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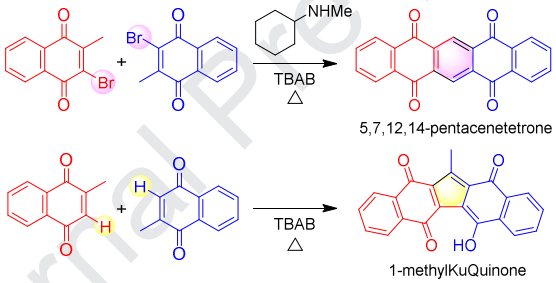
[a]*Department of Applied Biological Science, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan*

[b]*Graduate School for Life and Environmental Sciences, Kyoto Prefectural University, 1-5 Shimogamo Hangi-cho, Sakyo-ku, Kyoto 606-8522, Japan*

[*]Corresponding author.

[1]These authors contributed equally to this work.

[2]Present address: Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, Pennsylvania 15260, United States.



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[a]*Department of Applied Biological Science, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan*
[b]*Graduate School for Life and Environmental Sciences, Kyoto Prefectural University, 1-5 Shimogamo Hangi-cho, Sakyo-ku, Kyoto 606-8522, Japan*

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ABSTRACT

2-Bromo-3-methyl-1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone are highly reactive species known to dimerize in various ways. The product obtained in the dimerization of each compound is primarily dependent upon the solvent used. Ionic liquids represent a new class of solvents having non-molecular (ionic) character. Replacement of a conventional organic solvent with an ionic solvent frequently changes the mechanism of a reaction. In this study, reactions of 2-bromo-3-methyl-1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone in ionic liquids were examined. Dimerization of 2-bromo-3-methyl-1,4-naphthoquinone or 2-methyl-1,4-naphthoquinone with *N*-methylcyclohexylamine in tetra-*n*-butylammonium bromide (TBAB), an ionic liquid, under an aerobic atmosphere afforded 5,7,12,14-pentacenetetrone and 1-methylKuQuinone, respectively. The use of TBAB as a solvent improved the yields of the products as compared with previously reported methods. The mechanism of each dimerization was also investigated.

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1. Introduction

1,4-Naphthoquinones are known to dimerize in various ways, depending on their structure and the particular set of conditions in use [1-3]. They serve as electrophiles and participate in 1,2-addition and 1,4-addition reactions with nucleophiles. In contrast, 1,4-dihydroxynaphthalenes, the reduced forms of 1,4-naphthoquinones, act as nucleophiles [1]. Thus, coupling between naphthoquinones and the corresponding 1,4-dihydroxynaphthalenes can occur to give dimeric products. 2-Methyl-1,4-naphthoquinones are known to produce dimeric products via their *o*-quinone methides. The *o*-quinone methides have both nucleophilic and electrophilic properties because they have a nucleophilic dienol/enol and an electrophilic α,β-unsaturated enone/ketone in the same molecule [1]. Baxter and coworkers reported that treatment of 2-bromo-3-methyl-1,4-naphthoquinone (**1**) with *N*-methylcyclohexylamine in EtOH afforded 5,7,12,14-pentacenetetrone (**2**) in 11% yield (**Scheme 1A**) [4]. Our group reported the following six different dimerizations of **1** (**Scheme 1B**) [5-7]. Treatment of **1** with hexamethylditin and CuI in the presence of [1,1′-bis(diphenylphosphino)ferrocene]palladium dichloride [Pd(dppf)Cl_2] in dioxane afforded a 2,2′-dimeric naphthoquinone **3** [5]. When **1** was treated with hexamethylditin, CuI and Na_2CO_3 in the presence of tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$] and (±)-2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl (BINAP) in DMF, an oxepin **4** was obtained [5]. Treatment of **1** with Cs_2CO_3 in DMF gave a dimeric epoxide **5** [5], whereas treatment of **1** with Na_2CO_3 in MeOH gave a tetrahydropyran **6** [6]. Switching only the solvent also results in different reactivity. For example, a 2*H*-naphtho[1,2-*b*]pyran **7** was obtained by treatment of **1** with 1-ethylpiperidine in THF, while treatment of **1** with 1-ethylpiperidine in CH_2Cl_2 afforded a diquinone **8** [7].

Baxter and coworkers reported that treatment of 2-methyl-1,4-naphthoquinone (**9**) with *N*-methylcyclohexylamine in EtOH gave **2** in 14% yield (**Scheme 2A**) [4]. Although the yield of the reaction was low, this method was considered useful because **2** can be prepared from inexpensive starting materials in a straightforward and reproducible way [8]. Our group reported a biomimetic dimerization of **9** affording a dimeric epoxide **10** in higher yield by treatment with a 5 M aqueous NaOH solution in EtOH under an aerobic atmosphere (**Scheme 2B**) [9].

Ionic liquids, salts that are liquid at temperature lower than 150 °C, represent a relatively new class of solvents with non-

∗ Corresponding author. Tel. +81-4-7122-9413; fax: +81-4-7123-9767; e-mail: kuramoch@rs.tus.ac.jp
[1]These authors contributed equally to this work.
[2]Present address: Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, Pennsylvania 15260, United States.

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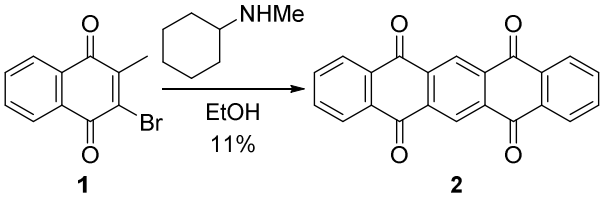
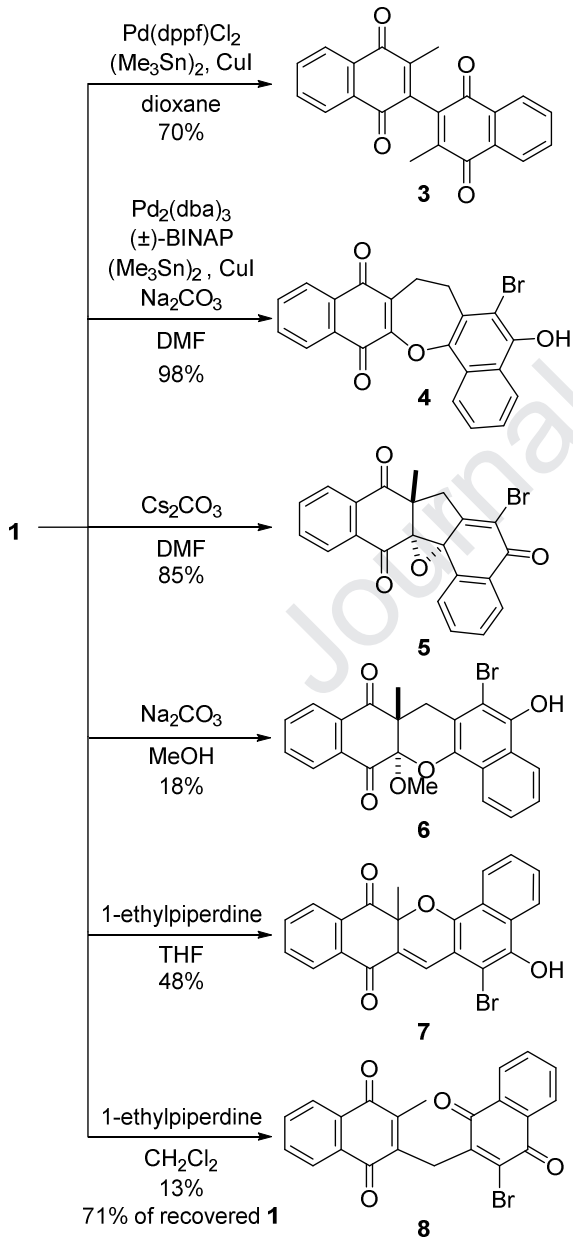
molecular (ionic) character [10]. They have emerged as useful solvents with high thermal and chemical stability, and have found several applications in synthetic chemistry. Notably, ionic liquids can exploit novel and unusual chemical reactivity [10-12]. This peculiar nature of ionic liquids motivated us to employ them as solvents for the "*chameleon-like*" dimerization of 1,4-naphthoquinones.

(A) Dimerization of **1** reported by Baxter and coworkers



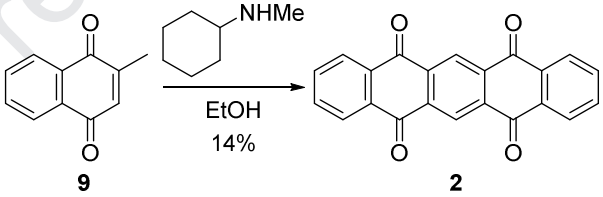
(B) Six different dimerizations reported by our group



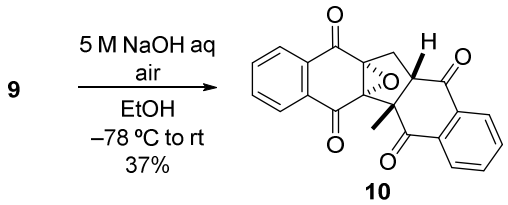
Scheme 1. Previous dimerizations of 2-bromo-3-methyl-1,4-naphthoquinone (**1**).

In this paper, dimerizations of **1** and **9** in tetra-*n*-butylammonium bromide (TBAB), an ionic liquid, are reported. Dimerizations of **1** and **9** in TBAB gave **2** and 1-methylKuQuinone (**11**), respectively. Both **2** and **11** have interesting properties. Compound **2** and its derivatives are promising organic candidates for use as high-capacity cathodes in rechargeable lithium batteries [13-16]. Additionally, compound **2** has been used as a starting material in the production of a new class of pentacene-based π-conjugated systems [8,17-21]. 1-MethylKuQuinone (**11**) was synthesized by Coletti and coworkers in 6% yield via treatment of 2-hydroxynaphthoquinone (**12**) and 1-bromopropane with Cs_2CO_3 in the presence of a catalytic amount of ferrocene in DMSO at 114 °C (**Scheme 3**) [22]. This compound possesses interesting absorption, fluorescence and electrochemical properties [23-25]. In addition to its chemical properties, **11** shows cytotoxic activities against human cancer cells [25]. Thus, a better and simpler methodology for the synthesis of **11** is needed. Our present method using TBAB as a solvent for the dimerizations of **1** and **9** improved the yields of **2** and **11**, respectively. Notably, the use of TBAB as a solvent and a reagent provided a novel dimerization mode of **9**. The reaction mechanism for the formation of **11** by dimerization of **9** was also elucidated by determination of the reaction intermediate and ^{13}C labeling experiments.

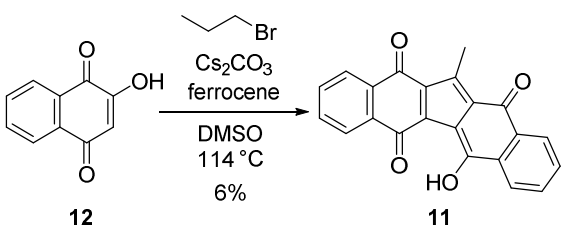
(A) Dimerization of **9** reported by Baxter and coworkers



(B) Dimerization of **9** reported by our group



Scheme 2. Previous Dimerizations of 2-Methyl-1,4-naphthoquinone (**9**).



Scheme 3. Previous synthesis of 1-methylKuQuinone (**11**).

2. Results and discussion

Dimerization of 2-bromo-3-methyl-1,4-naphthoquinone (**1**) in ionic liquids was examined (**Table 1**). Treatment of **1** with *N*-

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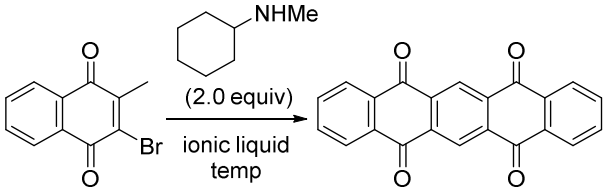
methylcyclohexylamine (2.0 equiv) in TBAB (52 equiv) at 120 °C under an aerobic atmosphere gave **2** in 17% yield (entry 1). The melting point (Mp) of TBAB is 103 °C. Thus, TBAB is a liquid at the reaction temperature of 120 °C. Because compound **1** is unstable under basic conditions, the low yield is due to decomposition of **1** accompanied by formation of **2**. Dimerization of **1** with *N*-methylcyclohexylamine (2.0 equiv) in TBAB (50 equiv) and refluxing toluene gave **2** in lower (7%) yield (entry 2). The reaction did not proceed in the absence of *N*-methylcyclohexylamine (entry 3). These results indicate that the use of TBAB and *N*-methylcyclohexylamine as solvent and base, respectively, is important for this dimerization. The use of tetra-*n*-butylammonium chloride (TBAC; Mp = 70°C), tetra-*n*-butylphosphonium bromide (TBPB; Mp = 100–103 °C), tetra-*n*-butylphosphonium tetrafluoroborate (n-$Bu_4P{\cdot}BF_4$; Mp = 96–99 °C), or 1-butyl-3-methylimidazolium chloride ([Bmim]Cl; Mp = ~70 °C) as the ionic liquid all decreased the yield of **2** (entries 4−7). The reaction in tetra-*n*-butylammonium iodide (TBAI; Mp = 141–143 °C) at 145 °C resulted in decomposition of **1** (entry 8). The melting point of TBAI is higher than those of other liquid ions used in this study, suggesting that TBAI induces thermal decomposition of **1**.

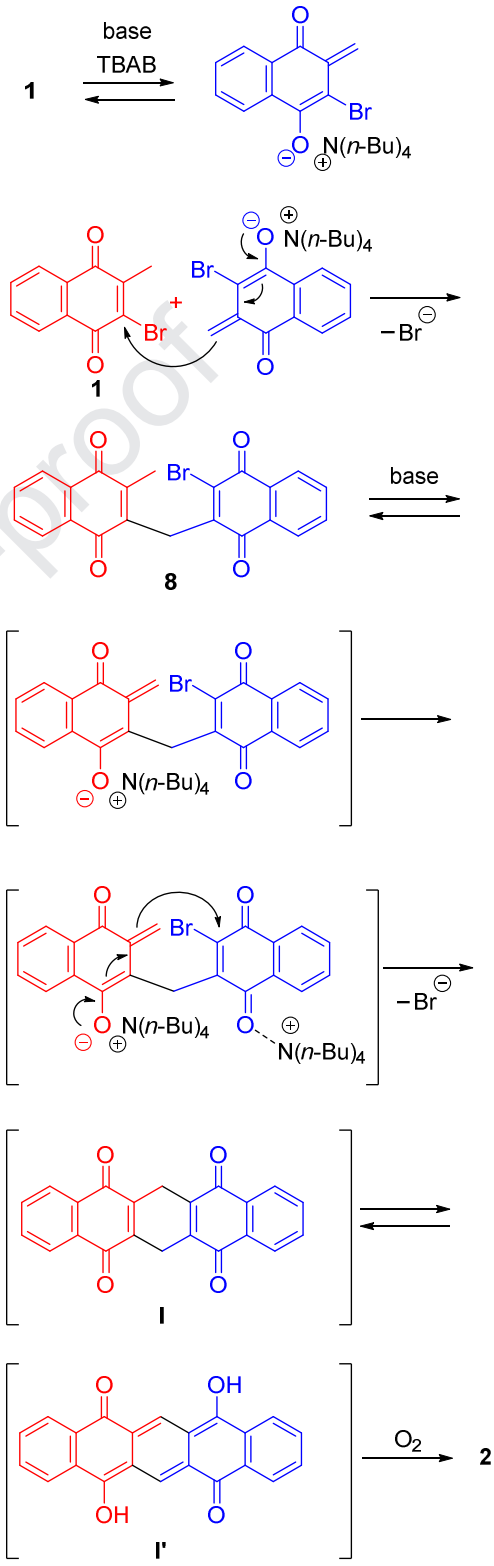
Table 1.
Dimerization of 2-bromo-3-methyl-1,4-naphthoquinone (**1**) in ionic liquids.



entry	ionic liquid (equiv)	solvent	temp (°C)	time (min)	yield (%)[a]
1	TBAB (52)	–	120	45	17[b]
2	TBAB (50)	toluene	reflux	60	7[b]
3[c]	TBAB (50)	–	120	300	–[d]
4	TBAC (50)	–	100	60	9[b]
5	TBPB (50)	–	110	30	13[b]
6	n-$Bu_4P{\cdot}BF_4$ (50)	–	110	30	10[b]
7	[Bmim]Cl (50)	–	80	50	4[b]
8	TBAI (50)	–	145	50	0[e]

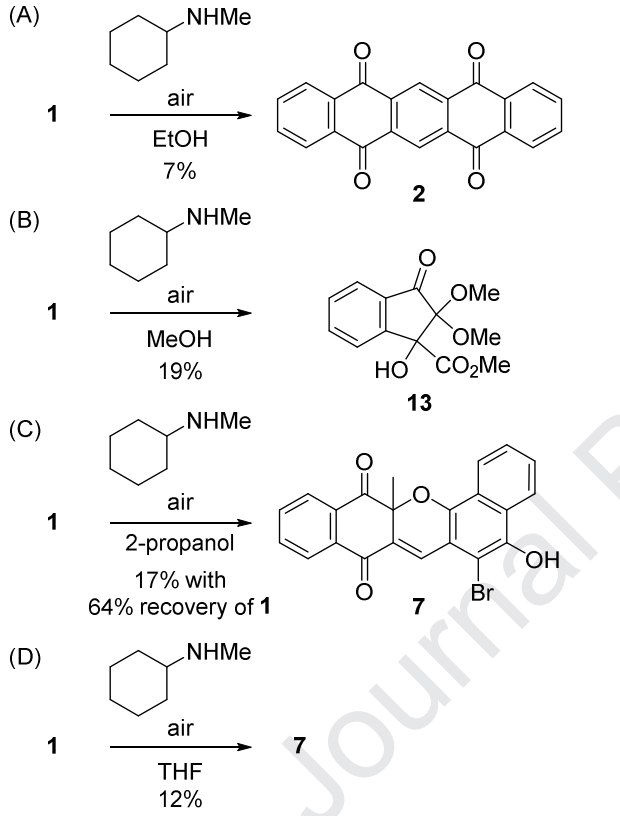
[a] Isolated yield.
[b] TLC analysis showed the starting material **1** was fully consumed. Decomposition of **1** was accompanied by formation of **2**.
[c] Without *N*-methylcyclohexylamine.
[d] TLC analysis showed that formation of **2** was not observed and unreacted starting material **1** was observed.
[e] Compound **1** decomposed, and **2** was not obtained.

The mechanism for the dimerization of **1** in TBAB is proposed in **Scheme 4**. First, the diquinone **8** is formed by coupling **1** to its *o*-quinone methide [7]. A base-induced enolization of **8**, an intramolecular 1,4-addition, and elimination of the bromide ion affords diquinone **I**, which is in equilibrium with its dienol form **I′**. Interaction between the carbonyl oxygen and the tetra-*n*-butylammonium cation should activate the unsaturated ketone and induces the 1,4-addition. Finally, oxidation of the tautomeric mixture of diquinoids **I** and **I′** by oxygen yields **2**.



Scheme 4. Mechanism for formation of **2** from **1**.

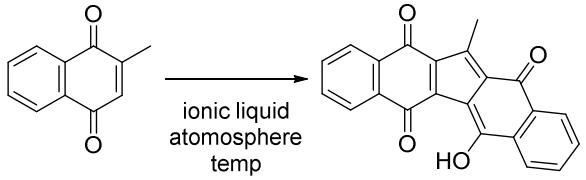
We examined the conventional solvents for the dimerization of **1** (**Scheme 5**). According to the procedure reported by Baxter and coworkers [4], treatment of **1** with *N*-methylcyclohexylamine in EtOH under an aerobic atmosphere gave **2** in 7% yield (**Scheme 5A**). Surprisingly, treatment of **1** with *N*-methylcyclohexylamine in MeOH gave **13** in 19% yield (**Scheme 5B**). Decomposition of **1** was accompanied by formation of **13**. The reaction in 2-propanol gave 2*H*-naphtho[1,2-*b*]pyran **7** [7] in 17% yield with 64% recovery of **1** (**Scheme 5C**). The use of THF as a solvent gave **7** in 12% (**Scheme 5D**). When DMF was used as a solvent, decomposition of **1** occurred. These results are the reason why we call the dimerization of 1,4-naphthoquinones "*chameleon-like*".



Scheme 5. Dimerization of **1** in EtOH (A), MeOH (B) and 2-propanol (C), and THF (D).

Next, dimerization of **9** in ionic liquids was examined (**Table 2**). When **9** was heated with *N*-methylcyclohexylamine (2.0 equiv) in TBAB (11 equiv) at 130 °C under an aerobic atmosphere, 1-methylKuQuinone (**11**) was obtained in 30% yield (entry 1). In this reaction, decomposition of **9** was accompanied by formation of **11**, resulting in the low yield of **11**. The reaction proceeded in the absence of *N*-methylcyclohexylamine (entry 2) and under an oxygen atmosphere (entry 3). Dimerization of **9** by TBAB in a refluxing toluene (bp = 110.6 °C) under an oxygen atmosphere afforded **11** in 17% yield (entry 4). When the reaction of **9** with TBAB was performed in a refluxing ethanol (bp = 78.4 °C), the formation of **11** was not observed (entry 5). When the reaction was performed in TBAC at 100 °C, no reaction occurred (entry 6). However, the reaction in TBAC at 130 °C yielded **11** in 15% yield (entry 7). These results suggest that the dimerization might proceed at temperatures higher than 110 °C. But, treatment of **9** with TBAB in DMF at 130 °C gave a complex mixture (entry 8). When **9** was heated at 145 °C in

Table 2.
Dimerization of 2-methyl-1,4-naphthoquinone (**9**) in ionic liquids.



9 **11**

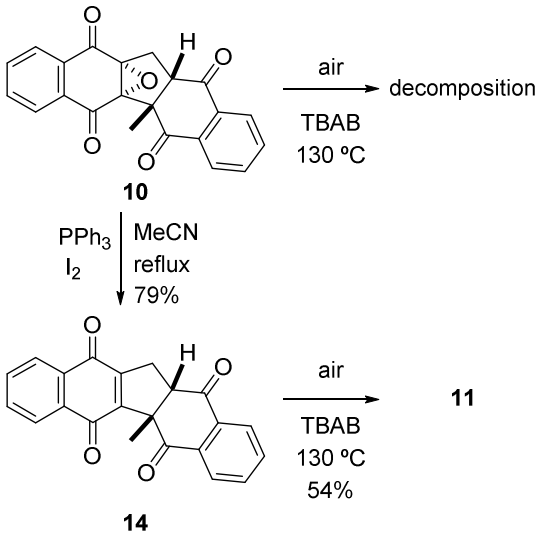
entry	ionic liquid (equiv)	atmosphere	solvent	temp (°C)	time (h)	yield (%)[a]
1[b]	TBAB (11)	air	–	130	1	30[c]
2	TBAB (11)	air	–	130	9	22[c]
3	TBAB (11)	O_2	–	130	7	19[c]
4	TBAB (10)	O_2	toluene	reflux	6.5	17[c]
5	TBAB (10)	O_2	ethanol	reflux	7	0[d]
6	TBAC (10)	O_2	–	100	7	0[d]
7	TBAC (10)	O_2	–	130	7	15[c]
8	TBAB (10)	O_2	DMF	130	7	0[e]
9	TBAI (10)	O_2	–	145	7	0[e]

[a] Isolated yield.
[b] In the presence of *N*-methylcyclohexylamine (3.0 equiv).
[c] TLC analysis showed the starting material **9** was fully consumed. Decomposition of **9** was accompanied by formation of **11**.
[d] No reaction occurred. Almost all the starting material was recovered.
[e] Compound **9** decomposed, and **11** was not obtained.

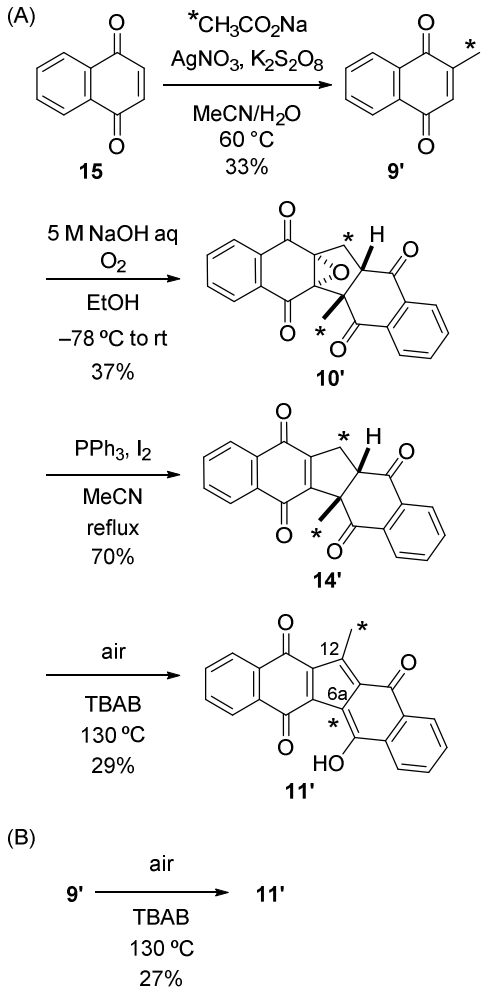
TBAI, decomposition of **9** occurred (entry 9). TBAI induces thermal decomposition of **9**. These results indicate that the reaction temperature, solvent, and ionic liquid used in this reaction are considered major factors in this dimerization.

To determine the intermediate in the dimerization of **9**, two hypothetical intermediates **10** and **14** were subjected to the reaction conditions (**Scheme 6**). Compound **14** was prepared by reduction of the epoxide in **10** [7] with PPh_3 and iodine. Heating **10** in TBAB at 130 °C under an aerobic atmosphere resulted in the decomposition of **10**. On the other hand, when **14** was heated in TBAB at 130 °C, **11** was obtained in 55% yield. These results indicate that **14** is a potential intermediate in the conversion of **9** to **11**.

To elucidate the reaction pathway and mechanism of the formation of **11** from **9**, a ^{13}C-labeled 1-methylKuQuinone **11′** was synthesized from 2-(methyl-^{13}C)-1,4-naphthoquinone (**9′**) (**Scheme 7**). Compound **9′** was prepared by treatment of 1,4-naphthoquinone (**15**) with silver nitrate and potassium persulfate in the presence of sodium acetate-2-^{13}C (**Scheme 7A**). Treatment of **9′** with a 5 M aqueous NaOH solution under an oxygen atmosphere in EtOH gave dimer **10′** in 37% yield. Reduction of the epoxide in **10′** with PPh_3 and iodine afforded **14′**. Heating **14′** in TBAB under an aerobic atmosphere gave ^{13}C-labeled 1-methylKuQuinone **11′** in 29% yield. Strong ^{13}C NMR signals derived from C-5a (or C-6a) and the methyl group at C-12 of **11′** were observed at 125.4 and 14.2 ppm, respectively (**Table S1** and **Fig. S21** in the Supplementary material). The coupling



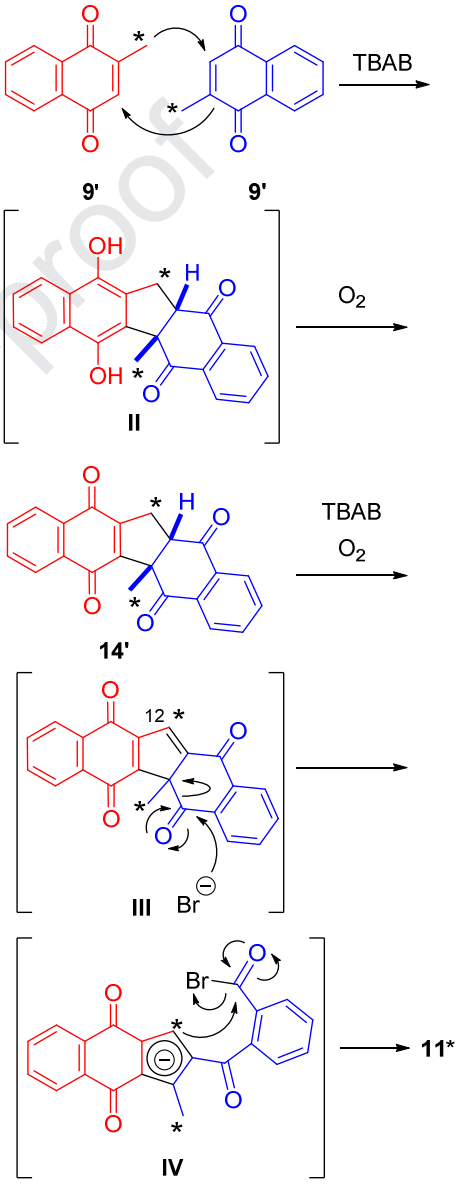
Scheme 6. Reactions of **10** and **14** in TBAB under an aerobic atmosphere.



Scheme 7. Synthesis of ^{13}C-labeled 1-methylKuQuinone **11′** from 1,4-naphthoquinone (**15**) (A) and via dimerization of 2-(methyl-^{13}C)-1,4-naphthoquinone (**9′**) (B).

constant between the ^{13}C-labeled carbons in **11′** is 2.8 Hz, indicating a long-range $^{3}J_{C\text{-}C}$ coupling. When 2-(methyl-^{13}C)-1,4-naphthoquinone (**9′**) was heated in TBAB, compound **11′** was obtained in 27% yield (**Scheme 7B**).

Taking the results obtained in **Schemes 6** and **7** together, the mechanism for the dimerization of **9′** is proposed in **Scheme 8**. Sequential intermolecular and intramolecular Michael reactions of **9′**, followed by oxidation of the resulting hydroquinone **II** with molecular oxygen gives **14′** [26,27]. Further oxidation of the cyclopentene moiety in **14′** affords **III**. The addition of bromide ion to the carbonyl group in **III** and a C−C bond cleavage reaction affords an acyl bromide **IV**. The cyclopentadienyl anion in **IV** is stabilized by the three carbonyl groups adjacent to the cyclopentadienyl ring, and acts as a good leaving group to promote C−C bond cleavage [27-30]. The ring-closing reaction occurs at the less hindered unsubstituted carbon in the cyclopentadienyl anion to give **11′**.



Scheme 8. Proposed Mechanism for the Formation of **11′** from **9′**.

In order to prove the existence of the intermediates **III** and **IV** in **Scheme 8**, compound **14** was treated with NaOMe under an oxygen atmosphere in MeOH (**Scheme 9**). This reaction afforded a cyclopentadienyl anion **16** in 69% yield. This result strongly supports the existence of the intermediates **III** and **IV**. The formation of **16** from **14** is explained by the oxidative double bond formation in **14**, followed by methanolysis of the resultant

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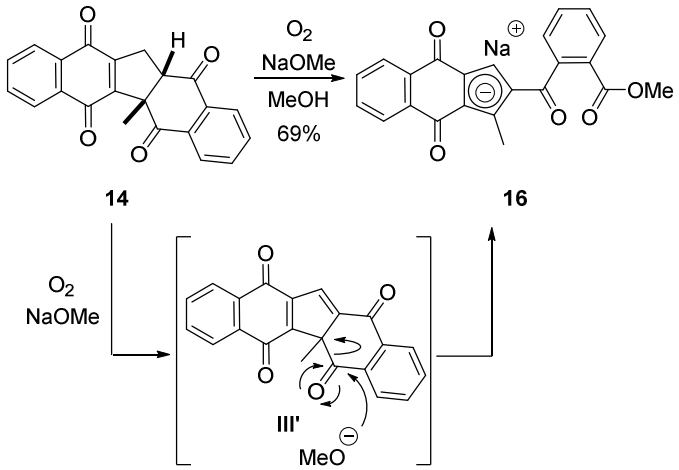
intermediate **III′**. The driving source of the methanolysis should be the high stability of the cyclopentadienyl anion in **16**.



Scheme 9. Formation of cyclopentadienyl anion **16** from compound **14**.

3. Conclusion

In this study, dimerizations of 2-bromo-3-methyl-1,4-naphthoquinone (**1**) and 2-methyl-1,4-naphthoquinone (**9**) in TBAB, an ionic liquid, were reported. Treatment of **1** with *N*-methylcyclohexylamine in TBAB at 120 °C afforded 5,7,12,14-pentacenetetrone (**2**) in 17% yield. The yield of **2** is slightly higher than that previously reported for the dimerization of **1** using EtOH as a solvent (entry 1 in **Table 1** versus **Scheme 1A**). The presence of *N*-methylcyclohexylamine is necessary for formation of **2**. The dimerization of **1** also proceed in other ionic liquids including TBAC, TBPB, *n*-$Bu_4P{\cdot}BF_4$, and [Bmim]Cl to give **2**. Treatment of **9** with *N*-methylcyclohexylamine in TBAB at 130 °C afforded 1-methylKuQuinone (**11**) in 30% yield. The present method greatly improves the yield of **11** compared with the reported method (entry 1 in **Table 2** versus **Scheme 3**). Furthermore, using the present method, compound **11** was purified by repeated centrifugation and washing with MeOH. The reaction mechanism was elucidated by determination of the reaction intermediates and ^{13}C labeling experiments using 2-(methyl-^{13}C)-1,4-naphthoquinone (**9′**). The present study demonstrates not only the potential utility of ionic liquids as solvents for the dimerization of 1,4-naphthoquinones, but also the potential utility of 1,4-naphthoquinones as versatile intermediates for the divergent syntheses of numerous 1,4-naphthoquinone dimers.

4. Experimental section

4.1. General Information

All solvents and reagents were used without further purification unless otherwise noted. Analytical TLC was performed using Silica gel 60 F_{254} plates (0.25 mm, normal phase) (Merck). Flash column chromatography was performed using Silica gel 60 (particle size 40–63 μm; 230–400 mesh ASTM) (SiliCycle). Melting point (Mp) data were determined using a MM-2 instrument (Shimadzu) and uncorrected. IR spectra were recorded on a FT-720 spectrometer (Horiba), using KBr pellets. ^1H and proton-decoupled ^{13}C ($^{13}C\{^1H\}$) NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 and 100 MHz, respectively), using chloroform-*d* ($CDCl_3$) or methanol-d_4 (CD_3OD). Chemical shift values are expressed in δ (ppm) relative to tetramethylsilane (TMS, δ 0.00 ppm) or the solvent resonance ($CDCl_3$, δ 77.0 ppm for $^{13}C\{^1H\}$ NMR; CD_3OD, δ 3.30 ppm for ^1H NMR, δ 49.0 ppm for $^{13}C\{^1H\}$ NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, m = multiplet), coupling constants (*J*; Hz), and integration. Mass spectra were obtained by a JEOL high-resolution double-focusing mass spectrometer (JMS-700) using fast atom bombardment (FAB), or a Bruker Fourier transformation-ion cyclotron resonance (FT-ICR) mass spectrometer (solariX) using electrospray ionization (ESI), or an Applied Biosystems hybrid quadrupole time-of-flight (QTOF) mass spectrometer (API QSTAR pulsar i) using ESI. Compound **1** was prepared from commercially available **9** according to the reported procedure [31].

*4.2. General Procedure for Dimerization of 2-Bromo-3-methyl-1,4-naphthoquinone (**1**) in an Ionic Liquid (**Table 1**)*

A mixture of **1** (75.0 mg, 299 μmol, 1.0 equiv) and TBAB (5.00 g, 15.5 mmol, 52 equiv) was heated in an oil bath under an aerobic atmosphere in the presence of *N*-methylcyclohexylamine (80.0 μL, 608 μmol, 2.0 equiv) at 120 °C for 45 min. The mixture was diluted with EtOAc and water. After the layers were separated, the organic layer was washed with a 1 M aqueous HCl solution, water, and brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography using toluene as the eluent to afford **2** (8.8 mg, 17%) as a pale brown solid. The ^1H NMR spectrum of **2** was identical with that reported for **2** [32].

In entry 2, following the general procedure, the reaction of **1** (50.0 mg, 199 μmol) in the presence of *N*-methylcyclohexylamine (52.0 μL, 395 μmol) and TBAB (3.21 g, 9.96 mmol) in a refluxing toluene (6 mL) for 60 min gave **2** (2.3 mg, 7%). In entry 3, the reaction of **1** (50.0 mg, 199 μmol) was performed in TBAB (3.21 g, 9.96 mmol) at 120 °C for 300 min. No significant TLC changes were observed during 300 min. In entry 4, the reaction of **1** (75.2 mg, 300 μmol) in the presence of *N*-methylcyclohexylamine (80.0 μL, 608 μmol) in TBAC (4.17 g, 15.0 mmol) at 100 °C for 60 min gave **2** (4.6 mg, 9%). In entry 5, the reaction of **1** (75.5 mg, 301 μmol) in the presence of *N*-methylcyclohexylamine (80.0 μL, 608 μmol) in TBPB (5.10 g, 15.0 mmol) at 110 °C for 30 min gave **2** (6.8 mg, 13%). In entry 6, the reaction of **1** (75.3 mg, 300 μmol) in the presence of *N*-methylcyclohexylamine (80.0 μL, 608 μmol) in *n*-$Bu_4P{\cdot}BF_4$ (5.19 g, 15.0 mmol) at 110 °C for 30 min gave **2** (5.1 mg, 10%). In entry 7, the reaction of **1** (75.1 mg, 299 μmol) in the presence of *N*-methylcyclohexylamine (80.0 μL, 608 μmol) in [Bmim]Cl (2.62 g, 15.0 mmol) at 80 °C for 50 min gave **2** (2.1 mg, 4%).

*4.3. General Procedure for Dimerization of 2-Bromo-3-methyl-1,4-naphthoquinone (**1**) in a Conventional Solvent (**Scheme 5**)*

A solution of **1** (75.0 mg, 299 μmol, 1.0 equiv) and *N*-methylcyclohexylamine (80.0 μL, 608 μmol, 2.0 equiv) in EtOH (3 mL) was stirred under an aerobic atmosphere at rt for 7 h. The solution was concentrated. The residue was purified by silica gel column chromatography using toluene as the eluent to afford **2** (3.5 mg, 7%). The ^1H NMR spectrum of **2** was identical with that reported for **2**.

In **Scheme 5C**, following the general procedure, the reaction of **1** (50.0 mg, 199 μmol) with *N*-methylcyclohexylamine (52.0 μL, 395 mmol) in 2-propanol (3 mL) at rt for 8 h, and purification by silica gel column chromatography using hexanes/EtOAc (5/1) as the eluent gave **7** (7.2 mg, 17%) and

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recovered **1** (31.9 mg, 64%). The ^{1}H NMR spectrum of **7** was identical with that reported for **7** [7].

In **Scheme 5D**, following the general procedure, the reaction of **1** (50.0 mg, 199 μmol) with *N*-methylcyclohexylamine (52.0 μL, 395 mmol) in THF (3 mL) at rt for 12 h, and purification by silica gel column chromatography using hexanes/EtOAc (5/1) as the eluent gave **7** (5.9 mg, 12%).

*4.4. Methyl 1-hydroxy-2,2-dimethoxy-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**13**) (**Scheme 5B**)*

Following the general procedure described in section 4.3, the reaction of **1** (116 mg, 462 μmol) with *N*-methylcyclohexylamine (162 μL, 1.23 mmol) in methanol (30 mL) at rt for 8 h, and purification by silica gel column chromatography using hexanes/EtOAc (5/1~3/1) as the eluent gave **13** (23.6 mg, 19%) as a pale yellow oil. IR (neat) ν_{max} = 3477, 3010, 2953, 2845, 1728, 1622, 1604, 1464 cm^{-1}; ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.71 (td, *J* = 7.6, 0.8 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.54 (td, *J* = 7.6, 0.8 Hz, 1H), 4.01 (s, 1H), 3.69 (s, 3H), 3.55 (s, 3H), 3.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.2, 170.7, 150.0, 135.9, 134.0, 130.1, 124.2, 124.0, 102.1, 82.1, 53.6, 51.84, 51.77; HRMS (ESI/FT-ICR) *m*/*z*: $[M+H]^+$ Calcd for $C_{13}H_{15}O_6$ 267.0863; Found 267.0864.

*4.5. General Procedure for Dimerization of 2-Methyl-1,4-naphthoquinone (**9**) in an Ionic Liquid (**Table 2**)*

A mixture of **9** (99.8 mg, 580 μmol, 1.0 equiv) and TBAB (2.10 g, 6.51 mmol, 11 equiv) was heated in an oil bath under an aerobic atmosphere in the presence of *N*-methylcyclohexylamine (230 μL, 1.75 mmol, 3.0 equiv) at 130 °C for 1 h. The mixture was diluted with EtOAc and water. After the layers were separated, the organic layer was washed with a 1 M aqueous HCl solution, water, and brine, dried over Na_2SO_4, and concentrated. The residue was diluted with MeOH and centrifuged (3500 rpm, 1 min). After the supernatant was removed, the precipitate was washed with MeOH. This washing process was repeated five times to give **11** (29.6 mg, 30%). The ^{1}H NMR data of **11** was identical with that reported for **11** [22]. The ^{13}C{1H} NMR data of **11** was in good agreement with that reported for **11**, except for the chemical shift at the methyl group at C-12 [22]. We assigned all signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **11** through the analysis of the ^{1}H–^{13}C heteronuclear multiple-bond correlation (HMBC) spectrum of **11** (**Table S1** in the Supplementary material).

In entry 2, following the general procedure, the reaction of **9** (50.2 mg, 292 μmol) in TBAB (1.02 g, 3.16 mmol) under an aerobic atmosphere at 130 °C for 9 h in the absence of *N*-methylcyclohexylamine gave **11** (10.9 mg, 22%). In entry 3, the reaction of **9** (152.4 mg, 885 μmol) in TBAB (3.00 g, 9.30 mmol) under an oxygen atmosphere at 130 °C for 7 h gave **11** (28.8 mg, 19%). In entry 4, the reaction of **9** (50.6 mg, 294 μmol) in TBAB (935 mg, 2.90 mmol) in a refluxing toluene under an oxygen atmosphere at 130 °C for 6.5 h gave **11** (8.4 mg, 17%). In entry 5, the reaction of **9** (50.0 mg, 290 μmol) in TBAC (806 mg, 2.90 mmol) under an oxygen atmosphere at 130 °C for 7 h gave **11** (7.6 mg, 15%).

*4.6. 5a-Methyl-12,12a-dihydro-5H-dibenzo[b,h]fluorene-5,6,11,13(5aH)-tetraone (**14**)*

Iodine (72.9 mg, 0.574 mmol) and PPh_3 (148 mg, 0.562 mmol) were added to a solution of **10** [9] (50.5 mg, 0.141 mmol) in MeCN (5 mL) at rt. The mixture was refluxed by heating in an oil bath for 4.5 h. The reaction was quenched by the addition of water, and the resulting mixture was diluted with EtOAc. The organic layer was collected, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography using hexanes/EtOAc (10/1) as the eluent to afford **14** (37.8 mg, 79%) as a red brown amorphous solid. Mp = 151–152 °C; IR (KBr) ν_{max} = 2929, 1685, 1664, 1618, 1591, 1458, 1431 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–8.04 (m, 4H), 7.81–7.70 (m, 4H), 3.50–3.41 (m, 2H), 3.14–3.04 (m, 1H), 1.85 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.2, 195.8, 183.2, 182.3, 149.9, 149.8, 135.1, 134.4, 133.9, 133.7, 133.6, 133.2, 132.4, 127.7, 127.1, 126.8, 126.2, 61.8, 57.1, 33.7, 22.4 (one aromatic carbon signal is overlapped); HRMS (ESI/QTOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{22}H_{14}O_4Na$ 365.0784; Found 365.0792.

*4.7. Synthesis of **11** from **14***

A mixture of **14** (15.0 mg, 43.8 μmol) and TBAB (0.650 g, 2.02 mmol) was heated at 130 °C in an oil bath under an aerobic atmosphere for 6 h. The mixture was diluted with $CHCl_3$ and water. After the layers were separated, the organic layer was washed with a 3 M aqueous H_2SO_4 solution, water and brine, dried over Na_2SO_4, and concentrated. The residue was diluted with MeOH (3 mL) and centrifuged (3500 rpm, 1 min). After the supernatant was removed, the precipitate was washed with MeOH (3 mL). This washing process was repeated five times to give **11** (8.1 mg, 54%). The ^{1}H NMR spectrum of **11** was identical with that of our authentic sample.

*4.8. 2-(Methyl-^{13}C)-1,4-naphthoquinone (**9′**)*

A solution of 1,4-naphthoquinone **15** (436 mg, 2.76 mmol), sodium acetate-2-^{13}C (156 mg, 1.88 mmol), and $AgNO_3$ (160 mg, 0.941 mmol) in a 1:1 mixture of MeCN and water (14 mL) was degassed. $K_2S_2O_8$ (2.49 g, 9.21 mmol) was added to the mixture at rt. The mixture was stirred at 60 °C by heating in an oil bath under an argon atmosphere for 3 h. The resultant mixture was diluted with EtOAc and water to give a biphasic solution. The organic layer was collected, washed with water and brine, dried over Na_2SO_4, and concentrated to give a residue. The residue was purified via silica gel column chromatography using hexanes/EtOAc (50/1) as the eluent to give **9′** (108 mg, 33%) as a yellow solid and recovered **15** (124 mg, 28%). Mp = 98–99 °C; IR (KBr) ν_{max} = 3064, 3047, 2949, 2922, 2852, 1666, 1622, 1593 cm^{-1}; ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.13–8.05 (m, 2H), 7.75–7.71 (m, 2H), 6.86–6.84 (m, 1H), 2.20 (dd, *J* = 129.3, 1.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.7, 133.7, 133.6, 132.3, 133.2, 126.5, 126.1, 16.5 (The signals derived from other carbons were not observed, because the signal of the ^{13}C-labeled carbon was greatly enhanced); HRMS (FAB/double-focusing MS) *m*/*z*: $[M+H]^+$ Calcd for $^{12}C_{10}{}^{13}CH_9O_2$ 174.0636; Found 174.0637.

*4.9. 11a,12-Dihydro-5b-(methyl-^{13}C)-5a,12a-epoxy-11H-dibenzo[b,h]fluorene-5,6,11,13(5bH)-tetrone-12-^{13}C (**10′**)*

A 5.0 M aqueous NaOH solution (1.00 mL, 5.00 mmol) in ethanol (20 mL) was bubbled by oxygen gas at −78 °C. Compound **9′** (100 mg, 0.577 mmol) was added to the solution at −78 °C, and the mixture was stirred under an oxygen atmosphere. The reaction was warmed up to rt, and the mixture was stirred at rt for 30 min. The reaction was quenched by the addition of water, and the resulting mixture was diluted with EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc three times. The combined organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified via silica gel chromatography using hexanes/EtOAc (10/1) as the eluent to afford **10′** (37.9 mg, 37%) as a white solid. Mp = 194–195 °C; IR (KBr) ν_{max} = 3066, 3014,

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2941, 1697, 1593, 1464 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.17–8.15 (m, 1H), 8.10–8.07 (m, 1H), 7.97–7.92 (m, 2H), 7.76–7.68 (m, 4H), 3.63 (dd, *J* = 129.9, 14.8 Hz, 1H), 2.95 (dd, *J* = 7.8, 7.8 Hz, 1H), 2.81 (ddd, *J* = 129.9, 14.8, 7.8 Hz, 1H), 1.69 (d, *J* = 129.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 134.6, 134.5, 134.2, 127.52, 127.47, 127.1, 127.0, 29.0, 18.0 (The signals derived from other carbons were not observed, because the signals of the ^{13}C-labeled carbons were greatly enhanced); HRMS (FAB/double-focusing MS) *m/z*: $[M+H]^+$ Calcd for $^{12}C_{20}{}^{13}C_2H_{15}O_5$ 361.0987; Found 361.0984.

*4.10. 5a-(Methyl-^{13}C)-12,12a-dihydro-5H-dibenzo[b,h]fluorene-5,6,11,13(5aH)-tetraone-12-^{13}C (**14′**)*

Iodine (37.0 mg, 0.291 mmol) and PPh_3 (75.9 mg, 0.289 mmol) were added to a solution of **10′** (19.7 mg, 54.7 μmol) in MeCN (3 mL) at rt. The mixture was refluxed by heating in an oil bath for 19 h. The reaction was quenched by the addition of water, and the resulting mixture was diluted with EtOAc. The organic layer was collected, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified via silica gel chromatography using hexanes/EtOAc (10/1) as the eluent to afford **14′** (13.3 mg, 70%) as a pale brown amorphous solid. IR (KBr) ν_{max} = 2956, 2925, 2854, 1685, 1666, 1618, 1593, 1456 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13–8.04 (m, 4H), 7.81–7.70 (m, 4H), 3.48 (ddd, *J* = 130.6, 18.2, 8.6 Hz, 1H), 3.43 (m, 1H), 3.06 (ddd, *J* = 130.6, 18.2, 8.2 Hz, 1H), 1.85 (d, *J* = 130.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 135.1, 134.4, 133.9, 133.6, 127.7, 127.1, 126.7, 126.2, 33.7 (d, *J* = 1.1 Hz), 22.4 (d, *J* = 1.1 Hz) (The unassigned signal at 127.3 ppm was also observed. The signals derived from other carbons were not observed, because the signals of the ^{13}C-labeled carbons were greatly enhanced); HRMS (FAB/double-focusing MS) *m/z*: $[M+H]^+$ Calcd for $^{12}C_{20}{}^{13}C_2H_{15}O_4$ 345.1037; Found 345.1037.

*4.11. 6-Hydroxy-12-(methyl-^{13}C)-5H-dibenzo[b,h]fluorene-5,11,13-trione-5a-^{13}C (**11′**)*

A mixture of **14′** (14.4 mg, 41.8 μmol) in TBAB (703 mg, 2.18 mmol) was heated at 130 °C in an oil bath under an aerobic atmosphere for 6 h. The mixture was diluted with EtOAc and water. After the layers were separated, the organic layer was washed with a 3 M aqueous H_2SO_4 solution, water and brine, dried over Na_2SO_4, and concentrated. The residue was diluted with MeOH (3 mL) and centrifuged (4000 rpm, 1 min). After the supernatant was removed, the precipitate was washed with MeOH (3 mL). This washing process was repeated fifteen times to give **11′** (4.1 mg, 29%) as a red purple solid. Mp = >250 °C; IR (KBr) ν_{max} =3443, 3068, 3030, 2922, 1666, 1622, 1593 cm^{-1}; ^1H NMR (400 MHz,$CDCl_3$) δ 18.09 (s, 1H), 8.28–8.24 (m, 4H), 8.28–7.71 (m, 4H), 2.96 (d, *J* = 129.48 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 135.0, 133.0, 127.8, 127.2, 125.4 (d, *J* = 2.8 Hz), 14.2 (d, *J* = 2.8 Hz) (The unassigned signal at 127.4 ppm was also observed. The signals derived from other carbons were not observed, because the signals of ^{13}C-labeled carbons were greatly enhanced); HRMS (FAB/double-focusing MS) *m/z*: $[M-H]^-$ Calcd for $^{12}C_{20}{}^{13}C_2H_{11}O_4$ 341.0724; Found 341.0722.

*4.12. Synthesis of **11′** from **9′***

A mixture of **9′** (49.8 mg, 0.288 mmol) in TBAB (0.93 g, 2.89 mmol) was heated at 130 °C in an oil bath under an aerobic atmosphere for 9 h. The mixture was diluted with EtOAc and water. After the layers were separated, the organic layer was washed with a 3 M aqueous H_2SO_4 solution, water and brine, dried over Na_2SO_4, and concentrated. The residue was diluted with MeOH (4 mL) and centrifuged (3500 rpm, 2 min). After the supernatant was removed, the precipitate was washed with MeOH (3 mL). This washing process was repeated fourteen times to give **11′** (13.4 mg, 27%). The ^1H NMR spectrum of **11′** was identical with that of our authentic sample.

*4.13. Sodium 2-(2-(methoxycarbonyl)benzoyl)-3-methyl-4,9-dioxo-4,9-dihydro-1H-cyclopenta[b]naphthalenide (**16**)*

A 0.5 M NaOMe solution in MeOH (5.00 mL, 2.50 mmol) was added to **14** (10.0 mg, 29.2 μmol). The resultant mixture was stirred at rt under an oxygen atmosphere for 30 min. The reaction was quenched by the addition of water, and the resulting mixture was diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic layer was collected, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified via silica gel chromatography using hexanes/EtOAc (2/1) and EtOAc/MeOH (10/1) as the eluents to afford **16** (8.0 mg, 69%) as an orange amorphous solid. Mp = 180 °C (decomposition); IR (KBr) ν_{max} = 2924, 1722, 1711, 1579, 1550, 1493, 1483, 1444, 1427, 1385 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 8.06 (d, *J* = 7.4 Hz,1H), 7.99 (d, *J* = 7.1 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.63 (dd, *J* = 7.7, 7.4 Hz, 1H), 7.55–7.50 (m, 3H), 7.44 (d, *J* = 7.5 Hz, 1H), 6.71 (s, 1H), 3.69 (s, 3H), 2.81 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) δ 196.7, 182.5, 180.8, 169.0, 145.9, 142.0, 139.5, 138.5, 132.9, 132.7, 132.5, 130.9, 130.7, 130.5, 129.8, 129.1, 128.0, 127.1, 126.9, 125.3, 125.1, 52.7, 15.5; HRMS (FAB/double-focusing MS) *m/z*: $[M-Na]^-$ Calcd for $C_{23}H_{15}O_5$ 371.0921; Found 371.0920, and *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{15}O_5Na_2$ 417.0715; Found 417.0719.

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Appendix A. Supplementary Material

Supplementary data to this article can be found online at https://.

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Highlights

· Dimerizations of 3-methyl-1,4-naphthoquinones in TBAB were developed.

· The use of TBAB as a solvent improved the yield of 5,7,12,14-pentacenetetrone.

· The use of TBAB as a solvent improved the yield of 1-methylKuQuinone.

· The reaction mechanisms for the dimerizations were elucidated.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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