Total Synthesis of (±)-Plumbazeylanone, A Naphthoquinone Trimer from *Plumbago zeylanica*[1)]

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We have investigated the total synthesis of (±)-plumbazeylanone (1), a naphthoquinone trimer based on two different pathways (I) and (II). The synthetic approach based on pathway (I) was not successful. However, the first synthesis of 1 from plumbagin (2a) was achieved by utilizing an unsymmetrical methylene-bridged dimer (20b), with a naphthoquinone unit and a naphthalene unit as a key intermediate, based on pathway (II), in 11 steps with an overall yield of 5.9%. This synthesis features regioselective nucleophilic 1,2-addition of the naphthyllithium reagent 4a to the C-1 position of naphthoquinone 20b, and the regio- and stereoselective dienone-phenol-type rearrangement of the 1,2-adduct 21b (1,2-migration of the naphthyl group to the C3-position on 21b) with 2 N-NaOH.

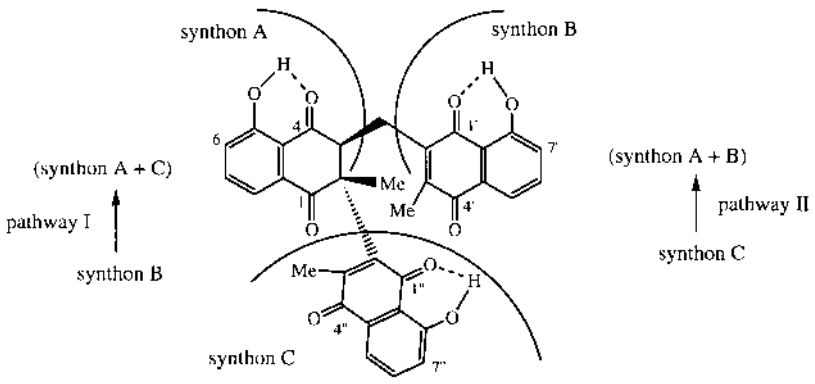
Key words naphthoquinone trimer; plumbazeylanone; total synthesis; nucleophilic 1,2-addition; dienone-phenol rearrangement

The roots of the perennial herb *Plumbago zeylanica* (Plumbaginaceae) have long been used in a variety of medicinal applications (*e.g.*, abortifacient, ulcers, astringent, leprosy, syphilis, and carcinoma, *etc.*)[2)] in many Asian countries. Since 1971, several naphthoquinones[3)] have been isolated from this plant including plumbazeylanone (**1**) and plumbagin (**2a**). The latter compound demonstrates *in vitro* immuno-suppressive and cytotoxic activity against primary cell cultures of granulocytes.[4)] However, the essential active ingredient that provides the biological activity in medicinal applications of this plant has not yet been established. To determine the active ingredient is important, especially due to the absence of constituents such as alkaloids, saponins, and glycosides in the roots of this plant.

In this context, naturally occurring plumbazeylanone is an optically inactive compound, whose structure was revised through X-ray crystallography by Thomson *et al*. as shown in Chart 1.[3g)] Among the naphthoquinones in this plant, plumbazeylanone (**1**) was chosen as a synthetic target due not only to its unique structure, but also in order to determine the most active constituent in the medicinal application of this plant. In addition, this material is a trimeric naphthoquinone derivative analogous to conocurvone, an active anti HIV (human immunodeficiency virus) constituent isolated from a *Conospermum* sp.[5)] Our retro-synthetic examination of plumbazeylanone revealed the following two synthetic disconnections (Chart 1). Retrosynthesis leads to pathway (I), which involves a linkage between synthon A and synthon C, followed by introduction of synthon B, including the methylene group. By contrast, pathway (II) involves construction of the methylene-bridged dimer with synthons A and B, followed by introduction of synthon C.

Recently, we published a preliminary communication of the first total synthesis of (±)-plumbazeylanone (**1**).[1)] We now provide greater detail and experimental procedures and also describe some of the ancillary studies that facilitated achievement of the synthesis.

First, we examined the synthesis of plumbazeylanone (**1**) based on pathway (I) (Chart 2), in which (i) nucleophilic 1,2-addition reaction of the naphthyllithium reagent **4a** to the C-1 position of the naphthoquinone **2**, followed by dienone-phenol-type rearrangement of 1-oxo-1,4-dihydronaphthalene derivative **5** (1,2-migration of the naphthyl group to the C-3 position of **5**) is required, followed by (ii) condensation reaction between **10** and **3d**, and demethylation of **11** to construct the target compound **1**. However, the following problems must be solved in order to establish a total synthesis of **1** by this pathway; (i) how can regioselective 1,2-addition of **4a** to the C-1 position of **2** be achieved, (ii) how can regioselective 1,2-migration of the naphthyl group to the C-3 position on **5**



1: Plumbazeylanone

Chart 1

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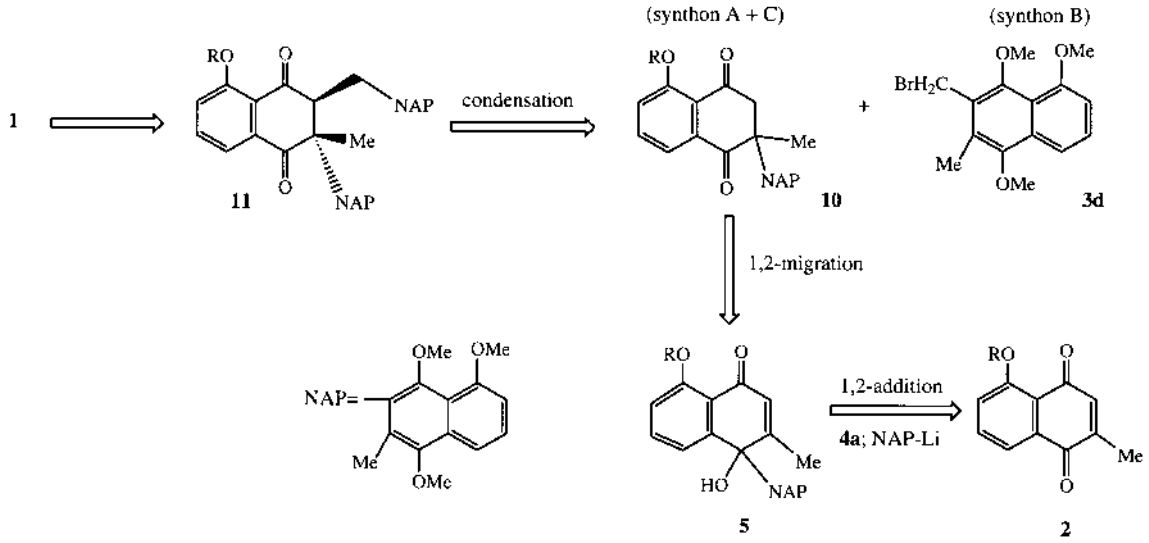

Chart 2

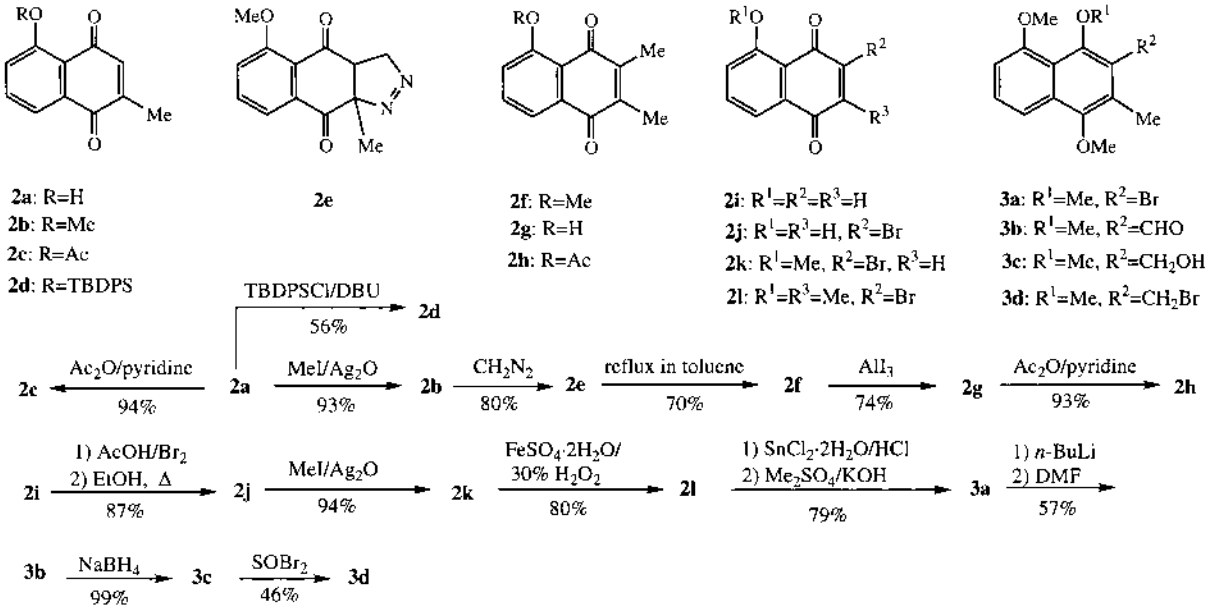

Chart 3

be achieved.

As a prelude to the key regioselective 1,2-addition reaction, preliminary model experiments with various naphthoquinones **2** as electrophiles were examined using organolithium reagents, **4a**, **4b** (phenyllithium), and **4c** (*n*-butyllithium) as nucleophiles.

The naphthoquinones **2b**,[3f] **2c**, **2d**, **2e**,[3f] **2f**,[3f] **2g**, and **2h** and naphthalenes **3a**, **3d**[6] used in this reaction were prepared from the corresponding compounds **2a** and **2i** through the reaction sequences shown in Chart 3.

The results of nucleophilic addition reactions are shown in Chart 4 and Table 1. Reaction of **2a**, having a naphtholic hydroxyl group at the C-5 position, with naphthyllithium reagent **4a** prepared by reaction of bromonaphthalene **3a** with *n*-butyllithium gave the C-1 1,2-adduct **5a** (26.0%), the C-4 1,2-adduct **6a** (30.0%), and the C-3 1,4-adduct **7a** (22.5%) (run 1). The structures of **5a** and **6a** were assigned by ^{1}H-NMR spectra. In the ^{1}H-NMR spectrum of **5a**, the proton signal for C_8-OH (δ 12.71), which disappeared upon addition of D_2O, was observed at lower field as a singlet owing to formation of a hydrogen bond between the C-1 carbonyl group and the C-8 hydroxyl. The proton signal for C_4-OH (δ 8.70) was observed at lower field due to the formation of a hydrogen bond between the C-4 hydroxyl group and the C-1′ methoxyl group on the naphthyl group. This data indicated that the naphthyl group is bonded to the C-4 position in **5a**. On the other hand, observation of the proton signals for C_4-OH (δ 8.25) and C_5-OH (δ 7.23), which disappeared upon addition of D_2O, in ^{1}H-NMR spectrum of **6a**, indicated that the naphthyl group was located at the C-4 position in **6a**.

In reactions of **2b** and **2f** protected with CH_3I at the C5-hydroxyl group, using reagents **4a** or **4b**, the desired 1,2-addition products at the C-1 position of the corresponding naphthoquinones were not obtained (runs 2 and 6). Reactions of **2c** or **2m** protected with Ac_2O or $AlCl_3$ at the C5-hydroxyl group were carried out using reagent **4a**. These reactions

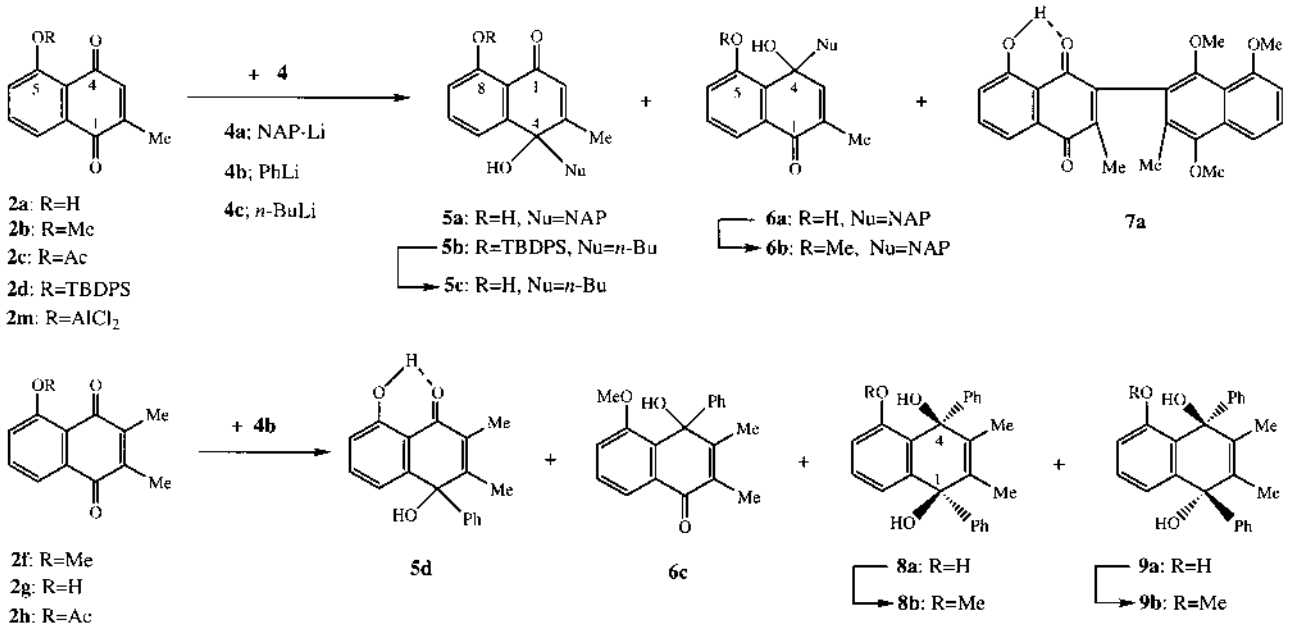

Chart 4

Table 1. Nucleophilic Reactions of Organolithium Compounds **4a**, **4b** and **4c** with Naphthoquinones, **2a**, **2b**, **2c**, **2d**, **2f**, **2g**, **2h**, and **2m**

Run	Electrophiles **2**	Nucleophiles **4**	Temperature (°C)	Product (yield, %)[a]			
				1,2-Adduct at C-1 (**5**)	1,2-Adduct at C-4 (**6**)	Others	
1	**2a**	**4a**	−78	**5a** (26.0)	**6a** (30.0)	**7a** (22.5)	
2	**2b**	**4a**	−78	—	**6b** (46.6)	—	
3	**2c**	**4a**	−78	**5a** (25.0)	**6a** (22.5)	**7a** (23.0)	
4	**2m**	**4a**	−78	**5a** (15.5)	**6a** (13.0)	**7a** (10.5)	
5	**2d**	**4c**	−78	**5b** (59.0)	—	—	
6	**2f**	**4b**	0	—	**6c** (22.0)	**8b** (15.5)	**9b** (30.5)
7	**2g**	**4b**	0	**5d** (52.3)	—	**8a** (9.5)	**9a** (15.0)
8	**2h**	**4b**	0	**5d** (48.5)	—	**8a** (15.3)	**9a** (10.5)

a) Isolated yields after silica gel column chromatography.

gave similar results to reaction of **2a** with the reagent **4a** (runs 3 and 4). In the reaction of **2d**, protected with a bulky *tert*-butyldiphenylsilyl group (TBDPS) at the C5-hydroxyl, with reagent **4c**, regioselective 1,2-addition reaction proceeded to afford the C-1 1,2-adduct **5b** in 59% yield without formation of the C-4 1,2-addition product (run 5). This result indicated that introduction of the TBDPS group interfered with the 1,2-addition reaction to the C-4 position of the naphthoquinone moiety.

On the other hand, reactions of **2g** and **2h** having methyl groups at both C-2 and C-3 positions, with the reagent **4b**, gave the C-1 1,2-adduct **5d** and the double 1,2-adducts **8a** and **9a** at both C-1 and C-4 positions, respectively (runs 7 and 8). The stereochemistry of **8a** and **9a** were assigned on the basis of nuclear Overhauser enhancement and exchange spectroscopy (NOESY) experiments of the corresponding **8b** and **9b**, which were obtained from **8a** and **9a** by methylation, respectively. In the NOESY spectrum for **8b**, a correlation cross peak between the proton signal for C_4-OH (δ 4.68) and the proton signal for C_1-OH (δ 2.28) was observed. No correlation cross peak was observed between the proton signal for C_4-OH (δ 4.70) and the proton signal for C_1-OH (δ 2.56) in **9b**. This data indicated that **8b** and **9b** possessed relative *cis*- and *trans*-configurations between C-1 and C-4, respectively. Accordingly, **8a** and **9a** have the same relative configurations as those of **8b** and **9b**, respectively.

Based on the results of the model experiments, the synthetic approach toward **1** started with the naphthoquinone **2d** (Chart 5). Nucleophilic addition reaction of reagent **4a** to **2d** was examined. This reaction gave the desired 1,2-adduct **5e** in 28.5% yield and the 1,4-adduct **7b** in 42.7% yield. Although base and acid induced dienone-phenol-type re-

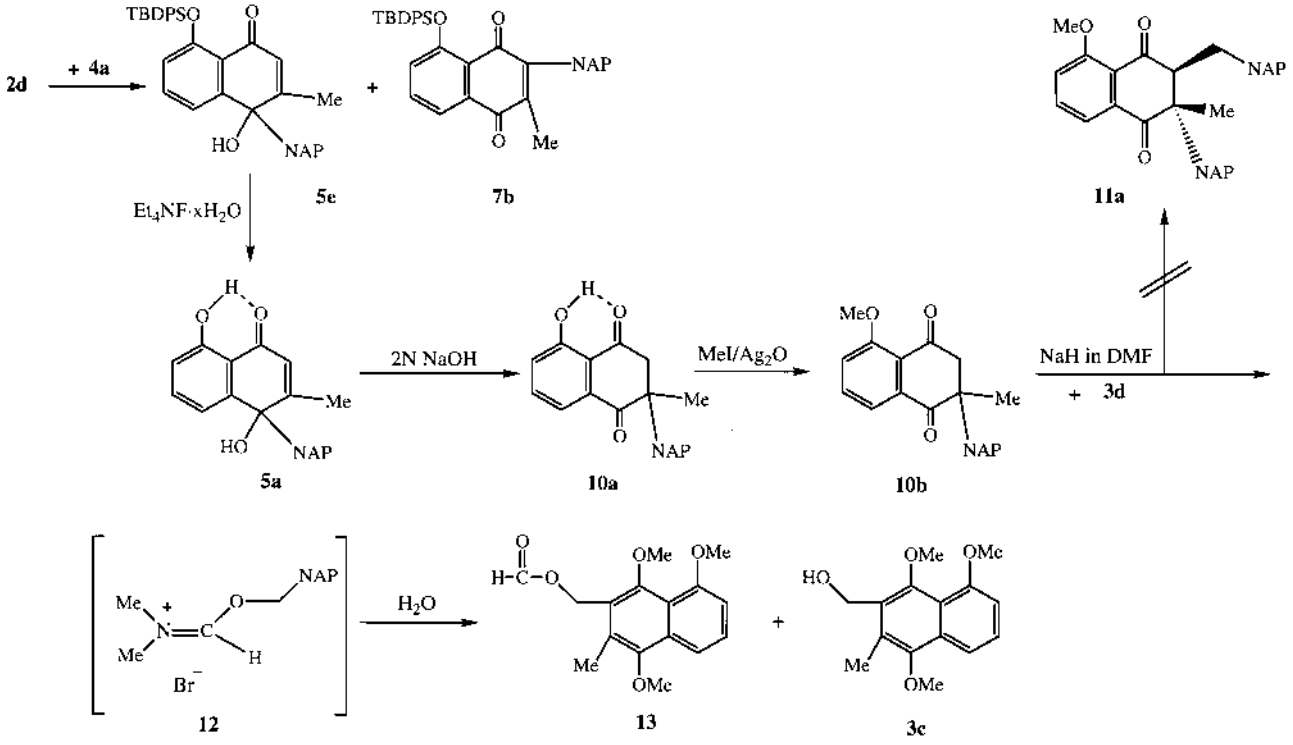

Chart 5

Table 2. Dienone-Phenol Type Rearrangement of **5a**

Run	Substrate (0.1 mmol)	Reagent	Solvent	Temp. (°C)	Time (h)	Product (yield, %)
1	**5a**	1 N NaOH	H_2O	180[a]	12	**10a** (9.5)
2		1 N KOH	H_2O	180[a]	20	**10a** (9.5)
3		2 N NaOH	H_2O	180[a]	12	**10a** (30.0)
4		2 N NaOH	H_2O/EtOH (1/1)	180[a]	12	**10a** (34.6)
5		2 N NaOH	Diglyme	125	0.5	**10a** (30.0)
6		2 N NaOH	Ethylene glycol	125	2	**10a** (10.0)
7		Et_3N	—	100	18	No reaction
8		*tert*-BuOK	DMSO[b]	80	13	**10a** (trace)
9		*tert*-BuOK	DMF[c]	50	48	Polymer
10		$BF_3 \cdot OEt_2$	CH_2Cl_2	0	0.5	Polymer
11		$ZnCl_2$	CH_2Cl_2	0	24	No reaction
12		$MgCl_2$	THF	Reflux	24	No reaction
13		$MgCl_2 \cdot OEt_2$	THF	Reflux	24	No reaction

a) Heating in a sealed tube. *b*) Dimethylsulfoxide. *c*) Dimethylformamide.

arrangement of **5e** (1,2-migration of the naphthyl group to the C3-position of **5e**) was examined, it did not proceed at all. Therefore, deprotection of the TBDPS group of **5e** with $Et_4N^+F^- \cdot xH_2O$ was performed to give the corresponding naphthoquinol **5a** in quantitative yield. The dienone-phenol-type rearrangement of **5a** with various reagents[7] was further investigated, and the results are summarized in Table 2. The best results were obtained using aqueous 2 N-NaOH with heating in a sealed tube to give the 1,2-migration product **10a** in 34.6% yield. The reaction of **10a** with CH_3I in the presence of Ag_2O gave the methylated compound **10b**.

Subsequently, condensation of the enolate generated from reaction of **10b** with sodium hydride (NaH) in dimethylformamide (DMF) with bromide **3d** gave formate **13** and alcohol **3c**, without formation of the desired methylene-bridged trimer **11a**. Compounds **13** and **3c** may be formed by hydrolysis of Vilsmeier–Haack adduct[8] **12** derived from DMF and **3d**. Accordingly, we had to abandon the synthesis of **1** *via* pathway (I).

On the basis of the information obtained from the above investigations, we next investigated the total synthesis of **1** utilizing **20b** as a key intermediate based on pathway (II), as shown in Chart 6. This pathway involves, (i) condensation reaction between naphthol **3e** and paraformaldehyde, followed by transformation to key intermediate **20b**, the unsymmetrical methylene-bridged dimer with a naphthoquinone unit and a naphthalene unit, (ii) 1,2-addition of **4a** to the C-1 position of **20b**, followed by dienone-phenol-type rearrangement of **21b** to construct the desired 1,2-migration product **11b**, and (iii) final demethylation of the six methoxyl groups in **11b**, followed by air oxidation to furnish the desired compound **1**.

The synthesis of key intermediate **20b** from **3e** was first

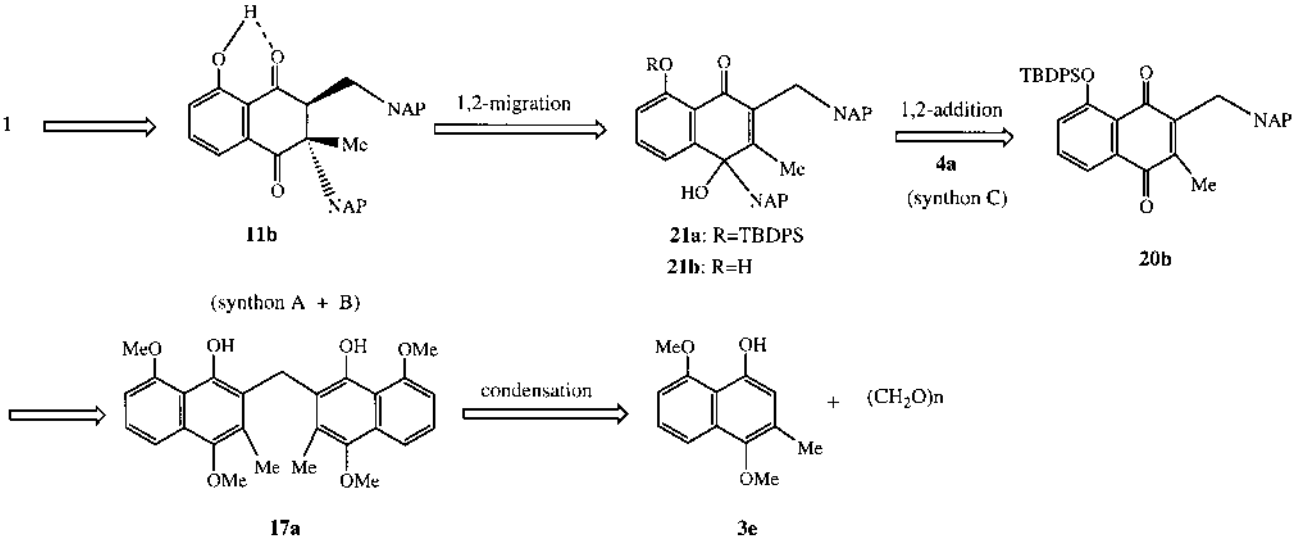

Chart 6

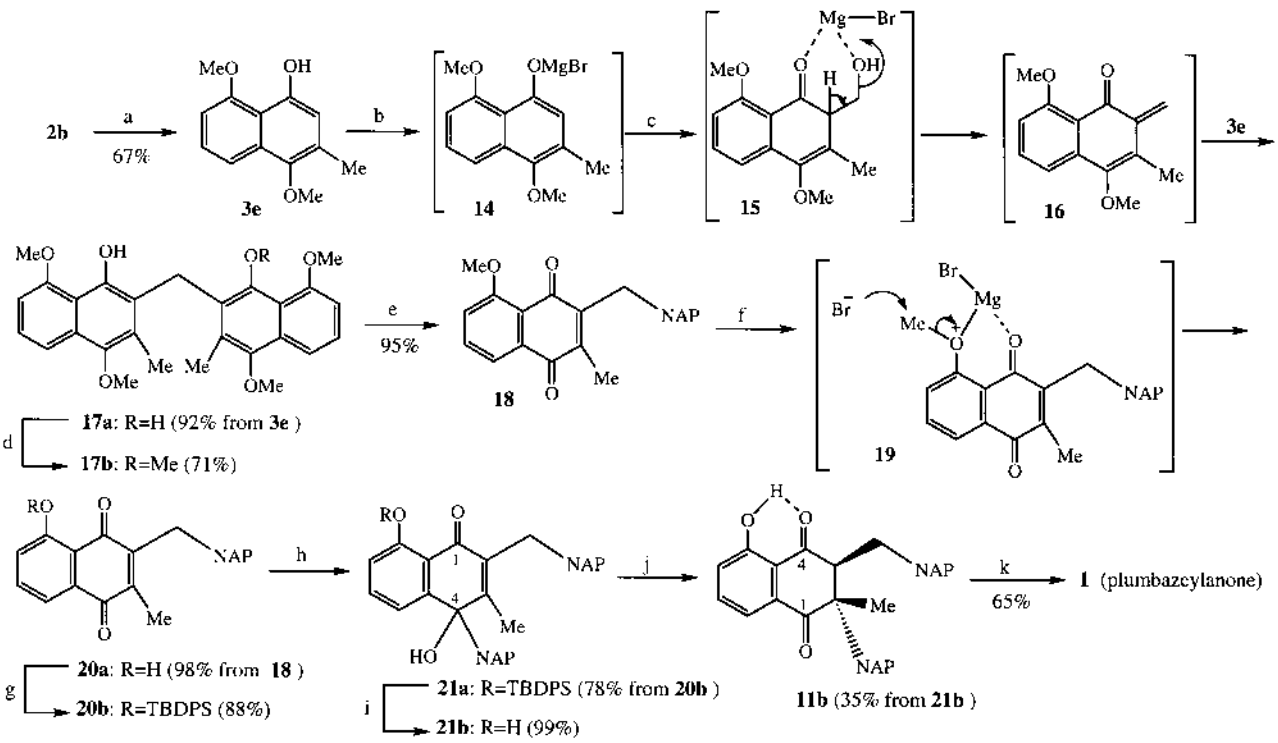

Chart 7

carried out. The naphthol **3e** was synthesized by reduction of **2b** with $SnCl_2 \cdot 2H_2O$/HCl followed by selective monomethylation with Me_2SO_4/KOH.[9] Treatment of **3e** with ethylmagnesium bromide (EtMgBr) and paraformaldehyde gave the symmetrical methylene-bridged dimer **17a**.[10] The formation of **17a** by this reaction can be explained as follows. The condensation of paraformaldehyde and **14** derived from the reaction of **3e** with EtMgBr may take place to form the corresponding adduct **15**, followed by dehydration to form the corresponding *o*-naphthoquinone methide **16**. Furthermore, addition of **3e** to **16** may proceed to yield **17a**.[11]

Selective monomethylation of the naphtholic hydroxyl group of **17a** with Me_2SO_4 in the presence of $Bu_4N^+HSO_4^-$ gave the corresponding compound **17b**. Moreover, oxidation of the naphthol moiety in **17b** using 10% $FeCl_3$ in MeCN gave the corresponding naphthoquinone **18** in 95% yield. Magnesium bromide hexahydrate ($MgBr_2 \cdot 6H_2O$) effected selective demethylation of the methoxyl group at the C-5 position in **18** to afford the corresponding naphthol **20a** in excellent yield. The mechanism for this demethylation can be postulated as follows. Selective nucleophilic attack of Br^- to the methyl group of the methoxyl group at the C-5 position in

19, derived from **18**, with $MgBr_2 \cdot 6H_2O$, in which the oxygen atom of the methoxyl group is chelated to a magnesium atom with the carbonyl group at the C-4 position, followed by hydrolysis to yield the demethylated compound **20a**. The naphtholic hydroxyl group of **20a** was protected with a TBDPS group to afford the corresponding *O*-silylated compound **20b** as a key intermediate in 88% yield.

Next, examination of the synthesis of target compound **1** from **20b** was initiated. The regioselective nucleophilic addition of the naphthyllithium reagent **4a** to the C-1 position of **20b** in tetrahydrofuran (THF) proceeded at −78 °C under a nitrogen atmosphere to give the expected 1,2 adduct **21a** (78%) in high yield. Deprotection of the TBDPS group of **21a** with $Et_4N^+F^- \cdot xH_2O$ gave the corresponding naphthol **21b** in quantitative yield. Dienone-phenol-type rearrangement of **21b** using aqueous 2 N-NaOH with heating in a sealed tube was then performed. Base-induced 1,2-migration of the naphthyl group to the C-3 position of **21b** proceeded with no detectable generation of a diastereoisomer, to give the stereoselective 1,2-migration product **11b** in 35% yield, along with polymeric product as the major product.

The structure of the product **11b** was assigned by means of spectral analyses, including IR, ^{1}H-NMR, and ^{13}C-NMR comparisons of **11b** and **10a**, ^{1}H–^{13}C COSY (^{1}H–^{13}C shift correlation spectroscopy), and ^{1}H-detected heteronuclear multiple bond connectivity (HMBC) experiments. **11b** showed the following features (i) naphthoquinone absorptions at 1688, 1649 cm^{-1} in the IR spectrum, (ii) two carbonyl carbon signals due to the naphthoquinone moiety were observed at δ 206.95 (C-4) and δ 194.82 (C-1) in the ^{13}C-NMR spectrum, (iii) the HMBC spectrum indicated that the proton at δ 2.03 (C_2-Me) showed long-range correlations with the carbons at δ 194.8 (C-1), 57.0 (C-2), 57.7 (C-3), and 134.29 (C-2″), respectively. This data indicate that the naphthyl group at the C-4 position in **21b** has migrated to the C-3 position. The stereochemistry of **11b** was assigned on the basis of NOESY experiments. The observation of correlation cross peaks between the proton signal for C_2-Me (δ 2.03) and the methylenic proton signals for C_3-CH_2 (δ 2.85 and 3.25) indicated that C_2-Me and C_3-H possess a *trans*-relative configuration.

Finally, demethylation of **11b** with AlI_3 in benzene,[12] followed by air oxidation afforded (±)-plumbazeylanone (**1**) in 65% yield, mp 245—248 °C. All physical data for the synthetic compound **1** were identical with those of the natural product.[3e,g]

The first total synthesis of (±)-**1** consists of 11 steps from plumbagin (**2a**) and an overall yield of 5.9%. In this total synthesis, regioselective 1,2-addition reaction of naphthyllithium reagent **4** to the C-1 position of **20b** was achieved by using the *O*-silylated compound **20b** protected with a bulky TBDPS group at the naphtholic hydroxyl group of **20a**. Furthermore, stereoselective dienone-phenol-type rearrangement of **21b** to **11b** could be performed using a base such as 2 N-NaOH with heating.

Investigations of the biological activity of the synthetic compound **1** are in progress.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer and ^{1}H- and ^{13}C-NMR spectra with JEOL JNM-EX90, JNM-GX270 and JNM-GSX500 spectrometers, with tetramethylsilane as an internal standard ($CDCl_3$ and C_6D_6 solution). Mass spectra were recorded on a JEOL JMS-D300 spectrometer. Elemental analyses were done using a Yanaco CHN-MT-3 apparatus. Wako silica gel C-200 (200 mesh) and Merck Kieselgel 60 F_{254} were used for column chromatography and thin-layer chromatography (TLC), respectively. Each organic extract was dried over Na_2SO_4. High-performance liquid chromatography (HPLC) was performed on a Wakosil 5C4-200 column (25 cm×4.6 mm i.d. for analytical scale or 25 cm×20 mm i.d. for preparative scale) with aqueous methanol (40—60%), using a Shimadzu LC-6A apparatus for monitoring at 254 nm.

5-Methoxy-2-methyl-1,4-naphthoquinone (2b) Silver (I) oxide (3.5 g, 15 mmol), followed by MeI (1.0 g, 7.0 mmol) was added to a solution of **2a** (1.0 g, 5.3 mmol) in anhydrous $CHCl_3$ (10 ml) and the whole was sealed with bonbenrole. After the mixture was stirred at room temperature for 5 h, Ag_2O and MeI, as described above were further added, the whole was stirred overnight. The reaction mixture was filtered and the filtrate washed with 10% NaOH until the red color of the aqueous layer had faded. The organic layer was further washed with H_2O, dried, filtered, and evaporated *in vacuo*. The residue was recrystallized from ether–hexane to give 993 mg (93%) of **2b**, yellow needles, mp 94—96 °C. IR (KBr) cm^{-1}: 1656, 1631, 1582. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 2.14 (3H, d, J=1.5 Hz, C2-Me), 4.00 (3H, s, C5-OMe), 6.74 (1H, q, J=1.5 Hz, C2-H), 7.29 (1H, dd, J=1.3, 8.5 Hz, C6-H), 7.66 (1H, dd, J=8.5, 8.6 Hz, C7-H), 7.76 (1H, dd, J=1.3, 8.6 Hz, C8-H). ^{13}C-NMR ($CDCl_3$) δ: 15.8 (C2-Me), 56.5 (C5-OMe), 117.7 (C6), 119.4 (C8), 120.0 (C4a), 134.7 (C7), 137.9 (C3), 145.4 (C2), 159.4 (C5), 184.5 (C4), 185.8 (C1). HR-MS Calcd for $C_{12}H_{10}O_3$: 202.0630. Found 202.0644.

5-Acetoxy-2-methyl-1,4-naphthoquinone (2c) Acetic anhydride (9 ml) was added to a solution of **2a** (376 mg, 2.0 mmol) in pyridine (3 ml) at 0 °C and the mixture was stirred at room temperature for 2 h. The reaction mixture was poured onto crushed ice and stirred at room temperature for 2 h, and the whole was extracted with ether. The organic layer was washed with saturated $NaHCO_3$, diluted HCl, and H_2O, then dried, filtered, and evaporated *in vacuo*. The residue was recrystallized from ether–hexane to yield 41 mg (94%) of **2c**, as yellow plates, mp 116—117 °C. IR (KBr) cm^{-1}: 1759, 1658, 1626. ^{1}H-NMR ($CDCl_3$) δ: 2.16 (3H, d, J=1.54 Hz, C2-Me), 2.44 (3H, s, OCOMe), 6.71 (1H, q, J=1.54 Hz, C3-H), 7.35 (1H, dd, J=1.54, 8.14 Hz, C6-H), 7.73 (1H, dd, J=7.69, 8.14 Hz, C7-H), 8.07 (1H, dd, J=1.54, 7.69 Hz, C8-H). HR-MS Calcd for $C_{13}H_{10}O_4$: 230.0579. Found 230.0585.

5-*tert*-Butyldiphenylsilyloxy-2-methyl-1,4-naphthoquinone (2d) *tert*-Butyldiphenylsilyl chloride (TBDPSCl; 2.69 g, 9.8 mmol) was added at 5 °C to a solution of **2a** (470 mg, 2.5 mmol) in anhydrous benzene (20 ml) and the whole was stirred for 2 h. 1,8-Diazabicyclo[5,4,0]-7-undecene (DBU; 1.19 g, 7.8 mmol) was added slowly to the resultant mixture and the whole was stirred for 15 min. The precipitates were separated from the solution by filtration and the filtrate was washed with H_2O, dried, filtered, and evaporated *in vacuo*. The residue was subjected to silica gel chromatography with benzene to give 586 mg (54.8%) of **2d**, as colorless needles ($CHCl_3$–petroleum ether), mp 128—129 °C. IR (KBr) cm^{-1}: 1655, 1630. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.11 (9H, s, *tert*-Bu), 2.07 (3H, d, J=1.25 Hz, C2-Me), 6.67 (1H, d, J=1.25 Hz, C3-H), 6.68 (1H, d, J=7.47 Hz, C6-H), 7.11 (1H, t, J=7.47 Hz, C7-H), 7.18—7.37 (6H, m, aromatic-H), 7.58 (1H, d, J=7.47 Hz, C8-H), 7.67—7.69 (4H, m, aromatic-H). HR FAB-MS *m*/*z*: Calcd for $C_{27}H_{27}O_3Si$: 427.1729. Found 427.1743.

5-Hydroxy-2,3-dimethyl-1,4-naphthoquinone (2g) A solution of aluminum powder (54 mg, 2.0 mmol) and I_2 (553 mg, 2.1 mmol) in anhydrous benzene (5 ml) was stirred under a nitrogen atmosphere for 30 min. The mixture was stirred for 2 h, until the red-purple color had faded. A solution of **2f** (108 mg, 0.5 mmol) in anhydrous benzene (8 ml) was added to the above mentioned solution (AlI_3) and the whole was stirred at room temperature for 1 h. The reaction mixture was poured into ice water and acidified with diluted HCl, and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried, and evaporated *in vacuo*. The residue was subjected to silica gel column chromatography with hexane–AcOEt (20 : 1, v/v) to yield 74 mg (73.5%) of **2g**, as orange crystals (ether–hexane), mp 120—121 °C. IR (KBr) cm^{-1}: 3432, 1656, 1632. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.98 (3H, s, C2 or C3-Me), 2.33 (3H, s, C2 or C3-Me), 7.15—7.27 (1H, m, aromatic-H), 7.47—7.67 (2H, m, aromatic-H), 12.17 (1H, s, OH). HR-MS Calcd for $C_{12}H_{10}O_3$: 202.0630. Found 202.0643. *Anal*. Calcd for $C_{12}H_{10}O_3$: C,71.28; H, 4.99. Found: C,71.18; H, 5.02.

5-Acetoxy-2,3-dimethyl-1,4-naphthoquinone (2h) Compound **2h**, as orange crystals ($CHCl_3$–hexane), mp 111—114 °C was synthesized from **2g** in 93% yield by a procedure similar to that used for **2c**. IR (KBr) cm^{-1}: 1763, 1656, 1623. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 2.12 (3H, s, C2 or C3-Me),

2.14 (3H, s, C2 or C3-Me), 2.45 (3H, s, OCOMe), 7.31 (1H, dd, J=1.54, 8.13 Hz, C6-H), 7.69 (1H, dd, J=7.69, 8.13 Hz, C7-H), 8.05 (1H, dd, J=1.54, 7.69 Hz, C8-H). HR-MS Calcd for $C_{14}H_{12}O_4$: 244.0735. Found 244.0693. *Anal*. Calcd for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 68.80; H, 4.98.

3-Bromo-5-hydroxy-1,4-naphthoquinone (2j) Bromine (0.3 ml) was added to a solution of **2i** (1.0 g, 5.75 mmol) in AcOH (10 ml) under a nitrogen atmosphere in the dark and the mixture was stirred for 15 min. The reaction mixture was poured onto crushed ice and the whole was stirred for 10 min. The precipitates were separated from the solution by filtration and washed with H_2O. The resultant product was dissolved in EtOH, and the whole was stirred with heating at 80 °C for 10 min. The mixture was poured into ice–water, and the precipitates were separated by filtration. The residue was recrystallized from $CHCl_3$–hexane to yield 1.25 g (86.5%) of **2j**, orange plates, mp 168—168.5 °C. IR (KBr) cm^{-1}: 3406, 1654, 1636. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 7.30 (1H, dd, J=1.83, 7.63 Hz, C6-H), 7.50 (1H, s, C2-H), 7.63—7.71 (2H, m, C7, C8-H), 11.73 (1H, s, C5-OH). ^{13}C-NMR (CDCl3) δ: 113.93 (C4a), 119.88 (C8), 124.72 (C6), 131.63 (C8a), 137.19 (C7), 139.29 (C3), 141.19 (C2), 162.06 (C5), 181.62 (C1 or C4), 182.86 (C1 or C4). HR-MS Calcd for $C_{10}H_5O_3Br$: 251.9421, 253.9401. Found 251.9457, 253.9426.

3-Bromo-5-methoxy-1,4-naphthoquinone (2k) Compound **2k**, as yellow needles (acetone), mp 154—155 °C was synthesized from **2j** in 94.4% yield by a procedure similar to that used for **2b**. IR (KBr) cm^{-1}: 1671, 1648. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 4.02 (3H, s, OMe), 7.28—7.34 (1H, m, aromatic-H), 7.44 (1H, s, C2-H), 7.71—7.74 (2H, m, aromatic-H). ^{13}C-NMR ($CDCl_3$) δ: 56.5 (C5-OMe), 118.05 (C6), 118.55 (C4a), 119.44 (C8), 132.63 (C8a), 135.53 (C7), 138.27 (C2), 142.55 (C3), 160.31 (C5), 176.14 (C1 or C4), 182.52 (C1 or C4). HR-MS Calcd for $C_{11}H_7O_3Br$: 265.9577, 267.9557. Found 265.9561, 267.9571.

3-Bromo-5-methoxy-2-methyl-1,4-naphthoquinone (2l) Dimethylsulfoxide (DMSO; 20 ml), followed by $FeSO_4 \cdot 7H_2O$ (1.0 g) was added to a solution of **2k** (1.0 g, 3.97 mmol) in anhydrous dioxane (20 ml) at room temperature under a nitrogen atmosphere, and the mixture was stirred for 30 min. To the resultant reaction mixture was added slowly 30% H_2O_2 (6.0 ml), dioxane (8.0 ml), and DMSO (14.0 ml), and stirred for 30 min The reaction mixture was poured into ice–water (300 ml) and stirred for 30 min. The precipitates were separated from the solution by filtration and recrystallized from EtOH to give 851 mg (80.1%) of **2l**, as yellow needles, mp 163—165 °C. IR (KBr) cm^{-1}: 1667, 1607. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.34 (3H, s, C2-Me), 4.01 (3H, s, C5-OMe), 7.29 (1H, dd, J=0.92, 8.55 Hz, C6-H), 7.67 (1H, dd, J=7.63, 8.55 Hz, C7-H), 7.76 (1H, dd, J=0.92, 7.63 Hz, C8-H). ^{13}C-NMR ($CDCl_3$) δ: 17.49 (C2-Me), 56.51 (C5-OMe), 117.78 (C6), 118.93 (C4a), 119.73 (C8), 133.75 (C8a), 135.07 (C7), 141.39 (C3), 146.05 (C2), 160.01 (C5), 176.00 (C1 or C4), 182.19 (C1 or C4). HR-MS Calcd for $C_{12}H_9O_3Br$: 279.9734, 281.9714. Found 279.9736, 281.9707.

3-Bromo-1,4,5-trimethoxy-2-methylnaphthalene (3a) Compound **2l** (2.0 g, 7.09 mmol) was dissolved in hot 95% EtOH (82 ml). After cooling to room temperature, a suspension of $SnCl_2 \cdot 2H_2O$ (4.89 g, 21.56 mmol) in conc. HCl (4.94 ml) was added dropwise slowly to the pasty mixture at room temperature under a nitrogen atmosphere, and the whole was stirred for 30 min. To the reaction mixture was added dropwise Me_2SO_4 (12.12 ml) followed by 25% aqueous KOH (25.8 ml), and the mixture stirred for 20 min. The reaction mixture was poured into ice–water and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried, evaporated *in vacuo*. The residue was subjected to silica gel column chromatography with hexane–AcOEt (20 : 1, v/v) to yield 1.75 g (79.4%) of **3a**, as colorless needles (ether–hexane), mp 94—96 °C. IR (KBr) cm^{-1}: 1578, 1456. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.52 (3H, s, C2-Me), 3.84 (3H, s, C1-OMe), 3.86 (3H, s, C4-OMe), 4.00 (3H, s, C5-OMe), 6.87 (1H, d, J=7.63 Hz, C6-H), 7.41 (1H, dd, J=7.63, 8.55 Hz, C7-H), 7.67 (1H, dd, J=0.92, 8.55 Hz, C8-H). ^{13}C-NMR ($CDCl_3$) δ: 16.95 (C2-Me), 56.32 (C5-OMe), 61.4 (C1 and C4-OMe), 106.38 (C6), 114.81 (C8), 119.38 (C3), 119.84 (C4a), 126.64 (C7), 128.21 (C2), 130.18 (C8a), 149.70 (C4), 150.10 (C1), 155.79 (C5). HR-MS Calcd for $C_{14}H_{15}O_3Br$: 310.0203, 312.0183. Found 310.0224, 312.0190. *Anal*. Calcd for $C_{14}H_{15}O_3Br$: C, 54.04; H, 4.86. Found: C, 54.00; H, 4.96.

1,4,5-Trimethoxy-2-methylnaphthalene-3-carbaldehyde (3b) To a cooled (−78 °C) solution of **3a** (620 mg, 2.0 mmol) in anhydrous THF (3 ml) was added dropwise a solution of 1.66 M *n*-butyllithium in *n*-hexane (2.4 ml, 4.0 mmol) under an argon atmosphere during 5 min. After the mixture was stirred for 15 min, dimethyformamide (DMF; 0.62 ml, 8.0 mmol) was added and the mixture was stirred at −78 °C for 15 min. The reaction was quenched with saturated NH_4Cl solution and extracted with $CHCl_3$. The organic layer was washed with H_2O, dried, filtered, and evaporated *in vacuo*. The residue was subjected to silica gel chromatography with hexane–AcOEt (20 : 1, v/v) to give 295 mg (56.8%) of **3b**, as light yellow plates (EtOH), mp 96—98 °C. IR (KBr) cm^{-1}: 1681, 1612. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.62 (3H, s, C2-Me), 3.83 (3H, s, C1-OMe), 3.93 (3H, s, C4-OMe), 4.05 (3H, s, C5-OMe), 6.91 (1H, d, J=7.63 Hz, C6-H), 7.55 (1H, dd, J=7.63, 8.24 Hz, C7-H), 7.72 (1H, dd, J=0.92, 8.24 Hz, C8-H), 10.72 (1H, s, CHO). ^{13}C-NMR ($CDCl_3$) δ: 13.00 (C2-Me), 56.17 (C5-OMe), 61.15 (C1-OMe), 65.08 (C4-OMe), 106.22 (C6), 114.90 (C8), 118.65 (C4a), 126.05 (C3), 126.90 (C2), 129.69 (C7), 134.23 (C8a), 150.36 (C1), 157.18 (C4), 160.55 (C5), 193.35 (C2-CHO). HR-MS Calcd for $C_{15}H_{16}O_4$: 260.1048. Found 260.1067. *Anal*. Calcd for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.41; H, 6.17.

3-(Hydroxymethyl)-1,4,5-trimethoxy-2-methylnaphthalene (3c) To a solution of **3b** (260 mg, 1.0 mmol) in anhydrous MeOH (20 ml) was added dropwise a solution of $NaBH_4$ (12 mg, 0.32 mmol) in MeOH (5 ml) at 0 °C under a nitrogen atmosphere. After the mixture was stirred for 30 min, a solution of $NaBH_4$ (6 mg, 0.16 mmol) in MeOH (5 ml) was further added, the whole was stirred for 30 min. The reaction mixture was poured into ice–water and extracted with $CHCl_3$. The organic layer was washed with H_2O, dried, filtered, and evaporated *in vacuo*. The residue was recrystallized from $CHCl_3$–hexane to give 261.4 mg (99.8%) of **3c**, as colorless plates, mp 111—114 °C. IR (KBr) cm^{-1}: 3520, 1614, 1592. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.49 (3H, s, C2-Me), 3.83 (3H, s, C1-OMe), 3.86 (3H, s, C4-OMe), 4.01 (3H, s, C5-OMe), 4.92 (2H, s, –CH_2–), 6.85 (1H, d, J=7.32 Hz, C6-H), 7.40 (1H, dd, J=7.32, 8.55 Hz, C7-H), 7.69 (1H, dd, J=0.92, 8.55 Hz, C8-H). ^{13}C-NMR ($CDCl_3$) δ: 12.14 (C2-Me), 56.04 (C5-OMe), 57.71 (–CH_2–), 61.13 (C1-OMe), 63.27 (C4-OMe), 105.63 (C6), 114.72 (C8), 119.01 (C4a), 126.51 (C7), 127.08 (C3), 130.25 (C2), 131.12 (C8a), 150.06 (C1), 151.27 (C4), 156.13 (C5). MS m/z: 262 (M^+). *Anal*. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.70; H, 6.88.

3-(Bromomethyl)-1,4,5-trimethoxy-2-methylnaphthalene (3d) To a solution of thionyl bromide ($SOBr_2$; 412 mg, 2.0 mmol) in anhydrous benzene (20 ml) was added dropwise anhydrous pyridine (0.2 ml) followed by a solution of **3c** (360 mg, 1.37 mmol) in anhydrous benzene (5 ml) at 40—50 °C and the mixture was stirred at room temperature for 1 h. The reaction mixture was poured into ice–water and extracted with benzene. The organic layer was washed with H_2O, dried, filtered, and evaporated *in vacuo*. The residue was subjected to silica gel column chromatography with hexane–AcOEt (45 : 1, v/v) to give 205 mg (46%) of **3d**, as a yellow oil. IR (KBr) cm^{-1}: 1614, 1594, 1572. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.50 (3H, s, C2-Me), 3.84 (3H, s, C1-OMe), 3.95 (3H, s, C4-OMe), 4.01 (3H, s, C5-OMe), 4.86 (2H, s, –CH_2–), 6.85 (1H, d, J=7.47 Hz, C6-H), 7.41 (1H, dd, J=7.47, 8.35 Hz, C7-H), 7.69 (1H, dd, J=1.10, 8.35 Hz, C8-H). MS m/z: 324 (M^+).

General Procedure A for Nucleophilic Addition of Naphthyllithium Reagent (4a) to Electrophiles (2a, 2b, 2c, 2m) To a cooled (−78 °C) solution of **3a** (155 mg, 0.5 mmol) in anhydrous THF (4 ml) was added dropwise a solution of 1.56 M *n*-butyllithium in *n*-hexane (0.35 ml, 0.55 mmol) under an argon atmosphere during 5 min. After the mixture was stirred for 30 min, a solution of the electrophile (0.2 mmol) in anhydrous THF (4 ml) was added and the mixture was stirred at −78 °C for 30 min, then poured onto crushed ice and saturated NH_4Cl solution and extracted with $CHCl_3$. The organic layer was washed with H_2O, dried, filtered, and evaporated *in vacuo*, and the residue subjected to silica gel chromatography using the designated solvents as an eluent.

General Procedure B for the Nucleophilic Addition of Organolithium Reagents (4b or 4c) to Electrophiles (2d, 2g, 2f, 2h) To a cooled (0 °C) solution of the electrophile (1.12 mmol) in anhydrous THF (28 ml) was added dropwise a solution of 1.03 M phenyllithium in cyclohexane (**4b**; 3.26 ml, 3.36 mmol), or 1.56 M *n*-butyllithium in *n*-hexane (**4c**; 0.14 ml, 2.24 mmol) under an argon atmosphere and the mixture was stirred at 0 °C for 30 min. The reaction mixture was worked up according to the general procedure A described above.

Reaction of 4a with 2a Reaction of **4a** with **2a** was carried out at 0 °C for 30 min and worked up according to the general procedure A described above. Purification of the crude product by silica gel chromatography used $CHCl_3$–hexane–AcOEt (1 : 20 : 1, v/v/v) as an eluent. The first eluate gave 5-hydroxy-2-methyl-3-(1,4,5-trimethoxy-2-methyl-3-naphthyl)-1,4-naphthoquinone (**7a**), as orange crystals (ether–hexane), mp 95—96 °C in 22.5% yield. The second eluate gave 4,5-dihydroxy-2-methyl-4-(1,4,8-trimethoxy-3-methyl-2-naphthyl)-1(4*H*)-naphthalenone (**6a**), as orange crystals (ether–hexane), mp 185—187 °C in 30% yield. The final eluate gave 4,8-dihydroxy-3-methyl-4-(1,4,8-trimethoxy-3-methyl-2-naphthyl)-1(4*H*)-naphthalenone (**5a**), as yellow crystals (ether–hexane), mp 153—154 °C in 26% yield. **7a**: IR (KBr) cm^{-1}: 3382, 1668, 1634. ^{1}H-NMR (300 MHz, $CDCl_3$) δ:

2.00 (3H, s, C2 or C3′-Me), 2.17 (3H, s, C2 or C3′-Me), 3.63 (3H, s, C4′-OMe), 3.90 (3H, s, C1′-OMe), 4.00 (3H, s, C8′-OMe), 6.89 (1H, d, J=7.63 Hz, C7′-H), 7.29 (1H, dd, J=0.92, 8.24 Hz, C6-H), 7.47 (1H, dd, J=7.63, 8.24 Hz, C6′-H), 7.65 (1H, dd, J=7.63, 8.24 Hz, C7-H), 7.74 (1H, dd, J=0.92, 8.24 Hz, C5′-H), 7.75 (1H, dd, J=0.92, 8.24 Hz, C8-H), 12.12 (1H, s, C5-OH). HR-MS Calcd for $C_{25}H_{22}O_6$: 418.1416. Found 418.1379. *Anal*. Calcd for $C_{25}H_{22}O_6$: C, 71.76; H, 5.30. Found: C, 71.86; H, 5.20. **6a**: IR (KBr) cm^{-1}: 3504, 3272, 1662, 1646. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.45 (3H, s, C2-Me), 2.08 (3H, s, C3′-Me), 3.66 (3H, s, C4′-OMe), 4.06 (6H, s, C1′ and C8′-OMe), 6.91 (1H, s, C3-H), 6.92 (1H, d, J=7.93 Hz, C7′-H), 7.03 (1H, d , J=7.63 Hz, C6-H), 7.23 (1H, s, C5-OH), 7.40 (1H, t, J=7.63 Hz, C7-H), 7.45 (1H, dd, J=7.93, 8.24 Hz, C6′-H), 7.66 (1H, d, J=8.24 Hz, C5′-H), 7.81 (1H, dd, J=0.61, 7.63 Hz, C8-H), 8.25 (1H, s, C4-OH). HR-MS Calcd for $C_{25}H_{24}O_6$: 420.1579. Found 420.1586. *Anal*. Calcd for $C_{25}H_{24}O_6$: C, 71.41; H, 5.75. Found: C, 71.50; H, 5.85. **5a**: IR (KBr) cm^{-1}: 1654, 1607, 1569. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.83 (3H, s, C3′-Me), 1.92 (3H, s, C3-Me), 3.72 (3H, s, C4′-OMe), 4.05 (3H, s, C1′-OMe), 4.08 (3H, s, C8′-OMe), 6.32 (1H, s, C2-H), 6.67 (1H, br s, C7-H), 6.89 (1H, d, J=8.55 Hz, C5-H), 6.99 (1H, d, J=7.63, 0.92 Hz, C7′-H), 7.29—7.33 (1H, m , C6-H), 7.51 (1H, dd, J=7.63, 8.24 Hz, C6′-H), 7.71 (1H, dd, J=0.92, 8.24 Hz, C5′-H), 8.70 (1H, s, C4-OH), 12.71 (1H, s, C8-OH). ^{13}C-NMR ($CDCl_3$) δ: 12.38 (C3-Me), 20.42 (C3′-Me), 56.33 (C8′-OMe), 61.03 (C4′-OMe), 64.83 (C1′-OMe), 77.90 (C4), 107.04 (C7′), 113.78 (C8a), 114.92 (C4a), 116.98 (C5), 118.41 (C7), 118.67 (C8a), 125.77 (C2), 127.91 (C6′), 130.95 (C4a′), 135.74 (C6), 135.78 (C4a), 149.01 (C3), 151.22 (C4), 152.84 (C1′), 155.82 (C8′), 162.33 (C8), 189.76 (C1). MS m/z: 420 (M$^+$). *Anal*. Calcd for $C_{25}H_{24}O_6$: C, 71.41; H, 5.75. Found: C, 71.35; H, 5.70.

Methylation of 6a Methylation of **6a** was carried out and worked up by a procedure similar to that used for **2b**. Purification of the crude product by recrystallization from $CHCl_3$–hexane gave 4-hydroxy-5-methoxy-2-methyl-4-(1,4,8-trimethoxy-3-methyl-2-naphthyl)-1(4*H*)-naphthalenone (**6b**), as yellow crystals , mp 135—137 °C in 94.4% yield. IR (KBr) cm^{-1}: 3448, 1635, 1580. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.66 (3H, s, C2-Me), 2.04 (3H, s, C3′-Me), 3.38 (3H, s, C4′-OMe), 3.66 (3H, s, C1′-OMe), 4.02 (3H, s, C5 or C8′-OMe), 4.06 (3H, s, C5 or C8′-OMe), 6.86—7.01 (3H, m, C3-H, C6-H, and C7′-H), 7.29—7.40 (2H, m, C7-H and C6′-H), 7.67 (1H, d, J=7.97 Hz, C5′-H), 7.85 (1H, d, J=8.24 Hz, C8-H), 8.36 (1H, s, C4-OH). HR-MS Calcd for $C_{26}H_{26}O_6$: 434.1729. Found 434.1704.

Reaction of 4b with 2g Reaction of **4b** with **2g** was carried out at 0 °C for 30 min and worked up according to the general procedure B described above. Purification of the crude product by silica gel chromatography employed hexane–AcOEt (5 : 1, v/v) as an eluent. The first eluate gave 4,8-dihydroxy-2,3-dimethy1-4-phenyl-1(4*H*)-naphthalenone (**5d**), as yellow crystals (ether–hexane), mp 175—177 °C in 52.3% yield. The second eluate gave *cis*-2,3-dimethyl-1,4-diphenyl-1,4-dihydronaphthalen-1,4,5-triol (**8a**), as yellow crystals (ether–hexane), mp 190—195 °C in 9.5% yield. The final eluate gave *trans*-2,3-dimethyl-1,4-diphenyl-1,4-dihydronaphthalen-1,4,5-triol (**9a**), as yellow crystals (ether–hexane), mp 130—135 °C in 15% yield. **5d**: IR (KBr) cm^{-1}: 3450, 1642, 1604. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.87 (3H, d, J=0.61 Hz, C2 or C3-Me), 2.00 (3H, d, J=0.61 Hz, C2 or C3-Me), 2.64 (1H, s, C4-OH), 6.77—6.81 (1H, m, aromatic-H), 6.83—6.86 (1H, m, aromatic-H), 7.19—7.37 (6H, m, 6×aromatic-H), 12.78 (1H, s, C8-OH). ^{13}C-NMR ($CDCl_3$) δ: 10.95 (C2-Me), 20.42 (C3-Me), 74.15 (C4), 113.28 (C8a), 116.34 (C7), 118.84 (C5), 125.77 (C2), 125.01 (C2′ and C6′), 127.23 (C4′), 128.47 (C3′ and C5′), 130.52 (C4a), 135.48 (C6), 148.67 (C3), 161.30 (C8), 189.56 (C1). HR-MS Calcd for $C_{18}H_{16}O_3$: 280.1099. Found 280.1069. *Anal*. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.32; H, 5.65. **8a**: IR (KBr) cm^{-1}: 3564, 3394, 1584. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.52 (3H, s, C2-Me or C3-Me), 1.65 (3H, s, C2-Me or C3-Me), 2.34 (1H, s, C1-OH), 2.84 (1H, s, C4-OH), 6.64 (1H, dd, J=1.22, 7.94 Hz, C6-H), 6.70 (1H, dd, J=1.22, 7.94 Hz, C8-H), 7.08 (1H, t, J=7.94 Hz, C7-H), 7.20—7.44 (11H, m, C5-OH and aromatic-H). ^{1}H-NMR (CD_3COCD_3) δ: 1.49 (3H, s, C2-Me or C3-Me), 1.61 (3H, s, C2-Me or C3-Me), 6.03 (1H, s, C1-OH), 4.84 (1H, s, C4-OH), 6.47 (1H, dd, J=1.22, 7.94 Hz, C6-H), 6.70 (1H, dd, J=1.22, 7.94 Hz, C8-H), 6.98 (1H, t, J=7.94 Hz, C7-H), 7.13—7.62 (10H, m, C5-OH and aromatic-H), 8.00 (1H, s, C5-OH). ^{13}C-NMR ($CDCl_3$) δ: 12.76 (C2 or C3-Me), 14.81 (C2 or C3-Me), 75.16 (C1 or C4), 75.63 (C1 or C4), 115.81 (C6), 120.34 (C8), 129.74 (C7), 154.47 (C5), 125.71, 125.92, 125.97, 126.57, 127.04, 128.02, 128.04, 132.39, 132.93, 141.51, 143.34 and 146.54 (aromatic- and olefinic-C). MS m/z: 358 (M$^+$). **9a**: IR (KBr) cm^{-1}: 3432, 1588. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.55 (3H, d, J=0.88 Hz, C2-Me or C3-Me), 1.76 (3H, d, J=0.88 Hz, C2-Me or C3-Me), 2.46 (1H, s, C1-OH), 3.37 (1H, s, C4-OH), 6.64 (1H, dd, J=1.22, 7.94 Hz, C6-H), 6.93 (1H, dd, J=1.22, 7.94 Hz, C8-H), 7.15 (1H, t, J=7.94 Hz, C7-H), 7.20—7.44 (10H, m, 10×aromatic-H). MS m/z: 358 (M$^+$).

Methylation of 8a Methylation of **8a** was carried out and worked up by a procedure similar to that used for **2b**. Purification of the crude product by recrystallization from $CHCl_3$–hexane gave *cis*-5-methoxy-2,3-dimethyl-1,4-diphenyl-1,4-dihydronaphthalen-1,4-diol (**8b**), as white plates, mp 193—196 °C in 94% yield. IR (KBr) cm^{-1}: 3492, 3392, 1586. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.52 (3H, s, C2-Me), 1.62 (3H, s, C3-Me), 2.28 (1H, s, C1-OH), 3.45 (3H, s, C5-OMe), 4.68 (1H, s, C4-OH), 6.65 (1H, dd, J=1.22, 7.94 Hz, C6-H), 6.88 (1H, dd, J=1.22, 7.94 Hz, C8-H), 7.14 (1H, t, J=7.94 Hz, C7-H), 7.16—7.49 (10H, m, aromatic-H). HR-MS Calcd for $C_{25}H_{24}O_3$: 372.1725 . Found 372.1718. *Anal*. Calcd for $C_{25}H_{24}O_3$: C, 80.62; H, 6.50. Found: C, 80.82; H, 6.46.

Methylation of 9a Methylation of **9a** was carried out and worked up by a procedure similar to that used for **2b**. Purification of the crude product by recrystallization from $CHCl_3$–hexane gave *trans*-5-methoxy-2,3-dimethyl-1,4-diphenyl-1,4-dihydronaphthalen-1,4-diol (**9b**), as white plates, mp 163—166 °C in 94% yield. IR (KBr) cm^{-1}: 3494, 3418, 1599. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.58 (3H, s, C2-Me), 1.76 (3H, s, C3-Me), 2.56 (1H, s, C1-OH), 3.39 (3H, s, C5-OMe), 4.70 (1H, s, C4-OH), 6.68 (1H, dd, J=1.22, 7.94 Hz, C6-H), 7.13 (1H, dd, J=1.22, 7.94 Hz, C8-H), 7.17—7.60 (11H, m, C7-H and aromatic-H). HR-MS Calcd for $C_{25}H_{24}O_3$: 372.1725. Found 372.1727. *Anal*. Calcd for $C_{25}H_{24}O_3$: C, 80.62; H, 6.50. Found: C, 80.55; H, 6.56.

Reaction of 4a with 2b Reaction of **4a** with **2b** was carried out for 15 min and worked up according to the general procedure A described above. Purification of the crude product by silica gel chromatography used hexane–AcOEt (20 : 1, v/v) as an eluent. The eluate gave **6b** in 46.6% yield.

Reaction of 4b with 2f Reaction of **4b** with **2f** was carried out at 0 °C for 30 min and worked up according to the general procedure B described above. Purification of the crude product by silica gel chromatography used hexane–AcOEt (10 : 1, v/v) as an eluent. The first eluate gave **8b** in 15.5% yield. The second eluate gave 4-hydroxy-5-methoxy-2,3-dimethyl-4-phenyl-1(4*H*)-naphthaleneone (**6c**) as light yellow needles (ether–hexane), mp 197—200 °C in 8.6% yield. The final eluate gave **9b** in 30.5% yield. **6c**: IR (KBr) cm^{-1}: 3518, 3462, 1640, 1584. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.88 (3H, s, C3-Me), 2.00 (3H, s, C2-Me), 3.60 (3H, s, C5-OMe), 5.01 (1H, s, C4-OH), 7.00 (1H, dd, J=1.10, 7.91 Hz, C6-H), 7.20—7.32 (5H, m, aromatic-H), 7.41 (1H, t, J=7.91 Hz, C7-H), 7.91 (1H, dd, J=1.10, 7.91 Hz, C8-H). HR-MS Calcd for $C_{25}H_{24}O_3$: 294.1256. Found 294.1274. *Anal.* Calcd for $C_{25}H_{24}O_3$: C, 80.62; H, 6.50. Found: C, 80.73; H, 6.61.

Reaction of 4a with 2c Reaction of **4a** with **2c** was carried out at −78 °C for 30 min and worked up according to the general procedure A described above. Purification of the crude product by silica gel chromatography employed $CHCl_3$–hexane–AcOEt (1 : 20 : 1, v/v/v) as an eluent. The first eluate gave **7a** in 23% yield. The second eluate gave **6a** in 22.5% yield. The final eluate gave **5a** in 25% yield.

Reaction of 4b with 2h Reaction of **4b** with **2h** was carried out at 0 °C for 15 min and worked up according to the general procedure B described above. Purification of the crude product by silica gel chromatography used hexane–AcOEt (5 : 1, v/v/v) as an eluent. The first eluate gave **5d** in 48.5% yield. The second eluate gave *cis*-isomer **8a** in 15.3% yield. The final eluate gave *trans*-isomer **9a** in 10.5% yield.

Reaction of 4a with 2m Reaction of **4a** with **2m** which was prepared from **2a** (1 mmol) and $AlCl_3$ (0.5 mmol), in THF was carried out at room temperature for 30 min and worked up according to the general procedure B described above. Purification of the crude product by silica gel chromatography used $CHCl_3$–hexane–AcOEt (1 : 20 : 1, v/v/v) as an eluent. The first eluate gave **7a** in 10.5% yield. The second eluate gave **6a** in 13% yield. The final eluate gave **5a** in 15.5% yield.

Reaction of 4c with 2d Reaction of *n*-butyl lithium **4c**, (0.14 ml, 0.22 mmol) with **2d** (86 mg, 0.2 mmol) was carried out at −78 °C for 30 min and worked up according to the general procedure B described above. Purification of the crude product by silica gel chromatography employed hexane–AcOEt (20 : 1, v/v/v) as an eluent. The eluate gave 4-*n*-butyl-8-*tert*-butyldiphenylsilyloxy-4-hydroxy-3-methy1-1(4*H*)-naphthalenone (**5b**) as white crystals (ether–hexane), mp 162—164 °C in 59% yield. IR (KBr) cm^{-1}: 3376, 1656, 1629, 1589. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.75 (3H, t, J=6.16 Hz, –CH_2–C$\underline{H}_3$), 1.26—2.00 (6H, m, –C$\underline{H}_2\underline{CH}_2\underline{CH}_2$–$CH_3$), 1.15 (9H, s, *tert*-Bu), 2.08 (3H, d, J=1.32 Hz, C3-Me), 2.23 (1H, s, C4-OH), 6.20 (1H, br s, C2-H), 6.48 (1H, dd, J=1.25, 7.92 Hz, C7-H), 7.16 (1H, t, J=7.92 Hz, C6-H), 7.25—7.40 (7H, m, C8-H and aromatic-H), 7.75—7.84 (4H, m, aromatic-H). FAB-MS m/z:485 (M$^+$+1). *Anal*. Calcd for $C_{31}H_{36}O_3Si$: C, 76.81; H, 7.49. Found: C, 76.95; H, 7.53.

Desilylation of 5b Tetraethylammmonium fluoride (75 mg, 0.50 mmol)

was added under a nitrogen atmosphere to a solution of **5b** (26 mg, 0.050 mmol) in anhydrous THF (3 ml) at 0 °C and the whole was stirred for 60 min. The reaction was quenched with saturated NH_4Cl solution (5 ml) and extracted with $CHCl_3$. The organic layer was washed with H_2O, dried, and concentrated. The residue was purified by silica gel chromatography. The eluate with hexane–AcOEt (10 : 1, v/v) gave 16.1 mg (99.6 %) of 4-*n*-butyl-4,8-dihydroxy-3-methy1-1(4*H*)-naphthalenone (**5c**) as a yellow oil. IR (KBr) cm^{-1}: 3824, 1652, 1607. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.74 (3H, t, J=6.37 Hz, –CH_2–CH_3), 1.04—2.02 (6H, m, –$CH_2CH_2CH_2$–CH_3), 1.15 (9H, s, *tert*-Bu), 2.15 (3H, d, J=1.32 Hz, C3-Me), 2.40 (1H, s, C4-OH), 6.20 (1H, s, C2-H), 6.86 (1H, dd, J=1.25, 8.13 Hz, C7-H), 7.22 (1H, dd, J=1.25, 8.79 Hz, C5-H), 7.49 (1H, dd, J=8.13, 8.79 Hz, C6-H), aromatic-H), 12.44 (1H, s, C8-OH). HR-MS Calcd for $C_{15}H_{18}O_3$: 246.1256. Found 246.1271. *Anal.* Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.27; H, 7.32.

Nucleophilic Addition Reaction of 4a with 2d Reaction of **4a** with **2d** was carried out at −78 °C for 60 min and worked up according to the general procedure A described above. Purification of the crude product by silica gel chromatography used hexane–AcOEt (20 : 1, v/v) as an eluent. The first eluate gave recovered **2d** (43 mg, 20%). The second eluate gave 5-*tert*-butyldiphenylsilyloxy-2-methyl-3-(1,4,5-trimethoxy-2-methyl-3-naphthyl)-1,4-naphthoquinone (**7b**), as orange crystals (EtOH), mp 99—100 °C in 42.7% yield. The final eluate gave 8-*tert*-butyldiphenylsilyloxy-4-hydroxy-3-methyl-4-(1,4,8-trimethoxy-3-methyl-2-naphthyl)-1(4*H*)-naphthalenone (**5e**), as yellow crystals (EtOH), mp 99—101 °C, in 16.7% yield. **7b**: IR (KBr) cm^{-1}: 1658, 1620, 1584. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.08 (9H, s, *tert*-Bu), 1.91 (3H, s, C2-Me), 2.18 (3H, s, C3′-Me), 3.66 (3H, s, C4′-OMe), 3.91 (3H, s, C1′-OMe), 3.99 (3H, s, C8′-OMe), 6.73—7.93 (13H, m, 13×aromatic-H). HR FAB-MS *m*/*z*: Calcd for $C_{41}H_{40}O_6Si$: 657.2672 . Found 657.2670. *Anal*. Calcd for $C_{41}H_{40}O_6Si$: C, 74.97; H, 6.14. Found: C, 74.77; H, 6.18. **5e**: IR (KBr) cm^{-1}: 3356, 1665, 1646, 1589. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.19 (9H, s, *tert*-Bu), 1.88 (6H, s, C3 and C3′-Me), 3.72 (3H, s, C4′-OMe), 4.04 (6H, s, C1′ and C8′-OMe), 6.30 (1H, s, C2-H), 6.45 (1H, d, J=7.83 Hz, C7-H), 6.56—7.10 (3H, m, C7′-H, C6-H, and C5-H), 7.25—7.42 (6H, m, aromatic-H), 7.44—7.78 (6H, m, C6′-H, C5′-H, and aromatic-H), 8.55 (1H, s, C4-OH). HR FAB-MS *m*/*z*: Calcd for $C_{41}H_{42}O_6Si$: 659.2828. Found 659.2812. *Anal*. Calcd for $C_{41}H_{42}O_6Si$: C, 85.07; H, 7.31. Found: C, 85.01; H, 7.43.

Desilylation of 5e Desilylation of **5e** was carried out at room temperature for 2 h and worked up by a procedure similar to that used for **5c** from **5b**. Purification of the crude product by silica gel chromatography using hexane–AcOEt (5 : 1, v/v) as an eluent, gave **5a** in 99% yield.

General Procedure for Dienone-Phenol-Type Rearrangement of 5a (1,2-Migration Reaction) Method A with Bases: To a suspension or solution of **5a** (42 mg, 0.1 mmol) in various solvents (5 ml), was added a base, namely, aqueous NaOH or KOH at the designated concentration (2 ml), Et_3N (5 ml without solvent), or *tert*-BuOK (1 mmol), and the whole was heated at the designated temperatures shown in Table 2. Reactions using aqueous NaOH or KOH solution were carried out in a sealed tube. The reaction mixture was poured onto crushed ice and acidified with diluted HCl, and extracted with $CHCl_3$. The organic layer was washed with H_2O, dried, filtered, and evaporated *in vacuo*, and the residue purified by silica gel chromatography using hexane–ether (10 : 1, v/v) as eluent. The eluate gave 5-hydroxy-2-methyl-2-(1,4,8-trimethoxy-3-methyl-2-naphthyl)-2,3-dihydronaphthalen-1,4-dione (**10a**), as light yellow crystals (hexane), mp 137—139 °C. Yields and reaction conditions are listed in Table 3. IR (KBr) cm^{-1}: 3480, 1688, 1650, 1612, 1569. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.82 (3H, s, C2-Me), 2.65 (3H, s, C3′-Me), 3.05 (1H, d, J=16.48 Hz, C3-H), 3.55 (3H, s, C1′-OMe), 3.70 (3H, s, C8′-OMe), 3.81 (3H, s, C4′-OMe), 3.96 (1H, d, J=16.48 Hz, C3-H), 6.79 (1H, d, J=7.63 Hz, C7′-H), 6.91—6.95 (1H, m, C7-H), 7.34 (1H, dd, J=7.63, 8.55 Hz, C6′-H), 7.50—7.51 (2H, m, C6 and C8-H), 7.63 (1H, d, J=8.55 Hz, C5′-H), 11.26 (1H, s, C5-OMe). ^{13}C-NMR ($CDCl_3$) δ: 14.76 (C3′-Me), 23.58 (C2-Me), 50.70 (C3), 54.42 (C2), 57.75 (C8′-OMe), 61.04 (C4′-OMe), 62.01 (C6′-OMe), 108.94 (C7′), 115.38 (C5′), 117.28 (C4a), 119.16 (C8a′), 119.49 (C8), 120.43 (C6), 126.03 (C3′), 126.89 (C6′), 130.62 (C4a′), 132.15 (C2′), 136.38 (C7), 139.10 (C8a), 149.50 (C1′), 151.29 (C4′), 156.07 (C8′), 159.34 (C5), 195.98 (C1), 201.43 (C4). HR-MS Calcd for $C_{25}H_{24}O_6$: 420.1572. Found 420.1609. *Anal*. Calcd for $C_{25}H_{24}O_6$: C, 71.41; H, 5.75. Found: C, 71.22; H, 5.80.

Method B with Lewis acids: The reaction of **5a** (0.1 mmol) with various Lewis acids (0.2 mmol; $BF_3 \cdot OEt_2$, $ZnCl_2$, $MgCl_2 \cdot OEt_2$, $MgBr_2$) in several solvents (CH_2Cl_2, THF) were performed at the designated temperatures as shown in Table 2. The results are shown in Table 2.

Methylation of 10a Methylation of **10a** was carried out overnight and worked up by a procedure similar to that used for **2b** from **2a**. Purification of the crude product by recrystallization from ether–hexane gave 5-methoxy-2-methyl-2-(1,4,8-trimethoxy-3-methyl-2-naphthyl)-2,3-dihydronaphthalen-1,4-dione (**10b**), as light yellow crystals, mp 229—231 °C in 81% yield. IR (KBr) cm^{-1}: 1686, 1654, 1586. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.71 (3H, s, C2-Me), 2.61 (3H, s, C3′-Me), 2.91 (1H, d, J=15.12 Hz, C3-H), 3.46, 3.61, 3.72 (12H, each s, 3×aromatic-OMe), 3.82 (1H, d, J=15.12 Hz, C3-H), 6.69 (1H, d, J=7.69 Hz, C6 or C7′-H), 6.89 (1H, d, J=8.24 Hz, C6 or C7′-H), 7.25 (1H, t, J=7.97 Hz, C7 or C6′-H), 7.47 (1H, t, J=7.97 Hz, C7 or C6′-H), 7.55—7.58 (2H, m, C8 and C5′-H). HR-MS Calcd for $C_{26}H_{26}O_6$: 434.1729. Found 434.1694. *Anal*. Calcd for $C_{26}H_{26}O_6$: C, 71.87; H, 6.03. Found: C, 71.93; H, 6.01.

Reaction between 10b and 3d with NaH in DMF A solution of **10b** (15 mg, 0.036 mol) in anhydrous DMF (0.5 ml) was added to a solution of 55% NaH in oil suspension (3 mg, 0.07 mmol) in anhydrous DMF (0.5 ml) at 0 °C under an argon atmosphere and the mixture was stirred for 30 min. To the resulting mixture was added a solution of **3d** (35 mg, 0.11 mmol) in anhydrous DMF (0.5 ml) at 0 °C under an argon atmosphere and the whole was stirred at room temperature for 40 h. The reaction mixture was poured onto crushed ice and saturated NH_4Cl solution, and extracted with $CHCl_3$. The organic layer was washed with H_2O, dried, filtered, evaporated *in vacuo*, and the residue was subjected to silica gel chromatography using hexane–AcOEt (5 : 1, v/v) as an eluent. The first eluate gave 4 mg (13.1%) of 3-(formyloxymethyl)-1,4,5-trimethoxy-2-methynaphthalene (**13**), as orange crystals (ether–hexane), mp 79—82 °C. The second eluate gave 3 mg (20%) of **10b**, as light yellow crystals (ether–hexane). The final eluate gave 2 mg (7.3%) of **3c**, as colorless plates (ether–hexane). **13**: IR (KBr) cm^{-1}: 1713. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.43 (3H, s, C2-Me), 3.82 (3H, s, C1′-OMe), 3.85 (3H, s, C4′-OMe), 4.01 (3H, s, C5′-OMe), 5.49 (2H, s, –CH_2–), 6.87 (1H, d, J=7.15 Hz, C6-H), 7.44 (1H, dd, J=7.15, 7.52 Hz, C7-H), 7.70 (1H, dd, J=1.25, 7.52 Hz, C8-H), 8.17 (1H, m, –OCOH). HR-MS Calcd for $C_{16}H_{18}O_5$: 290.1154. Found 290.1136. *Anal*. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.39; H, 6.20.

4-Hydroxy-1,5-dimethoxy-2-methylnaphthalene (3e) A suspension of $SnCl_2 \cdot 2H_2O$ (207 mg, 0.92 mmol) in conc. HCl (0.207 ml) was added to a solution of **2b** (57 mg, 0.28 mmol) in 95% EtOH (2 ml) under a nitrogen atmosphere at 0 °C, and the mixture was stirred at room temperature for 20 min. To the reaction mixture, was added Me_2SO_4 (0.17 ml) followed by 25% aqueous KOH (1.1 ml) and the whole was stirred for 15 min. The reaction mixture was poured into ice water and acidified with diluted HCl, and the whole was extracted with ether. The ether layer was washed with H_2O, then dried and concentrated. The residue was subjected to silica gel column chromatography. The eluate with AcOEt–hexane (1 : 20, v/v) gave 41 mg (67%) of **3e**, mp 80—81 °C, as light yellow needles (ether–hexane). IR (KBr) cm^{-1}: 3390, 1632, 1612, 1582. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.37 (3H, s, C2-Me), 3.80 (3H, s, C1-OMe), 4.02 (3H, s, C5-OMe), 6.69 (1H, s, C3-H), 6.73 (1H, d, J=7.91 Hz, C6-H), 7.33 (1H, dd, J=7.91, 8.57 Hz, C7-H), 7.66 (1H, d, J=8.57 Hz, C8-H), 9.04 (1H, s, C4-OH). MS *m*/*z*: 218 (M^+). *Anal*. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.33; H, 6.55.

Bis(1-hydroxy-4,8-dimethoxy-3-methyl-2-naphthyl)methane (17a) A solution of ethyl bromide (648 mg, 6.5 mmol) in dry THF (5 ml) was added to a stirred mixture of Mg turnings (156 mg, 6.5 mmol) in dry THF (20 ml) under ultrasound irradiation, and the mixture was stirred at room temperature for 30 min. A solution of **3e** (1.09 g, 5.0 mmol) in THF (20 ml) was added dropwise to the Grignard reagent and the whole was stirred for 30 min. After evaporation of the solvent, paraformaldehyde (98 mg, 3.25 mmol) was added to the resultant residue dissolved in anhydrous benzene (80 ml), and the whole was refluxed under a nitrogen atmosphere for 2 h. The resultant solution was poured into saturated NH_4Cl in ice–water (100 ml), and extracted with $CHCl_3$ (×3). The $CHCl_3$ layer was washed with H_2O, dried and concentrated. The residue was subjected to silica gel chromatography. The eluate with hexane–AcOEt (20 : 1, v/v) gave 2.07 g (92.2%) of **17a**, as white crystals ($CHCl_3$–hexane), mp 224—226 °C. IR (KBr) cm^{-1}: 3404, 1626, 1606, 1578. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.26 (6H, s, C3 and C3′-Me), 3.72 (6H, s, C4 and C4′-OMe), 3.99 (6H, s, C8 and C8′-OMe), 4.41 (2H, s, –CH_2–), 6.70 (2H, d, J=7.63 Hz, C-7 and C-7′-H), 7.26 (2H, dd, J=7.63, 8.55 Hz, C-6 and C-6′-H), 7.64 (2H, d, J=8.55 Hz ,C-5 and C-5′-H), 9.53 (2H, s, C-1 and C-1′-OH). ^{13}C-NMR ($CDCl_3$) δ: 12.36 (C-3 and C-3′-Me), 23.99 (–CH_2–), 55.98 (C8 and C8′-OMe), 61.07 (C4- and C4′-OMe), 103.44 (C7 and C7′), 113.55 (C8a and C8a′), 115.65 (C5 and C5′), 122.46 (C2 and C2′), 124.73 (C6 and C6′), 128.60 (C3 and C3′), 129.86 (C4a and C4a′), 145.88 (C1 and C1′), 147.81 (C4 and C4′), 156.00 (C8 and C8′). HR-MS Calcd for $C_{27}H_{28}O_6$: 448.1886. Found 448.1899. *Anal*. Calcd for $C_{27}H_{28}O_6$: C, 72.30; H, 6.29. Found: C, 72.11; H, 6.38.

1,5-Dimethoxy-4-hydroxy-2-methyl-3-[(1,4,8-trimethoxy-3-methyl-2-naphthyl)methyl]naphthalene (17b) Tetra-*n*-butylbutylammonium hydrogensulfate (400 mg, 1.18 mmol), 2 N aqueous NaOH (8 ml), and Me_2SO_4 (600 mg, 4.76 mmol) were added to a solution of **17a** (1.07 g, 2.39 mmol) in anhydrous CH_2Cl_2 (15 ml), and the whole was stirred at room temperature for 30 min under a nitrogen atmosphere. The reaction mixture was poured into ice–water and extracted with ether. The organic layer was washed with H_2O, then dried and concentrated. The residue was subjected to silica gel chromatography. The eluate with CH_3CO_2Et–hexane (2 : 3, v/v) gave 761 mg (71.1%) of **17b** as colorless crystals (ether–hexane), mp 184—186 °C. IR. (KBr) cm^{-1}: 3380, 1629, 1607, 1589, 1571. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.19 (3H, s, C2-Me), 2.21 (3H, s, C3′-Me), 3.67 (3H, s, C1′-OMe), 3.71 (3H, s, C1-OMe), 3.75 (3H, s, C4′-OMe), 4.00 (3H, s, C5-OMe), 4.02 (3H, s, C8′-OMe), 4.50 (2H, s, –CH_2–), 6.73 (1H, d, J=7.63 Hz, C6-H), 6.83 (1H, d, J=7.63 Hz, C7′-H), 7.28 (1H, dd, J=7.63, 8.54 Hz, C7-H), 7.34 (1H, dd, J=7.63, 8.24 Hz, C6′-H), 7.64 (1H, d, J=8.54 Hz, C8-H), 7.67 (1H, dd, J=8.24 Hz, C5′-H), 9.54 (1H, s, C4-OH). ^{13}C-NMR ($CDCl_3$) δ: 12.57 (C3′-Me), 12.77 (C2-Me), 24.73 (–CH_2–), 56.07 (C8′-OMe), 56.28 (C5-OMe), 61.05 (C4′-OMe), 61.11 (C1-OMe), 62.20 (C1′-OMe), 103.48 (C6), 105.48 (C7′), 113.60 (C4a or C8a′), 114.71 (C5′), 115.73 (C8), 119.10 (C4a or C8a′), 122.21 (C3), 124.91 (C7), 125.36 (C6′), 128.76 (C2), 128.81 (C3′), 129.69 (C8a), 129.77 (C4a′), 132.05 (C2′), 146.11 (C4), 147.86 (C1′), 149.76 (C1), 150.43 (C4′), 156.03 (C5), 156.07 (C8′). HR-MS Calcd for $C_{28}H_{30}O_6$: 462.2042. Found 462.2026. *Anal*. Calcd for $C_{28}H_{30}O_6$: C, 72.71; H, 6.54. Found: C, 72.70; H, 6.57.

5-Methoxy-2-methyl-3-[(1,4,8-trimethoxy-3-methyl-2-naphthyl)methyl]-1,4-naphthoquinone (18) 10% $FeCl_3$ aqueous solution (5 ml) was added to **17b** (180 mg, 0.39 mmol) in CH_3CN (20 ml), and the mixture was stirred at room temperature for 1 h. The reaction mixture was poured into ice–water and extracted with $CHCl_3$ (×3). The $CHCl_3$ layer was washed with H_2O, dried, concentrated, and the residue subjected to silica gel chromatography. The eluate with CH_3CO_2Et–hexane (1 : 10, v/v) gave 168 mg (99%) of **18** as colorless needles ($CHCl_3$–hexane), mp 270—272 °C. IR (KBr) cm^{-1}: 1651, 1616, 1585. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.87 (3H, s, C2-Me), 2.41 (3H, s, C3′-Me), 3.70 (3H, s, C1′-OMe), 3.81 (3H, s, C4′-OMe), 3.94 (3H, s, C8′-OMe) , 3.99 (3H, s, C5-OMe), 4.24 (2H, s, –CH_2–), 6.81 (1H, d, J=7.81 Hz, C7′-H), 7.25 (1H, d, J=8.44 Hz, C6-H), 7.35 (1H, d, J=7.81, 8.26 Hz, C6′-H), 7.60 (1H, dd, J=7.71, 8.44 Hz, C7-H), 7.67 (1H, d, J=8.26 Hz, C5′-H), 7.70 (1H, d, J=7.71 Hz, C8-H). ^{13}C-NMR ($CDCl_3$) δ: 12.10 (C2 or C3′-Me), 13.61 (C2 or C3′-Me), 24.92 (–CH_2–), 56.15 (C8′-OMe), 56.44 (C5-OMe), 61.19 (C4′-OMe), 62.12 (C1′-OMe), 105.72 (C7′), 114.76 (C5′), 117.19 (C6), 118.87 (C8), 119.15 (C8a′), 120.95 (C4a), 125.79 (C6′), 127.42 (C3′), 129.59 (C2′), 130.10 (C4a′), 134.11 (C7), 134.53 (C8a), 140.65 (C2), 148.70 (C3), 149.95 (C4′), 150.48 (C1′), 155.80 (C8′), 159.33 (C5), 183.86 (C4), 185.58 (C1). HR-MS Calcd for $C_{27}H_{26}O_6$: 446.1729. Found 446.1749. *Anal*. Calcd for $C_{27}H_{26}O_6$: C, 72.63; H, 5.87. Found: C, 72.65; H, 5.89.

5-Hydroxy-2-methyl-3-[(1,4,8-trimethoxy-3-methyl-2-naphthyl)methyl]-1,4-naphthoquinone (20a) Magnesium bromide hexahydrate (3.52 g, 12 mmol) was added to a solution of **18** (223 mg, 0.50 mmol) dissolved in anhydrous toluene (50 ml) and the whole was refluxed for 12 h. The reaction was quenched with cooled water and saturated NH_4Cl solution, and the whole stirred for 30 min. The mixture was extracted with $CHCl_3$, and the $CHCl_3$ layer washed with H_2O, dried, concentrated, and the residue recrystallized from ether–hexane to yield 212 mg (97.9%) of **20a** as orange plates, mp 185—188 °C. IR (KBr) cm^{-1}: 1655, 1632, 1611. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.94 (3H, s, C2-Me), 2.44 (3H, s, C3′-Me), 3.68 (3H, s, C1′-OMe), 3.83 (3H, s, C4′-OMe), 3.94 (3H, s, C8′-OMe), 4.20 (2H, s, –CH_2–), 6.82 (1H, d, J=7.63 Hz, C7′-H), 7.22 (1H, dd, J=1.53, 7.94 Hz, C6-H), 7.37 (1H, dd, J=7.63, 8.54 Hz, C6′-H), 7.55 (1H, dd, J=7.63, 7.94 Hz, C7-H), 7.59 (1H, dd, J=1.53, 7.63 Hz, C8-H), 7.68 (1H, d, J=8.54 Hz, C5′-H), 12.27 (1H, s, C5-OH). ^{13}C-NMR ($CDCl_3$) δ: 12.73 (C2-Me), 13.59 (C3′-Me), 24.32 (–CH_2–), 56.14 (C8′-OMe), 61.29 (C4′-OMe), 62.22 (C1′-OMe), 105.78 (C7′), 114.81 (C5′), 115.02 (C4a), 118.78 (C8), 119.12 (C8a′), 123.61 (C6), 126.02 (C6′), 127.30 (C3′), 128.99 (C2′), 130.26 (C4a′), 132.38 (C8a), 135.79 (C7), 144.61 (C2), 146.66 (C3), 150.04 (C4′), 150.65 (C1′), 155.81 (C8′), 161.30 (C5), 184.65 (C1), 189.71 (C4). HR-MS Calcd for $C_{26}H_{24}O_6$: 432.1573. Found 432.1535. *Anal*. Calcd for $C_{26}H_{24}O_6$: C, 72.21; H, 5.59. Found: C, 72.18; H, 5.61.

5-*tert*-Butyldiphenylsilyloxy-2-methyl-3-[(1,4,8-trimethoxy-3-methyl-2-naphthyl)methyl]-1,4-naphthoquinone (20b) *tert*-Butyldiphenylsilyl chloride (TBDPSCl; 107.8 mg, 0.39 mmol) was added at 5 °C to a solution of **20a** (43.2 mg, 0.10 mmol) in anhydrous benzene (2 ml) and stirred for 2 min. 1,8-Diazabicyclo[5.4.0]-7-undecene (DBU; 190 mg, 1.26 mmol) was added slowly to the resultant mixture and the whole was stirred for 45 min. The precipitates were separated by filtration and the filtrate was washed with H_2O, dried, and concentrated. The residue was then subjected to silica gel chromatography. The eluate with $CHCl_3$–hexane–AcOEt (1 : 20 : 1, v/v/v) gave 59 mg (87.9%) of **20b** as yellow crystals (ether–hexane), mp 153—159 °C. IR (KBr) cm^{-1}: 1657, 1631, 1621, 1584. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.11 (9H, s, *tert*-Bu), 1.95 (3H, s, C2-Me), 2.46 (3H, s, C3′-Me), 3.73 (3H, s, C1′-OMe), 3.81 (3H, s, C4′-OMe), 3.96 (3H, s, C8′-OMe), 4.27 (2H, s, –CH_2–), 6.71 (1H, d, J=8.24 Hz, C6-H), 6.82 (1H, d, J=7.94 Hz, C7′-H), 7.13 (1H, t, J=7.94 Hz, C6′-H), 7.35 (1H, t, J=8.24 Hz, C7-H), 7.37—7.45 (6H, m, aromatic-H), 7.61 (1H, d, J=7.94 Hz, C5′-H), 7.68 (1H, d, J=8.24 Hz, C8-H), 7.74—7.76 (4H, m, aromatic-H). HR FAB-MS *m*/*z*: Calcd for $C_{42}H_{43}O_6Si$: 671.2828. Found 671.2823. *Anal*. Calcd for $C_{42}H_{43}O_6Si$: C, 75.08; H, 6.45. Found: C, 75.28; H, 6.50.

8-*tert*-Butyldiphenylsilyloxy-4-hydroxy-3-methyl-4-(1,4,8-trimethoxy-3-methyl-2-naphthyl)-2-[(1,4,8-trimethoxy-3-methyl-2-naphthyl)methyl]-1(4*H*)-naphthalenone (21a) *n*-Butyllithium (1.56 M in *n*-hexane; 0.35 ml, 0.55 mmol) was added to a solution of **3a** (155 mg, 0.50 mmol) in anhydrous THF (3 ml) at −78 °C under an argon atmosphere. The mixture was stirred at −78 °C for 30 min, then **20b** (134.2 mg, 0.2 mol) in THF (3 ml) was added slowly. The whole was stirred at −78 °C for 15 min and the reaction quenched with saturated aqueous NH_4Cl solution (10 ml). The mixture was extracted with $CHCl_3$ (50 ml×3), and the organic solution washed with H_2O, then dried and concentrated. The residue was purified by silica gel column chromatography. The eluate with $CHCl_3$–hexane–AcOEt (1 : 5 : 1, v/v/v) gave 140 mg (77.5%) of **21a** as colorless prisms, mp 186—189 °C (ethanol). IR (KBr) cm^{-1}: 1648, 1614, 1590, 1569. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.19 (9H, s, *tert*-Bu), 1.60 (3H, s, C3-Me), 1.65 (3H, s, C3″-Me), 2.34 (3H, s, C3′-Me), 3.49, 3.79, 3.94, 3.95, 4.00 (18H, each s, 6×aromatic-OMe), 4.24 (1H, d, J=14.97 Hz, –CH_2–), 4.48 (1H, d, J=14.97 Hz, –CH_2–), 6.43 (1H, d, J=8.24 Hz, aromatic-H), 6.52 (1H, br s, aromatic-H), 6.55 (1H, s, C4-OH), 6.77—6.80 (2H, m, aromatic-H), 6.90 (1H, d, J=7.63 Hz, aromatic-H), 7.25—7.44 (8H, m, aromatic-H), 7.59 (1H, d, J=8.24 Hz, aromatic-H), 7.65 (1H, d, J=8.24 Hz, aromatic-H), 7.75—7.88 (4H, m, aromatic-H). HR FAB-MS *m*/*z*: Calcd for $C_{56}H_{59}O_9Si$: 903.3928. Found 903.3956. *Anal*. Calcd for $C_{56}H_{59}O_9Si$: C, 74.39; H, 6.58. Found: C, 74.36; H, 6.59.

4,8-Dihydroxy-3-methyl-4-(1,4,8-trimethoxy-3-methyl-2-naphthyl)-2-[(1,4,8-trimethoxy-3-methyl-2-naphthyl)methyl]-1(4*H*)-naphthalenone (21b) A 1.0 M solution of *n*-Bu_4N·F in THF (0.1 ml, 0.1 mmol) was added under a nitrogen atmosphere to a solution of **21a** (361 mg, 0.40 mmol) in anhydrous THF (2 ml) at 0 °C and stirred for 60 min. The reaction was quenched with saturated NH_4Cl solution (10 ml) and extracted with $CHCl_3$. The organic layer was washed with H_2O, dried, concentrated, and the residue subjected to silica gel chromatography. The eluate with $CHCl_3$–hexane–AcOEt (1 : 1 : 1, v/v/v) gave 263 mg (99%) of **21b** as yellow crystals ($CHCl_3$–hexane), mp 142—143 °C. IR (KBr) cm^{-1}: 3356, 3320, 1639, 1596, 1569. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.66 (3H, s, C3-Me), 1.79 (3H, s, C3″-Me), 2.36 (3H, s, C3′-Me), 3.52 (3H, s, C4″-OMe), 3.75 (3H, s, C1′-OMe), 3.79 (3H, s, C4′-OMe), 3.94 (6H, s, C8″-and C1″-OMe), 4.02 (3H, s, C8′-OMe), 4.14 (1H, d, J=15.56 Hz, –CH_2–), 4.42 (1H, d, J=15.56 Hz, –CH_2–), 6.56 (1H, br s, C7-H), 6.80 (1H, d, J=7.43 Hz, C7″-H), 6.90—6.93 (1H, m, C5-H), 6.92 (1H, d, J=7.93 Hz, C7′-H), 7.24—7.27 (1H, m, C6-H), 7.32 (1H, dd, J=7.43, 8.55 Hz, C6″-H), 7.43 (1H, dd, J=7.93, 8.24 Hz, C6′-H), 7.61 (1H, d, J=8.55 Hz, C5″-H), 7.64 (1H, d, J=8.24 Hz, C5′-H), 8.50 (1H, s, C4-OH), 13.11 (1H, s, C8-OH). ^{13}C-NMR ($CDCl_3$) δ: 12.26 (C3 and C3″-Me), 13.52 (C3′-Me), 22.44 (–CH_2–), 56.16 (C8″-OMe), 56.33 (C8′-OMe), 60.75 (C4″-OMe), 61.08 (C4′-OMe), 62.24 (C1′-OMe), 64.55 (C1″-OMe), 78.74 (C4), 105.98 (C7″), 106.98 (C7′), 113.74 (C8a), 114.65 (C5′ and C5″), 116.87 (C5), 117.95 (C7), 118.35 (C8a′), 119.21 (C8a″), 125.64 (C6″), 126.01 (C3″), 127.28 (C6′), 127.89 (C2′), 129.00 (C2″), 129.90 (C4a″), 130.49 (C3′), 130.83 (C4a′), 133.55, 135.35 (C6), 138.55 (C4a), 142.56 (C3), 148.66 (C2), 149.86 (C4′), 150.45 (C1′), 151.01 (C4″), 152.76 (C1″), 155.79 (C8″), 156.06 (C8’), 162.60 (C8), 188.85 (C1). HR-MS Calcd for $C_{40}H_{40}O_9$: 664.2672. Found 664.2657. *Anal*. Calcd for $C_{40}H_{40}O_9$: C, 72.27; H, 6.07. Found: C, 72.37; H, 6.01.

5-Hydroxy-2-methyl-2-(1,4,8-trimethoxy-3-methyl-2-naphthyl)-3-[(1,4,8-trimethoxy-3-methyl-2-naphthyl)methyl]-2,3-dihydronaphthalen-1,4-dione (11b) A solution of **21b** (50 mg, 0.075 mmol) in EtOH (1 ml) and aqueous 2 N NaOH (2 ml) was heated at 180 °C in a sealed tube for 25 min. The reaction mixture was poured into ice water and acidified with diluted HCl, and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried, concentrated, and the residue subjected to silica gel column chromatography. The eluate with $CHCl_3$–hexane–AcOEt (1 : 10 : 1, v/v/v)

gave 7.5 mg (15%) of **11b**, mp 214—215 °C, as yellow crystals (hexane). The second eluate gave 7.5 mg (13%) of **21b**. IR (KBr) cm^{-1}: 1690, 1650, 1612. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.03 (3H, s, C2-Me), 2.17 (3H, s, C3′-Me), 2.64 (3H, s, C3″-Me), 2.82 (1H, t, J=12.82 Hz, –CH_2–), 3.25 (1H, d, J=12.82 Hz, –CH_2–), 3.50 (3H, s, C4″-Me), 3.56 (3H, s, C1″-OMe), 3.61 (3H, s, C4′-OMe), 3.68 (3H, s, C1′-OMe), 3.78 (3H, s, C8′-OMe), 3.92 (1H, s, C8″-OMe), 4.25 (1H, br s, C3-H), 6.78 (1H, d, J=7.02 Hz, C7′-H), 6.83 (1H, d, J=7.63 Hz, C7″-H), 6.94 (1H, d, J=8.24 Hz, C6-H), H), 7.31 (1H, dd, J=7.02, 8.55 Hz, C6′-H), 7.34 (1H, dd, J=7.63, 8.55 Hz, C6″-H), 7.52 (1H, dd, J=7.63, 8.24 Hz, C7-H), 7.59 (1H, dd, J=7.63 Hz, C8-H), 7.61 (1H, dd, J=8.55 Hz, C5′-H), 7.66 (1H, dd, J=8.55 Hz, C5″-H), 10.95 (1H, s, C5-OH). ^{13}C-NMR ($CDCl_3$) δ: 15.50 (C3′ and C3″-Me), 19.50 (C2-Me), 28.04 (–CH_2–), 30.93 (C3′-Me), 57.04 (C2), 57.21 (C8″-OMe), 57.72 (C3), 58.16 (C8′-OMe), 60.89 (C4″-OMe), 61.08 (C4′-OMe), 61.43 (C1′-OMe), 61.89 (C1″-OMe), 107.67 (C7″), 110.00 (C7′), 115.27 (C5″), 115.61 (C5′), 116.12 (C4a), 118.74 (C8), 119.31 (C8a″), 119.74 (C8a′), 120.34 (C6), 125.99 (C6″), 126.34 (C3′), 126.64 (C3″), 126.86 (C6′), 128.34 (C2′), 130.50 (C4a″), 130.57 (C4a′), 134.29 (C2″), 135.60 (C7), 138.75 (C8a), 148.84 (C1′), 149.85 (C4″), 150.96 (C1″), 151.61 (C4′), 156.13 (C8′ or C8″), 156.19 (C8′ or C8″), 159.38 (C5), 194.82 (C1), 206.95 (C4). HR-MS Calcd for $C_{40}H_{40}O_9$: 664.2672. Found 664.2648. *Anal*. Calcd for $C_{40}H_{40}O_9$: C, 72.27; H, 6.07. Found: C, 72.30; H, 6.09.

(±)-Plumbazeylanone (1) A solution of aluminum powder (124.86 mg, 4.62 mmol) and I_2 (881 mg, 6.94 mmol) in anhydrous benzene (5 ml) was stirred under nitrogen atmosphere for 30 min, then further aluminum powder (124.86 mg, 4.62 mmol) was added. The mixture was stirred for 30 min, after which the red-purple color had faded. A solution of **11b** (6.4 mg, 0.01 mmol) in benzene (2 ml) was then added to the above mentioned solution (AlI_3) and the whole was stirred at room temperature for 3 h. The reaction mixture was poured into ice water and acidified with diluted HCl, and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried, concentrated, and the residue subjected to silica gel column chromatography. The eluate with $CHCl_3$–hexane–AcOEt (1 : 10 : 1, v/v/v) gave 2.5 mg (45%) of 5-hydroxy-2-(8-hydroxy-3-methyl-1,4-dioxo-2-naphthyl)-3-[(8-hydroxy-3-methyl-1,4-dioxo-2-naphthyl)methyl]-2-methyl-2,3-dihydronaphthalen-1,4-dione (**1**), mp 245—248 °C, as orange crystals ($CHCl_3$–hexane). IR (KBr) cm^{-1}: 1694, 1654, 1630. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.83 (3H, s, C2-Me), 2.35 (3H, s, C3′ or C3″-Me), 2.51 (3H, s, C3′ or C3″-Me), 2.75 (1H, dd, J=3.12, 13.08 Hz, –CH_2–), 3.27 (1H, dd, J=9.34, 13.08 Hz, –CH_2–), 4.31 (1H, dd, J=3.12, 9.34 Hz, C3-H), 7.08—7.72 (9H, m, aromatic-H), 11.43, 11.47 and 11.57 (3H, each s, aromatic-OH). ^{13}C-NMR ($CDCl_3$) δ: 13.50 (C3″-Me), 13.70 (C2-Me), 21.12 (C3′-Me), 24.13 (–CH_2–), 55.75 (C2), 57.72 (C3), 114.56 (C8a′ or C8a″), 115.13 ((C8a′ or C8a″), 116.41 (C4a), 119.00 (C5′ or C5″), 119.26 (C5′ or C5”), 119.73 (C8), 123.43 (C7′ or C7″), 123.81 (C7′ or C7″), 124.16 (C6), 131.44 (C4a′ or C4a″), 131.85 (C4a′ or C4a″), 132.81 (C8a), 136.16 (C6′ or C6″), 136.46 (C6′ or C6″), 137.12 (C7), 143.53 (C2″), 147.07 (C3′ or C3″), 147.27 (C3′ or C3″), 148.73 (C2′), 160.45 (C5), 161.05 (C8’ or C8″), 161.23 (C8′ or C8″), 184.12 (C4′ or C4″), 183.66 (C4′ or C4″), 189.78 (C1′ or C1″), 190.06 (C1′ or C1″), 196.35 (C1), 202.82 (C4). HR-MS Calcd for $C_{34}H_{24}O_9$: 576.1420. Found 576.1427. *Anal*. Calcd for $C_{34}H_{24}O_9$: C, 70.83; H, 4.20. Found: C, 70.73; H, 4.25.

References and Notes

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