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Biomimetic synthesis of the dinaphthofuranquinone violet-quinone, utilizing oxidative dimerization with the ZrO_2/O_2 system

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Abstract—The first total and biomimetic synthesis of violet-quinone (**1**), which has a dinaphthofuranquinone (DNFQ) framework, is described. This synthesis features the oxidative dimerization of 1-naphthol **4** and the construction of the DNFQ framework by photochemical ring closure of 2,2′-binaphthoquinone **7** as a key intermediate. Compound **7** was prepared by the novel oxidative dimerization of **4** with a semiconductor (such as ZrO_2) in the presence of dioxygen, followed by oxidation of the resulting 2,2′-binaphthyl-1,1′-quinone **6** with HNO_3.

1. Introduction

Among natural biarylquinones, dinaphthofuranquinones (DNFQ) such as violet-quinone (**1**)[1] and balsaminone A (**2**),[2] and dibenzofuranquinones (DBFQ) such as popolohuanone E (**3**),[3] having the dibenzofuran-1,4-dione moiety as a key structural element, have been isolated from several plants and marine products. Compounds **2** and **3** show antipruritic activity[2] and selective cytotoxicity against A549 non-small cell lung cancer cells, respectively (Fig. 1).[3]

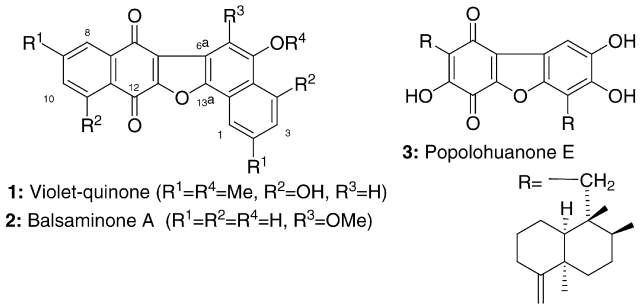

Figure 1.

A possible biogenetic pathway to biarylfuranquinones **E** (DNFQs and DBFQs) would involve (i) the oxidative biaryl coupling of the corresponding two aryls **A** (1-naphthols or phenols), (ii) selective oxidation of biaryls **B**, and (iii) subsequent intramolecular ring closure of biarylquinones **C** or **D** to form the corresponding furan rings, as shown in Figure 2.[3] There is some support for such a biogenetic pathway. Thus, violet-quinone (**1**), along with diosindigo B (**6c**) and biramentaceone (**7c**), which are related to the intermediates **C** and **D**, have been isolated from the heartwood of *Diospyros melanoxyloin*,[1] and its congener *Diospyros celebica*[4] also contains dihydrodiosindigo B (**5c**), corresponding to **B**, together with **6c** and **7c** (refer to Fig. 2, Schemes 2 and 3).

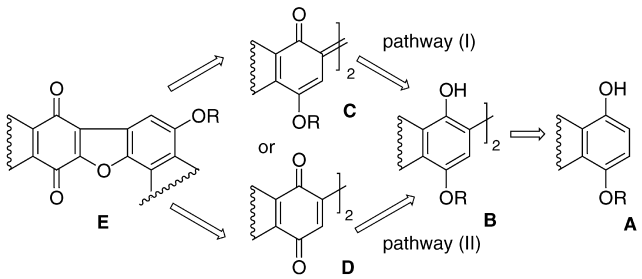

Figure 2.

Although the synthesis of **3** has been explored[5] owing to the biological activity of **3**, as described above, a total synthesis has not yet been achieved. Violet-quinone (**1**) has an analogous framework (the diarylfuran-1,4-dione moiety) to popolohuanone E (**3**). From the viewpoint of the structure–cytotoxic activity relationship of **3**, compound **1** is of great interest as a synthetic target. As yet, its synthesis has not yet been accomplished.

Several methods have been developed for the preparation of

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2,2′-binaphthyl derivatives such as **B**, **C** and **D** by the oxidative dimerization of 1-naphthols. These involve chemical,[6] electrolytic,[7] thermal disproportionation[8] and air oxidation[9] reactions. However, the reactions are difficult to control, mostly showing poor selectivity and low yield of the desired products, accompanied with side reactions.

Recently, much attention has been focused on the use of various semiconductor catalysts,[10] particularly TiO_2, to achieve a variety of organic reactions and syntheses on the basis of the concept of green chemistry.[11] More recently, we developed a new and efficient method for the direct synthesis of 2,2′-binaphthyls, utilizing an oxidative dimerization of 1-naphthols (NPOH), with semiconductors such as ZrO_2 and activated charcoal (Act-C) in the presence of dioxygen (O_2).[12]

This method has stimulated further studies with the aim of applying it to biomimetic synthesis of natural products. Here, we present the first total synthesis of violet-quinone (**1**), utilizing the oxidative dimerization of NPOH **4b** with the ZrO_2/O_2 reagent system.

2. Results and discussion

2.1. Synthetic plan

For our feasibility study, we envisioned the biomimetic synthesis of DNFQ **1** through pathway (I) or (II), based on our biogenetic hypotheses mentioned above (Fig. 2).

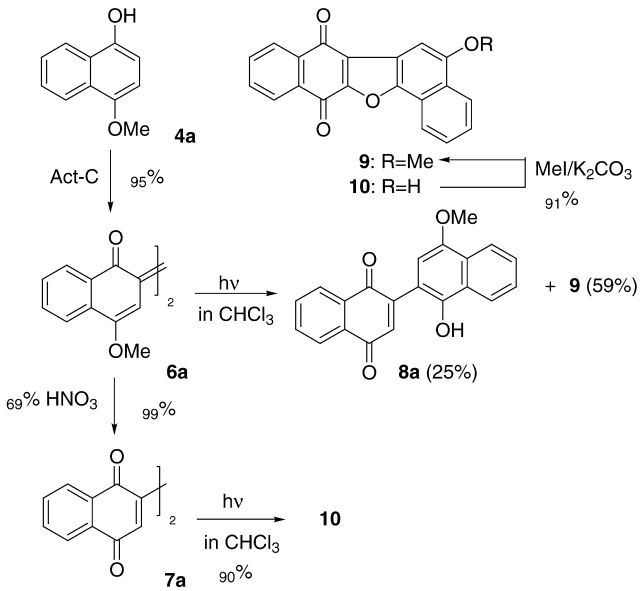
Pathway (I) consists of the formation of 2,2′-binaphthyl-1,1′-quinone (**6**; BNPTQ), which is related to intermediate **C**, by the oxidative dimerization of NPOH **4** and the construction of DNFQ framework by intramolecular ring closure of **6**. In contrast, pathway (II) involves the formation of 2,2′-binaphthoquinone (**7**; BNPQ), which is related to intermediate **D**, and the construction of DNFQ framework by ring closure of **7**. These approaches are attractive because of the simplicity of the reaction and its possible involvement in biosynthesis of naturally occurring DNFQs and DBFQs as described above.

2.2. Preliminary experiments for synthesis of violet-quinone

As a prelude to the synthesis of violet-quinone (**1**), preliminary experiments using 4-methoxy-1-naphthol **4a** as a model substrate were examined. These were based on pathways (I) and (II) described above (Scheme 1).

First, BNPTQ **6a**,[13a] the required model intermediate in pathway (I), was prepared in 95% yield by the oxidative dimerization of **4a** with the Act-C/O_2 system[12] in MeCN. The reaction with the ZrO_2/O_2 system under similar conditions gave **6a** (75%) along with 4-methoxy-1,2-naphthoquinone (17%). Subsequently, **6a** could be easily converted to BNPQ **7a**[13d] as the model intermediate in pathway (II), in 99% yield, by oxidation with 69% HNO_3.

Several methods have been reported for the construction of the DNFQ framework by ring closure of BNPTQs or



Scheme 1.

BNPQs. These include photochemical,[13a,d] thermal,[13e] and chemical (with acid[13d] or base[13f–h]) reactions. We examined the photolysis of **6a** and **7a** under various conditions.

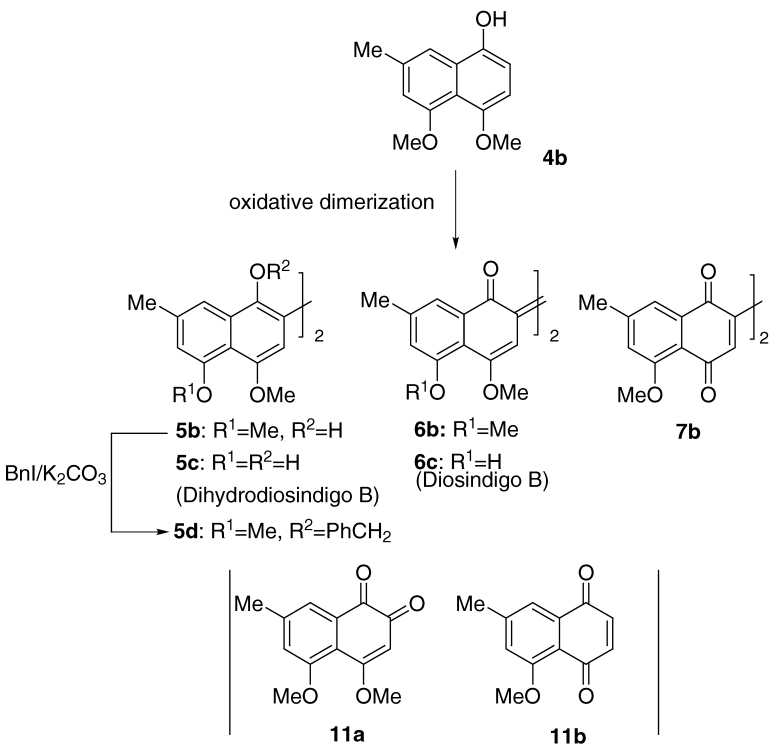
The photolysis of **6a** using a 60 W Hg lamp in $CHCl_3$ with a Pyrex vessel for a long time (80 h) gave **8a**[13a] in 88% yield. When we used a 450 W Hg lamp under similar conditions but for a short time (1 h), DNFQ **9** (59%) and **8a** (25%) were obtained. In the photolysis of **7a**, the best result was obtained with a 450 W Hg lamp in $CHCl_3$ for 2 h, affording DNFQ **10** in 90% yield, and methylation of **10** with CH_3I gave **9** in 91% yield. This mechanism for the photochemical conversion of **7a** into **10** was proposed to proceed via ring closure with rearrangement.[13d,i] The synthetic compounds **9**[13a] and **10**[13d,e] were identical with the corresponding compounds reported previously. In addition, the structures **9** and **10** were confirmed by analyses of the IR, ^{1}H-, ^{13}C NMR spectra with the aid of 2D NMR analyses.

2.3. First total synthesis of violet-quinone

On the basis of the results and information obtained from the above model experiments, the synthesis of **1** utilizing **7b** as the key intermediate was investigated based on pathway (II). First, NPOH **4b** was synthesized according to the protocol reported previously.[14a,b,15a]

In order to obtain BNPOH **5b** or BNPTQ **6b** as a precursor for obtaining **7b**, oxidative dimerization of **4b** using several reagents was examined (Table 1 and Scheme 2). The reaction with Ag_2O gave a mixture of **5b**, **6b** and the *ortho*-naphthoquinone **11a** (entry 1). However, **5b** could not be isolated because it proved very susceptible to air oxidation and decomposition. The structure **5b** was thus confirmed by converting this compound into the benzylated derivative **5d**.

In the case of the well-known AgO/HNO_3 system,[6m] the desired compound **7b** was obtained in one step, but the yield was not satisfactory (entry 2). Laatsch[15a] reported that the



Scheme 2.

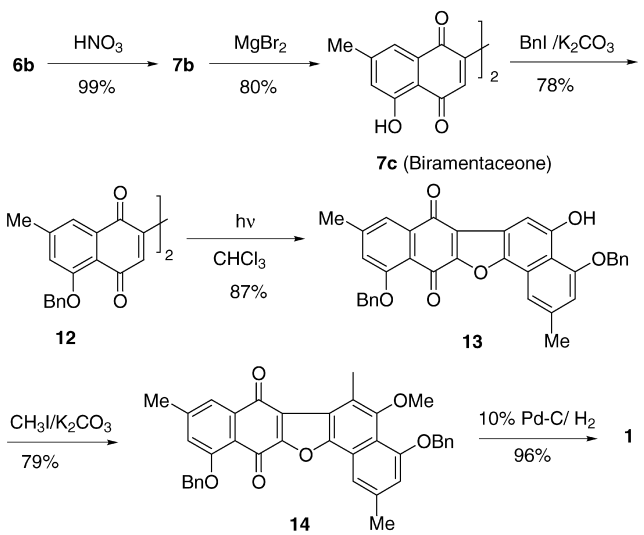
oxidative dimerization of **4b** with the Ag_2O/NEt_3 system[6n] gave only **6b** without any by-product. Re-examination of the reaction by us afforded **6b** (92%) together with the *para*-naphthoquinone **11b** (4%) (entry 3). The best result was obtained by employing the novel oxidative dimerization with the ZrO_2/O_2 reagent system, which we recently developed, affording BNPTQ **6b**[15a] selectively in excellent yield (entry 5). Subsequent oxidation of **6b** with 69% HNO_3 produced **7b**[15a] in 99% yield. When **6b** prepared by means of the above oxidation was used without purification, **7b** was obtained in a similar yield.

Furthermore, the synthesis of **1** from the resulting **7b** was investigated, as shown in Scheme 3. Magnesium bromide ($MgBr_2$) effected demethylation of the methoxyl group of **7b** to produce **7c** as a natural product, the so-called biramentaceone,[15a] in 80% yield. The naphtholic hydroxyl group of **7c** was protected with a benzyl group using benzyl iodide[16] in the presence of K_2CO_3 to yield BNPQ **12**. Subsequently, the ring closure of **12** was achieved by means of photolysis[13a,b] using a 450 W Hg lamp in $CHCl_3$ with a Pyrex vessel for 1 h to give DNFQ **13** in 87% yield. Next, compound **14** was obtained by methylation of **13** with methyl iodide. Finally, the reductive deprotection of the benzyl group of **14** with 10% Pd/C–H_2 gave violet-quinone (**1**) in 96% yield, as a violet solid. All physical data, such as the melting point, MS (Mass), IR (infrared) and ^1H NMR spectra of the synthetic product **1** were identical with those of the natural product.[1]

Table 1. Oxidative dimerization of **4b** with various reagents

Entry	Reagent	Time (h)	Product (isolated yield, %)				
			5d	**6b**	**7b**	**11a**	**11b**
1[a,b]	Ag_2O	0.5	30[c]	34	—	8	—
2[b]	AgO/HNO_3	0.5	—	—	50	—	17
3[b]	Ag_2O/NEt_3	0.5	—	92	—	—	4
4[a]	Act-C[d]/O_2	24	20[c]	44	—	11	9
5[e]	ZrO_2/O_2	19	—	96	—	—	—

[a] This reaction with Ag_2O in $CHCl_3$ gave a complex mixture containing **5b**. In order to isolate **5b**, we performed column chromatography of the reaction mixture under various conditions. However, all the attempts were unsuccessful, producing mainly solid mixtures of **5b** and **6b**. Furthermore, the mixture of **5b** and **6b** was treated with benzyl iodide/K_2CO_3 to give **5d** together with non-reacted **6b**.
[b] Under air at 23 °C.
[c] Yield from **4b**.
[d] Activated charcoal.
[e] Using a dioxygen (O_2)-saturated solvent (MeCN) at 70 °C.



Scheme 3.

2.4. Structure of violet-quinone

There is, to our knowledge, only one article relating to violet-quinone (**1**). This was published by Shidhu et al. in 1981.[1] In this article, a structural analysis of naturally occurring **1** based on the analysis of ^{1}H NMR spectrum was described. However, 2D NMR methods and ^{13}C NMR spectroscopy were not employed. We therefore confirmed the structure of the synthetic compound **1** by means of detailed analyses of the ^{1}H- and ^{13}C NMR spectra with the aid of various 2D NMR experiments.[17]

All ^{1}H- and ^{13}C NMR signal assignments, except for those of the carbons C6a and C6b, were confirmed by means of H–H COSY, C–H COSY and HMBC spectral analyses and by comparison of the spectra with those of the reference compounds **9**, **10** (which were synthesized by us), and balsaminone A (**2**) described in a previous report [2] (refer to Table 2 and Fig. 3).

The ^{1}H NMR spectrum of **1** showed the following signals: (i) two singlets (δ 2.52 and δ 2.47) due to the C2- and C9-methyl protons, a singlet (δ 4.18) due to the C5-methoxyl protons, and a singlet (δ 7.35) assignable to the C6-proton; (ii) a singlet (δ 12.12) due to the hydrogen-bonded hydroxyl at C-11 was observed at lower field than a singlet (δ 9.41) due to the C4-hydroxyl group. The ^{13}C NMR spectrum of **1** displayed signals for all 23 carbons in the molecule: one methoxyl, two carbonyls, two aromatic methyls and 18 aromatic carbons, five of which were protonated, eight quaternary, and five bearing oxygen (Table 2). Accordingly, the above data proved that violet-quinone has the structure **1**.

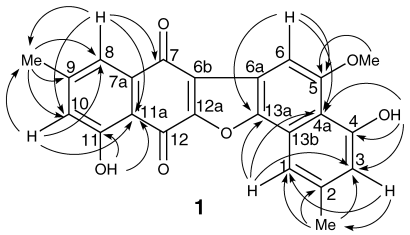


Figure 3. Long-range correlation in the HMBC spectrum of violet-quinone (**1**).

3. Conclusion

The first and biomimetic synthesis of the natural product violet-quinone (**1**) using BNTQ **7b** as a key intermediate was accomplished, based on pathway (II), in 11 steps from methyl 3-methyl-2-butenoate[14a] as a starting material with an overall yield of ca. 13%. In this first synthesis, a key intermediate **7b** was selectively synthesized in excellent yield by utilizing a novel oxidative dimerization of **4b** with the ZrO_2/O_2 system. Furthermore, the construction of the DNFQ framework from BNPQ **12** was achieved by photolysis using a 450 W Hg lamp. The structure of violet-quinone has been established as **1** by this synthesis. Investigations of the biological activity of the synthetic compounds **1**, **9** and **10** are in progress.

Table 2. ^{13}C and ^{1}H NMR spectral data (δ, ppm) for compounds **1**,[a] **2**,[a] **9**[a] and **10**[b]

Carbon no.	Violet-quinone (**1**)		Balsaminone A (**2**)[2]		**9**[c]		**10**[c]	
	^{13}C	^{1}H[d]	^{13}C	^{1}H	^{13}C	^{1}H[d]	^{13}C	^{1}H[d]
1	112.2	7.75 br s	121.2	8.48 m	121.0	8.43 d (8.2)	120.0	8.35 m
2	140.8		127.8	7.67 m	128.0	7.70 dt (8.2, 1.2)	127.9	7.79 br t (7.9)
3	115.9	6.92 d (0.9)	127.1	7.67 m	127.4	7.63 dt (8.2, 1.2)	126.8	7.71 br t (7.9)
4	155.3		123.1	8.34 m	123.7	8.38 d (8.2)	123.4	8.35 m
4a	113.1		125.6		127.1		125.7	
5	156.1		142.8		154.3		146.9	
6	95.0	7.35 s	134.7		96.5	7.46 s	98.6	7.55 s
6a	123.2[e]		114.6		125.3		124.1	
6b	125.4[e]		118.9		119.4		119.0	
7	181.3		174.6		174.3		173.4	
7a	133.3		133.7		133.4[f]		132.7	
8	121.3	7.57 d (0.9)	127.4	8.30 m	126.9[f]	8.25 m	125.9[f]	8.18 m
9	148.3		134.2	7.80 m	133.9[f]	7.78 m	133.78[f]	7.91 m
10	124.7	7.09 br s	133.8	7.80 m	133.8[f]	7.78 m	133.82[f]	7.91 m
11	162.9		126.7	8.30 m	126.7[f]	8.25 m	126.0[f]	8.18 m
11a	113.2		132.3		132.9[f]		132.3	
12	178.8		180.2		182.1		181.2	
12a	152.2		153.1		152.5		152.2	
13a	149.8		148.8		149.0		152.4	
13b	118.9		125.0		121.5		120.7	
2-Me	21.7	2.52 s						
4-OH		9.41 s						
5-OMe	55.8	4.18 s			56.2	4.12 s		
5-OH				6.33 s				10.54 s
6-OMe			63.4	4.09 s				
9-Me	22.2	2.47 s[f]						
11-OH		12.12 s						

[a] Data recorded in $CDCl_3$ at 300 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR).
[b] Data recorded in CD_3SOCD_3 at 300 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR).
[c] Assignment based on ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY and HMBC spectra.
[d] Coupling constants (J in Hz) are in parentheses.
[e] Only the chemical schift of a methyl proton signal (δ 2.47) at the C9 position was different from that (δ 2.74) in the previous report.[1]
[f] Interchangeable.

4. Experimental

4.1. General

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-AL300 and JNM-alpha 500 spectrometers, with tetramethylsilane as an internal standard ($CDCl_3$, CD_3COCD_3 or CD_3SOCD_3 solution). Mass spectra were recorded on a JEOL JMS-D300 or Shimadzu QP-5000 spectrometer. Elemental analyses were done using a Yanaco CHN-MT-3 apparatus. Merck Kieselgel 60 (230–400 mesh), Wako silica gel C-200 (200 mesh) and Merck Kieselgel 60 F_{254} were used for flash column chromatography, column chromatography and thin-layer chromatography (TLC), respectively. Each organic extract was dried over $MgSO_4$ or Na_2SO_4. Photolyses were conducted with a Eikohsha 60 W low-pressure or 450 W high-pressure mercury lamp and irradiation was performed through a Pyrex vessel. The semiconductors, such as ZrO_2 and activated charcoal powders, are commercially available (Wako Pure Chemical Industries, Ltd, Japan).

4.1.1. Oxidative dimerization of 4a. *Method A* (*with the Act-C/O_2 system*). A slurry of activated charcoal powder (1 g) and **4a** (100 mg, 0.58 mmol) in a dioxygen-saturated MeCN (15 ml) was vigorously stirred at 70 °C for 16 h under normal laboratory light. A similar result was obtained in the dark. The insoluble reagent was filtered off and washed with MeCN, and then the filtrate was evaporated. The residue was subjected to flash column chromatography on silica gel. The eluate with CH_2Cl_2/hexane (1:1, v/v) gave 95 mg (95%) of 4,4′-dimethoxy-[2,2′]binaphthalenylidene-1,1′-dione (**6a**), as deep blue needles, mp 257–258 °C (lit.[13a] 256–258 °C). IR (KBr) cm^{-1}: 1606, 1584, 1561. ^{1}H NMR ($CDCl_3$) δ: 4.08 (6H, s, 4 and 4′-OMe), 7.48 (2H, broad t, J=7.7 Hz, 7 and 7′-H), 7.61 (2H, broad t, J=7.7 Hz, 6 and 6′-H), 7.79 (2H, broad d, J=7.7 Hz, 8 and 8′-H), 8.17 (2H, broad d, J=7.7 Hz, 5 and 5′-H), 8.42 (2H, s, 3 and 3′-H). LR-MS m/z: 344 (M^+). HR-MS calcd for $C_{22}H_{16}O_4$: 344.1044. Found: 344.1029.

Method B (*with the ZrO_2/O_2 system*). A slurry of ZrO_2 powder (5 g) and **4a** (100 mg, 0.58 mmol) in dioxygen-saturated MeCN (15 ml) was vigorously stirred at 70 °C for 1.5 h under normal laboratory light. The insoluble reagent was filtered off and washed with MeCN, and then the filtrate was evaporated. The residue was purified by the same method described above to give **6a** (75%) and 19 mg (17%) of 4-methoxy-1,2-naphthoquinone, as yellow needles (hexane–AcOEt), mp 192–193 °C (lit.[13j] 188–189 °C). IR (KBr) cm^{-1}: 1700, 1627, 1607, 1588. ^{1}H NMR ($CDCl_3$) δ: 4.03 (3H, s, 4-OMe), 5.99 (1H, s, 3-H), 7.59 (1H, dt, J=7.9, 1.3 Hz, 6 or 7-H), 7.70 (1H, dt, J=7.9, 1.3 Hz, 6 or 7-H), 7.87 (1H, dd, J=7.9, 1.3 Hz, 5-H), 8.13 (1H, dd, J=7.7, 1.5 Hz, 8-H). ^{13}C NMR ($CDCl_3$) δ: 56.81 (C4–OMe), 103.04 (C3), 124.73 (Ar–C), 129.05 (Ar–C), 130.33 (C4a or C8a), 131.52 (Ar–C), 131.96 (C4a or C8a), 134.96 (Ar–C), 168.68 (C4), 179.39 (C1 or C2), 179.49 (C1 or C2). LR-MS m/z: 188 (M^+). HR-MS calcd for $C_{11}H_8O_3$: 188.0479. Found: 188.0475.

4.1.2. Oxidation of 6a with 69% HNO_3. A mixture of 69% HNO_3 (2 ml) and **6a** (46 mg, 0.27 mmol) was stirred at 0 °C for 15 min. The reaction mixture was poured into a large volume of ice–water. The precipitated product was recrystallized from $CHCl_3$ to yield 42 mg (99%) of 2,2′-binaphthalenyl-1,4,1′,4′-tetraone (**7a**), as yellow needles, mp 288 °C (decomp.) (lit.[13b] 270–280 °C). IR (KBr) cm^{-1}: 1664, 1613, 1587. ^{1}H NMR ($CDCl_3$) δ: 7.07 (2H, s, 3 and 3′-H), 7.75–7.80 (4H, m, Ar–H), 8.12–8.16 (4H, m, Ar–H). LR-MS m/z: 314 (M^+). HR-MS calcd for $C_{20}H_{10}O_4$: 314.0576. Found: 314.0561.

4.1.3. Photolysis of 6a. *Method A* (*with a* 450 W *mercury lamp*). A solution of **6a** (25 mg, 0.15 mmol) in an argon-saturated $CHCl_3$ (10 ml) in a Pyrex vessel was irradiated using a 450 W high-pressure Hg lamp for 1 h, and then evaporated. The residue was subjected to flash column chromatography on silica gel. The eluate with CH_2Cl_2/hexane (2:1, v/v) gave 6 mg (25%) of 1′-hydroxy-4′-methoxy-[2,2′]binaphthalenyl-1,4-dione (**8a**) and 14 mg (59%) of 5-methoxy-dinaphtho[1,2-*b*;2′,3′-*d*]furan-7,12-dione (**9**).

Compound **8a**. Deep violet needles (benzene), mp 189 °C (lit.[13c] 185–186 °C). IR (KBr) cm^{-1}: 3328, 1655, 1590. ^{1}H NMR ($CDCl_3$) δ: 3.99 (3H, s, 4′-OMe), 6.56 (1H, s, 3′-H), 7.15 (1H, s, 3-H), 7.57–7.60 (2H, m, Ar–H), 7.81–7.85 (2H, m, Ar–H), 8.14–8.28 (3H, m, Ar–H), 8.39–8.42 (1H, m, Ar–H), 8.51 (1H, s, 1′-OH). ^{13}C NMR ($CDCl_3$) δ: 55.81 (C4′-OMe), 104.65 (C3′), 114.43 (C2′), 121.73 (C8′), 123.77 (C5′), 126.30 (C5 or C8), 126.72 (C6′ or C7′), 127.32 (C8a′), 127.55 (C6′ or C7′), 127.76 (C5 or C8), 127.99 (C4a′), 131.75 (C4a or C8a), 132.57 (C4a or C8a), 134.05 (C6 or C7), 134.82 (C6 or C7), 138.89 (C3), 145.48 (C1′), 149.71 (C4′), 150.00 (C2), 184.49 (C1 or C4), 188.49 (C1 or C4). LR-MS m/z: 330 (M^+). HR-MS calcd for $C_{21}H_{14}O_4$: 330.0888. Found: 330.0922.

Compound **9**. Orange needles ($CHCl_3$–hexane), mp 291.5–292.5 °C (lit.[13a] 293–295 °C). IR (KBr) cm^{-1}: 1665, 1590. LR-MS m/z: 328 (M^+).

Method B (*with a* 60 W *mercury lamp*). Photolysis of **6a** (25 mg, 0.15 mmol) was carried out under a 60 W low-pressure Hg lamp at 23 °C for 80 h by the same procedure under the conditions described above (method A) for the photolysis of **6a**. The crude product was purified by flash column chromatography on silica gel. The eluate with CH_2Cl_2/hexane (2:1, v/v) gave 21 mg (88%) of **8a**.

4.1.4. Photolysis of 7a. Photolysis of **7a** (20 mg, 0.06 mmol) was carried out at 23 °C for 2 h by the same procedure under the conditions described above (method A) for the photolysis of **6a**. The crude product was purified by recrystallization from $CHCl_3$–MeOH to yield 18 mg (90%) of 5-hydroxy-dinaphtho[1,2-*b*;2′,3′-*d*]furan-7,12-dione (**10**) as red needles, mp 305–308 °C (lit.[13e] 360 °C). IR (KBr) cm^{-1}: 3310, 1654, 1592. LR-MS m/z: 314 (M^+). HR-MS calcd for $C_{20}H_{10}O_4$: 314.0576. Found: 314.0560.

4.1.5. Methylation of 10. CH_3I (24 μl, 0.4 mmol) was added to a solution of **10** (30 mg, 0.10 mmol) and anhydrous K_2CO_3 (132 mg) in dry DMF (12 ml), and the solution was

stirred vigorously at 23 °C for 4 h. The reaction mixture was poured into ice–water, neutralized with 10% HCl, and extracted with $CHCl_3$. The organic layer was washed with H_2O, dried and concentrated. The residue was purified by recrystallization from $CHCl_3$–MeOH to yield 28 mg (91%) of **9**.

4.1.6. Oxidative dimerization of 1-naphthol 4b with various reagents. *Method A* (*entry* 1) (*with* Ag_2O). A mixture of **4b** (50 mg, 0.23 mmol) in $CHCl_3$ (10 ml) containing 1.5 equiv. of Ag_2O (80 mg, 0.344 mmol) was stirred at 23 °C in an air atmosphere for 1 h. The solvent was removed and the residue was subjected to flash column chromatography on silica gel using CH_2Cl_2/hexane (1:2, v/v) as an eluent to give a mixture of **5b** and **6b**, and 4,5-dimethoxy-7-methyl-1,2-naphthoquinone (**11a**). Benzyl iodide (268 μl, 2.26 mmol) was added to a solution of the mixture of **5b** and **6b**, and anhydrous K_2CO_3 (312 mg) in dry DMF (5 ml), and the solution was stirred vigorously at 23 °C for 40 min. The reaction mixture was poured into ice–water, neutralized with 10% HCl, and extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried and concentrated. The residue was subjected to flash column chromatography on silica gel. The eluate with hexane/AcOEt (10:1, v/v) gave 1,1′-dibenzyloxy-4,5, 4′,5′-tetramethoxy-[2,2′]binaphthalenyl-1,1′-diol (**5d**) and 4,5,4′,5′-tetramethoxy-7,7′-dimethyl-[2,2′]binaphthalenyli-dene-1,1′-dione (**6b**). Yields are listed in Table 1.

Compound **5d**. Pale yellow powder (AcOEt), mp 203.5–204.0 °C. IR (KBr) cm^{-1}: 2922, 1604. ^1H NMR ($CDCl_3$) δ: 2.50 (6H, s, 7 and 7′-Me), 3.91 (6H, s, 4 and 4′-OMe), 4.02 (6H, s, 5 and 5′-OMe), 4.71 (4H, s, 2×–CH_2–Ar), 6.78 (2H, d, J=1.29 Hz, 6 and 6′-H), 7.17 (2H, s, 3 and 3′-H), 7.20–7.30 (10H, m, Ar–H), 7.67 (2H, d, J=1.29 Hz, 8 and 8′–H). ^{13}C NMR ($CDCl_3$) δ: 22.23 (7- and 7′–Me), 56.55 (5-OMe), 56.62 (4-OMe), 75.14 (–CH$_2$–Ar), 108.27 (C3), 109.07 (C6), 114.49 (C8), 116.21 (C2), 127.46 (C4a), 127.87 (Ar–C), 128.10 (Ar–C), 128.35 (Ar–C), 132.104 (C8a), 136.65 (C7), 137.32 (Ar–C), 145.16 (C1), 152.82 (C4), 157.13 (C5). LR-MS m/z: 614 (M^+). HR-MS: calcd for $C_{40}H_{38}O_6$: 614.2658. Found: 614.2642. Anal. Calcd for $C_{40}H_{38}O_6$: C, 78.15; H, 6.23. Found: C, 78.13; H, 6.20.

Compound **6b**. Deep violet needles, mp 236.5–237 °C (lit.[15a] 228 °C). IR (KBr) cm^{-1}: 1589. ^1H NMR ($CDCl_3$) δ: 2.43 (6H, s, 7 and 7′-Me), 3.92 (6H, s, 4 and 4′-OMe), 4.05 (6H, s, 5 and 5′-OMe), 6.98 (2H, broad t, J=0.9 Hz, 6 and 6′-H), 7.70 (2H, broad t, J=0.9 Hz, 8 and 8′-H), 8.37 (2H, s, 3 and 3′-H). ^{13}C NMR ($CDCl_3$) δ: 21.76 (7 and 7′-Me), 56.08 (Ar–OMe), 56.91 (Ar–OMe), 103.21 (C3 and C3′), 117.99, 118.18 (C6 and C6′,or C8 and C8′), 121.74 (C6 and C6′,or C8 and C8′), 130.32 (Ar–C), 133.60 (Ar–C), 140.27 (Ar–C), 156.14 (Ar–C), 159.46 (Ar–C), 188.93 (C1 and C1′). HR-MS calcd for $C_{26}H_{24}O_6$: 432.1566. Found: 432.1563. Anal. Calcd for $C_{26}H_{24}O_6$: C, 72.21; H, 5.59. Found: C, 72.35; H, 5.56.

Compound **11a**. Orange powder ($CHCl_3$–hexane), mp 175.0–175.5 °C. IR (KBr) cm^{-1}: 1642, 1603, 1580. ^1H NMR ($CDCl_3$) δ: 2.42 (3H, s, 7 and 7-Me), 3.92, 3.97 (6H, each s, 4 and 5-OMe), 5.89 (1H, s, 3-H), 7.07 (1H, br s, 6-H), 7.63 (1H, d, J=0.74 Hz, 8-H). ^{13}C NMR ($CDCl_3$) δ: 21.6 (7-Me), 56.75, 56.81 (4 and 5-OMe), 102.1 (C3), 116.2 (C4a), 120.8, 123.8 (C6 and C8), 132.2 (C8a), 143.8 (C7), 158.2 (C5), 172.7 (C4), 179.1, 180.6 (C1 and C2). LR-MS m/z: 232 (M^+). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.20; H, 5.19.

Method B (*entry 2*) (*with AgO*/40% *HNO*$_3$). To a mixture of **4b** (50 mg, 0.229 mmol) and AgO (284 mg, 2.29 mmol) in acetone (5 ml) was added 40% HNO_3 (1.5 ml) over 5 min. The reaction mixture was stirred at room temperature for 30 min, diluted with water and extracted with $CHCl_3$. The extracts were washed with brine, dried over $MgSO_4$ and evaporated. The residue was purified by flash column chromatography on silica gel. The eluate with $CHCl_3$/AcOEt (20:1, v/v) gave 23 mg (50%) of 5,5′-dimethoxy-7,7′-dimethyl-[2,2′]binaphthalenyl-1,4,1′,4′-tetraone (**7b**) and 8 mg (17%) of 5-methoxy-8-methyl-1,4-naphthoquinone (**11b**).

Compound **7b**. Yellow amorphous powder ($CHCl_3$–MeOH), mp 279–281 °C (lit.[15a] 310 °C). IR (KBr) cm^{-1}: 1649, 1601, 1587. ^1H NMR ($CDCl_3$) δ: 2.50 (6H, s, 7 and 7′-Me), 4.02 (6H, s, 5 and 5′-OMe), 6.94 (2H, s, 3 and 3′-H), 7.13 (2H, broad s, 6 and 6′-H), 7.59 (2H, broad s, 8 and 8′-H). HR-MS calcd for $C_{24}H_{18}O_6$: 402.1098. Found: 402.1133. Anal. Calcd for $C_{24}H_{18}O_6$: C, 72.64; H, 4.51. Found: C, 72.60; H, 4.50.

Compound **11b**. Yellow needles (benzene), mp 169.5–170 °C (lit.[14b] 164–166 °C). IR (KBr) cm^{-1}: 1651, 1559. ^1H NMR ($CDCl_3$) δ: 2.48 (3H, s, 7-Me), 4.00 (3H, s, 5-OMe), 6.84 (2H, s, 2 and 3-H), 7.11 (1H, s, 6-H), 7.55 (1H, s, 8-H). HR-MS calcd for $C_{12}H_{10}O_3$: 202.0627. Found: 202.0614.

Method C (*entry* 3) (*with* Ag_2O/NEt_3). A mixture of **4b** (100 mg, 0.58 mmol) in $CHCl_3$ (20 ml) containing 0.2% NEt_3 and 20 equiv. of Ag_2O (2.66 g) was stirred at 23 °C in an air atmosphere for 1 h. The solvent was removed and the residue was subjected to flash column chromatography on silica gel. The eluate with CH_2Cl_2/hexane (1:2, v/v) gave **7b** and **11b**. Yields are listed in Table 1.

Method D (*entry* 4) (*with the Act-Cl*/O_2 *system*). Oxidation of **4b** (100 mg, 0.58 mmol) was carried out at 70 °C for 24 h by the same procedure under the conditions described above (method A) for the oxidative dimerization of **4a**. The crude product was purified by flash column chromatography on silica gel. The eluate with CH_2Cl_2/hexane (1:2, v/v) gave **5d**, **6b**, **11a** and **11b**. Yields are listed in Table 1.

Method E (*entry* 5) (*with the* ZrO_2/O_2 *system*). Oxidation of **4b** (100 mg, 0.58 mmol) was carried out at 70 °C for 19 h by the same procedure under the conditions described above (method B) for the oxidative dimerization of **4a**. The crude product was purified by recrystallization from benzene to yield **6b** (96%).

4.1.7. Oxidation of 6b with 69% HNO_3. A mixture of 69% HNO_3 (3 ml) and **6b** (80 mg, 0.17 mmol) was stirred at 0 °C for 15 min. The reaction mixture was poured into a large volume of ice–water. The precipitated product was

recrystallized from $CHCl_3$/MeOH to yield 73 mg (99%) of **7b**.

4.1.8. 5,5′-Dihydroxy-7,7′-dimethyl-[2,2′]binaphthalenyl-1,4,1′,4′-tetraone (biramentaceone) (7c). Magnesium bromide (2.2 g, 12 mmol) was added to a solution of **7b** (200 mg, 0.5 mmol) dissolved in anhydrous toluene (30 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 was washed with H_2O, dried, concentrated, and then the residue was subjected to flash column chromatography on silica gel. The eluate with hexane/AcOEt (5:1, v/v) gave 150 mg (80%) of **7c** as an orange amorphous powder ($CHCl_3$–MeOH), mp 264–265 °C (decomp.) (lit.[15a] 260 °C). IR (KBr) cm^{-1}: 3426, 1665, 1641, 1574. ^1H NMR ($CDCl_3$) δ: 2.45 (6H, s, 7 and 7′-Me), 7.01 (2H, s, 3 and 3′-H), 7.12 (2H, dd, J=0.9, 1.7 Hz, 6 and 6′-H), 7.49 (2H, dd, J=0.9, 1.7 Hz, 8 and 8′-H), 11.79 (2H, s, 5 and 5′-OH). HR-MS calcd for $C_{22}H_{14}O_6$: 374.0786. Found: 374.0787. Anal. Calcd for $C_{22}H_{14}O_6$: C, 70.58; H, 3.77. Found: C, 70.47; H, 3.75.

4.1.9. 5,5′-Bis-benzyloxy-7,7′-dimethyl-[2,2′]binaphthalenyl-1,4,1′,4′-tetraone (12). Benzyl iodide (72 μl, 0.54 mmol) was added to a solution of **7c** (20 mg, 0.054 mmol) and anhydrous K_2CO_3 (76 mg) in dry DMF (10 ml), and the solution was stirred vigorously at 23 °C for 1 h. The reaction mixture was poured into ice–water, neutralized with 10% HCl, and extracted with $CHCl_3$. The organic layer was washed with H_2O, dried and concentrated. The residue was subjected to flash column chromatography on silica gel. The eluate with benzene/acetone (40:1, v/v) gave 24 mg (78%) of **12** as yellow amorphous powder ($CHCl_3$–MeOH), mp 192–193 °C. IR (KBr) cm^{-1}: 1654, 1598. ^1H NMR ($CDCl_3$) δ: 2.46 (6H, s, 7 and 7′-Me), 5.31 (4H, s, $-OCH_2$), 6.95 (2H, s, 3 and 3′-H), 7.17 (2H, broad d, J=0.7 Hz, 6 and 6′-H), 7.33–7.60 (10H, m, Ar–H), 7.58 (2H, broad d, J=0.7 Hz, 8 and 8′-H). HR-MS calcd for $C_{36}H_{26}O_6$: 554.1722. Found: 554.1740. Anal. Calcd for $C_{36}H_{26}O_6$: C, 77.96; H, 4.73. Found: C, 77.92; H, 4.70.

4.1.10. 4,11-Bis-benzyloxy-5-hydroxy-2,9-dimethyl-dinaphtho[1,2-*b*;2′,3′-*d*]furan-7,12-dione (13). A solution of **17** (20 mg, 0.036 mmol) in argon-saturated $CHCl_3$ (10 ml) in a Pyrex vessel was irradiated using a 450 W high-pressure Hg lamp for 1 h, and then evaporated. The residue was subjected to flash column chromatography on silica gel. The eluate with CH_2Cl_2/hexane (2:1, v/v) gave 18 mg (87%) of **13** as red needles ($CHCl_3$–MeOH), mp 258–258.5 °C. IR (KBr) cm^{-1}: 3406, 1662, 1598, 1505. ^1H NMR ($CDCl_3$) δ: 2.49 (3H, s, 9-Me), 2.54 (3H, s, 2-Me), 5.29 (2H, s, C4–OCH_2), 5.30 (2H, s, C11–OCH_2), 6.90 (1H, broad s, 3-H), 7.18 (1H, broad s, 10-H), 7.43 (1H, s, 6-H), 7.31–7.73 (10H, m, Ar–H), 7.73 (1H, broad d, J=0.9 Hz, 8-H), 7.93 (1H, broad d, J=0.9 Hz, 1-H), 9.39 (1H, s, 5-OH). ^{13}C NMR ($CDCl_3$) δ: 22.01 (C2–*Me*), 22.31 (C9–*Me*), 70.98 (C11–O*CH*$_2$), 72.09 (C4–O*CH*$_2$), 101.10 (C6), 110.08 (C3), 113.58 (C4a), 114.65 (C1), 118.37 (C11a), 120.21 (C10), 120.55 (C13b), 121.17 (C8), 122.70 (C6a or C6b), 123.27 (C6a or C6b), 126.67 (Ar–C), 127.83 (Ar–C), 128.14 (Ar–C), 128.66 (Ar–C), 129.10 (Ar–C), 129.17 (Ar–C), 134.80 (Ar–C), 135.86 (C7a), 136.25 (Ar–C), 138.40 (C2), 146.60 (C9), 147.08 (C13a), 153.56 (C5), 154.12 (C12a), 155.67 (C4), 159.89 (C11), 174.12 (C12), 181.49 (C7). HR-MS calcd for $C_{36}H_{26}O_6$: 554.1722. Found: 554.1867. Anal. Calcd for $C_{36}H_{26}O_6$: C, 77.96; H, 4.73. Found: C, 77.99; H, 4.75.

4.1.11. 4,11-Bis-benzyloxy-5-methoxy-2,9-dimethyl-dinaphtho[1,2-*b*;2′3′-*d*]furan-7,12-dione (14). Methyl iodide (0.14 μl, 2.29 mmol) was added to a solution of **13** (100 mg, 0.19 mmol) and anhydrous K_2CO_3 (260 mg) in dry DMF (10 ml), and the solution was stirred at 23 °C for 2 h with vigorous stirring. The reaction mixture was poured into ice–water, and extracted with $CHCl_3$. The organic layer was washed with H_2O, dried and concentrated. The residue was subjected to flash column chromatography on silica gel. The eluate with AcOEt/hexane (1:1, v/v) gave 85 mg (79%) of **14** as red needles ($CHCl_3$–MeOH), mp 322–324 °C. IR (KBr) cm^{-1}: 1662, 1598, 1567. ^1H NMR ($CDCl_3$) δ: 2.50 (3H, s, 2-Me), 2.55 (3H, s, 9-Me), 4.05 (3H, s, 5-OMe), 5.21 (2H, s, 4-OCH_2), 5.31 (2H, s, 11-OCH_2), 6.95 (1H, broad s, 3-H), 7.18 (1H, broad s, 10-H), 7.43 (1H, s, 6-H), 7.33–7.73 (10H, m, Ar-H), 7.73 (1H, s, 8-H), 7.93 (1H, s, 1-H). HR-MS calcd for $C_{37}H_{28}O_6$: 568.1878. Found: 568.1926. Anal. Calcd for $C_{37}H_{28}O_6$: C, 78.15; H, 4.96. Found: C, 78.13; H, 4.99.

4.1.12. 4,11-Dihydroxy-5-methoxy-2,9-dimethyl-dinaphtho[1,2-*b*;2′,3′-*d*]furan-7,12-dione (violet-quinone) (1). Compound **14** (46 mg, 0.08 mmol) was hydrogenated in the presence of 10% Pd/C (20 mg) in ethyl acetate (8 ml). The catalyst was removed, and the filtrate was concentrated. The residue was subjected to flash column chromatography on silica gel. The eluate with CH_2Cl_2 gave 30 mg (96%) of **1** as violet solid ($CHCl_3$–MeOH), mp 332–335 °C (lit.[1] 335–338 °C). IR (KBr) cm^{-1}: 3370, 1664, 1640, 1607. HR-MS calcd for $C_{23}H_{16}O_6$: 388.0942. Found: 388.0957. Anal. Calcd for $C_{23}H_{16}O_6$: C, 71.13; H, 4.15. Found: C, 71.23; H, 4.18.

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