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A NEW SYNTHETIC ROUTE TO 2-HYDROXYNAPHTHALENE-1-CARBOXYLIC ACID DERIVATIVES. AN EFFICIENT ACCESS TO THE NAPHTHALENE MOIETY OF NEOCARZINOSTATIN CHROMOPHORE [1]

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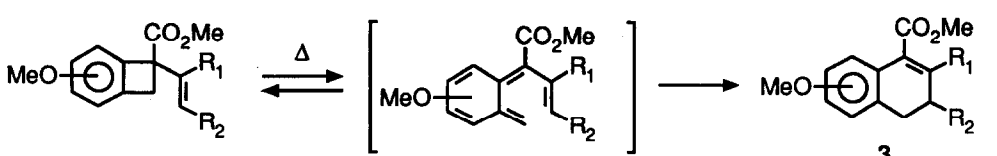
Thermolyses of the 1-carbomethoxy-1-alkenyloxybenzocyclobutenes **4a-d** produced the dihydronaphthalenes **7a-d** via chemoselective electrocyclic reaction of E-*o*-quinodimethanes in good yields. Then, **7a,b,d** were easily converted to the 2-naphthol **9** (R_1=R_2=H) by sequential dehydrogenation and deprotection. The method of conversion developed here has been successfully applied to an efficient synthesis of the methanolysis product **12** of neocarzinostatin chromophore **10**.

While the electrocyclic reaction (ECR) of *o*-quinodimethane, generated in situ by thermolysis of benzocyclobutenes, has been one of powerful tools for the construction of hetero- and carbocyclic compounds[2], few detailed and systematic studies have been reported so far. Our own studies in this area have focused on the investigations from a view point of the competition with the other pericyclic reaction, e.g. [1,5]sigmatropic reaction, and the development of methods for the construction of oxygen containing heterocycles and naphthalenes has guided our synthetic efforts[3]. In a previous communication[4], we showed that the thermolysis of methyl 1-alkenylbenzocyclobutenyl-1-carboxylates **1** led to smooth ECR via E-*o*-quinodimethane **2** to give the corresponding dihydronaphthalenes **3** in excellent yields as illustrated in Scheme 1.



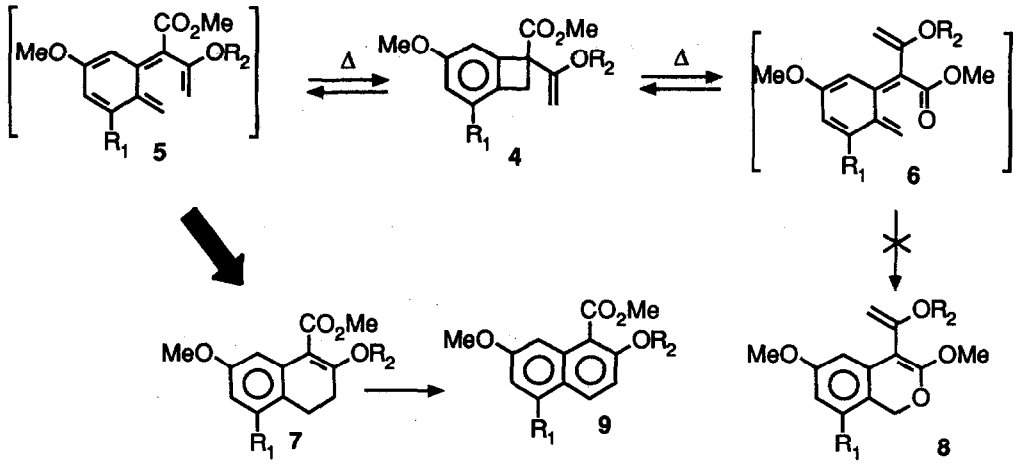
R_1 , R_2 = alkyl, alicyclic, aryl
1

2

3

Scheme 1

We reasoned that even if the alkenyl part at C-1 in **1** was an enol group such as enol ester or silyl enol ether, the thermolysis of **4**, should similarly proceed via E-*o*-quinodimethane **5**, not Z-isomer **6** leading to isochromenes **8**, to give the dihydronaphthalene **7** which could then be converted to the highly functionalized naphthalenes **9** by dehydrogenation. (Scheme 2) This paper describes the realization of transformation (**4**→**9**) and application of the methodology to an efficient synthesis of the naphthalene moiety of neocarzinostatin chromophore (NCS–chr.) **10**.

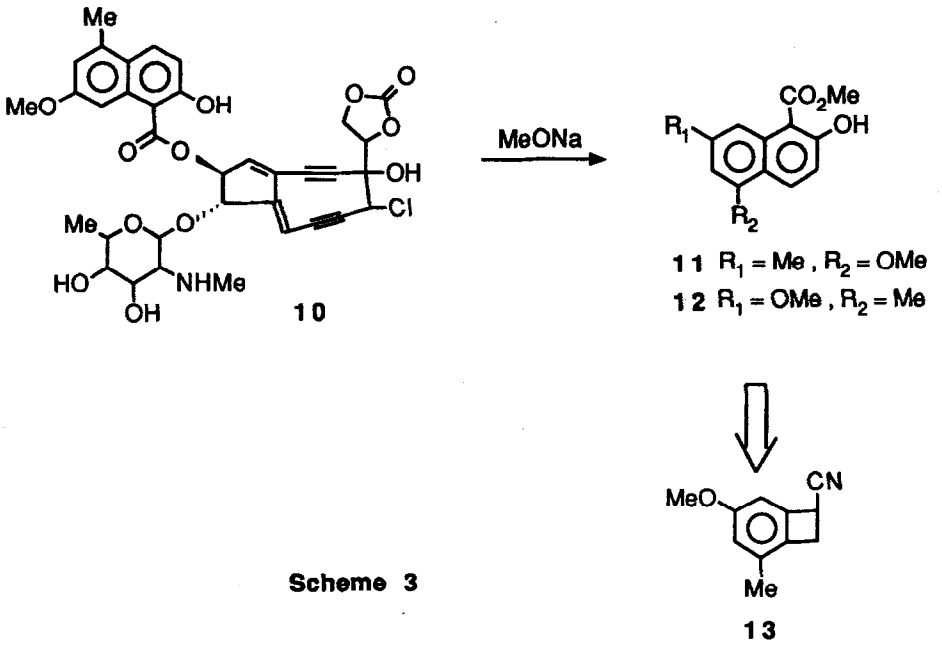


Scheme 2

NCS-chr. **10**, a non-protein component of the antitumor antibiotic neocarzinostatin isolated from the culture filtrate of *Streptomyces carzinostaticus* var. F-41 by Ishida[5], has attracted considerable interest from synthetic organic chemists worldwide due not only to the biological profile[6] but also to its intriguing structural features[7]. During the course of structural studies of NCS-chr. Edo and co-workers isolated the naphthol **11**[8] from the methanolysis products of **10** and elucidated the structure by spectroscopic analyses. Thereafter the structure **11** was revised to **12** by the synthesis through a completely unambiguous route by Shibuya[9]. Our strategy for the synthesis of **12** is to use the newly developed transformation starting from a suitably functionalized benzocyclobutene **13**[10]. (Scheme 3)

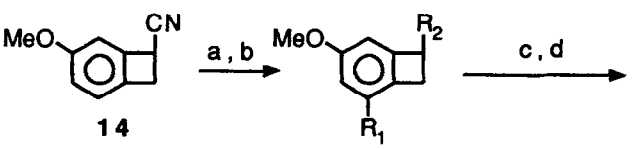
Results and Discussion

As a preliminary experiment for clarifying the predominance of two kinds of competitive ECR, we examined the thermolysis of four substrates **4a-d**, which were derived from a readily available 1-cyano-5-methoxybenzocyclobutene **14**[11] as outlined in Scheme 4. Thus, hydrolysis of **14** followed by esterification of the resulting acid **15** gave the methyl ester **16** in 94% yield. Treatment of **16** with lithium diisopropylamide (LDA) and acetic anhydride afforded an inseparable mixture of the enol acetate **4a** and the methyl ketone **18** in a ratio of 3.5:1[12] (from the integration of ^{1}H-NMR). On the other hand, the following three substrates **4b-d** were

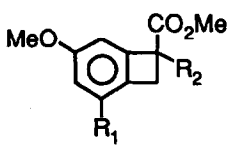


Scheme 3

constructed from the methyl ketone **18**, which was prepared in 89% yield by treatment of **16** with LDA and acetaldehyde followed by Swern oxidation of the resulting diastereomeric alcohol **17**. The methyl ketone **18** was treated with LDA-ethyl chloroformate and lithium hexamethyldisilazide-diethyl chlorophosphate to give the enol carbonate **4b** and enol phosphate **4c** in 80% and 51% yield, respectively. The silyl enol ether **4d**, prepared by exposure of **18** to *t*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf) and triethylamine[13], was extremely moisture sensitive, so that the crude product was immediately submitted to thermolysis.



15 $R_1 = H$, $R_2 = CO_2H$
16 $R_1 = H$, $R_2 = CO_2Me$
19 $R_1 = Me$, $R_2 = CO_2H$
20 $R_1 = Me$, $R_2 = CO_2Me$



16 $\xrightarrow{e}$ **4a** $R_1 = H$, $R_2 = Ac$ + **18**

to **4b,e** : f

4c : g

4d,f : h

4b $R_1 = H$, $R_2 = CO_2Me$

4c $R_1 = H$, $R_2 = PO(OEt)_2$

4d $R_1 = H$, $R_2 = Si(Me)_2{}^tBu$

4e $R_1 = Me$, $R_2 = CO_2Et$

4f $R_1 = Me$, $R_2 = Si(Me)_2{}^tBu$

17 $R_1 = H$, $R_2 = CH(OH)Me$

18 $R_1 = H$, $R_2 = COMe$

21 $R_1 = Me$, $R_2 = CH(OH)Me$

22 $R_1 = Me$, $R_2 = COMe$

Reagents : a, KOH, EtOH, H_2O ; b, for **15** , MeOH, H_2SO_4, for **19** , AcCl, MeOH; c, LDA, MeCHO; d, $(COCl)_2$, DMSO, NEt_3; e, LDA, Ac_2O; f, LDA, $ClCO_2Et$; g, $LiN(TMS)_2$, $ClPO(OEt)_2$, h, TBSOTf, NET_3.

Scheme 4

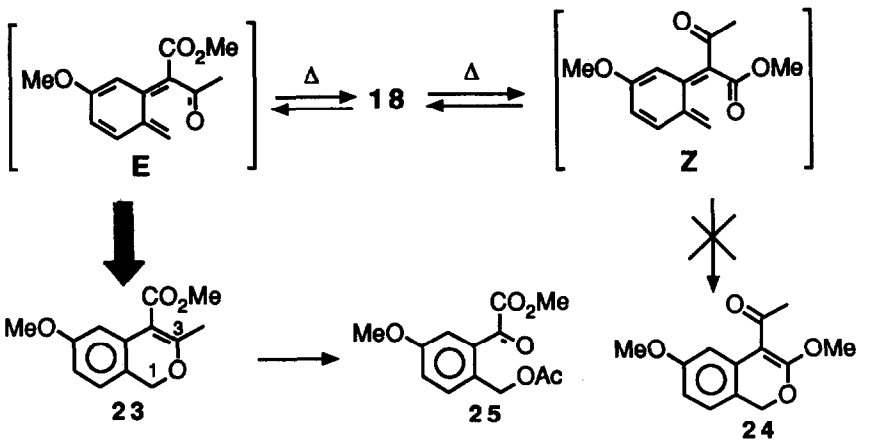
The thermolyses of **4a-d** thus obtained were conducted at 180 °C in a solution of degassed *o*-dichlorobenzene (ODB) under argon atmosphere and were completed within 1h to afford exclusively the expected dihydronaphthalenes **7b-d**. Otherwise the thermolysis of an inseparable mixture of **4a** and **18** resulted in the formation of two chromatographically separable products **7a** and **23**. The structure of product resulting from **18** was assigned as **23** on the basis of the two (C-3 - C-3 Me) and the three bonds (C-3 - C-1 CH_2) ^{13}C-^1H long range couplings in the ^{13}C-NMR spectra. In addition, it was further confirmed by Lemieux-Johnson oxidation of **23** producing the acetate **25**, whose IR spectrum ($\upsilon^{max}_{CHCl_3}$ 1740 and 1690 cm^{-1}) showed no carbonate absorption. The exclusive formation of the isochromene **23**, not **24**, showed that the thermolysis of 1-carbalkoxy-1-acylbenzocyclobutene would similarly proceed via E-*o*-quinodimethane. (Scheme 5) These results were summarized in Table 1.

Table 1. Conversion of the Benzocyclobutenes **4** to the Naphthalenes **9**

Substrate	Reaction Time of Thermolysis, min	Product (Yield, %)	Yield of **9** %
4a	20	**7a** (47)*+**23** (9)*	97 (from **7a**)
4b	30	**7b** (94)	100
4c	45	**7c** (47)	86
4d	30	**7d** (/)	63 (from **18**)
4e	10	**7e** (83)	100
4f	60	**7f** (/)	46**

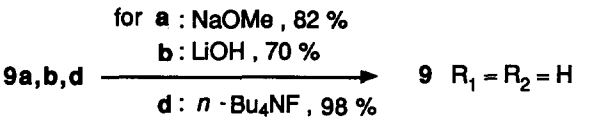
* Yields from the ester **16**.

** Overall yield from **22** to **12**.



Scheme 5

We next examined the dehydrogenation of **7** to the naphthalenes **9**[14]. Treatment of **7a-d** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing toluene gave **9a-d** in excellent yields as shown in Table 1. Finally, **9a,b,d** were easily converted to the naphthol **9** (R_1=R_2=H) by the standard procedures shown in Scheme 6. All attempts to convert the phosphate **9c** into the naphthol were unsuccessful.

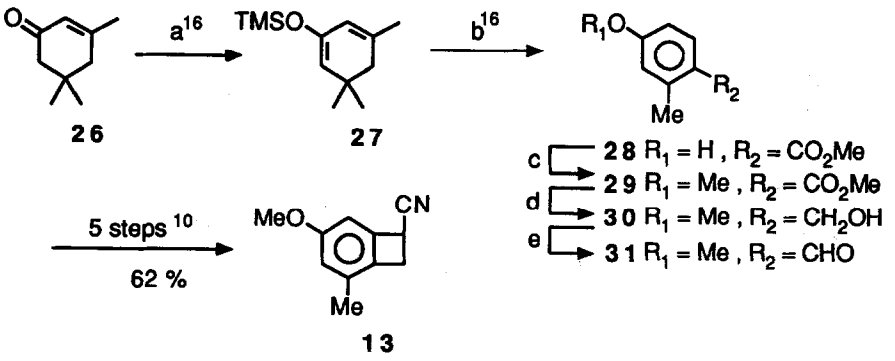


Scheme 6

Synthesis of the Naphthalene Moiety of NCS-chr.

With the successful transformation of benzocyclobutenes to 2-naphthols we were ready to effect its application to the synthesis of the naphthol **12**. Although the starting benzocyclobutene **13** was previously been synthesized in this laboratory[10], two serious problems, the low overall yield (4%) from *m*-methoxytoluene to **13** and the lack of regioselectivity (desired/undesired=2/1)[15] in the Vilsmeier formylation of *m*-methoxytoluene for the preparation of **31**, have still remained. We now focused our attention on the efficient construction of **31**. After a considerable amount of experimentation, the aim was nicely realized by using the reaction developed by Rubottom[16]. Thus, on heating a mixture of methyl propiolate and the silyl dienol ether **27**, derived from isophorone **26**, in toluene under reflux, the benzoate **28** was produced in 93% yield. Sequential methylation, reduction with lithium aluminum hydride, and pyridinium chlorochromate (PCC) oxidation of **28** provided in 90% yield the desired aldehyde **31** which was then converted to **13** via a standard five-step sequence[10] in 62% overall yield. (Scheme 7)

Since the preliminary studies have demonstrated that the two routes, via enol carbonate and silyl enol ether, were superior to the others for the preparation of **9** (R_1=R_2=H), we decided to examine two approaches for the access to **12**. Subjection of **13** to the same four-step sequence



Reagents: a , LDA , TMSCl ; b , ≡—CO_2Me , Δ ; c , MeI , K_2CO_3 ; d , $LiAlH_4$; e , PCC .

Scheme 7

of reactions as that employed for **14** afforded **22** in 80% overall yield. The conversion of methyl ketone **22** to the enol carbonate **4e** was effected in 80% yield. On heating a solution of **4e** in ODB at 180 °C, the reaction was completed for 10 min to afford in yield of 83% the dihydronaphthalene **7e**, which was then dehydrogenated with DDQ to give the naphthalene **9e** quantitatively (Table 1). The target naphthol **12** [mp 109-110 °C (lit.[8] mp 104-105°C)] was obtained in 97% yield from **9e** by hydrolysis with potassium carbonate. The synthetic sample of **12** was indistinguishable from the authentic sample by using the gamut of chromatographic and spectroscopic techniques.

Alternatively, treatment of **22** with TBSOTf in the presence of triethylamine gave the labile silyl enol ether **4f**, which was immediately heated at 180 °C for 1h to afford **7f**. The dihydronaphthalene **7f** thus obtained was treated with DDQ in a one-pot operation to give the naphthalene **9f**. Desilylation of the crude **9f** with tetra-*n*-butylammonium fluoride furnished **12**, which was identical with the authentic material prepared via enol carbonate, in 46% yield from **22**. (Table 1) The two routes to **12**, a methanolysis product of NCS-chr., reported here are quite practical since they require eight steps from the benzocyclobutene **13** and proceed in 51% and 37% overall yield, respectively.

In summary, we have developed a highly efficient and chemoselective ECR via E-*o*-quinodimethane, generated in situ by the thermolysis of 1-carbomethoxy-1-alkenyloxybenzocyclobutenes, leading to the 1-carbomethoxy-2-naphthols. The methodology has been successfully applied to a practical synthesis of a segment of the physiologically important molecule.

Experimental Section

Melting points were determined by a Yanako micromelting point apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a JEOL JNM-GX 500 (500 MHz), JEOL JNM-FX-90A (90MHz), or JEOL PMX-60 (60MHz) spectrometer in deuteriochloroform solutions with tetramethylsilane as an internal standard. Chemical shifts are reported in ppm (from TMS). When peak multiplicities are reported, the following abbreviations are used : s, singlet ; d, doublet ; t, triplet ; q, quartet ; m, multiplet ; br, broadened. ^{13}C-NMR spectra were obtained on a JEOL PS-100 spectrometer operating at a frequency of 25 MHz. Infrared spectra were obtained on a Hitachi 125 grating spectrophotometer as a chloroform solution. Ordinary mass spectra were measured with a JEOL JMS-O1SG-2 instrument, while high-resolution mass spectroscopy was performed on a JEOL JMS-DX303 spectrometer. All reactions were run under an atmosphere of argon. Solvents were freshly distilled prior to use : tetrahydrofuran (THF), toluene, and diethyl ether (Et_2O) were distilled from sodium and kept over sodium wire : dichloromethane (CH_2Cl_2) and *o*-dichlorobenzene were distilled from phosphorus pentoxide and CH_2Cl_2 was kept over 4 Å molecular sieves. Unless otherwise noted, all reaction mixtures were dried, after workup, over anhydrous magnesium sulfate. Column chromatography was carried out with silica gel (Kieselgel 60, 70-230 mesh, Merck). All chromatography solvents were distilled prior to use.

Methyl 5-methoxybenzocyclobutene-1-carboxylate (16). A solution of 1-cyano-5-methoxybenzocyclobutene **14**[11] (3.3 g, 20.8 mmol) and potassium hydroxide (5.8 g, 104 mmol) in EtOH-H_2O (5:1, 60 mL) was refluxed for 2 h. After evaporation of the solvent, the aqueous residue was washed with Et_2O. The aqueous phase was acidified with 10% HCl and extracted with Et_2O. The extracts were washed with brine and dried. Evaporation of the solvent *in vacuo* afforded the crude acid **15** (3.7 g), which was submitted to the next reaction without further purification.

A solution of **15** (3.7 g) and five drops of conc. H_2SO_4 in MeOH (50 mL) was refluxed for 1h. After removal of the solvent, the residue was extracted with Et_2O, washed with brine, and dried. Evaporation of the solvent *in vacuo* followed by chromatography on silica gel (ethyl acetate- hexane, 1:9) gave the ester **16** (3.7 g, 94%) as a colorless oil : IR ($CHCl_3$) 1730 cm^{-1} ; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 3.38 (2H , d , J = 4.1 Hz) , 3.73 (3H , s) , 3.77 (3H , s) , 4.24 (1H , t , J = 4.1 Hz) , 6.75-6.85 (2H , m) , 7.00 (1H , d , J = 9.1 Hz) ; MS *m/z* 192 (M^+) ; HRMS , calcd for $C_{11}H_{12}O_3$ *m/z* 192.0786 , found *m/z* 192.0794.

Methyl 1-(1-hydroxyethyl)-5-methoxybenzocyclobutene-1-carboxylate (17). *n*-BuLi (1.54 M in hexane , 6.8 mL , 10.5 mmol) was added to a solution of diisopropylamine (1.12 g , 11.1 mmol) in dry THF (20 mL) at -78 °C and the resulting mixture was stirred at the same temperature for 20 min. Then a solution of the ester **16** (1.19 g , 6.2 mmol) in dry THF (10 mL) was added dropwise to the mixture at -78 °C. After being stirred for 20 min, acetaldehyde (0.36 g , 8.08 mmol) was added and the stirring was continued for 10 min, then the mixture was quenched with saturated aqueous NH_4Cl and the organic layer was separated. The aqueous phase was extracted with ethyl acetate, and the combined organic phases were washed with water and dried. Evaporation of the solvent followed by chromatography on silica gel (ethyl acetate-hexane , 1:2) gave a solid which was recrystallized from Et_2O-hexane to afford the alcohol **17** (1.46 g , 100 %), an inseparable mixture of diastereomers, as colorless needles : mp 63-65 °C ; IR($CHCl_3$) 3500 , 1720 cm^{-1} ; ^{1}H-NMR($CDCl_3$, 90 MHz) δ 1.37 (3H , d , J = 6.4 Hz) , 2.57 (1H , br s , D_2O disappeared) , 3.33 (1H , d , J =13.8 Hz) , 3.53 (1H , d , J =13.8 Hz) , 3.83 (3H , s) , 3.89 (3H , s) , 4.29 (1H , q , J = 6.4 Hz) , 6.88 (1H , d , J = 2.0 Hz) , 6.92 (1H , dd , J = 9.1 and 2.0 Hz) , 7.24 (1H , d , J = 9.1 Hz) ; MS *m/z* 236 (M^+). Anal. calcd for $C_{13}H_{16}O_4$: C , 66.08 ; H , 6.83. Found : C , 66.06 ; H , 6.87.

Methyl 1-acetyl-5-methoxybenzocyclobutene-1-carboxyate (18). Oxalyl chloride (0.18 g , 1.38 mmol) was added dropwise to a cooled(-78 °C) solution of dimethyl sulfoxide (0.21 g , 2.68 mmol) in dry CH_2Cl_2 (7 mL). After 20 min at -78 °C, a solution of the alcohol **17** (0.25 g , 1.04 mmol) in dry CH_2Cl_2 (3 mL) was added and stirring was continued for a

further 20 min ; triethylamine (0.52 g , 5.18 mmol) was then added and the reaction mixture was allowed to warm to 0 °C. After being stirred at 0 °C for 1 h, water was added to the reaction mixture which was extracted with CH_2Cl_2, then the extracts were washed with brine, dried, and evaporated. The residue was chromatographed on silica gel (ethyl acetate-hexane , 1:4) to afford the ketone **18** (0.23 g , 89%) as a colorless oil : IR ($CHCl_3$) 1730 , 1705 cm^{-1} ; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 2.19 (3H , s) , 3.54 (1H , br s) , 3.56 (1H , br s) , 3.71 (3H , s) , 3.73 (3H , s) , 6.71-6.95 (2H , m) , 7.00 (1H , d , *J* = 9.1 Hz) ; MS *m/z* 234 (M^+) ; HRMS , calcd for $C_{13}H_{14}O_4$ *m/z* 234.0893 , found *m/z* 234.0878.

Reaction of 16 with LDA and acetic anhydride. A solution of the ester **16** (0.15 g , 0.79 mmol) in dry THF (2.5 mL) was added dropwise to a solution of LDA (1.9 mmol), prepared by the same manner as for **17**, in dry THF (5 mL) at -78 °C. After being stirred for 40 min, a solution of acetic anhydride (0.2 g , 1.98 mmol) in dry THF (0.5 mL) was added and the stirring was continued for 15 min, then the reaction mixture was allowed to warm to room temperature. After being stirred at the same temperature for 80 min, saturated aqueous NH_4Cl was added to the mixture at 0 °C. The resulting mixture was extracted with ethyl acetate and the extracts were washed with 5% HCl and brine, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel (ethyl acetate-hexane , 1:4) to give an inseparable mixture (0.14 g) of the enol acetate **4a** and the methyl ketone **18** in a ratio of 3.5:1, which was determined by integration of the ^{1}H-NMR, as an oil : IR ($CHCl_3$) 1760 , 1740 cm^{-1} ; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 2.15 (2.31H , s) , 2.25 (0.69H , s) , 3.32 (0.77H , d , *J* = 14.0 Hz) , 3.65-3.89 (0.46H , m) , 3.74 (3H s) , 3.78 (0.77H , d , *J* = 14.0 Hz) , 3.79 (3H , s) , 4.99 (0.77H , d , *J* = 1.8 Hz) , 5.13 (0.77H , d , *J* = 1.8 Hz) , 6.75-6.90 (2H , m) , 6.95-7.12 (1H , m).

Methyl 1-(1-ethoxycarbonyl)-5-methoxybenzocyclobutene-1-carboxylate (4b). A solution of **18** (0.83 g , 3.53 mmol) in dry THF (5 mL) was added dropwise to a solution of LDA (4.56 mmol) in dry THF (11 mL) at -78 °C. After being stirred at -78 °C for 20 min, hexamethylphosphoric triamide (HMPA) (8 mL) and ethyl chloroformate (0.5 g , 4.6 mmol) was added successively, then the reaction mixture was allowed to warm to room temperature, stirred for further 40 min, and quenched with saturated aqueous NH_4Cl. The resulting mixture was extracted with Et_2O and the extracts were washed with water, dried , and evaporated to give a residue which was chromatographed on silica gel (ethyl acetate - hexane, 1:4) to afford the enol carbonate **4b** (0.86 g , 80 %) as a colorless oil : IR ($CHCl_3$) 1755 and 1735 cm^{-1} ; ^{1}H-NMR($CDCl_3$, 90 MHz) δ 1.33 (3H , t , *J* = 7.7Hz) , 3.34 (1H , d , *J* = 13.3 Hz) , 3.76 (3H , s) , 3.80 (3H , s) , 3.82 (1H , d , *J* = 13.3 Hz) , 4.26 (2H , q , *J* = 7.7 Hz) , 5.14(2H , s) , 6.78-6.94 (2H , m) , 7.06 (1H , d , *J* = 8.6 Hz) ; MS *m/z* 306 (M^+) ; HRMS , calcd for $C_{16}H_{18}O_6$ *m/z* 306.1104 , found *m/z* 306.1068.

Methyl 1-(1-diethylphosphonyloxyvinyl)-5-methoxybenzocyclobutene-1-carboxylate (4c). *n*-BuLi (1.52 M in hexane , 1.41 mL , 1.73 mmol) was added to a solution of hexamethyldisilazane (0.3 g , 1.85 mmol) in dry THF (6.5 mL) at -78 °C and resulting mixture was stirred at the same temperature for 15 min. Then a solution of **18** (0.27 g , 1.15 mmol) in dry N,N,N',N'-tetramethylethylenediamine (1.5 mL) was added dropwise to the mixture at -78°C. After being stirred for 15 min, diethyl chlorophosphate (0.32 g , 1.87 mmol) was added, then the mixture was allowed to warm to 0°C, stirred for 20 min, and quenched with saturated aqueous NH_4Cl. After evaporation of the solvent, the residue was extracted with Et_2O and the extracts were washed successively with 5 % HCl and brine, dried, and evaporated to give a residue which was chromatographed on silica gel (ethyl acetate - hexane , 3:7) to afford the enol phosphate **4c** (0.22 g , 51 %) as a pale yellow oil : IR ($CHCl_3$) 1750 cm^{-1} ; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1.34 (6H , dt , *J* = 7.1 and 0.5 Hz) , 3.35 (1H , d , *J* = 13.4 Hz) , 3.75 (3H , s) , 3.79 (3H , s) 3.92 - 4.32 (5H , m) , 4.81 (1H , dd , *J* = 2.9 and 1.9 Hz) , 5.11 (1H , dd , *J* = 2.9 and 1.9 Hz) , 6.77 - 6.91 (2H , m) , 7.06 (1H , d , *J* = 7.2 Hz) ; MS *m/z* 370 (M^+) ; HRMS , calcd for $C_{17}H_{23}O_7P$ *m/z* 370.1181 , found *m/z* 370.1185.

Methyl 7-(1-*t*-butyldimethylsilyloxyvinyl)-5-methoxybenzocyclobutene-1-carboxylate (4d). *t*-Butyldimethylsilyl trifluoromethanesulfonate (TBSOTf) (0.76 g, 2.88 mmol) was added dropwise to a solution of **1g** (0.45 g, 1.92 mmol) and triethylamine (0.35 g, 3.47 mmol) in dry CH_2Cl_2 (13 mL) at 0 °C and the mixture was allowed to warm to room temperature. After being stirred for 2 h, the reaction mixture was washed with chilled saturated aqueous $NaHCO_3$ and the solvent was evaporated *in vacuo* to give a residue which was taken up into Et_2O. The ethereal solution was washed with water, dried, and evaporated to give the silyl enol ether **4d** (0.63 g, 94 %) as a colorless oil, which was used to the next reaction without further purification : ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 0.16, 0.17 (3H each, s), 0.88 (9 H, s), 3.29 (1H, d, *J* =13.7 Hz), 3.71, 3.77 (3H each, s), 3.79 (1H, d, *J* = 13.7 Hz), 4.17 (1H, d, *J* = 2.3 Hz), 4.28 (1H, d, *J* = 2.3 Hz), 6.78 (1H, dd, *J* = 8.6 and 2.5 Hz), 6.84 (1H, s), 7.01 (1H, d, *J* = 8.6 Hz).

Thermolysis of a mixture of 4a and 1g. A solution of a mixture (128 mg) of **4a** and **1g** in degassed *o*-dichlorobenzene (ODB) (10 mL) was heated at 180 °C for 20 min. Evaporation of the solvent followed by chromatography on silica gel (ethyl acetate - hexane, 9:1) gave the isochromene **23** (15.6 mg, 9 %) as a colorless oil : IR ($CHCl_3$) 1705 cm^{-1} ; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 2.28, 3.81, 3.86 (3H each, s), 4.96(2H, s), 6.72(1H, dd, *J* = 8.3 and 2.4 Hz), 6.92(1H, d, *J* = 8.3 Hz), 7.31(1H, d, *J* = 2.4 Hz) ; ^{13}C-NMR ($CDCl_3$, 25 MHz) δ 20.14(q), 51.43(q), 55.42(q), 68.87(t), 107.68(s), 109.20(d), 111.72(d), 119.30(s), 124.70(d), 130.69(s), 159.81(s), 165.97(s), 167.79(s) ; MS *m/z* 234 (M^+); HRMS, calcd for $C_{13}H_{14}O_4$ *m/z* 234.0892, found *m/z* 234.0888. From less polar fractions (ethyl acetate–hexane, 3 : 7), the dihydronaphthalene **7a** (91.7 mg, 47 %) was obtained as a colorless oil : IR ($CHCl_3$) 1760, 1730 cm^{-1} ; ^{1}H–NMR ($CDCl_3$, 90MHz) δ 2.21 (3H, s), 2.43–2.64 (2H, m), 2.81–3.05 (2H, m), 3.77, 3.86 (3H each, s), 6.70 (1H, dd, *J*=8.2 and 2.7Hz), 6.87 (1H, d, *J*=2.7Hz), 7.06 (1H, d, *J*=8.2Hz); MS *m/z* 276 (M^+); HRMS, calcd for $C_{15}H_{16}O_5$ *m/z* 276.0997, found *m/z* 276.0996.

Lemieux - Johnson oxidation of 23. Sodium metaperiodate (944 mg, 4.41 mmol) was added to a stirred solution of **23** (68.9 mg, 0.294 mmol) and a catalytic amount of osmium tetraoxide in Et_2O - H_2O (1:1, 8 mL) at room temperature. After being stirred for 10 h, NaCl was added to the mixture and the resulting mixture was filtered through Celite. After separation of organic layer, the aqueous phase was extracted with Et_2O and the combined organic phases were washed with brine and dried. Evaporation of the solvent *in vacuo* followed by chromatography on silica gel (ethyl acetate - hexane, 1:4) gave the acetate **25** (50.6 mg, 65 %) as a colorless oil : IR ($CHCl_3$) 1740, 1690 cm^{-1} ; ^{1}H-NMR($CDCl_3$, 90 MHz) δ 2.09, 3.85, 3.96(3H each, s), 5.34(2H, s), 7.12(1H, dd, *J* = 8.6 and 2.7 Hz), 7.28(1H, d, *J* = 2.7 Hz), 7.45(1H, d, *J* = 8.6 Hz) ; MS *m/z* 266 (M^+) ; HRMS, calcd for $C_{13}H_{14}O_6$ *m/z* 266.0790, found *m/z* 266.0804.

Thermolysis of 4b. A solution of **4b** (59 mg, 0.225 mmol) in ODB (2.5 mL) was heated at 180 °C for 30 min. Evaporation of the solvent *in vacuo* followed by chromatography on silica gel (ethyl acetate - hexane, 1:4) afforded the dihydronaphthalene **7b** (64.7 mg, 94 %) as a colorless oil : IR($CHCl_3$) 1760, 1730 cm^{-1} ; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1.37(3H, t, *J* = 7.1 Hz), 2.53-3.05(4H, m), 3.77, 3.87(3H each, s), 4.30(2H, q, *J* = 7.1 Hz), 6.71(1H, dd, *J* = 8.4 and 2.7 Hz), 6.91(1H, d, *J* = 2.7 Hz), 7.06(1H, d, *J* = 8.4 Hz) ; MS *m/z* 306 (M^+) ; HRMS, calcd for $C_{16}H_{18}O_6$ *m/z* 306.1089, found *m/z* 306.1089.

Thermolysis of 4c. A solution of **4c** (40.6 mg, 0.11 mmol) in ODB (2 mL) was heated for 45 min. Chromatography on silica gel (ethyl acetate - hexane, 3:7) gave **7c** (19.1 mg, 47 %) as a pale yellow oil : IR ($CHCl_3$) 1730 cm^{-1} ; ^{1}H-NMR($CDCl_3$, 90 MHz) δ 1.24 - 1.46(6H, m), 2.10 - 2.50(4H, m), 3.77, 3.88(3H each, s), 4.02 - 4.38(4H, m), 6.60 - 6.75(2H, m), 7.06(1H,

d , J = 7.2 Hz) ; MS *m/z* 370 (M^+) ; HRMS , calcd for $C_{17}H_{23}O_7P$ *m/z* 370.1181 , found *m/z* 370.1170.

Thermolysis of 4d. A solution of the crude **4d** (0.63 g , 1.92 mmol) in ODB (13 mL) was heated for 30 min. Evaporation of the solvent afforded the crude **7d** (0.6 g , 95 %) as a colorless oil , which was submitted to the next reaction without further purification : ^{1}H-NMR($CDCl_3$, 90 MHz) δ 0.22(6H , s) , 0.93 (9H, s), 2.22 - 2.54(2H , m) , 2.64 - 2.95(2H ,m) , 3.76 , 3.82(3H each , s) , 6.59(1H , dd , J = 8.2 and 3.4 Hz) , 6.76(1H , d , J = 3.4 Hz) , 6.99(1H , d , J = 8.2 Hz).

DDQ oxidation of 7a. A solution of **7a** (82.3 mg , 0.3 mmol) and DDQ (81.1 mg , 0.36 mmol) in dry toluene (5 mL) was refluxed for 30 min. After filtration through Celite, the filtrate was concentrated to give a residue which was chromatographed on silica gel (ethyl acetate - hexane 3:7) to afford the naphthalene **9a** (79.5 mg , 97 %) as colorless prisms , mp 113 - 114 °C , by recrystallization from Et_2O : IR ($CHCl_3$) 1770 , 1730 cm^{-1} ; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 2.33 , 3.91 , 4.01(3H each , s) , 7.08(1H , d , J = 8.8 Hz) , 7.15(1H , dd , J = 8.8 and 2.4 Hz) , 7.43(1H , d , J = 2.4 Hz) , 7.74(1H , d , J = 9.0 Hz) , 7.86(1H , d , J = 9.0 Hz) ; MS *m/z* 274 (M^+). Anal. Calcd for $C_{15}H_{14}O_5$: C , 65.69 ; H , 5.15 . Found : 65.93 ; H , 4.98.

DDQ oxidation of 7b. A solution of **7b** (26.2 mg , 0.086 mmol) and DDQ (23 mg , 0.1 mmol) in dry toluene (2 mL) was refluxed for 2 h. Chromatography on silica gel (ethyl acetate - hexane , 1:4) gave **9b** (26 mg , 100 %) as a colorless oil : IR ($CHCl_3$) 1760 , 1720 cm^{-1} ; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1.41(3H , t , J = 7.1 Hz) , 3.91 , 4.01(3H each , s) , 4.35(2H , q , J = 7.1 Hz) , 7.17(1H , d , J = 8.8 Hz) , 7.21(1H , dd , J = 8.8 and 2.4 Hz) , 7.49(1H , d , J = 2.4 Hz) , 7.75 (1H , d , J = 8.8 Hz) , 7.88(1H , d , J = 8.8 Hz) ; MS *m/z* 304 (M^+) ; HRMS , calcd for $C_{16}H_{16}O_6$ *m/z* 304.0947 , found *m/z* 304.0944.

DDQ oxidation of 7c. A solution of **7c** (18.6 mg , 0.05 mmol) and DDQ (13.7 mg , 0.06 mmol) in dry toluene (2 mL) was refluxed for 2.5 h. Chromatography on silica gel (ethyl acetate - hexane , 3:7) gave **9c** (16.0 mg , 86 %) as a pale yellow oil : IR($CHCl_3$) 1725 cm^{-1} ; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1.35(6H , dt , J = 7.1 and 1.2 Hz) , 3.91 , 4.04(3H each , s) , 4.23(4H , dq , J = 8.1 and 7.1 Hz) , 7.13(1H , dd , J = 9.0 and 2.5 Hz) , 7.20(1H , br d , J = 2.5 Hz) , 7.45(1H , dd , J = 9.0 and 1.0 Hz) , 7.73 (1H , d , J = 8.8 Hz) , 7.83(1H , d , J = 8.8 Hz) ; MS *m/z* 368 (M^+) ; HRMS , calcd for $C_{17}H_{21}O_7P$ *m/z* 368.1025 , found *m/z* 368.1033.

DDQ oxidation of 7d. A solution of **7d** (0.6 g , 1.72 mmol) and DDQ (0.52 g, 2.25 mmol) in dry tolueue (10 mL) was refluxed for 30 min. Chromatography on silica gel (ethyl acetate–hexaue, 1:9) gave **9d** (0.42 g, 70 %) as a pale yellow oil:IR ($CHCl_3$) 1720 cm^{-1}; ^{1}H–NMR ($CDCl_3$, 90MHz) δ 0.25 (6H, s),1.01 (9H, s), 3.38, 3.98 (3H each, s), 6.85–7.05 (3H, m), 7.59–7.72 (2H,m); MS *m/z* 364 (M^+); HRMS, calcd for $C_{19}H_{26}O_4Si$ *m/z* 346.1601, found *m/z* 346.1598.

Methyl 2–hydroxy–7–methoxynaphthalene–1–carboxylate 9 (R_1=R_2=H). From 9a. Dry MeOH (0.05 mL) was added dropwise to a stirred suspension of NaH (41.0 mg, 1.02 mmol) in dry THF (2 mL) at 0°C and resulting mixture was stirred at the same temperature for 5 min. A solution of the acetate **9a** (70.2 mg, 0.26 mmol) in dry THF (2 mL) was added to the mixture at 0°C, then the reaction mixture was stirred for 5 min. After addition of 10% HCl, the solvent was evaporated to give a residue which was extracted with ethyl acetate. The extracts were washed with brine, dried, and concentrated *in vacuo*. Chromatography on silica gel (ethyl acetate–hexane, 1:4) gave the naphthol **9** (R_1=R_2=H) (48.6 mg, 82 %) as colorless prisms, mp 109–110°C, by recrystallization from Et_2O: IR($CHCl_3$) 1655,1630 cm^{-1}; ^{1}H–NMR ($CDCl_3$, 90MHz) δ 3.92, 4.08 (3H each, s), 6.99 (1H, d, J=8.8Hz), 7.01(1H, dd, J=8.8 and 2.5Hz),7.63 (1H,

d, J=8.8Hz), 7.79 (1H, d, J=8.8Hz), 8.17 (1H, d, J=2.5Hz), 12.29(1H, s, D_2O disappeared); MS m/z 232 (M^+). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.27; H, 5.32. Found : C, 67.23 ; H, 5.21.

From 9b. LiOH. H_2O (17 mg, 0.41 mmol) was added to a solution of **9b** (41.7 mg, 0.14 mmol) in THF–H_2O (4:1, 1.25 mL) and the mixture was stirred at room temperature for 2.7 h. After evaporation of the solvent, water was added and the resulting mixture was extracted with $CHCl_3$. The extracts were washed with brine, dried, and concentrated *in vacuo* to give a residue which was chromatographed on silica gel (ethyl acetate–hexane, 1:9) to give **9** (R_1=R_2=H) (22.4 mg, 70 %) as colorless prisms, mp 109–110°C, by recrystallization from Et_2O.

From 9d. Tetra–*n*–butylammonium fluoride (1M in THF, 0.22 mL, 0.22 mmol) was added dropwise to a solution of **9d** (63 mg, 0.18 mmol) in dry THF (2 mL) at 0°C. The mixture was allowed to warm to room temperature under stirring for 1 h and the solvent was evaporated *in vacuo* to give a residue which was chromatographed on silica gel (ethyl acetate–hexane, 1:9) to afford **9** (R_1=R_2=H) (41.5 mg, 98 %) as colorless prisms, mp 109–110°C, by recrystallization from Et_2O.

4-Methoxy–2–methylbenzaldehyde (31). Potassium carbonate (0.5 g, 3.62 mmol) was added to a solution of methyl 4-methoxy–2–methylbenzoate **28**[16] (0.55 g, 3.31 mmol) and methyl iodide (0.52 g, 3.69 mmol) in acetone (17 mL) and the resulting mixture was heated under reflux for 5 h. To the reaction mixture was added potassium carbonate (0.25 g, 1.81 mmol) and methyl iodide (0.25 g, 1.77 mmol) and the mixture was further refluxed for 14 h. After evaporation of the solvent, water was added. The mixture was extracted with Et_2O and the extracts were washed with brine, dried, and concentrated *in vacuo* to give the ester **29** (0.58 g, 97 %) as a colorless oil, which was used in the next reaction without purification: IR ($CHCl_3$) 1715 cm^{-1} ; ^{1}H–NMR ($CDCl_3$, 60MHz) δ 2.57 (3H, s), 3.83 (6H, s), 6.74(2H, m), 7.90 (1H, d, J=10.0Hz).

A soluiton of **29** (0.57 g, 3.14 mmol) in dry THF (10 mL) was added dropwise to a suspension of $LiAlH_4$ (0.42 g, 11.1 mmol) in dry THF (18 mL) at 0°C. The mixture was stirred at room temperature for 2 h, then cooled to 0°C, and quenched by slow addition of wet Et_2O. After filtration through Celite, the filtrate was concentrated *in vacuo* to give the alcohol **30** (0.45 g, 100 %) as a colorless oil, which was also submitted to the next reaction without further purification: IR($CHCl_3$) 3630 cm^{-1} ; ^{1}H–NMR ($CDCl_3$, 90MHz) δ 1.59 (1H, s, D_2O disappeared), 2.37, 3.81 (3H each, s), 4.63 (2H, d, J=5.4Hz), 6.73(1H, dd, J =9.9 and 2.3Hz), 6.76 (1H, s), 7.23 (1H, d, J=9.9Hz).

A solution of **30** (43.5 mg, 0.29 mmol) in dry CH_2Cl_2 (0.5 mL) was added to a solution of PCC (93.0 mg, 0.443 mmol) in dry CH_2Cl_2 (1 mL) at room tempreature, and the mixture was stirred for 1.3 h. After addition of Florisil, the mixture was diluted with Et_2O and filtered through Celite. Concentration of the filtrate *in vacuo* followed by chromatography on silica gel (ethyl acetate–hexane, 1:9) yielded the aldehyde **31**[17] (40.1 mg, 93 %) as a colorless oil : IR ($CHCl_3$) 1680 cm^{-1} ; ^{1}H–NMR ($CDCl_3$, 60MHz) δ 2.64, 3.93 (3H each, s), 6.83–6.92 (2H, m), 7.71 (1H, d, J=8.7Hz).

5–Methoxy–3–methylbenzocyclobutene–1–carboxylic acid (19). A solution of 1–cyano–5–methoxy–3–methylbenzocyclobutene **13**[10] (1.72 g, 9.94 mmol) and potassium hydroxide (2.8 g, 50.0 mmol) in EtOH–H_2O (5:1, 42 mL) was heated under reflux for 10.5 h. After the same treatment as for **14**, the crude crystalline product was recrystallized from benzene to give the acid **19** (1.88 g, 98 %), mp 145–146°C , as colorless needles : IR($CHCl_3$) 1710 cm^{-1}; ^{1}H–NMR ($CDCl_3$, 90MHz) δ 2.18 (3H, s), 3.27 (1H, br s), 3.31 (1H, br s), 37.3 (3H, s), 4.21 (1H, m), 6.61 (2H, br s); MS m/z 192 (M^+). Anal. Calcd for C_{11} $H_{12}O_3$: C, 68.73 ; H,6.29. Found : C, 68.84 ; H,6.45.

Methyl 5–methoxy–3–methylbenzocyclobutene–1–carboxylate (20). Acetyl chloride (0.59 g, 7.45 mmol) was added dropwise to a stirred dry MeOH (18 mL) at 0°C. After being stirred at room temperature for 10 min, a solution of the acid **19** (1.78 g, 9.27 mmol) in dry MeOH(18 mL) was added to the mixture and the resulting solution was stirred for 10 h. Evaporation of the solvent followed by addition of water gave a residue which was extracted with

Et_2O and the extracts were washed with saturated aqueous $NaHCO_3$ and water. The dried ethereal solution was concentrated *in vacuo* to give a residue which was chromatographed on silica gel (ethyl acetate–hexane, 1:4) to afford the ester **20** (1.82 g, 95 %) as a colorless oil : IR ($CHCl_3$) 1735 cm^{-1}; ^1H-NMR ($CDCl_3$, 90MHz) δ 2.17 (3H, s), 3.31 (2H, d, *J*=4.0Hz), 3.74, 3.76 (3H each, s), 4.20 (1H, t, *J*=4.0Hz), 6.60 (2H, br s); MS *m/z* 206(M^+); HRMS, calcd for $C_{12}H_{14}O_3$ *m/z* 206.0943, found *m/z* 206.0946.

Methyl 1-(1-hydroxyethyl)-5-methoxy-3-methylbenzocyclobutene -1-carboxylate (21). A solution of **20** (0.22 g, 1.08 mmol) in dry THF (4 mL) was added to a solution of LDA (1.75 mmol) in dry THF (6 mL) at – 78°C. The resulting solution was treated with acetaldehyde (0.071 g, 5.03 mmol) according to the same procedure as for the preparation of **17**. The crude product was chromatographed on silica gel (ethyl acetate–hexane, 1:4) to give the alcohol **21** (0.26 g, 97 %), an inseparable mixture of diastereomers, as a colorless oil: IR ($CHCl_3$) 1715 cm^{-1}; ^1H-NMR ($CDCl_3$, 90MHz) δ 1.11–1.35 (3H, m), 2.18 (3H, s), 2.62 (1H, br s, D_2O disappeared), 3.00–3.50 (2H, m), 3.71, 3.78 (3H each, s), 3.98–4.33 (1H, m), 6.62 (2H, br s); MS *m/z* 250 (M^+); HRMS, calcd for $C_{14}H_{18}O_4$ *m/z* 250. 1205, found *m/z* 250.1174.

Methyl 1-acetyl-5-methoxy-3-methylbenzocyclobutene-1-carboxylate (22). The alcohol **21** (0.26 g, 1.04 mmol), a mixture of diastereomers, was oxidized under the conditions of Swern, described for the preparation of **18**, and the product was chromatographed on silica gel (ethyl acetate–hexane, 1:9) to yield **22** (0.23 g, 89 %) as colorless prisms, mp 55–56°C, after recrystallization from Et_2O–hexane: IR ($CHCl_3$) 1730, 1715 cm^{-1}; ^1H-NMR ($CDCl_3$, 90MHz) δ 2.18, 2.27 (3H each, s), 3.36 (2H, s), 3.78(6H, s), 6.66 (1H, br s), 6.69 (1H, br s); MS *m/z* 248 (M^+). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73 ; H, 6.50. Found: C, 67.80 ; H, 6.51.

Methyl 1-(1-ethoxycarbonyloxyvinyl)-5-methoxy-3-methylbenzocyclobutene-1-carboxylate (4e). A solution of **22** (0.28 g, 1.15 mmol) in dry THF (2 mL) was added dropwise to a solution of LDA (1.55 mmol) in dry THF (4 mL) at –78°C. After being stirred for 30 min at the same temperature, HMPA (3 mL) was added and then the mixture was stirred for 30 min. Ethyl chloroformate (0.17 g, 1.57 mmol) was added dropwise to the mixture at –78°C, the solution was then allowed to warm to 0°C over 1 h and quenched with saturated aqueous NH_4Cl. After separation of the organic layer, the aqueous phase was extracted with Et_2O and the extracts were washed with brine, dried, and concentrated *in vacuo* to leave a residue which was chromatographed on silica gel (ethyl acetate–hexane, 1:9) to give the enol carbonate **4e** (0.3 g, 80 %) as a colorless oil:IR ($CHCl_3$) 1760, 1740 cm^{-1}, ^1H-NMR ($CDCl_3$, 90MHz) δ 1.34 (3H, t, *J*=7.1Hz), 2.17(3H, s), 3.28 (1H, d, *J*=13.8Hz), 3.74, 3.77 (3H each, s), 3.80 (1H, d, *J*=13.8Hz), 4.24 (2H, q, *J*=7.2Hz), 5.12 (2H, s), 6.66 (1H, br s), 6.69 (1H, br s); MS *m/z* 320 (M^+); HRMS, calcd for $C_{17}H_{20}O_6$ *m/z* 320.1260, found *m/z* 320.1228.

Thermolysis of 4e. A solution of **4e** (14.6 mg, 0.048 mmol) in ODB (1.5 mL) was heated at 180°C for 10 min. Evaporation of the solvent followed by chromatography on silica gel (ethyl acetate–hexane, 1:9) gave **7e** (12.1 mg, 83 %) as a colorless oil : IR ($CHCl_3$) 1760, 1730 cm^{-1}, ^1H-NMR ($CDCl_3$, 90MHz) δ 1.37 (3H, t, *J*=7.1Hz), 2.27 (3H, s), 2.45–3.30 (4H, m), 3.76, 3.86 (3H each, s), 4.30 (2H, q, *J*=7.1Hz), 6.63 (1H, d, *J*=2.6Hz), 6.72 (1H, d, *J*=2.6Hz); MS *m/z* 320 (M^+). Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74 ; H, 6.29. Found : C, 63.99 ; H, 6.41.

Methyl 2-ethoxycabonyloxy-7-methoxy-5-methylnaphthalene-1-carboxylate (9e). A solution of **7e** (149 mg, 0.47 mmol) and DDQ (125 mg, 0.55 mmol) in dry toluene (6 mL) was heated under reflux for 30 min. After filtration through Celite, the filtrate was concentrated and chromatographed on silica gel (ethyl acetate–hexane, 1:9) to give **9e** (148 mg, 100 %) as colorless prisms, mp 106–107°C, by recrystallization from Et_2O–hexane : IR($CHCl_3$) 1765, 1730 cm^{-1}; ^1H-NMR ($CDCl_3$, 90MHz) δ 1.40 (3H, t, *J*=7.1Hz), 2.64, 3.88, 4.01 (3H each, s), 4.35 (2H, q, *J*=7.1Hz), 7.04 (1H, br s), 7.10 (1H, d, *J*=9.0Hz), 7.26 (1H, br s), 8.02 (1H, d,

J=9.0Hz); MS *m/z* 318 (M^+). Anal. Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found : C, 64.08; H, 5.77.

Methyl 2-hydroxy-7-methoxy-5-methylnaphthalene-1-carboxylate (12). From 9e. Potassium carbonate (66 mg, 0.48 mmol) was added to a solution of **9e** (76 mg, 0.24 mmol) in MeOH–H_2O (1.25 :1, 4.5mL) and the mixture was heated under reflux for 4 h. After the mixture had been cooled in an ice–water bath, 10 % HCl was added to acidify and the solvent was evaporated *in vacuo*. The resulting aqueous phase was extracted with Et_2O, then the ethereal extracts were washed with brine, dried, and evaporated *in vacuo* to give a residue which was chromatographed on silica gel (ethyl acetate–hexane, 1:9) to give **12** (83.5 mg, 88 %) as colorless leaflets, mp 109–110°C (lit[8]. mp 104–105°C), by recrystallization from Et_2O : IR ($CHCl_3$) 1650 cm^{-1}; ^1H–NMR ($CDCl_3$, 500MHz) δ 2.63, 3.92, 4.10 (3H each, s), 6.88(1H, d, *J*=2.5Hz), 7.02(1H, d, *J*=9.2Hz), 8.02 (1H, d, *J*=9.2Hz), 8.06(1H, d, *J*=2.5Hz), 12.14 (1H, s, D_2O disappeared); MS *m/z* 246 (M^+).

From 22 via silyl enol ether 4f. TBSOTf (64.4 mg, 0.24 mmol) was added dropwise to a stirred solution of **22** (30.5 mg, 0.12 mmol) and triethylamine (26.3 mg, 0.26 mmol) in dry Et_2O (1.5 ml) at 0°C. After being stirred for 3 h, TBSOTf (64.4 mg, 0.24 mmol) and triethylamine (26.3 mg, 0.26 mmol) were added to the reaction mixture and the solution was further stirred for 2 h at 0°C. After filtration through Celite, the filtrate was washed with saturated aqueous NH_4Cl, dried, and concentrated *in vacuo* to give the crude silyl enol ether **4f** (62.3 mg), as a colorless oil, which was taken up into ODB (1.8 ml). The resulting solution was heated at 180°C for 1 h, then the solution was cooled to room temperature. After addition of DDQ (30 mg, 0.13 mmol), the resulting mixture was heated at 120°C for 30 min, filtered through Celite and the filtrate was concentrated *in vacuo* to give the crude naphthalene **9f** (61.1mg) as a colorless oil, which was submitted to the next reaction without further purification: IR ($CHCl_3$) 1725 cm^{-1}; ^1H–NMR ($CDCl_3$, 90MHz) δ 0.18 (6H, s), 0.94 (9H, s), 2.53, 3.79, 3.91 (3H each, s), 6.81 (2H, s), 6.86 (1H, d, *J*=9.1Hz), 7.77 (1H, d, *J*=9.1Hz); MS *m/z* 360 (M^+); HRMS, calcd for $C_{20}H_{28}O_4Si$ *m/z* 360.1757, found *m/z* 360.1759. Tetra-*n*-butylammonium fluoride (1M in THF, 0.15 mL, 0.15 mmol) was added dropwise to a stirred solution of **9f** (61.1 mg) in dry THF (2 mL) at 0°C. After being stirred at room temperature for 1 h, evaporation of the solvent followed by chromatography on silica gel (ethyl acetate–hexane, 1:9) yielded **12** (14 mg, 46 % from **22**) as colorless leaflets, mp 109–110°C, by recrystallization from Et_2O–hexane.

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References and Notes

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