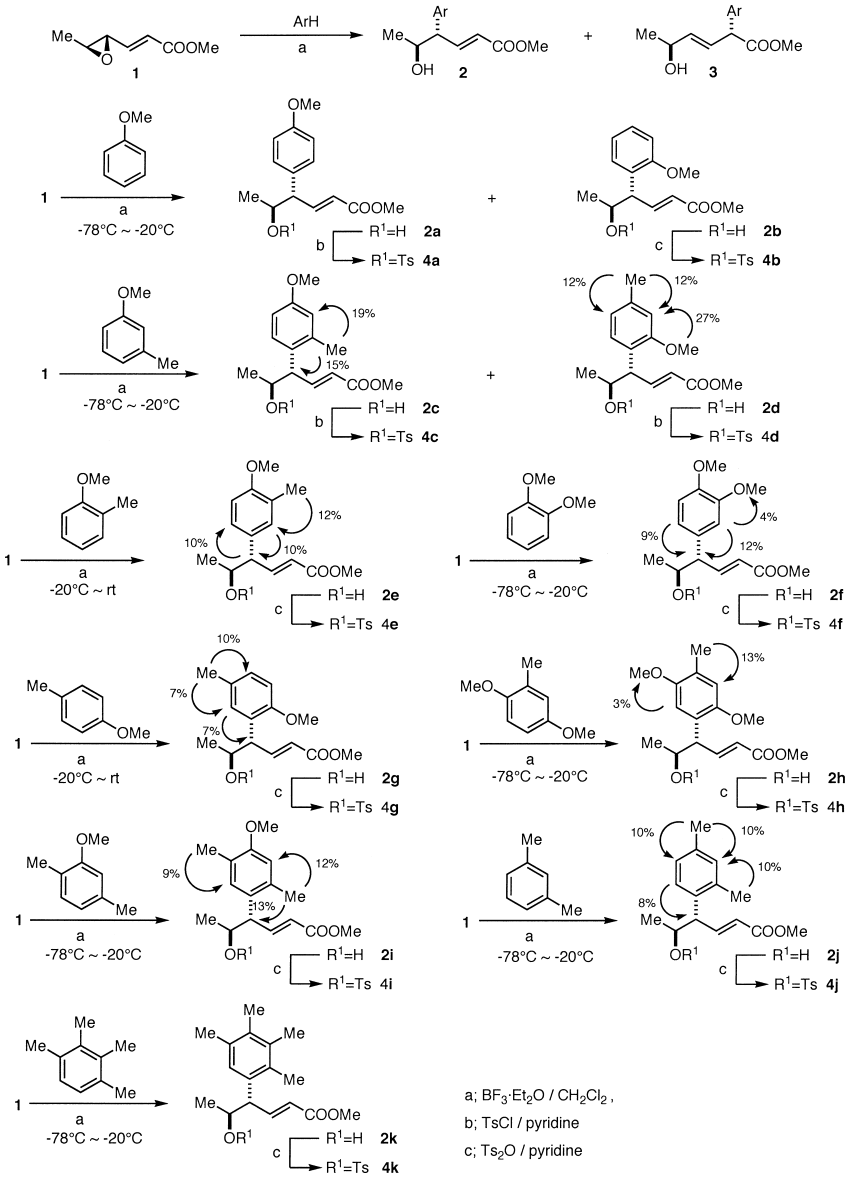


Chart 2. NOE Experiments Were Carried Out in the Substrates **2c**—**j**

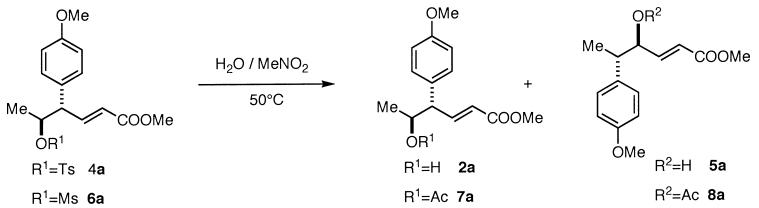
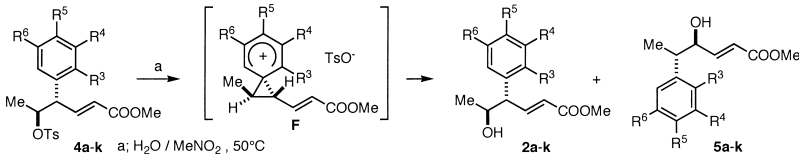


Chart 3

troalkane such as nitroethane, 2-nitropropane, and nitrobenzene was found to be less reactive than nitromethane by NMR analysis of the reaction mixture. Moreover, water-saturated solvents such as *n*-butyronitrile, cyclohexanone, DMF, isopropyl ether, ethyl acetate, 1,2-dichloroethane, and benzene did not promote the 1,2-rearrangement reaction for **5d** at 50 °C. It was apparent that nitromethane was the best solvent for 1,2-migration reaction using substrate **4a**. Nitromethane or dimethylsulfoxide (DMSO) is reported to be the best solvent for solvolysis reaction by Winstein *et al.*[6] The dielectric constant of nitromethane (ε=35.9) is similar to that of DMF (ε=36.7), while solvent effect on solvolysis reaction was not explained by only dielectric constant. Then, solvolysis of ten kinds of substrates was carried out under the same reaction condition as **4a** and the results were shown in Table 1. To investigate the influence of the substituent in the aromatic ring, solvolysis of three groups of substrates was carried out. In the case of the same type substrate **4e**, **f** without substituent at *ortho*-position as **4a**, solvolysis reaction smoothly occurred to afford **2e**, **f** and **5e**, **f** in moderate yield.

Table 1. Solvolysis of (4,5)-*anti*-4-Aryl-5-tosyloxy-2(*E*)-hexenoate Derivatives



Entry	Tosylate (g)	R^3	R^4	R^5	R^6	Time (d)	Recovered **4** (%)	**2** (yield, %)	**5** (yield, %)	Ratio (**2** : **5**)
1	**4a** (0.939)	H	H	OMe	H	5	8	10	70	1 : 7
2	**4e** (1.01)	H	Me	OMe	H	3	18	6	51	1 : 8.5
3	**4f** (1.00)	H	OMe	OMe	H	4	3	12	52	1 : 4.3
4	**4b** (0.671)	OMe	H	H	H	7	16	31	21	1.5 : 1
5	**4d** (1.723)	OMe	H	Me	H	3	0	38	47	1 : 1.2
6	**4g** (1.01)	OMe	H	H	Me	7	7	28	19	1.5 : 1
7	**4h** (1.19)	OMe	H	Me	OMe	4	11	19	15	1.3 : 1
8	**4c** (1.00)	Me	H	OMe	H	3	10	55	17	3.2 : 1
9	**4i** (1.148)	Me	H	OMe	Me	5	5	46	28	1.6 : 1
10	**4j** (1.01)	Me	H	Me	H	12	7	29	25	1.2 : 1
11	**4k** (1.148)	Me	Me	Me	Me	5	3	69	21	3.3 : 1

The 1,2-migration products **5e**, **f** were predominantly obtained (entries 2, 3). The second group substrates **4b**, **d**, **g**, **h** possessing the methoxyl group at *ortho*-position were subjected to solvolysis reaction to provide **2b**, **d**, **g**, **h** and **5b**, **d**, **g**, **h** in moderate yield (entries 4—7). In these cases, the product selectivity was not observed. The third group substrates **4c**, **i**—**k** possessing the methyl group at *ortho*-position were subjected to solvolysis reaction to yield **2c**, **i**—**k** and **5c**, **i**—**k** in moderate yield (entries 8—11). The reaction products **2b**—**k** were identical with the synthesized **2b**—**k**, respectively. To confirm the 4,5-*anti*-configuration of the 1,2-migration products **5a**—**k**, the substrate **5c** was selected for the structure elucidation. Catalytic hydrogenation of **5c** followed by the consecutive alkaline hydrolysis and γ-lactone formation using dicyclohexyl carbodiimide (DCC) gave γ-lactone **9c** in 70% overall yield, which was identical with the authentic sample **9c**[7] (Chart 4). The structures of the residual **5a**, **b**, **d**—**k** were deduced by the similarity of the NMR spectrum of **5c**.

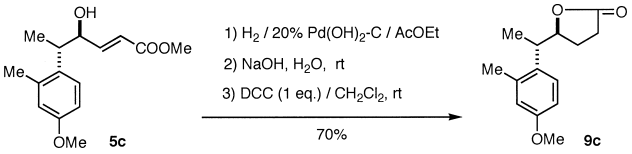


Chart 4

Disscussion

It was apparent that the solvolysis reaction of (4,5)-*anti*-4-aryl-5-tosyloxy-2(*E*)-hexenoates **4a**—**k** gave **2a**—**k** and 1,2-migration products **5a**—**k** along with the complete inversion. The product selectivity between **2a**—**k** and **5a**—**k** was found to be subtly governed by the substituent and substitution pattern in the aromatic ring of the substrates **4a**—**k**. When both **2a** and **5a** were individually exposed to the solvolysis condition (TsOH in H_2O-saturated $MeNO_2$ at 50 °C for 5 d), both substrates were intact, respectively. This experiment indicates that the reaction is kinetically controlled and the rate-determining stage might be until the formation of the reaction intermediate. Both substrates **2a** and **5a** could be formed from the common intermediate which is corresponding to the σ-bridged phenonium ion **F** as shown in Table 1. We already reported that treatment of (4,5)-*anti*-4-aryl-5-tosyloxy-hexanoates under a solvolytic condition afforded a **G**-lactonization product along with the complete 1,2-aryl migration *via* the σ-bridged phenonium ion intermediate.[1] In the case of **4a** without substituent at *ortho*-position, the plausible reaction course is considered as follow. After the formation of phenonium ion intermediate **I**, H_2O as nucleophile attacks at both C(4)- and C(5)-positions along with inversion to afford **5a** as a major product and **2a** as a minor product. This product selectivity can be rationalized by considering that the reactivity of C(4)-carbenium ion corresponding to the allyl carbenium ion is higher than that of C(5)-carbenium ion as shown in Chart 5.

In the case of the solvolysis of **4b** possessing the methoxyl group at *ortho*-position, two possible intermediates **II** and **III** are considered as shown in Chart 5. The formation of **2b** and **5b** is explained by way of the phenonium ion intermediate **II**, and **2b** is presumed to be also formed *via* an oxonium ion intermediate **III** which is corresponded to the methoxyl oxygen participation at the C(5)-position. Consequently, product selectivity might be not observed. Ramsey *et al.* reported the presence of such an oxonium ion **10** and the σ-bridged phenonium ion **11** based on the ionization of *o*-anisylethyl chloride **12** in $SbF_5 \cdot SO_2$ at −70 °C and $SbF_5 \cdot SO_2 \cdot BF_3$ at −20 °C, respectively, by means of ^{1}H-NMR measurement of the resulting reaction mixture as shown in Chart 5.[8] In the case of the solvolysis of **4c**, **i**—**k** possessing the methyl group at *ortho*-position, two possible intermediates **IV** and **V** are considered as shown in Chart 6. The formation of **2c**, **k** and **5c**, **k** is explained by way of the phenonium ion intermediate **IV**, and the preferential formation of **2c**, **k** could be considered an alternative pathway. Although such an alternative pathway should be present in literature, the detailed structure of the intermediate has not yet been determined.[9]

Conclusion

The solvolysis reaction of (4,5)-*anti*-4-aryl-5-tosyloxy-2(*E*)-hexenoates **4a**—**k** gave (4,5)-*anti*-4-aryl-5-hydroxy-2(*E*)-hexenoates **2a**—**k** and (4,5)-*anti*-5-aryl-4-hydroxy-

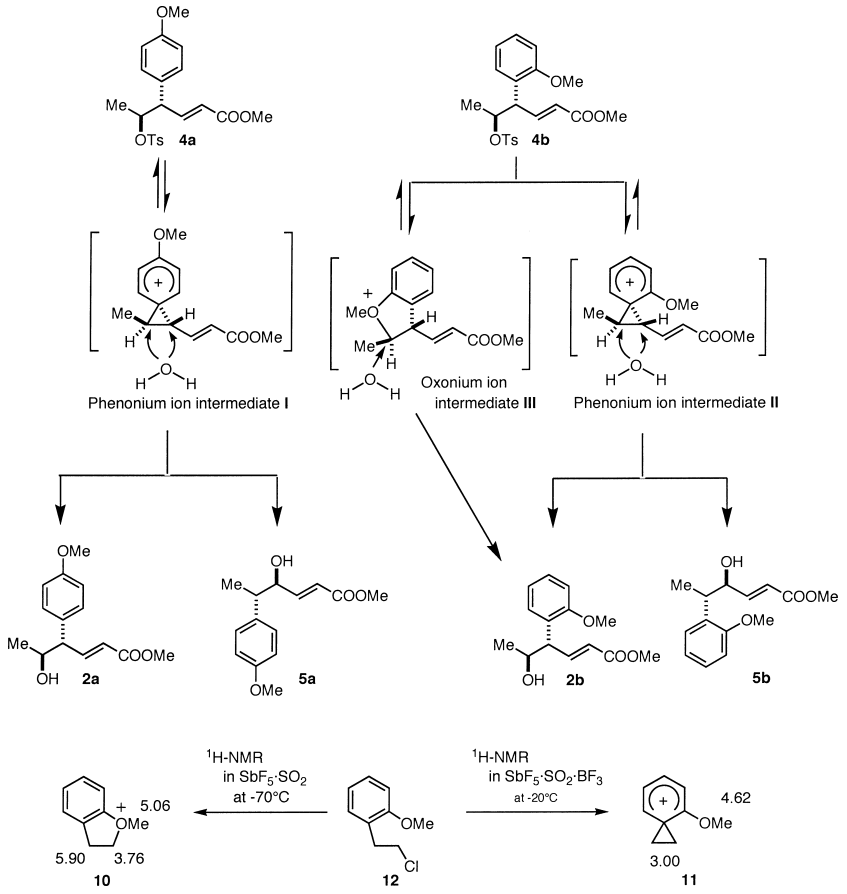


Chart 5

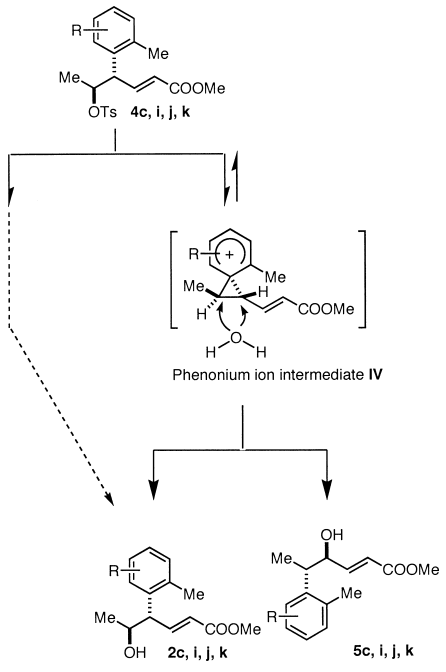


Chart 6

2(*E*)-hexenoates **5a**—**k** along with the complete inversion. This 1,2-aryl migration was induced by treatment with heating in water-saturated nitromethane. On the basis of the substituent effect on the aromatic ring, this 1,2-aryl migration is thought to proceed *via* the σ-bridged phenonium ion. The product selectivity between **2a**—**k** and **5a**—**k** was found to be governed by the substituent and substitution pattern in the aromatic ring of the substrates **4a**—**k**.

Experimental

^{1}H-NMR spectra were recorded by a JEOL EX 400 spectrometer (Tokyo, Japan). Spectra were taken with 5—10% (w/v) solution in $CDCl_3$ with Me_4Si as an internal reference. Mass spectra and the fast atom bombardment mass spectra (FAB-MS) were obtained with a JEOL JMS-600H (matrix; glycerol, *m*-nitrobenzyl alcohol) spectrometer. IR spectra were recorded on a JASCO FT/IR-300 spectrometer. All evaporations were performed under reduced pressure. For column chromatography, silica gel (Kieselgel 60) was employed.

Methyl (4,5)-*anti*-4-(4′-Methoxyphenyl)-5-hydroxy-2(*E*)-hexenoate 2a and Methyl (4,5)-*anti*-4-(2′-Methoxyphenyl)-5-hydroxy-2(*E*)-hexenoate 2b To a solution of **1** (5.83 g, 0.041 mol) and anisole (6.93 g, 0.082 mol) in CH_2Cl_2 (30 ml) was added $BF_3 \cdot Et_2O$ (5.1 ml, 0.041 mol) at −78 °C, and the whole mixture was stirred for 1 h at −78 °C, and for 1 h at −20 °C. The reaction mixture was diluted with brine and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and evaporated to provide a residue, which was chromatographed on silica gel (200 g, *n*-hexane : AcOEt=85 : 15) to afford **2b** (0.229 g, 3%) and **2a** (4.908 g, 53%) as a colorless oil, respectively, in elution order. Compound **2a** was identical with the reported **2a**.[4] **2b**: IR (neat): 3444, 1720 cm^{-1}; ^{1}H-NMR: δ 1.11 (3H, d, J=6 Hz), 1.84 (1H, d, J=4 Hz), 3.72 (3H, s), 3.79 (1H, t, J=8 Hz), 3.82 (3H, s), 4.19 (1H, ddq, J=4, 8, 8 Hz), 5.91 (1H, d, J=15.6 Hz), 6.88 (1H, d, J=8 Hz), 6.93 (1H, t, J=8 Hz), 7.15 (1H, d, J=8 Hz), 7.23 (1H, t, J=8 Hz), 7.34 (1H, dd, J=8, 15.6 Hz). *Anal.* Calcd for $C_{14}H_{18}O_4 \cdot H_2O$: C, 66.00; H, 7.32. Found: C, 66.03; H, 7.63.

Methyl (4,5)-*anti*-4-(2′-Methyl-4′-methoxyphenyl)-5-hydroxy-2(*E*)-hexenoate 2c and Methyl (4,5)-*anti*-4-(4′-Methyl-2′-methoxyphenyl)-5-hydroxy-2(*E*)-hexenoate 2d To a solution of **1** (6.05 g, 0.043 mol) and *m*-methoxytoluene (4.68 g, 0.12 mol) in CH_2Cl_2 (80 ml) was added $BF_3 \cdot Et_2O$ (5.3 ml, 0.043 mol) at −78 °C, and the whole mixture was stirred for 1 h at −78 °C, and for 1 h at –20 °C. The reaction mixture was worked up in the

same way as **2a** to afford **2d** (3.18 g, 28%) and **2c** (5.75 g, 51%) as a colorless oil, respectively, in elution order. **2c**: IR (neat): 3443, 1720 cm^{-1}; ^{1}H-NMR: δ 1.12 (3H, d, J=6.5 Hz), 1.74 (1H, br s), 2.31 (3H, s), 3.58 (1H, ddd, J=2, 7.5, 8 Hz), 3.71 (3H, s), 3.78 (3H, s), 4.10 (1H, dq, J=6.5, 7.5 Hz), 5.86 (1H, dd, J=2, 15.5 Hz), 6.73 (1H, s), 6.75 (1H, d, J=7.5 Hz), 7.08 (1H, d, J=1, 7.5 Hz), 7.23 (1H, dd, J=8, 15.5 Hz). *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7. 63. Found: C, 67.86; H, 7.74. MS (FAB) *m/z*: 265 (M^++1). **2d**: IR (neat): 3444, 1695 cm^{-1}; ^{1}H-NMR: δ 1.10 (3H, d, J=6 Hz), 1.74 (1H, br s), 2.33 (3H, s), 3.71 (3H, s), 3.77 (1H, ddd, J=1, 7, 8.5 Hz), 3.80 (3H, s), 4.17 (1H, dq, J=7, 6 Hz), 5.89 (1H, dd, J=1, 15.6 Hz), 6.69 (1H, s), 6.74 (1H, d, J=7.5 Hz), 7.01 (1H, d, J=7.5 Hz), 7.33 (1H, dd, J=8.5, 15.6 Hz). *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.72; H, 7.69. MS (FAB) *m/z*: 265 (M^++1).

Methyl (4,5)-*anti*-4-(3′-Methyl-4′-methoxyphenyl)-5-hydroxy-2(*E*)-hexenoate 2e To a solution of **1** (11.38 g, 0.08 mol) and *o*-methoxytoluene (19.53 g, 0.16 mol) in CH_2Cl_2 (150 ml) was added $BF_3\cdot Et_2O$ (10 ml, 0.08 mol) at −78 °C, and the whole mixture was stirred for 1 h at −78 °C, and for 1 h at −20 °C. The reaction mixture was worked up in the same way as **2a** to afford **2e** (14.7 g, 70%) as a colorless oil. **2e**: IR (neat): 3444, 1714 cm^{-1}; ^{1}H-NMR: δ 1.08 (3H, d, J=6 Hz), 2.12 (1H, br s), 2.18 (3H, s), 3.25 (1H, ddd, J=2, 6, 8 Hz), 3.69 (3H, s), 3.78 (3H, s), 4.02 (1H, dq, J=6, 6 Hz), 5.87 (1H, dd, J=2, 16 Hz), 6.74 (1H, d, J=8 Hz), 6.93 (1H, d, J=2 Hz), 6.95 (1H, dd, J=2, 8 Hz), 7.24 (1H, d, J=8, 16 Hz). *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.88; H, 7.84. MS (FAB) *m/z*: 265 (M^++1).

Methyl (4,5)-*anti*-4-(3′,4′-Dimethoxyphenyl)-5-hydroxy-2(*E*)-hexenoate 2f To a solution of **1** (4.26 g, 0.03 mol) and 1,2-dimethoxybenzene (8.29 g, 0.06 mol) in CH_2Cl_2 (60 ml) was added $BF_3\cdot Et_2O$ (3.75 ml, 0.03 mol) at −78 °C, and the whole mixture was stirred for 1 h at −78 °C, and for 1 h at −20 °C. The reaction mixture was worked up in the same way as **2a** to afford **2f** (8.40 g, 90%) as a colorless oil. **2f**: IR (CCl_4): 3560, 1715 cm^{-1}; ^{1}H-NMR: δ 1.07 (3H, d, J=6 Hz), 2.12 (1H, br s), 3.24 (1H, ddd, J=2, 6, 8 Hz), 3.66 (3H, s), 3.80 (3H, s), 3.82 (3H, s), 4.01 (1H, dq, J=6, 6 Hz), 5.86 (1H, dd, J=2, 16 Hz), 6.66 (1H, d, J=2 Hz), 6.70 (1H, dd, J=2, 8 Hz), 6.78 (1H, d, J=8 Hz), 7.22 (1H, d, J=8, 16 Hz). *Anal.* Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.10; H, 7.43. MS (FAB) *m/z*: 265 (M^++1).

Methyl (4,5)-*anti*-4-(5′-Methyl-2′-methoxyphenyl)-5-hydroxy-2(*E*)-hexenoate 2g To a solution of **1** (11.38 g, 0.08 mol) and 4-methoxytoluene (19.54 g, 0.16 mol) in CH_2Cl_2 (150 ml) was added $BF_3\cdot Et_2O$ (10 ml, 0.08 mol) at −78 °C, and the whole mixture was stirred for 1 h at −78 °C, and for 1 h at −20 °C. The reaction mixture was worked up in the same way as **2a** to afford **2g** (10.72 g, 51%) as a colorless oil. **2g**: IR (CCl_4): 3570, 1720 cm^{-1}; ^{1}H-NMR: δ 1.10 (3H, d, J=6 Hz), 2.15 (1H, br s), 2.26 (3H, s), 3.70 (3H, s), 3.76 (1H, ddd, J=2, 6, 8 Hz), 3.78 (3H, s), 4.17 (1H, dq, J=6, 6 Hz), 5.90 (1H, dd, J=2, 16 Hz), 6.77 (1H, d, J=8 Hz), 6.94 (1H, d, J=2 Hz), 7.34 (1H, dd, J=8, 16 Hz). *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.14; H, 7.63. Found: C, 67.74; H, 7.82. MS (FAB) *m/z*: 265 (M^++1).

Methyl (4,5)-*anti*-4-(4′-Methyl-2′,5′-dimethoxyphenyl)-5-hydroxy-2(*E*)-hexenoate 2h To a solution of **1** (4.26 g, 0.03 mol) and 2,5-dimethoxytoluene (9.13 g, 0.06 mol) in CH_2Cl_2 (60 ml) was added $BF_3\cdot Et_2O$ (3.75 ml, 0.03 mol) at −78 °C, and the whole mixture was stirred for 1 h at −78 °C, and for 1 h at −20 °C. The reaction mixture was worked up in the same way as **2a** to afford **2h** (5.55 g, 63%) as a colorless oil. **2h**: IR (neat): 3443, 1714 cm^{-1}; ^{1}H-NMR: δ 1.09 (3H, d, J=6 Hz), 2.12 (1H, br s), 2.17 (3H, s), 3.68 (3H, s), 3.72 (1H, ddd, J=2, 6, 8 Hz), 3.74 (3H, s), 3.75 (3H, s), 4.15 (1H, dq, J=6, 6 Hz), 5.88 (1H, dd, J=2, 16 Hz), 6.60 (1H, s), 6.68 (1H, s), 7.31 (1H, dd, J=8, 16 Hz). *Anal.* Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.01; H, 7.72. MS (FAB) *m/z*: 295 (M^++1).

Methyl (4,5)-*anti*-4-(2′,5′-Dimethyl-4′-methoxyphenyl)-5-hydroxy-2(*E*)-hexenoate 2i To a solution of **1** (4.26 g, 0.03 mol) and 1,4-dimethyl-2-methoxybenzene (12.17 g, 0.09 mol) in CH_2Cl_2 (50 ml) was added $BF_3\cdot Et_2O$ (3.78 ml, 0.03 mol) at −78 °C, and the whole mixture was stirred for 1 h at −78 °C, and for 1 h at −20 °C. The reaction mixture was worked up in the same way as **2a** to afford **2i** (6.89 g, 84%) as a colorless oil. **2i**: IR (neat): 3422, 1719 cm^{-1}; ^{1}H-NMR: δ 1.07 (3H, d, J=7 Hz), 2.13 (3H, s), 2.23 (1H, br s), 2.27 (3H, s), 3.53 (1H, dd, J=8.5, 8.5 Hz), 3.66 (3H, s), 3.77 (3H, s), 4.06 (1H, dq, J=8.5, 7 Hz), 5.82 (1H, d, J=16 Hz), 6.59 (1H, s), 6.87 (1H, s), 7.21 (1H, dd, J=8.5, 16 Hz). *Anal.* Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.78; H, 8.05. MS (FAB) *m/z*: 301 (M^++Na).

Methyl (4,5)-*anti*-4-(2′,4′-Dimethylphenyl)-5-hydroxy-2(*E*)-hexenoate 2j To a solution of **1** (4.26 g, 0.03 mol) and *m*-xylene (6.37 g, 0.06 mol) in CH_2Cl_2 (60 ml) was added $BF_3\cdot Et_2O$ (3.75 ml, 0.03 mol) at −78 °C, and the whole mixture was stirred for 1 h at −78 °C, and for 1 h at −20 °C. The reaction mixture was worked up in the same way as **2a** to afford **2j** (4.09 g, 55%). **2j**: IR (neat): 3443, 1723 cm^{-1}; ^{1}H-NMR: δ 1.08 (3H, d, J=6 Hz), 2.25 (3H, s), 2.27 (3H, s), 2.35 (1H, br s), 3.58 (1H, ddd, J=2, 8, 8 Hz), 3.66 (3H, s), 4.09 (1H, dq, J=8, 6 Hz), 5.82 (1H, dd, J=2, 16 Hz), 6.93—6.99 (2H, m), 7.02 (1H, d, J=8 Hz), 7.23 (1H, dd, J=8, 16 Hz). *Anal.* Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.10; H, 8.39. MS (FAB) *m/z*: 249 (M^++1).

Methyl (4,5)-*anti*-4-(2′,3′,4′,5′-Tetramethylphenyl)-5-hydroxy-2(*E*)-hexenoate 2k To a solution of **1** (4.26 g, 0.03 mol) and 1,2,3,4-tetramethylbenzene (12.08 g, 0.09 mol) in CH_2Cl_2 (50 ml) was added $BF_3\cdot Et_2O$ (3.78 ml, 0.03 mol) at −78 °C, and the whole mixture was stirred for 1 h at −78 °C, and for 1 h at −20 °C. The reaction mixture was worked up in the same way as **2a** to afford **2k** (6.89 g, 94%). **2k**: IR (neat): 3435, 1719 cm^{-1}; ^{1}H-NMR: δ 1.10 (3H, d, J=6.5 Hz), 1.91 (1H, br s), 2.16 (3H, s), 2.20 (6H, s), 2.24 (3H, s), 3.68 (1H, ddd, J=2, 9, 9 Hz), 3.69 (3H, s), 4.11 (1H, dq, J=9, 6.5 Hz), 5.86 (1H, dd, J=2, 16 Hz), 6.80 (1H, s), 7.26 (1H, dd, J=9, 16 Hz). *Anal.* Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.87; H, 8.76. MS (FAB) *m/z*: 299 (M^++Na).

Methyl (4,5)-*anti*-4-(4′-Methoxyphenyl)-5-tosyloxy-2(*E*)-hexenoate 4a A mixture of **2a** (2.773 g, 0.011 mol), *p*-toluenesulfonyl chloride (TsCl, 3.14 g, 0.016 mol), pyridine (8 ml) was stirred for 1 d at rt. The reaction mixture was diluted with H_2O, which was extracted with ether. The organic layer was washed with 1 M aqueous HCl and 7% aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$ and evaporated to give a residue, which was chromatographed on silica gel (80 g, *n*-hexane : AcOEt=5 : 1) to afford **4a** (2.02 g, 73%) as a colorless oil. **4a**: IR (neat): 1730, 1376 cm^{-1}; ^{1}H-NMR: δ 1.24 (3H, d, J=6 Hz), 2.44 (3H, s), 3.48 (1H, t, J=8 Hz), 3.70 (3H, s), 3.77 (3H, s), 4.83 (1H, dq, J=8, 6 Hz), 5.75 (1H, d, J=16 Hz), 6.80 (2H, d, J=9 Hz), 6.94 (1H, dd, J=8, 16 Hz), 7.00 (2H, d, J=9 Hz), 7.28 (2H, d, J=9 Hz), 7.70 (2H, d, J=9 Hz). *Anal.* Calcd for $C_{21}H_{24}SO_6$: C, 62.36; H, 5.98. Found: C, 62.57; H, 6.08. MS (FAB) *m/z*: 405 (M^++1).

Methyl (4,5)-*anti*-4-(4′-Methoxyphenyl)-5-mesyloxy-2(*E*)-hexenoate 6a A mixture of **2a** (1.9 g, 0.0076 mol), methanesulfonyl chloride (MsCl, 1.4 g, 0.012 mol), pyridine (8 ml) was stirred for 1 d at rt. The reaction mixture was worked up in the same way as **4a** to afford **6a** (1.775 g, 93%) as a colorless oil. **6a**: IR (neat): 1721, 1655 cm^{-1}; ^{1}H-NMR: δ 1.38 (3H, d, J=7 Hz), 2.82 (3H, s), 3.57 (1H, t, J=8 Hz), 3.74 (3H, s), 3.79 (3H, s), 4.97(1H, dq, J=8, 7 Hz), 5.91 (1H, d, J=16 Hz), 6.89 (2H, d, J=9 Hz), 7.13 (2H, d, J=9 Hz), 7.20 (1H, dd, J=8, 16 Hz). *Anal.* Calcd for $C_{15}H_{20}SO_6$: C, 54.86; H, 6.14. Found: C, 54.91; H, 6.13. MS (FAB) *m/z*: 329 (M^++1).

Methyl (4,5)-*anti*-4-(2′-Methoxyphenyl)-5-tosyloxy-2(*E*)-hexenoate 4b A mixture of **2b** (0.63 g, 0.0025 mol), *p*-toluenesulfonic anhydride (Ts_2O, 0.99 g, 0.003 mol), pyridine (3 ml) was stirred for 1 d at rt. The reaction mixture was worked up in the same way as **4a** to afford **4b** (0.723 g, 71%) as a colorless oil. **4b**: IR (KBr): 1721 cm^{-1}; ^{1}H-NMR: δ 1.28 (3H, d, J=6.3 Hz), 2.39 (3H, s), 3.69 (3H, s), 3.76 (3H, s), 3.83 (1H, dd, J=7.3, 9.3 Hz), 5.05 (1H, dq, J=7.3, 6.3 Hz), 5.75 (1H, d, J=16.1 Hz), 6.77 (1H, d, J=8.3 Hz), 6.84 (1H, t, J=7.3 Hz), 7.00 (1H, dd, J=9.3, 16.1 Hz), 7.00 (1H, d, J=7.3 Hz), 7.19 (1H, t, J=7.3 Hz), 7.24 (2H, d, J=8.3 Hz), 7.65 (2H, d, J=8.3 Hz). *Anal.* Calcd for $C_{21}H_{24}SO_6$: C, 62.36; H, 5.98. Found: C, 62.60; H, 5.87. MS (FAB) *m/z*: 405 (M^++1).

Methyl (4,5)-*anti*-4-(2′-Methyl-4′-methoxyphenyl)-5-tosyloxy-2(*E*)-hexenoate 4c A mixture of **2c** (1.464 g, 0.0054 mol), *p*-toluenesulfonyl chloride (TsCl, 1.55 g, 0.0083 mol), pyridine (4 ml) was stirred for 1 d at rt. The reaction mixture was worked up in the same way as **4a** to afford **4c** (2.034 g, 89%). **4c**: IR (neat): 1714 cm^{-1}; ^{1}H-NMR: δ 1.25 (3H, d, J=6.4 Hz), 2.23 (3H, s), 2.44 (3H, s), 3.67 (3H, s), 3.74 (1H, t, J=8.4 Hz), 3.75 (3H, s), 4.78 (1H, dq, J=8.4, 6.4 Hz), 5.68 (1H, d, J=15.6 Hz), 6.66 (1H, br s), 6.67 (1H, br d, J=8.4 Hz), 6.88 (1H, dd, J=8.4, 15.6 Hz), 6.91 (1H, d, J=8.4 Hz), 7.29 (2H, d, J=8.4 Hz), 7.73 (2H, d, J=8.4 Hz). *Anal.* Calcd for $C_{22}H_{26}SO_6$: C, 63.14; H, 6.23. Found: C, 62.74; H, 6.34. MS (FAB) *m/z*: 419 (M^++1).

Methyl (4,5)-*anti*-4-(4′-Methyl-2′-methoxyphenyl)-5-tosyloxy-2(*E*)-hexenoate 4d A mixture of **2d** (0.488 g, 0.0018 mol), *p*-toluenesulfonyl chloride (TsCl, 0.718 g, 0.0037 mol), pyridine (2 ml) was stirred for 1 d at rt. The reaction mixture was worked up in the same way as **4a** to afford **4d** (0.773 g, quantitative yield). **4d**: IR (neat): 1715 cm^{-1}; ^{1}H-NMR: δ 1.28 (3H, d, J=6.4 Hz), 2.30 (3H, s), 2.43 (3H, s), 3.69 (3H, s), 3.72 (3H, s), 3.78 (1H, t, J=8.4 Hz), 5.02 (1H, dq, J=8.4, 6.4 Hz), 5.67 (1H, br s), 5.73 (1H, d, J=15.8 Hz), 6.64 (1H, br d, J=7.5 Hz), 6.86 (1H, d, J=7.5 Hz), 6.99 (1H, dd, J=8.4, 15.8 Hz), 7.24 (2H, d, J=8.2 Hz), 7.66 (2H, d, J=8.2 Hz). *Anal.* Calcd for $C_{22}H_{26}SO_6\cdot 1/4H_2O$; C, 62.47; H, 6.31. Found: C, 62.35; H, 6.36. MS (FAB) *m/z*: 419 (M^++1).

Methyl (4,5)-*anti*-4-(3′-Methyl-4′-methoxyphenyl)-5-tosyloxy-2(*E*)-

hexenoate 4e A mixture of **2e** (1.28 g, 0.0048 mol), *p*-toluenesulfonic anhydride (Ts_2O, 2.49 g, 0.0072 mmol), pyridine (10 ml) was stirred for 1 d at rt. The reaction mixture was worked up in the same way as **4a** to afford **4e** (1.59 g, 78%). **4e**: IR (neat): 1725 cm^{-1}; ^{1}H-NMR: δ 1.22 (3H, d, J=6 Hz), 2.11 (3H, s), 2.40 (3H, s), 3.40 (1H, ddd, J=2, 6, 8 Hz), 3.67 (3H, s), 3.75 (3H, s), 4.80 (1H, dq, J=6, 6 Hz), 5.72 (1H, dd, J=2, 16 Hz), 6.67 (1H, d, J=8 Hz), 6.78 (1H, d, J=2 Hz), 6.83 (1H, dd, J=2, 8 Hz), 6.91 (1H, dd, J=8, 16 Hz), 7.23 (2H, d, J=8 Hz), 7.66 (2H, d, J=8 Hz). *Anal.* Calcd for $C_{22}H_{26}SO_6$; C, 63.14; H, 6.26. Found: C, 63.15; H, 6.38. MS (FAB) *m/z*: 419 (M^++1).

Methyl (4,5)-*anti*-4-(3′,4′-Dimethoxyphenyl)-5-tosyloxy-2(*E*)-hexenoate 4f A mixture of **2f** (1.67 g, 0.006 mol), *p*-toluenesulfonic anhydride (Ts_2O, 3.11 g, 0.0091 mmol), pyridine (15 ml) was stirred for 1 d at rt. The reaction mixture was worked up in the same way as **4a** to afford **4f** (2.47 g, 94%). **4f**: IR (neat): 1725 cm^{-1}; ^{1}H-NMR: δ 1.21 (3H, d, J=6 Hz), 2.36 (3H, s), 3.42 (1H, ddd, J=2, 6, 8 Hz), 3.65 (3H, s), 3.76 (3H, s), 3.79 (3H, s), 4.80 (1H, dq, J=6, 6 Hz), 5.73 (1H, dd, J=2, 16 Hz), 6.51 (1H, d, J=2 Hz), 6.59 (1H, dd, J=2, 8 Hz), 6.71 (1H, d, J=8 Hz), 6.94 (1H, ddd, J=2, 6, 8 Hz), 7.21 (2H, d, J=8 Hz), 7.62 (2H, d, J=8 Hz). *Anal.* Calcd for $C_{22}H_{26}SO_7$; C, 60.81; H, 6.03. Found: C, 60.75; H, 6.10. MS (FAB) *m/z*: 434 (M^+).

Methyl (4,5)-*anti*-4-(5′-Methyl-2′-methoxyphenyl)-5-tosyloxy-2(*E*)-hexenoate 4g A mixture of **2g** (1.58 g, 0.006 mol), *p*-toluenesulfonic anhydride (Ts_2O, 3.07 g, 0.009 mmol), pyridine (12 ml) was stirred for 1 d at rt. The reaction mixture was worked up in the same way as **4a** to afford **4g** (2.12 g, 85%). **4g**: IR (neat): 1715 cm^{-1}; ^{1}H-NMR: δ 1.26 (3H, d, J=6 Hz), 2.18 (3H, s), 2.40 (3H, s), 3.67 (3H, s), 3.69 (3H, s), 3.76 (1H, ddd, J=2, 6, 8 Hz), 5.04 (1H, dq, J=6, 6 Hz), 5.73 (1H, dd, J=2, 16 Hz), 6.63 (1H, d, J=8 Hz), 6.75 (1H, d, J=2 Hz), 6.94 (1H, dd, J=2, 8 Hz), 6.97 (1H, dd, J=6, 16 Hz), 7.21 (2H, d, J=8 Hz), 7.62 (2H, d, J=8 Hz). *Anal.* Calcd for $C_{22}H_{26}SO_6$; C, 63.14; H, 6.26. Found: C, 62.92; H, 6.38. MS (FAB) *m/z*: 419 (M^++1).

Methyl (4,5)-*anti*-4-(4′-Methyl-2′,5′-dimethoxyphenyl)-5-tosyloxy-2(*E*)-hexenoate 4h A mixture of **2h** (1.48 g, 0.005 mol), *p*-toluenesulfonic anhydride (Ts_2O, 2.58 g, 0.0075 mmol), pyridine (12 ml) was stirred for 1 d at rt. The reaction mixture was worked up in the same way as **4a** to afford **4h** (1.42 g, 79%). **4h**: IR (neat): 1715 cm^{-1}; ^{1}H-NMR: δ 1.27 (3H, d, J=6 Hz), 2.14 (3H, s), 2.39 (3H, s), 3.65 (3H, s), 3.66 (3H, s), 3.68 (3H, s), 3.75 (1H, ddd, J=2, 6, 8 Hz), 5.02 (1H, dq, J=6, 6 Hz), 5.75 (1H, dd, J=2, 16 Hz), 6.41 (1H, s), 6.55 (1H, s), 7.00 (1H, dd, J=8, 16 Hz), 7.20 (2H, d, J=8 Hz), 7.61 (2H, d, J=8 Hz). *Anal.* Calcd for $C_{23}H_{28}SO_7$; C, 61.59; H, 6.29. Found: C, 61.38; H, 6.58. MS (FAB) *m/z*: 449 (M^++1).

Methyl (4,5)-*anti*-4-(2′,5′-Dimethyl-4′-methoxyphenyl)-5-tosyloxy-2(*E*)-hexenoate 4i A mixture of **2i** (2.766 g, 0.0099 mol), *p*-toluenesulfonic anhydride (Ts_2O, 4.9 g, 0.015 mmol), pyridine (20 ml) was stirred for 1 d at rt. The reaction mixture was worked up in the same way as **4a** to afford **4i** (3.153 g, 73%). **4i**: IR (neat): 1715 cm^{-1}; ^{1}H-NMR: δ 1.23 (3H, d, J=6.5 Hz), 2.09 (3H, s), 2.21 (3H, s), 2.42 (3H, s), 3.66 (3H, s), 3.69 (1H, ddd, J=2, 8, 8 Hz), 4.87 (1H, dq, J=8, 6.5 Hz), 5.66 (1H, dd, J=2, 16 Hz), 6.53 (1H, s), 6.69 (1H, s), 6.86 (1H, dd, J=8, 16 Hz), 7.27 (2H, d, J=8 Hz), 7.70 (2H, d, J=8 Hz). *Anal.* Calcd for $C_{23}H_{28}SO_6$; C, 63.87; H, 6.53. Found: C, 63.66; H, 6.58. MS (FAB) *m/z*: 433 (M^++1).

Methyl (4,5)-*anti*-4-(2′,4′-Dimethylphenyl)-5-tosyloxy-2(*E*)-hexenoate 4j A mixture of **2j** (1.51 g, 0.006 mol), *p*-toluenesulfonic anhydride (Ts_2O, 4.09 g, 0.012 mmol), pyridine (15 ml) was stirred for 1 d at rt. The reaction mixture was worked up in the same way as **4a** to afford **4j** (2.02 g, 82%). **4j**: IR (neat): 1714 cm^{-1}; ^{1}H-NMR: δ 1.23 (3H, d, J=7 Hz), 2.20 (3H, s), 2.24 (3H, s), 2.43 (3H, s), 3.66 (3H, s), 3.75 (1H, ddd, J=2, 8, 8 Hz), 4.87 (1H, dq, J=8, 7 Hz), 5.66 (1H, dd, J=2, 16 Hz), 6.85 (1H, dd, J=8, 16 Hz), 6.86 (1H, d, J=8 Hz), 6.90—6.94 (2H, m), 7.27 (2H, d, J=8 Hz), 7.71 (2H, d, J=8 Hz). *Anal.* Calcd for $C_{22}H_{26}SO_5$; C, 65.65; H, 6.51. Found: C, 65.37; H, 6.74. MS (FAB) *m/z*: 403 (M^++1).

Methyl (4,5)-*anti*-4-(2′,3′,4′,5′-Tetramethylphenyl)-5-tosyloxy-2(*E*)-hexenoate 4k A mixture of **2k** (2.644 g, 0.01 mol), *p*-toluenesulfonic anhydride (Ts_2O, 4.89 g, 0.015 mmol), pyridine (20 ml) was stirred for 1 d at rt. The reaction mixture was worked up in the same way as **4a** to afford **4k** (3.016 g, 70%). **4k**: IR (neat): 1715 cm^{-1}; ^{1}H-NMR: δ 1.25 (3H, d, J=6.5 Hz), 2.11 (3H, s), 2.13 (3H, s), 2.14 (3H, s), 2.19 (3H, s), 2.42 (3H, s), 3.67 (3H, s), 3.82 (1H, ddd, J=2, 9, 9 Hz), 4.90 (1H, dq, J=9, 6.5 Hz), 5.68 (1H, dd, J=2, 16 Hz), 6.62 (1H, s), 6.92 (1H, dd, J=9, 16 Hz), 7.25 (2H, d, J=8 Hz), 7.69 (2H, d, J=8 Hz). *Anal.* Calcd for $C_{24}H_{30}SO_5$; C, 66.95; H, 7.02. Found: C, 66.76; H, 7.07. MS (FAB) *m/z*: 431 (M^++1).

Solvolysis of 4a A solution of **4a** (0.939 g, 0.0023 mol) in water-saturated nitromethane (120 ml) was stirred for 5 d at 50 °C. The reaction mixture was diluted with water and extracted with ether. The organic layer was washed with 7% aqueous $NaHCO_3$ and dried over $MgSO_4$. Evaporation of the organic solvent gave a residue, which was chromatographed on silica gel (20 g) to afford **4a** (0.076 g, 8% recovery) from *n*-hexane : AcOEt=50 : 1 elution, **5a** (0.405 g, 70%) from *n*-hexane : AcOEt=30 : 1 elution and **2a** (0.057 g, 10%) from *n*-hexane : AcOEt=5 : 1 elution. Compound **2a** was identical with the above-mentioned **2a**. **5a**: IR (neat): 3472, 1716 cm^{-1}; ^{1}H-NMR: δ 1.28 (3H, d, J=7 Hz), 2.92 (1H, dq, J=7, 7 Hz), 3.71 (3H, s), 3.78 (3H, s), 4.35 (1H, ddd, J=2, 5, 7 Hz), 5.99 (1H, dd, J=2, 15 Hz), 6.85 (2H, d, J=9 Hz), 6.90 (1H, dd, J=5, 15 Hz), 7.13 (2H, d, J=9 Hz). *Anal.* Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.64; H, 7.29. MS (FAB) *m/z*: 251 (M^++1).

Solvolysis of 6a A solution of **6a** (0.749 g, 0.0023 mol) in water-saturated nitromethane (120 ml) was stirred for 8 d at 50 °C. The reaction mixture was worked up in the same way as **4a** to afford **6a** (0.034 g, 5%), **5a** (0.242 g, 42%) and **2a** (0.065 g, 12%).

Acetylation of 2a A solution of **2a** (0.518 g, 0.002 mol) and Ac_2O (0.42 g, 0.0041 mol) in pyridine (2 ml) was stirred for 1 d at rt. The reaction mixture was diluted with H_2O and extracted with ether. The organic layer was washed with 1 M aqueous HCl, 7% aqueous $NaHCO_3$ and dried over $MgSO_4$. Evaporation of the organic solvent gave a residue, which was chromatographed on silica gel (20 g, *n*-hexane : AcOEt=10 : 1) to afford **7a** (0.545 g, 90%). **7a**: IR (neat): 1730, 1657 cm^{-1}; ^{1}H-NMR: δ 1.19 (3H, d, J=7 Hz), 2.00 (3H, s), 3.44 (1H, ddd, J=1, 9, 9 Hz), 3.67 (3H, s), 3.76 (3H, s), 5.16 (1H, dq, J=9, 7 Hz), 5.79 (1H, dd, J=1, 16 Hz), 6.83 (2H, d, J=8 Hz), 7.08 (2H, d, J=8 Hz), 7.09 (1H, dd, J=9, 16 Hz). *Anal.* Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.34; H, 6.88. MS (FAB) *m/z*: 293 (M^++1).

Acetylation of 5a A solution of **5a** (0.169 g, 0.0007 mol) and Ac_2O (0.14 g, 0.0014 mol) in pyridine (2 ml) was stirred for 1 d at rt. The reaction mixture was worked up in the same way as **2a** to afford **8a** (0.176 g, 89%). **8a**: IR (neat): 1726, 1662 cm^{-1}; ^{1}H-NMR: δ 1.27 (3H, d, J=7 Hz), 2.06 (3H, s), 2.98 (1H, dq, J=7, 7 Hz), 3.66 (3H, s), 3.77 (3H, s), 5.46 (1H, ddd, J=2, 6, 7 Hz), 5.78 (1H, dd, J=2, 16 Hz), 6.71 (1H, dd, J=6, 16 Hz), 6.81 (2H, d, J=8 Hz), 7.07 (2H, d, J=8 Hz). *Anal.* Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.50; H, 6.90. MS (FAB) *m/z*: 293 (M^++1).

Solvolysis of 4e A solution of **4e** (1.01 g, 0.0024 mol) in water-saturated nitromethane (120 ml) was stirred for 3 d at 50 °C. The reaction mixture was worked up in the same way as **4a** to afford **4e** (0.18 g, 18% recovery), **5e** (0.32 g, 51%) and **2e** (0.04 g, 6%). Compound **2e** was identical with the above-mentioned **2e**. **5e**: IR (neat): 3462, 1724 cm^{-1}; ^{1}H-NMR: δ 1.25 (3H, d, J=8 Hz), 2.18 (3H, s), 2.55 (1H, br s), 2.83 (1H, dq, J=4, 8 Hz), 3.68 (3H, s), 3.77 (3H, s), 4.31 (1H, ddd, J=2, 4, 4 Hz), 5.98 (1H, dd, J=2, 16 Hz), 6.73 (1H, d, J=8 Hz), 6.88 (1H, dd, J=4, 16 Hz), 6.96 (1H, d, J=2 Hz), 6.97 (1H, dd, J=2, 8 Hz). *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.46; H, 7.73. MS (FAB) *m/z*: 287 (M^++Na).

Solvolysis of 4f A solution of **4f** (1.00 g, 0.0023 mol) in water-saturated nitromethane (120 ml) was stirred for 4 d at 50 °C. The reaction mixture was worked up in the same way as **4a** to afford **4f** (0.03 g, 3% recovery), **5f** (0.34 g, 52%) and **2f** (0.076 g, 12%). Compound **2f** was identical with the above-mentioned **2f**. **5f**: IR (neat): 3500, 1714 cm^{-1}; ^{1}H-NMR: δ 1.27 (3H, d, J=8 Hz), 1.92 (1H, br s), 2.90 (1H, dq, J=4, 8 Hz), 3.68 (3H, s), 3.82 (3H, s), 3.83 (3H, s), 4.35 (1H, ddd, J=2, 4, 4 Hz), 5.97 (1H, dd, J=2, 16 Hz), 6.69 (1H, d, J=2 Hz), 6.73 (1H, dd, J=2, 8 Hz), 6.79 (1H, d, J=8 Hz), 6.89 (1H, dd, J=4, 16 Hz). *Anal.* Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.11; H, 7.38. MS (FAB) *m/z*: 303 (M^++Na).

Solvolysis of 4b A solution of **4b** (0.671 g, 0.0017 mol) in water-saturated nitromethane (100 ml) was stirred for 7 d at 50 °C. The reaction mixture was worked up in the same way as **4a** to afford **4b** (0.106 g, 16% recovery), **5b** (0.085 g, 21%) and **2b** (0.127 g, 31%). Compound **2b** was identical with the above-mentioned **2b**. **5b**: IR (neat): 3454, 1716 cm^{-1}; ^{1}H-NMR: δ 1.25 (3H, d, J=7 Hz), 2.34—2.48 (1H, m), 3.47 (1H, dq, J=4, 7 Hz), 3.71 (3H, s), 3.82 (3H, s), 4.49 (1H, ddd, J=2, 4, 5 Hz), 6.02 (1H, dd, J=2, 16 Hz), 6.87 (1H, d, J=8 Hz), 6.93 (1H, t, J=7 Hz), 6.94 (1H, dd, J=5, 16 Hz), 7.15—7.23 (2H, m). *Anal.* Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.59; H, 7.49. MS (FAB) *m/z*: 251 (M^++1).

Solvolysis of 4d A solution of **4d** (1.723 g, 0.0041 mol) in water-saturated nitromethane (200 ml) was stirred for 3 d at 50 °C. The reaction mixture was worked up in the same way as **4a** to afford **5d** (0.508 g, 47%) and **2d** (0.411 g, 38%). Compound **2d** was identical with the above-mentioned **2d**. **5d**: IR (neat): 3474, 1719 cm^{-1}; ^{1}H-NMR: δ 1.24 (3H, d, J=7 Hz), 2.34 (3H, s), 3.45 (1H, dq, J=4, 7 Hz), 3.72 (3H, s), 3.82 (3H, s), 4.47—4.52 (1H, m), 6.03 (1H, dd, J=2, 16 Hz), 6.70 (1H, s), 6.76 (1H, d, J=8 Hz), 6.94 (1H, dd, J=4, 16 Hz), 7.05 (1H, d, J=8 Hz). *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.32; H, 7.61. MS (FAB) *m/z*: 265 (M^++1).

Solvolysis of 4g A solution of **4g** (1.01 g, 0.0024 mol) in water-saturated nitromethane (120 ml) was stirred for 7 d at 50 °C. The reaction mixture was worked up in the same way as **4a** to afford **4g** (0.071 g, 7% recovery), **5g** (0.12 g, 19%) and **2g** (0.18 g, 28%). Compound **2g** was identical with the above-mentioned **2g**. **5g**: IR (neat): 3458, 1714 cm^{-1}; ^{1}H-NMR: δ 1.22 (3H, d, J=8 Hz), 2.26 (3H, s), 2.38 (1H, br s), 3.40 (1H, dq, J=4, 8 Hz), 3.69 (3H, s), 3.77 (3H, s), 4.46 (1H, ddd, J=2, 4, 4 Hz), 6.01 (1H, dd, J=2, 16 Hz), 6.74 (1H, d, J=8 Hz), 6.92 (1H, dd, J=4, 16 Hz), 6.97 (1H, d, J=2 Hz), 6.98 (1H, dd, J=2, 8 Hz). *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.07; H, 7.70. MS (FAB) *m*/*z*: 287 (M^++Na).

Solvolysis of 4h A solution of **4h** (1.19 g, 0.0026 mol) in water-saturated nitromethane (120 ml) was stirred for 4 d at 50 °C. The reaction mixture was worked up in the same way as **4a** to afford **4h** (0.13 g, 11% recovery), **5h** (0.12 g, 15%) and **2h** (0.15 g, 19%). Compound **2h** was identical with the above-mentioned **2h**. **5h**: IR (neat): 3470, 1714 cm^{-1}; ^{1}H-NMR: δ 1.23 (3H, d, J=8 Hz), 2.18 (3H, s), 2.28 (1H, br s), 3.42 (1H, dq, J=4, 8 Hz), 3.69 (3H, s), 3.75 (3H, s), 3.76 (3H, s), 4.47 (1H, ddd, J=2, 4, 4 Hz), 6.00 (1H, dd, J=2, 16 Hz), 6.64 (1H, s), 6.68 (1H, s), 6.92 (1H, dd, J=4, 16 Hz). *Anal.* Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 64.99; H, 7.69. MS (FAB) *m*/*z*: 317 (M^++Na).

Solvolysis of 4c A solution of **4c** (1.00 g, 0.0024 mol) in water-saturated nitromethane (120 ml) was stirred for 3 d at 50 °C. The reaction mixture was worked up in the same way as **4a** to afford **4c** (0.10 g, 10% recovery), **5c** (0.11 g, 17%) and **2c** (0.35 g, 55%). Compound **2c** was identical with the above-mentioned **2c**. **5c**: IR (neat): 3472, 1715 cm^{-1}; ^{1}H-NMR: δ 1.27 (3H, d, J=7 Hz), 2.29 (3H, s), 3.18 (1H, dq, J=5, 7 Hz), 3.73 (3H, s), 3.78 (3H, s), 4.32—4.37 (1H, m), 6.05 (1H, dd, J=2, 16 Hz), 6.73 (1H, d, J=3 Hz), 6.74 (1H, dd, J=3, 8 Hz), 6.92 (1H, dd, J=4, 16 Hz), 7.15 (1H, d, J=8 Hz). *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.74; H, 8.05. MS (FAB) *m*/*z*: 265 (M^++1).

Solvolysis of 4i A solution of **4i** (1.148 g, 0.0023 mol) in water-saturated nitromethane (200 ml) was stirred for 5 d at 50 °C. The reaction mixture was worked up in the same way as **4a** to afford **4i** (0.054 g, 5% recovery), **5i** (0.208 g, 28%) and **2i** (0.337 g, 46%). Compound **2i** was identical with the above-mentioned **2i**. **5i**: IR (neat): 3419, 1725 cm^{-1}; ^{1}H-NMR: δ 1.24 (3H, d, J=6.5 Hz), 2.00 (1H, br s), 2.16 (3H, s), 2.26 (3H, s), 3.11 (1H, dq, J=6.5, 6.5 Hz), 3.69 (3H, s), 3.78 (3H, s), 4.33 (1H, ddd, J=2, 5, 6.5 Hz), 6.03 (1H, dd, J=2, 15 Hz), 6.61 (1H, s), 6.88 (1H, dd, J=5, 16 Hz), 6.96 (1H, s). *Anal.* Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.98; H, 8.15. MS (FAB) *m*/*z*: 301 (M^++Na).

Solvolysis of 4j A solution of **4j** (1.01 g, 0.0024 mol) in water-saturated nitromethane (120 ml) was stirred for 12 d at 50 °C. The reaction mixture was worked up in the same way as **4a** to afford **4j** (0.07 g, 7% recovery), **5j** (0.15 g, 25%) and **2j** (0.18 g, 29%). Compound **2j** was identical with the above-mentioned **2j**. **5j**: IR (neat): 3455, 1724 cm^{-1}; ^{1}H-NMR: δ 1.26 (3H, d, J=8 Hz), 1.98 (1H, br s), 2.26 (3H, s), 2.28 (3H, s), 3.17 (1H, dq, J=4, 8 Hz), 3.71 (3H, s), 4.37 (1H, ddd, J=2, 4, 4 Hz), 6.04 (1H, dd, J=2, 16 Hz), 6.90 (1H, dd, J=4, 16 Hz), 6.98 (1H, d, J=2 Hz), 6.99 (1H, dd, J=2, 8 Hz), 7.11 (1H, d, J=8 Hz). *Anal.* Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.25; H, 8.25. MS (FAB) *m*/*z*: 271 (M^++Na).

Solvolysis of 4k A solution of **4k** (1.148 g, 0.0027 mol) in water-saturated nitromethane (200 ml) was stirred for 5 d at 50 °C. The reaction mixture was worked up in the same way as **4a** to afford **4k** (0.034 g, 3% recovery), **5k** (0.152 g, 21%) and **2k** (0.507 g, 69%). Compound **2k** was identical with the above-mentioned **2j**. **5j**: IR (neat): 3472, 1693 cm^{-1}; ^{1}H-NMR: δ 1.26 (3H, d, J=6 Hz), 1.77 (1H, br s), 2.19 (3H, s), 2.21 (3H, s), 2.22 (3H, s), 2.27 (3H, s), 3.31 (1H, dq, J=7, 6 Hz), 3.73 (3H, s), 4.38 (1H, ddd, J=2, 5, 7 Hz), 6.08 (1H, dd, J=2, 16 Hz), 6.91 (1H, s), 6.95 (1H, d, J=5, 16 Hz). *Anal.* Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.68; H, 8.78. MS (FAB) *m*/*z*: 299 (M^++Na).

Conversion of 5c into γ-Lactone 9c A solution of **5c** (0.21 g, 0.0008 mol) in AcOEt (10 ml) was subjected to a catalytic hydrogenation in the presence of 20% $Pd(OH)_2$–C at rt and the reaction mixture was filtered off. The filtrate was condensed to give a residue, which was treated with 2 M aqueous NaOH (1 ml) and stirred for 1 h at rt. Acidification of the reaction mixture with 2 M aqueous HCl gave a crude carboxylic acid. A mixture of a crude carboxylic acid and DCC (0.15 g, 0.0007 mol) in CH_2Cl_2 (5 ml) was stirred for 1 d at rt. The whole mixture was condensed to give a residue, which was chromatographed on silica gel (20 g, benzene : AcOEt=10 : 1) to afford **9c** (0.13 g, 70%). **9c**: IR (neat): 1769 cm^{-1}; ^{1}H-NMR: δ 1.19 (3H, d, J=6.3 Hz), 1.99—2.05 (2H, m), 2.34 (3H, s), 2.62 (1H, dt, J=17.5, 8.5 Hz), 2.80 (1H, dt, J=17.5, 5.5 Hz), 3.00 (1H, dq, J=10.3, 6.3 Hz), 3.78 (3H, s), 4.58 (1H, ddd, J=6.8, 9.8, 10.3 Hz), 6.74 (1H, s), 6.75 (1H, d, J=6.8 Hz), 7.01 (1H, d, J=6.8 Hz). *Anal.* Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.23; H, 7.99. MS (FAB) *m*/*z*: 235 (M^++1). The NMR data of **9c** were identical with those of the authentic sample **9c** prepared by the reported method.[7]

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