Reactions of 1-Naphthols with π-Acceptor *p*-Benzoquinones: Oxidative Aryl Coupling *vs.* Non-Oxidative Electrophilic Arylation

Tetsuya TAKEYA,* Hiromu KONDO, Tsuyoshi OTSUKA, Hirohisa DOI, Iwao OKAMOTO, and Eiichi KOTANI

Showa Pharmaceutical University; 3–3165 Higashi-tamagawagakuen, Machida, Tokyo 194–8543, Japan.
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We investigated the reactions of various 1-naphthols (NPOHs; 1) with *p*-benzoquinones (Qs), such as 1,4-benzoquinone (BQ) and *p*-chloranil (CA), as π-electron acceptors. With electron-rich NPOHs 1a—c, oxidative biaryl coupling and subsequent dehydrogenation reaction took place selectively to give the corresponding 2,2′-binapthyl-1,1′-quinones 3a—c in excellent yield. In the case of electron-deficient NPOHs 1e, f, two different types of reactions occurred in the presence of $SnCl_4$ and ZrO_2 under similar conditions: $SnCl_4$ mediated oxidative dimerization and trimerization of NPOH, while ZrO_2 promoted electrophilic arylation of Qs with NPOH. The resulting products 3 would be useful synthetic intermediates for naturally occurring diosindigo B, biramentaceone and violet-quinone.

Key words 1-naphthol; 2,2′-binapthyl; π-acceptor; *p*-benzoquinone; oxidative coupling; arylation

The biaryl or triaryl framework is a central building block in a very large number of natural products.[1—4] Natural biaryls and triaryls have been isolated from several plants and show various biological activities.[4] The usual methods for construction of bi- and triaryl frameworks can be divided into the following categories: (i) oxidative biaryl coupling (so-called phenolic oxidation) of various arenas including metal phenolates[5] using a chemical method[6] or an electrochemical,[7] (ii) biaryl coupling between aryl halides and arylmetal compounds[8] or arylmetal species,[9] and (iii) electrophilic arylation of quinone derivatives with hydroxyarenes in the presence of acids or bases.[10—15]

Nature makes extensive use of the oxidative coupling reaction for the selective construction of complex compounds from simple starting materials, such as naphthols and phenols. We have focused on the oxidative coupling (or dimerization) of 1-naphthols (NPOHs) in order to develop a method for constructing biaryl substructures, aiming at biomimetic synthesis of natural products such as 2,2′-binaphthols, 2,2′-binapthylquinones and their derivatives.[4] Oxidizing reagents used in the oxidative coupling reaction of hydroxyarenes include a variety of metal salts,[16] Lewis acids[17,18] and nitrosonium salts,[19] and hypervalent iodine(III) reagents.[20] Recently, in particular, various oxidizing reagent systems for the coupling of 2-naphthols by using combinations of metal salts or metal complexes as a catalyst with aerial oxygen or dioxygen (O_2) have been developed: these catalysts include $FeCl_3$–SiO_2, $CuSO_4$–Al_2O_3, $CuSO_4$–montmorillonite, CuCl–amine complexes, CuCl(OH)–TMEDA, and oxovanadium(IV) complexes.[22] However, the choice of a suitable reagent for the synthesis of particular desired biaryls is still largely empirical. We have reported an oxidative coupling reaction *via* electron donor–acceptor (EDA) complexes of 1-naphthols with a Lewis acid such as $SnCl_4$ or a semiconductor including ZrO_2 in the absence or presence of dioxygen (O_2).[16,22,24] This EDA chemistry could provide the basis for a simple method of constructing biaryl frameworks, leading to a biomimetic synthesis of natural products.

On the other hand, since it is also well-known that *p*-benzoquinones such as 1,4-benzoquinone (BQ), *p*-chloranil (CA), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as π-electron acceptors[25,26] often form highly colored EDA (or charge-transfer) complexes with various donors, including arenes, charge-transfer (CT) interactions[27] might play a role in these electron-transfer reactions. In addition, many studies on thermal and photochemical reactions *via* CT complexes have been reported.[28—31] Furthermore, *p*-benzoquinones (Qs) and hydroquinones (QH_2) have attracted a great deal of attention because of the role of redox reactions of these Qs in a variety of biochemical electron transport reactions, including the conversion of NADH to NAD^+, photosynthetic reactions, and the reduction of cytochrome c.[32,33]

In general, halogenated CA and DDQ are not only powerful dehydrogenating reagents[34] for organic compounds such as steroids, but also effective electron-accepting photosensitizers[35] for oxidation of various compounds. Moreover, they can initiate various bond formation or cleavage reactions (*e.g.*, of C–C bond and C–O bonds).[36—40] Although there have been some studies on oxidative dimerizations[41—43] of arenes with CA or DDQ, the ability of these compounds to promote oxidative dimerization of 1-naphthols has not been studied in detail.

In order to characterize the behavior of 1-naphthol in EDA chemistry, as well as to develop new methods for construction of biaryl frameworks, we investigated the reactions of NPOH **1** with several organic acceptors, using BQ and CA in place of $SnCl_4$ as an inorganic acceptor (see above). In addition, the reactions of NPOH with reagent systems including combinations of Qs and $SnCl_4$ or ZrO_2 were examined. We now report the oxidative coupling reaction of NPOH **1** and the electrophilic arylation with **1** induced by π-acceptors, BQ and CA, in the absence or presence of $SnCl_4$ or ZrO_2.

Results and Discussion

Firstly, we investigated the oxidative biaryl coupling reaction of NPOHs **1a**—**f** (including precursors for the synthesis of natural products) and the naphthol ether **1d**[16] with Qs such as BQ, CA, and DDQ as π electron acceptors under various conditions. To determine the optimum conditions for

* To whom correspondence should be addressed. e-mail: takeya@ac.shoyaku.ac.jp

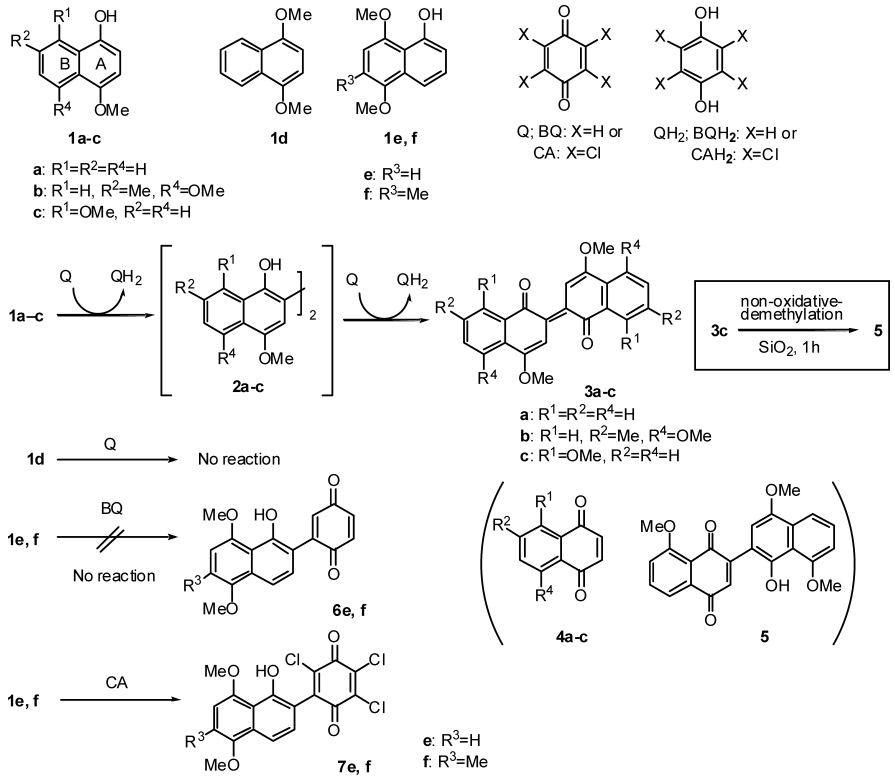

Chart 1. *p*-Benzoquinones (Q) -induced Reaction of 1-Napthols **1a—f**

the coupling reaction, detailed preliminary experiments on the oxidative dimerization were done with NPOH **1a** as a substrate at room temperature (23 °C), without light irradiation.

Several *p*-benzoquinones [BQ, CA, DDQ, *etc.*] and solvents saturated with argon (CH_2Cl_2, $MeNO_2$, *etc.*) were used, and the results are summarized in Table 1 and Chart 1. The addition of BQ dissolved in a solvent (CH_2Cl_2) to a solution of **1a** immediately afforded a light brown solution. This reaction mixture changed into a dark blue-colored solution with the passage of time at room temperature, and the biaryl coupling reaction proceeded. This observation suggests the formation of the EDA complex of BQ with **1a**. A new charge transfer absorption band was observed at 666 nm in the absorption spectrum of the BQ complex with **1a** in CH_2Cl_2. The best result was obtained with BQ in CH_2Cl_2 (run 1). That is, the reaction of **1a** using BQ in an argon saturated CH_2Cl_2 for 2 h afforded selectively the so-called Russig's Blue,[44] 2,2′-binaphthyl-1,1′-quinone (**3a**; BNPQ), in an almost quantitative yield, along with hydroquinone (BQH_2; 69%). The formation of BNPQ **3** is revealed by its characteristic dark blue color. When $MeNO_2$ was used in place of CH_2Cl_2 as a solvent under similar conditions, the yield of **3a** was slightly lower than that in CH_2Cl_2 (run 2). A similar result was obtained in the case of CA to afford **3a** as a major product, together with 2,3,5,6-tetrachlorohydroquinone (CAH_2)[45] (run 3). However, in the case of DDQ, **3a** was obtained in lower yield (51%), together with polymeric compounds (run 5).

Furthermore, we investigated other reagents commonly used for biaryl coupling reactions. The reaction of **1a** with Ag_2O gave **3a**, but the yield of **3a** was lower (run 23). In order to confirm the formation mechanism of **3** in the present oxidation, for example, the reaction of **2a** with CA (1.2 eq) was carried out to give **3a** in high yield (run 19 in Table 1). The above results indicate that **3** is produced *via* **2** by the oxidation of **1**.

Similar reactions were explored using **1b** or **1c**,[16] which can be used as precursors for the synthesis of binaphthyl natural products (Table 1).[21] When using **1b** as a substrate, a particular difference between the oxidations with BQ and CA was observed. The oxidation of **1b** with BQ for 3.5 h afforded BNPQ **3b** in excellent yield (run 8). In contrast with this result, the reaction with CA gave the napthoquinone **4b** (32%), along with a complex mixture of products, including polymeric compounds, without the formation of **3b** (run 9).

In the case of **1c** under similar conditions, **2c** and **5** were obtained along with a trace amount of **3c** (run 10). The best result was obtained with CA in CH_2Cl_2 for 24 h, affording 1′-hydroxy-2,2′-binaphthyl-1,4-quinone (**5**; HBNPQ) in good yield (run 11). TLC (thin layer chromatography) monitoring demonstrated the transformation of **3c** to HBNPQ **5** during the purification of the crude products by means of column chromatography using SiO_2.

To throw light on the formation of **5**, the reaction of the enol-ether **3c** with SiO_2 or CA in CH_2Cl_2 was examined. Pure **3c** was prepared by crystallization from the crude product obtained by work-up after the reaction of **1c** with Ag_2O in the presence of triethylamine (Et_3N) (run 25).[46] No reaction of **3c** with CA occurred (run 20), but in the case with only SiO_2 under argon, **5** was obtained in 91% yield (run 21). This suggests the participation of a Bronsted acid (Si-OH) site on the SiO_2 surface,[47] because proton sources, such as water (H_2O) and acids were not used in the work-up after the reaction according to the general procedure described in the experimental section. Indeed, the reaction of **3c** with HCl as

Table 1. Reactions of the Naphthol Derivatives with *p*-Benzoquinones (Q) as an Acceptor at 23 °C[a)]

Run	Substrate	Acceptor[a)] (1.2 eq)	Solvent	Time (h)	Product (isolated yield, %)		Recovered **1** (%)
1	**1a**	BQ	CH_2Cl_2	2	**3a** (99)		—[b)]
2	**1a**	BQ	$MeNO_2$	1.5	**3a** (97)		—
3	**1a**	CA	CH_2Cl_2	0.5	**3a** (89)	**4a** (6)	—[c)]
4	**1a**	CA	$MeNO_2$	1.5	**3a** (65)		—
5	**1a**	DDQ	CH_2Cl_2	0.5	**3a** (51)		—
6	**1a**	BQ[d)]	CH_2Cl_2	2	**2a** (78)	**3a** (20)	—
7	**1a**	CA[d)]	CH_2Cl_2	3	**2a** (80)	**3a** (16)	—
8	**1b**	BQ	$MeNO_2$[e)]	3.5	**3b** (96)		—
9	**1b**	CA	CH_2Cl_2	1	**4b** (32)		—
10	**1c**	BQ	$MeNO_2$[e)]	94	**2c** (66)	**5** (4)	30
11	**1c**	CA	CH_2Cl_2	24	**5** (84)		—
12	**1d**	BQ	CH_2Cl_2	24	No reaction		100
13	**1d**	CA	CH_2Cl_2	24	No reaction		100
14	**1e**	BQ	CH_2Cl_2	24	No reaction		100
15	**1e**	CA	CH_2Cl_2[f)]	24	**7e** (18)		80
16	**1f**	BQ	CH_2Cl_2	24	No reaction		100
17	**1f**	CA	CH_2Cl_2[f)]	24	**7f** (12)		80
18	**2a**	BQ	CH_2Cl_2	1	**3a** (98)		—
19	**2a**	CA	CH_2Cl_2	0.5	**3a** (98)		—
20	**3c**	CA	CH_2Cl_2	24	No reaction		100
21[g)]	**3c**	SiO_2	CH_2Cl_2	1	**5** (91)		—
22[h)]	**3c**	HCl	CH_2Cl_2	0.5	**5** (95)		—
23[i)]	**1a**	Ag_2O	$CHCl_3$	1	**2a** (20)	**3a** (75)	—
24[i)]	**1b**	Ag_2O/Et_3N	$CHCl_3$	0.5	**3b** (92)	**4** (4)	—
25	**1c**	Ag_2O/Et_3N	$CHCl_3$	1	**3c** (93)		—

a) The reactions of naphthols (0.25 mmol) with *p*-benzoquinones [BQ (1.2 eq), CA (1.2 eq) or DDQ (1.2 eq)] were carried out using argon-saturated solvent in a sealed tube with stirring under normal laboratory light. Similar results were obtained under air or in the dark. *b*) Hydroquinone (BQH_2; 69%) was also isolated with **3a**. *c*) 2,3,5,6-tetrachlorohydroquinone (CAH_2; 75%) could be also isolated with **3a**. *d*) This reaction was carried out with BQ (0.6 eq) or CA (0.6 eq) under the same conditions as above. *e*) Using CH_2Cl_2 in place of $MeNO_2$ as a solvent. Similar result was almost obtained, but the yield was slightly lower than that in $MeNO_2$. *f*) Using $MeNO_2$ in place of CH_2Cl_2 as a solvent. Similar result was almost obtained, but the yield was slightly lower than that in CH_2Cl_2. *g*) This reaction was carried out with SiO_2 used in the column chromatography. *h*) Using 10% HCl aqua. *i*) This result was reported by us previously (ref. 16). *j*) This result was reported previously by us (ref. 23).

Table 2. Reactions of the Naphthols **1e**, **f** with Various Reagents at 23 °C

Run	Substrate	Reagent	Solvent	Time (h)	Product (isolated yield, %)		Recovered **1** (%)
1[b)]	**1e**	$BQ/SnCl_4$	$MeNO_2$[f)]	0.5	**2e** (26)	**8e** (32)	12
2[b)]	**1e**	$CA/SnCl_4$	$MeNO_2$[f)]	0.5	**2e** (4)	**8e** (55)	—
3[c)]	**1e**	$O_2/SnCl_4$	CH_2Cl_2	1	**2e** (20)	**8e** (24)	33
4[d)]	**1e**	Ag_2O	CH_2Cl_2	1	**2e** (25)	**9** (30)	—
5[a)]	**1e**	BQ/ZrO_2	CH_2Cl_2	24	**6e** (11)		80
6[a)]	**1e**	CA/ZrO_2	CH_2Cl_2	5	**7e** (73)		10
7	**1e**	ZrO_2	CH_2Cl_2	24	No reaction		100
8[e)]	**1e**	$SnCl_4$	CH_2Cl_2	24	No reaction		100
9	**1f**	$BQ/SnCl_4$	$MeNO_2$[f)]	0.5	**2f** (2)	**8f** (56)	16
10	**1f**	$CA/SnCl_4$	$MeNO_2$[f)]	0.25	**2f** (1)	**8f** (31)	—
11[c)]	**1f**	$O_2/SnCl_4$	CH_2Cl_2	5	**2f** (8)	**8f** (19)	53
12	**1f**	BQ/ZrO_2	CH_2Cl_2	19	**6f** (20)		57
13	**1f**	CA/ZrO_2	CH_2Cl_2	1	**7f** (91)		—

a) This reaction of **1e** or **1f** (0.25 mmol) with BQ (1.0 eq) or CA (1.0 eq) in the presence of ZrO_2 (5 g) was carried out using argon-saturated solvent in a sealed tube with stirring under normal laboratory light. Similar results were obtained under air or in the dark. *b*) This reaction of naphthols (0.25 mmol) with BQ (1.0 eq) or CA (1.0 eq) in the presence of $SnCl_4$ (0.25 eq) was carried out using argon-saturated solvent in a sealed tube with stirring under normal laboratory light. Similar results were obtained under air or in the dark. *c*) This reaction of **1e** or **1f** (0.25 mmol) with $SnCl_4$ (0.25 eq) was carried out using dioxygen-saturated solvent in a sealed tube with stirring. This result was reported previously by us (ref. 22). *d*) With Ag_2O (1.5 eq) under air. This result was reported by us previously (ref. 22). *e*) With $SnCl_4$ (1.2 eq). *f*) Using CH_2Cl_2 in place of $MeNO_2$ as a solvent. Similar result was almost obtained, but the yield was slightly lower than that in $MeNO_2$.

a Bronsted acid in place of SiO_2 gave **5** in 95% yield (run 22). Accordingly, **5** is concluded to be formed by the SiO_2-induced demethylation of **3c**.

The oxidative coupling of **1c** was very sluggish, but selectively afforded **5** *via* **3c** in good yield (run 11). In all experiments with **1c** using BQ and CA, a longer period of reaction was required for completion of the reaction, in comparison with the cases of **1a, b**. This may be owing to the influence of hydrogen-bond formation[48)] between the hydroxyl proton (at C1) and the methoxyl group (at C8) in **1c**, as shown in Chart 2, though this remains to be confirmed. On the other hand, in the cases of the naphthol-ether **1d** with BQ or CA, the reaction did not proceed at all under similar conditions (runs 12,13).

Regioselective *ortho*/*ortho* coupling is more difficult to control in the reaction of 4-unsubstituted naphthalenes such as NPOHs **1e**, **f**, which lack substitution at the R^5 position (Chart 2). Although oxidative coupling reactions of naph-

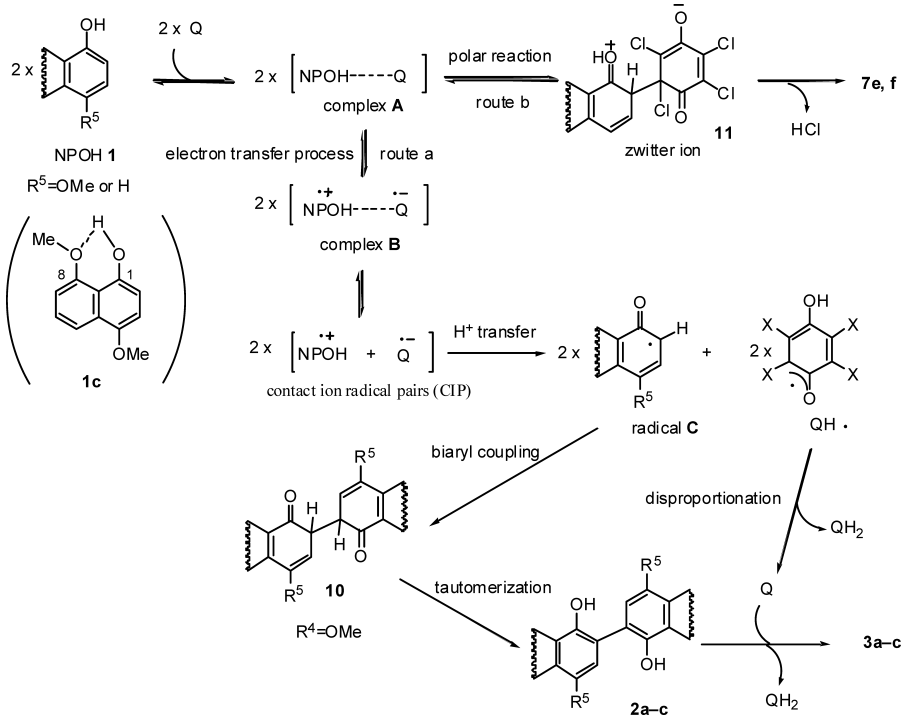

Chart 2. Proposed Mechanism for the Reactions of 1-Naphthol **1** Induced by *p*-Benzoquinones

thols by means of chemical methods and electrolysis have been studied extensively, mixtures of dimeric, polymeric and quinoid compounds were usually generated. Next, we investigated the reactions of NPOHs **1e**, **f**[16] using BQ or CA (Chart 1 and Table 1). When BQ was used as an acceptor, no reaction of **1e**, **f** occurred at all in both cases (runs 14, 16), while in the case with CA, the non-oxidative electrophilic arylation of CA with **1e**, **f** took place to give the corresponding napthol-quinone adducts (NPOH-Q; **7e**, **f**) in poor yields (runs 15, 17). The expected oxidative biaryl coupling reaction did not proceed at all.

In general, electron-donating or electron-accepting ability is reflected in the first oxidation or reduction potential of compounds.[49,50] Therefore, the oxidation potentials (the first half-wave potential ($E^{1/2}_{oxi}$), V *vs.* Ag/AgCl) of the first one-electron transfer from NPOH **1** in argon-saturated CH_2Cl_2 were measured by cyclic voltammetry (CV). These results were reported previously by us.[16] On the other hand, the redox potentials (the first redox potential (E^{o}_{redox}) V *vs.* Ag/AgCl) of Qs (BQ, CA and DDQ) in similar conditions were also measured by CV. Furthermore, the redox potential of BQ or CA in the presence of $SnCl_4$ in CH_2Cl_2 were measured by CV. The irreversible wave were observed in both cases, but it was not clear. The oxidation potentials of NPOH **1** as a donor in CH_2Cl_2 increased in the order of **1b** (+0.82 V)<**1a** (+0.95 V)=**1c** (+0.95 V)<**1d** (+1.06 V)<**1e** (+1.09 V)<**1f** (+1.14 V). NPOH **1b**, having two methoxyl groups, showed the lowest oxidation potential, whereas **1f**, which lacks a methoxyl group, showed the highest oxidation potential among NPOHs **1**.

On the other hand, the redox potentials of *p*-benzoquinones as π-acceptors in CH_2Cl_2 increased in the order of BQ (−0.59 V)<CA (−0.08 V)<DDQ (+0.48 V). The electrochemical results suggested that electron-rich NPOHs **1a**—**c** having –OMe at the R^5 position (oxidation potentials range from +0.82 to +0.95 V) are stronger donors than electron-deficient NPOH **1e**, **f** (+1.09 to +1.14 V). In addition, **1a**—**c** interact strongly with either BQ or CA, and one-electron transfer to Qs takes place more easily to form the corresponding radical cation species ($NPOH^{\cdot+}$) of NPOH.

The noteworthy features of the present reactions of NPOH **1a**—**f** with Qs were as follows.

(1) The hydroxyl group in **1a**—**c** was required for the formation of the binaphthyl derivatives **2** and **3**, based on the result of runs 12, 13.

(2) BNPQ **3a**—**c** were obtained in satisfactory to excellent yield by the reactions of the corresponding NPOHs **1a**—**c** with *p*-benzoquinones (1.2 eq) under mild conditions. These reactions can be conveniently performed with electron-rich NPOH having a methoxyl group at the R^5 position on ring A. Among **3a**—**c,** only **3c** could not be successfully isolated, since it is easily transformed into **5** on the SiO_2 used in column chromatography.

(3) However, there is an exception; in the case of **1b** with CA, the coupling reaction did not take place (run 9). The reason for this may be that **1b** is much more oxidizable than the other compounds because it has the lowest oxidation potential. In addition, CA is a stronger acceptor than BQ.

(4) In the case of electron-deficient NPOHs **1e**, **f** with BQ or CA, the biaryl coupling reaction did not proceed at all, presumably because they have higher oxidation potential.

The formation mechanism of **3a**—**c** or **7e**, **f** by the reaction of NPOH **1** with Qs (BQ or CA) can be rationalized in terms of the reaction sequence *via* route (a) (electron transfer process) or *via* route (b) (polar reaction process)[49] (Chart 2): route (a) is initiated by the formation of the EDA complex **B** between NPOH **1a**—**c** and Q (BQ or CA). In the case of **1a**—**c** as stronger donors, they can easily form complex **B**, as shown in Chart 2. Dissociation of complex **B** into contact ion radical pairs (CIP) of the radical cation species ($NPOH^{\cdot+}$)

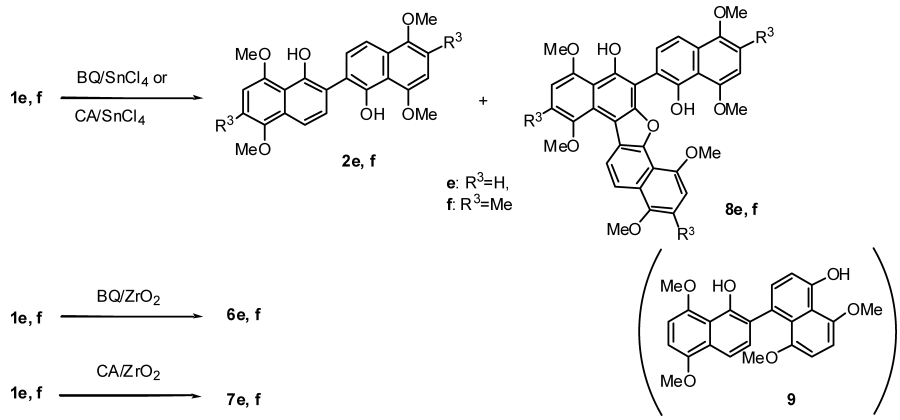

Chart 3. Reactions of 1-Napthols **1e, f** with *p*-Benzoquinones in the Presence of $SnCl_4$ or ZrO_2

and the radical anion species ($Q^{\cdot -}$) is expected, but the resulting radical cation ($NPOH^{\cdot +}$) itself does not seem to react, based on the results of runs 12 and 13. Therefore, we suggest that proton transfer from $NPOH^{\cdot +}$ to $Q^{\cdot -}$ and the formation of the napthoxy radical **C** ($NPO^{\cdot}$) cause the biaryl coupling reaction to occur, affording BNPOH **2a**—**c** in the present reaction. Finally, BNPQ **3a**—**c** can be formed by the oxidative dehydrogenation of **2** with Q, which is regenerated by the disproportionation[51] of two semiquinone radicals ($QH^{\cdot}$). Alternatively, NPOH **1e**, **f** can not form the complex **B** with either BQ or CA because of their higher oxidation potentials. Then, electrophilic arylation of CA involving the loss of HCl occurs to produce **7e**, **f** *via* the zwitterionic structure (route b).

As described above, in the reaction of **1e**, **f** with BQ or CA as an acceptor (runs 14—17, Table 1), the results were not satisfactory, because the desired biaryl coupling reaction did not take place or the electrophilic arylation did not smoothly proceed. The reactivity of electron-deficient NPOHs **1e**, **f** with Qs was very poor.

In the second stage, further investigations on the reaction of **1e**, **f** were carried out (Chart 3 and Table 2). In our preceding papers, we reported on the reaction of **1e**, **f** with the $O_2/SnCl_4$ system or Ag_2O. The reaction with the $O_2/SnCl_4$ system gave *ortho*/*ortho*-coupled products **2e**, **f** and the naphthol trimers **8e**, **f**, arising from the regioselective biaryl coupling of **1e**, **f** (runs 3, 4 in Table 2, and Chart 3). In the case with Ag_2O, the coupling reaction did not proceed regioselectivity, affording the *ortho*/*ortho*-coupled product **2e** and the *ortho*/*para*-coupled product **9** (run 4 in Table 2).

It is known that semiconductor metal oxides including ZrO_2 possess catalytically active Lewis and Bronsted acidic sites on their surface.[51,52] In order to overcome the above problem, therefore, we designed reagent systems including the combination of Qs (BQ or CA) with $SnCl_4$ or ZrO_2. The reaction with Qs in the presence of $SnCl_4$ or ZrO_2 was examined (Chart 3, Table 2). We found that two types of reactions occurred, depending on the addition of $SnCl_4$ or ZrO_2. With the $Qs/SnCl_4$ system, oxidative biaryl coupling of NPOH proceeded to give **2e**, **f** and **8e**, **f** in both cases. An improvement in the yields of these products was observed in both cases, as compared with those in run 3 and 11 described above. On the other hand, in the case of CA in the presence of ZrO_2, the electrophilic arylation of CA with NPOH took place to give the adducts **6** and **7** (runs 5, 6, 12, 13). The addition of ZrO_2 led to a remarkable increase in the yields of **7e**, **f** to 73% and 91% (runs 6, 13), respectively, as compared with those of runs 15 and 17 in Table 1. Besides **1e**, **f** reacted with BQ on addition of ZrO_2 to afford the adducts **6e**, **f** (runs 5, 12). The above results indicated that addition of $SnCl_4$ or ZrO_2 in the presence of Qs facilitates oxidative biaryl coupling of electron-deficient NPOHs **1e**, **f** or electrophilic arylation of Qs with **1e**, **f**, respectively. The different reactivities with the $Qs/SnCl_4$ system and the Qs/ZrO_2 system are discussed below.

The proposed mechanism for the $SnCl_4$-mediated oxidative coupling of NPOHs **1e**, **f** with Qs is illustrated in Chart 4. This is analogous to that proposed for the oxidative reaction of 1-naphthols with the $O_2/SnCl_4$ system reported previously by us.[21,22] This reaction is initiated by the preferential formation of complex D between **1** and $SnCl_4$ rather than Qs (route c). In fact, in the case of **1e**, **f** with Qs in the absence of $SnCl_4$, the biaryl coupling did not take place at all (refer to runs 14—17 in Table 1). In the present oxidation, $SnCl_4$ acts not only as a characteristic Lewis acid catalyst, but also as a mediator for electron transfer. Alternatively, Qs (BQ or CA) act as a one-electron acceptor and a one-proton acceptor, playing the same role as that of dioxygen (O_2) described in our preceding paper.[21,22] The different yields with Qs or with O_2 may be based on the difference of one-electron accepting ability from the anion radical species ($SC^{\cdot -}$) (for example, compare the yield of run 9 with that of run 11). Alternatively, the adducts **7** can be formed *via* electrophilic arylation with **1e**, **f** induced by Qs (BQ or CA) activated by ZrO_2; in other words, the ZrO_2-promoted electrophilic substitution reaction proceeds to produce **7**. The adduct **6** is similarly formed, with subsequent dehydrogenation; in other words, nucleophilic addition-oxidation reactions take place to afford **6**. A Brønsted acid (Zr–OH) site on the ZrO_2 surface is considered to act as an activator for Qs as electrophiles.[30,54,55]

Conclusion

In this study, we found that BQ and CA are efficient oxidizing reagents for the oxidative dimerization of NPOHs **1a**—**c** to 2,2′-binapthyl derivatives **3**. The resulting products **3** should be useful synthetic intermediates for naturally occurring diosindigo B, biramentaceone and violetquinone.[23] The reagent systems including the combination of

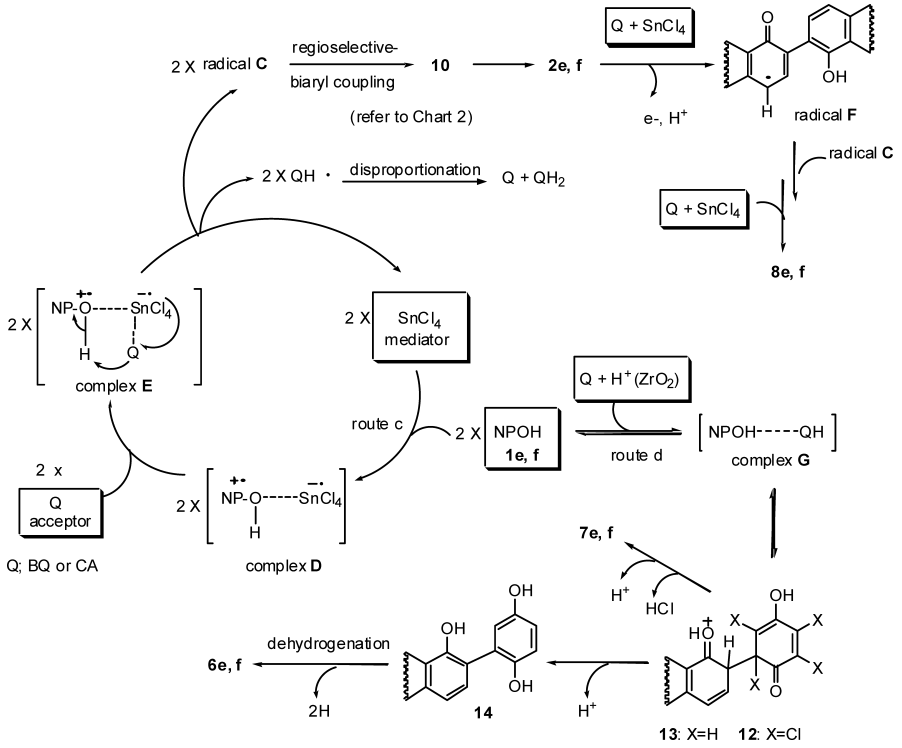

Chart 4. Proposed Mechanism for the Oxidative reaction of NPOH **1e**, **f** with the *p*-Benzoquinones in the Presence of $SnCl_4$ or ZrO_2

Qs (BQ or CA) and $SnCl_4$ or ZrO_2 promoted two different types of reactions of electron-deficient NPOHs **1e**, **f**: the oxidative biaryl coupling reaction of electron-deficient NPOH or the electrophilic arylation of the quinone with NPOH. This approach is attractive because of the simplicity of the reaction and its possible involvement in biosynthesis of biaryls and related natural products.

Experimental

General All melting points are uncorrected. IR and UV spectra were recorded on a JASCO IR-700 and a JASCO Ubest-55 spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL JNM-AL300 and JNM-alpha 500 spectrometers, with tetramethylsilane as an internal standard ($CDCl_3$ and CD_3SOCD_3 solution). Mass spectra were recorded on a JEOL JMS-D300 or a 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. Oxidation and reduction potentials were measured on a Yanaco P-1100 voltammetric analyzer by cyclic voltammetry. Storage and handling of $SnCl_4$: $SnCl_4$ should be stored in container with silica gel, blue, medium granule to minimize exposure to moisture; the container should be flushed with N_2 or Ar and tightly sealed; perform all manipulations under N_2 or argon. All reactions were carried out in the anhydrous state.

The Oxidation Potentials of 1a—f, the Reduction Potential of BQ, CA, DDQ, and the Charge-Transfer Absorptions of the EDA Complex of 1a with BQ or CA The oxidation potentials shown in Table 4, and the reduction potential of $SnCl_4$ were measured by cyclic voltammetry using an Ag/AgCl reference electrode at a platinum electrode with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte in an argon-saturated solvent (CH_2Cl_2).[16] The charge-transfer absorption described in the text was measured soon after mixing **1a** (7.65×10^{-5} M) with BQ (7.65×10^{-5} M) in argon-saturated CH_2Cl_2.

Synthesis of 1-Naphthols 1a—h Naphthols **1b**—**f**[16] were synthesized according to the protocol reported previously, and **1a** is commercially available (Tokyo Kasei Chemical Industries, Ltd., Japan).

General Procedure for the Reactions of NPOH 1 with Several *p*-Benzoquinones [1,4-Benzoquinone (BQ), 2,3,5,6-Tetrachloro-1,4-benzoquinone (*p*-chloranil; CA) or 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)] A solution of **1** (0.58 mmol) and *p*-benzoquinones (0.7 mmol; 1.2 eq) [CA (172 mg), BQ (76 mg), or DDQ (159 mg)] in a dry argon-saturated solvent (15 ml) (CH_2Cl_2 or $MeNO_2$) in a sealed tube was stirred at 23 °C (room temperature). The precipitate was separated from the solution by filtration and the filtrate was concentrated. The residue was subjected to flash column chromatography on silica gel.

Reaction of 1a with *p*-Benzoquinones Reaction of **1a** (50 mg, 0.29 mmol) with BQ (37 mg, 0.34 mmol) or CA (85 mg, 0.34 mmol) was carried out according to the general procedure for the reaction of NPOHs **1** with several *p*-benzoquinones described above. The crude product was subjected to flash column chromatography on silica gel with the designated solvents as follows: CH_2Cl_2–hexane (1 : 2; for **3a** in Table 1); CH_2Cl_2–hexane (3 : 1; for **3a** and **4a** in Table 1); CH_2Cl_2–hexane (1 : 2; for **2a** and **3a** in Table 1). Yields are listed in Table 1.

4,4′-Dimethoxy[2,2′]binaphthalenyl-1,1′-diol (2a) Colorless needles (benzene), mp 223—224 °C.[16] LR-MS *m/z*: 346 (M^+). IR, ^{1}H- and ^{13}C-NMR data were described previously by us.[16]

4,4′-Dimethoxy[2,2′]binaphthalenylidene-1,1′-dione (3a) Deep blue needles (benzene), mp 257—258 °C.[16] LR-MS *m/z*: 344 (M^+). IR, ^{1}H- and ^{13}C-NMR data were described previously by us.[16]

Isolation of Hydroquinone (BQH_2) Prepared by the Reaction of 1a with BQ Reaction of **1a** (50 mg, 0.29 mmol) with BQ (37 mg, 0.34 mmol) was carried out according to the general procedure for the reaction of NPOHs **1** with several *p*-benzoquinones described above. The crude product was subjected to flash column chromatography on silica gel with CH_2Cl_2–hexane (1 : 2) to give hydroquinone (BQH_2; 26 mg, 69%) and **3a** (99%).

Isolation of 3,4,5,6-Tetrachlorohydroquinone (CAH_2) Prepared by the Reaction of 1a with BQ Reaction of **1a** (50 mg, 0.29 mmol) with CA (85 mg, 0.34 mmol) was carried out according to the general procedure for the reaction of NPOHs **1** with several *p*-benzoquinones described above. The crude product was subjected to flash column chromatography on silica gel with CH_2Cl_2–hexane (1 : 2) to give 3,4,5,6-tetrachlorohydroquinone (CAH_2, 64 mg, 75%), **3a** (89%), and **4a** (6%).

Reaction of 1b with *p*-Benzoquinones Reaction of **1b** (50 mg, 0.24 mmol) with BQ (32 mg, 0.29 mmol) or CA (73 mg, 0.29 mmol) was carried out according to the general procedure for the reaction of NPOHs **1** with several *p*-benzoquinones described above. The crude product was subjected to flash column chromatography on silica gel with the designated solvents as follows: CH_2Cl_2–AcOEt (10 : 1 for **3b** in Table 1); CH_2Cl_2–hexane (1 : 2 for **4b** and **6** in Table 1). Yields are listed in Table 1.

4,5,4′,5′-Tetramethoxy-7,7′-dimethyl[2,2′]binaphthalenylidene-1,1′-dione (3b) Deep blue powder (benzene), mp 236.5—237.0 °C.[24] HR-MS Calcd for $C_{26}H_{24}O_6$: 432.1566, Found: 432.1563. IR, ^{1}H- and ^{13}C-NMR data were described previously by us.[24]

5-Methoxy-7-methyl-1,4-naphthoquinone (4b) Yellow needles (benzene), mp 169.5—170 °C.[24] HR-MS calcd for $C_{12}H_{10}O_3$: 202.0627. Found: 202.0614. IR, ^{1}H- and ^{13}C-NMR data were described previously by us.[24]

Reaction of 1c with *p*-Benzoquinones Reaction of **1c** (50 mg, 0.25 mmol) with BQ or CA was carried out according to the general procedure for the reaction of NPOHs **1** with several *p*-benzoquinones described above. The crude product was subjected to flash column chromatography on silica gel with the designated solvents as follows: hexane–AcOEt (2 : 1 for **5** in Table 1); CH_2Cl_2–hexane (2 : 1 for **2c** and **5** in Table 1). Yields for **2c** and **5** are listed in Table 1.

4,4′,8,8′-Tetramethoxy-2,2′-di-1,1′-naphthol (2c) Colorless needles ($CHCl_3$–hexane), mp 207—209 °C.[16] LR-MS *m/z*: 406 (M^+). IR, ^{1}H- and ^{13}C-NMR data were described previously by us.[16]

1′-Hydroxy-4′,8,8′-trimethoxy[2,2′]binaphthalenyl-1,4-dione (5) Deep purple needles (hexane–AcOEt), mp 120—122 °C.[24] HR-MS Calcd for $C_{23}H_{18}O_6$: 390.1100, Found: 390.1170. IR, ^{1}H- and ^{13}C-NMR data were described previously by us.[24]

Reaction of 1d with *p*-Benzoquinones These reactions did not proceed.

Reaction of 1e or 1f with BQ These reactions did not proceed.

Reaction of 1e or 1f with CA Reaction of **1e** (50 mg, 0.25 mmol) or **1f** (50 mg, 0.23 mmol) with CA was carried out according to the general procedure for the reaction of NPOHs **1** with several *p*-benzoquinones described above. The crude product was subjected to flash column chromatography on silica gel with the designated solvents as follows: CH_2Cl_2–hexane (1 : 5 for **7e** in Table 1); hexane–AcOEt (10 : 1 for **7f** in Table 1). Yields for **7e** and **f** are listed in Table 1.

2,3,5-Trichloro-6-(1-hydroxy-5,8-dimethoxynaphthalen-2-yl)[1,4]benzoquinone (7e) Deep blue granules (CH_2Cl_2–hexane), mp 243—243.5 °C. IR (KBr) cm^{-1}: 3376, 1675, 1628, 1566. ^{1}H-NMR ($CDCl_3$) δ: 3.96 (3H, s, -OMe), 4.01 (3H, s, -OMe), 6.74 (2H, s, 6′-H and 7′-H), 7.18 (1H, d, J=8.8 Hz, 3′-H), 7.80 (1H, d, J=8.8 Hz, 4′-H), 9.90 (1H, s, 1′-OH). ^{13}C-NMR ($CDCl_3$) δ: 56.4 (-OMe), 55.9 (-OMe), 104.4 (C6′), 104.7 (C7′), 113.2 (C4′), 113.4 (C8a′), 115.3 (C2′), 127.2 (C3′), 129.0 (C-4a′), 140.1 (C8′), 141.1 (C1′), 141.7 (C5′), 143.1 (C3), 150.3 (C6), 150.4 (C5), 152.1 (C2), 171.7 (C1), 174.5 (C4). LR-MS *m/z*: 414 (M^+). *Anal.* Calcd for $C_{18}H_{11}Cl_3O_5$: C, 52.27; H, 2.68; Cl,25.71. Found: C, 52.30; H, 2.70; Cl,25.75.

2,3,5-Trichloro-6-(1-hydroxy-5,8-dimethoxy-6-methylnaphthalen-2-yl)[1,4]benzoquinone (7f) Deep blue granules ($CHCl_3$–hexane), mp 225—227 °C. IR (KBr) cm^{-1}: 3308, 1683, 1623, 1570. ^{1}H-NMR ($CDCl_3$) δ: 2.44 (3H, s, 6-Me), 3.85 (3H, s, -OMe), 4.03 (3H, s, -OMe), 6.65 (1H, s, 7′-H), 7.18 (1H, d, J=8.82 Hz, 3′-H), 7.60 (1H, d, J=8.82 Hz, 4′-H), 9.74 (1H, s, 1′-OH). ^{13}C-NMR ($CDCl_3$) δ: 16.3 (C6′-Me), 56.3 (C8′-OMe), 61.1 (C5′-OMe), 107.8 (C7′), 112.2 (C6′), 113.0 (C4′), 114.1 (C8a′), 127.8 (C2′), 128.0 (C3′), 131.7 (C-4a′), 140.1 (C8′), 141.1 (C1′), 141.7 (C5′), 143.1 (C3), 148.0 (C6), 152.5 (C5), 152.6 (C2), 171.8 (C1), 174.6 (C4). LR-MS *m/z*: 426 (M^+). *Anal.* Calcd for $C_{19}H_{13}Cl_3O_5$: C, 53.36; H, 3.06; Cl, 24.87. Found: C, 53.39; H, 3.05; Cl, 24.90.

Reaction of 2a with *p*-Benzoquinones Oxidation of **2a** (50 mg, 0.15 mmol) with BQ (20 mg, 0.18 mmol) or CA (45 mg, 0.18 mmol) was carried out according to the general procedure for the reaction of NPOHs **1** with several *p*-benzoquinones described above. The crude product was subjected to flash column chromatography on silica gel with hexane–CH_2Cl_2 (2 : 1) to give **3a**. Yields for **3a** are listed in Table 1.

Reaction of 3c with CA This reaction did not proceed.

Demethylation of 3c to 5 with SiO_2 A slurry of SiO_2 powder (5 g) and **3c** (50 mg, 0.12 mmol) in argon-saturated CH_2Cl_2 (30 ml) was vigorously stirred at 23 °C under normal laboratory light. Then, the reaction mixture was stirred in a sealed tube until disappearance of the substrate (2,2′-binaphthyls). The insoluble reagent was filtered off and washed with the solvents used, and then the filtrate was evaporated. The residue was subjected to flash column chromatography on silica gel with CH_2Cl_2–AcOEt (20 : 1) to give **5** (91%) (Run 21 in Table 1).

Demethylation of 3c to 5 with HCl A solution of **3c** (50 mg, 0.12 mmol) and 10% HCl (46 μl) in CH_2Cl_2 (10 ml) was stirred at 23 °C for 30 min. The reaction mixture was poured into ice-water and extracted with CH_2Cl_2. The organic layer was washed with H_2O, then dried and concentrated. The residue was recrystallized from ether–hexane to give **5** (95%).

Oxidation of 1a with Ag_2O A solution of **1a** (50 mg, 0.29 mmol) in $CHCl_3$ (10 ml) containing 1.5 eq of Ag_2O (100 mg, 0.43 mmol) was stirred at 23 °C under air for 1 h. The solvent was removed and the residue was subjected to flash column chromatography on silica gel using hexane–CH_2Cl_2 (2 : 1) to give **2a** (20%) and **3a** (75%).

Oxidation of 1c with Ag_2O/Et_3N A mixture of **1c** (200 mg, 0.98 mmol) in $CHCl_3$ (15 ml) containing 0.2% NEt_3 (340 μl, 2.5 eq) and 10 eq of Ag_2O (2.27 g) was stirred at 23 °C in an air atmosphere for 1 h. The reaction mixture was filtered and solvent was evaporated. The residue was recrystallized from benzene–hexane to give 4,8,4′,8′-tetramethoxy[2,2′]binaphthalenylidene-1,1′-dione (**3c**; 93%) as deep purple needles ($CHCl_3$–hexane), mp 261—262 °C. IR (KBr) cm^{-1}: 1613, 1581, 1564. ^{1}H-NMR ($CDCl_3$) δ: 3.99 (6H, s, 8, 8′-OMe), 4.01 (6H, s, 4, 4′-OMe), 7.00 (2H, d, J=8.2 Hz, 7, 7′-H), 7.41 (2H, dd, J=0.9, 7.5 Hz, 5, 5′-H), 7.52 (2H, t, J=8.2 Hz, 6, 6′-H), 7.92 (2H, s, 3, 3′-H). ^{13}C-NMR ($CDCl_3$) δ: 55.90 (4, 4′-OMe), 56.32 (8, 8′-OMe), 102.28 (C3, C3′), 112.46 (C7, C7′), 114.61 (C5, C5′), 120.63 (C8a, C8a′), 133.35 (C4a, C4a′), 133.83 (C6, C6′), 134.49 (C2, C2′), 155.42 (C4, C4′), 159.90 (C8, C8′), 189.49 (C1, C1′). LR-MS *m/z*: 404 (M^+). HR-MS Calcd for $C_{24}H_{20}O_6$: 404.1254, Found: 404.1267. *Anal.* Calcd for $C_{24}H_{20}O_6$: C, 71.28; H, 4.98. Found: C, 71.08; H, 4.95.

General Procedure for Oxidation of 1-Naphthols 1 with *p*-Benzoquinones (CA or BQ) in the Presence of $SnCl_4$ A solution of **1** (50 mg, 0.24 mmol), $SnCl_4$ (7 μl, 0.03 mmol, 0.25 eq), and CA (60 mg, 1.0 eq) or BQ (26 mg, 1.0 eq) in argon-saturated CH_2Cl_2 (13 ml) in a sealed tube was stirred at 23 °C. The reaction mixture was poured into ice-water and extracted with CH_2Cl_2. The organic layer was washed with 10% HCl and H_2O, then dried and concentrated. The residue was subjected to flash column chromatography on silica gel with the designated solvents as follows: hexane–CH_2Cl_2 (2 : 1 for **2e** and **8e** in Table 2); hexane–AcOEt (10 : 1 for **2f** and **8f** in Table 2). Yields for **2e**, **f** and **8e**, **f** are listed in Table 1.

5,5′,8,8′-Tetramethoxy[2,2′]di-1,1′-naphthol (2e) Colorless needles (hexane–AcOEt), mp 257—260.5 °C.[16] HR-MS Calcd for $C_{24}H_{22}O_6$: 406.1416, Found: 406.1433. IR, ^{1}H- and ^{13}C-NMR data were described previously by us.[16]

12-(1′-Hydroxy-5′,8′-dimethoxynaphthalen-2′-yl)-1,4,7,10-tetramethoxy-13-oxa-dibenzo[*a*,*g*]fluoren-11-ol (8e) Light brown amorphous powder ($CHCl_3$–MeOH), mp 263—265 °C.[16] HR-MS Calcd for $C_{36}H_{30}O_9$: 606.1881, Found: 606.1887. IR, ^{1}H- and ^{13}C-NMR data were described previously by us.[16]

5,5′,8,8′-Trimethoxy-6,6′-dimethyl[2,2′]di-1,1′-naphthol (2f) Colorless needles (ether–hexane), mp 229—232 °C.[16] HR-MS Calcd for $C_{26}H_{26}O_6$: 434.1730, Found: 434.1746. IR, ^{1}H- and ^{13}C-NMR data were described previously by us.[16]

12-(1-Hydroxy-5,8-dimethoxy-6-methylnaphthalen-2-yl)-1,4,7,10-tetramethoxy-3,8-dimethyl-13-oxadibenzo[*a*,*g*]fluoren-11-ol (8f) Pale green amorphous powder ($CHCl_3$–hexane), mp 249—251 °C.[16] HR-MS Calcd for $C_{39}H_{36}O_9$: 648.2349, Found: 648.2386. IR, ^{1}H- and ^{13}C-NMR data were described previously by us.[16]

General Procedure for the Reaction of NPOHs 1e, f with *p*-Benzoquinones (BQ or CA) in the Presence of ZrO_2 A slurry of **1** (50 mg, 0.25 mmol), ZrO_2 powder (5 g), and CA (60 mg, 1.0 eq) or BQ (26 mg, 1.0 eq) in argon-saturated solvent (CH_2Cl_2 or $MeNO_2$; 15 ml) was vigorously stirred at 23 °C under normal laboratory light. The insoluble reagent was filtered off and washed with the solvent used, and then the filtrate was evaporated. The residue was subjected to flash column chromatography on silica gel with the designated solvents as follows: hexane–CH_2Cl_2 (2 : 1; for **6e** in Table 2); hexane–AcOEt (5 : 1; for **6f** in Table 2). Yields for **6e**, **f** and **7e**, **f** are listed in Table 1.

2-(1-Hydroxy-5,8-dimethoxynaphthalen-2-yl)[1,4]benzoquinone (6e) Deep green powder (hexane–CH_2Cl_2), mp 193.5—194.5 °C. IR (KBr) cm^{-1}: 3267, 1655, 1628, 1614, 1585. ^{1}H-NMR ($CDCl_3$) δ: 3.95 (3H, s, OMe), 4.01 (3H, s, OMe), 6.70 (1H, d, J=8.6 Hz, 6′ or 7′-H), 6.73 (1H, d, J=8.6 Hz, 6′ or 7′-H), 6.81 (1H, dd, J=2.6, 7.5 Hz, 5-H), 6.89 (1H, d, J=10.1 Hz, 6-H), 6.96 (1H, d, J=2.6 Hz, 3-H), 7.24 (1H, d, J=8.6 Hz, 3′-H), 7.75 (1H, d, J=8.6 Hz, 4′-H), 9.94 (1H, s, 1′-OH). ^{13}C-NMR ($CDCl_3$ δ: 55.8 (OMe), 56.5 (OMe), 104.3 (C6′ or C7′), 104.4 (C6′ or C7′), 113.0 (C4′), 115.4 (C2′ or C8a′), 115.6 (C2′ or C8a′),128.0 (C3′), 128.9 (C4a′), 134.8 (C3), 136.1 (C5), 137.2 (C6), 146.0 (C1), 150.2 (C8′), 150.4 (C5′), 152.6 (C2), 185.9 (C1), 187.9 (BQ-C4′). LR-MS *m/z*: 310 (M^+). HR-MS Calcd for $C_{18}H_{14}O_5$: 310.0837. Found 310.0856: *Anal.* Calcd for $C_{18}H_{14}O_5$: C, 69.67; H, 4.55. Found: C, 69.69; H, 4.58.

2-(1-Hydroxy-5,8-dimethoxy-6-methylnaphthalen-2-yl)[1,4]benzoquinone (6f) Deep blue powder (hexane–CH_2Cl_2), mp 143.5—144 °C. IR (KBr) cm^{-1}: 3280, 1654, 1624, 1585, 1388. ^{1}H-NMR ($CDCl_3$) δ: 2.43 (3H, s, Me), 3.84 (3H, s, OMe), 4.03 (3H, s, OMe), 6.63 (1H, s, 7′-H), 6.82

(1H, dd, J=2.57, 10.11 Hz, 5-H), 6.90 (1H, d, J=10.11 Hz, 6-H), 6.98 (1H, d, J=2.57 Hz, 3-H), 7.25 (1H, d, 3′-H), 7.57 (1H, d, J=8.64, 4′-H), 9.84 (1H, s, 1′-OH). ^{13}C-NMR ($CDCl_3$) δ: 16.3 (Me), 56.4 (OMe), 61.1 (OMe), 107.7 (C7′), 112.8 (C4′), 114.27 (C6′ or C8a′), 114.29 (C6′ or C8a′), 127.5 (C2′),128.7 (C3′), 131.5 (C4a′), 134.7 (C3), 136.1 (C5), 137.1 (C6), 145.8 (C1′), 148.0 (C8′), 152.5 (C5′), 153.1 (C2), 186.1 (C1), 187.9 (C4). LR-MS m/z: 324 (M^+). HR-MS Calcd for. $C_{19}H_{16}O_5$: 324.0993. Found: 324.1006. *Anal.* Calcd for $C_{19}H_{16}O_5$: C, 70.36; H, 4.97. Found: C, 70.40; H, 4.99.

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