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Photoinduced Reactions of *para*-Quinones with Bicyclopropylidene Leading to Diverse Polycyclic Compounds with Spirocyclopropanes

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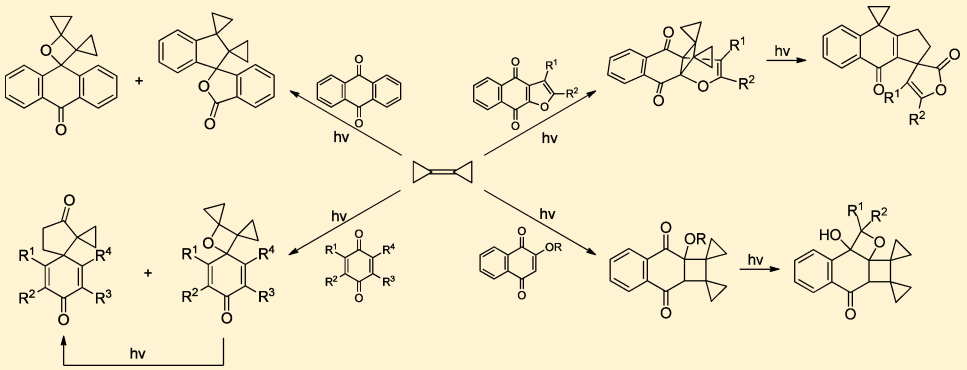
Supporting Information



ABSTRACT: Photoinduced reactions of bicyclopropylidene (BCP) with *para*-quinones (*p*-quinones) including benzoquinones, naphthoquinones, and anthraquinones were found to proceed via different cycloaddition pathways and lead to diverse polycyclic products bearing spiropropyl moiety. Photocycloaddition of BCP with benzoquinones gave spirooxetanes as the primary products, which upon irradiation were able to rearrange into the spiro[4.5]deca-6,9-diene-2,8-diones as secondary photoproducts. Chemoselectivity of the photocycloaddition of BCP with naphthoquinones relies largely on the substitution groups linked to the C=C in between the two carbonyl groups to give different types of products. Photoreaction of BCP with 9,10-anthraquinone gave not only the spirooxetane product, but also a novel spiro[indan-1,1′-phthalan]-3′-one product whose formation might be initiated by a transannular attack of the C4 cyclopropyl radical to the *para*-carbonyl group. Mechanisms involved in the formation of diverse primary or secondary products in the photoreactions of BCP with *p*-quinones were proposed. Some of the photoreactions also hold potentials as useful synthetic protocols for important spiropolycyclic compounds such as sesquiterpenes.

INTRODUCTION

Photoinduced cycloaddition reactions along with subsequent cascade reactions provide an efficient way to construct organic framework with diversified structures that are difficult to obtain by conventional thermal reactions.[1] Polycycles with cyclopropyl ring have been found to be frameworks in many natural products,[2] and the special reactivity of the highly strained cyclopropane-containing compounds have been extensively exploited in natural product synthesis.[3] The cycloadditions of methylenecyclopropanes with a variety of cyclophiles have drawn much recent research interest and proved to be a powerful tool in constructing various polycyclic systems.[4] However, the potential of methylenecyclopropane type strained alkenes in photoreactions has rarely been explored.[5]

Bicyclopropylidene (BCP) is an unconventional alkene with high angular strain by incorporating two cyclopropane rings.[6] Theoretical studies and X-ray crystal analysis have indicated that the C=C bond in BCP is 1.304 Å, significantly shorter than normal C=C bonds.[7] The relatively high HOMO energy and low ionization potential[8] enable BCP to be highly reactive in additions across its C=C bond toward a wide range of electrophilic cycloaddends. As a result of the systematic investigation of de Meijere and his co-workers[6] as well as other research groups[9] on thermal reactions of BCP under different conditions, BCP has emerged as a highly versatile synthetic building block. The photoinduced reactions of BCP with α-diketones including *N*-acetylisatin and isoquinoline-triones have also been investigated by us, and unusual products have been obtained via the photoinitiated sequential reactions or acid-mediated transformations of the photocycloadducts.[10]

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Photocycloaddition of *p*-quinones such as benzoquinones and naphthoquinones with alkenes was able to happen via nπ^* or $\pi\pi^*$ excited state to give the oxetane or cyclobutane type products.[11,12] The substitution groups on the quinones have shown significant influence on the photoreaction pathway partition. For example, photoinduced reactions of halogenated 1,4-benzoquinones with olefins or 1,1-diarylethenes have been reported to give unusual products with distributions highly dependent on the steric nature of quinones and olefins.[13] However, photoreactions of *p*-quinones with strained alkenes still remain to be explored. Here we report the photoinduced reactions of the highly strained alkene BCP with various *p*-quinones including benzoquinones and naphthoquinones bearing various substituents.

RESULTS AND DISCUSSION

It was reported that product distribution of photoreactions between *p*-quinones and olefins was mainly dependent on the nature of the excited state of quinones (nπ^* or $\pi\pi^*$ triplet state).[11] Meanwhile, the involvement of photoinduced electron transfer (PET) process and steric effect to the cycloaddition also play important roles and may cause a reaction site reversal.[12a,b,14] To examine the possibility of PET process involvement in the photoreactions between *p*-quinones and BCP, free energy change for electron transfer (ΔG_{ET}) between the triplet quinone and BCP has been evaluated using the Weller equation[15] (Table 1). The results showed that the PET process with BCP to all the quinones investigated was endergonic and it was unlikely to be involved in the photoreactions.

Table 1. Free Energy Change for Electron Transfer (ΔG_{ET})[a] between *p*-Quinones and BCP

entry	quinone	E_T[b]	$E_{1/2}^{red}$ (V)[c]	ΔG_{ET}[d]
1	benzoquinone (**1**)	50[16a]	−0.51[16b]	17
2	chlorobenzoquinone (**4**)	50[e]	−0.34[16b]	13
3	2,6-dichlorobenzoquinone (**5**)	50[e]	−0.18[16b]	9
4	naphthoquinone (**6**)	58[16c]	−0.76[12b]	15
5	2-methyl-1,4-naphthoquinone (**7**)	58[e]	−0.81[12b]	16
6	2-chloro-1,4-naphthoquinone (**8**)	58[e]	−0.59[12b]	11
7	2,3-dichloro-1,4-naphthoquinone (**9**)	58[e]	−0.49[12b]	8
8	9,10-anthraquinone (**15**)	61[12c]	−0.94[12c]	16

[a]Estimated by the Weller equation. [b]Triplet state energy in kcal/mol. [c]Half-wave reduction potential of the quinone (SCE, MeCN). [d]In kcal/mol. [e]Presumed to have the same E_T value as BQ and NQ, respecively.

Photoreaction of Benzoquinones 1−5 with BCP. Photoinduced reactions of 1,4-benzoquinone (**1**) with olefins are often supposed to take place from the lowest nπ^* triplet excited state via a preoxetane diradical intermediate.[12c,16a] Meanwhile, singlet exciplex and singlet diradical mechanism has also been suggested in some cases.[5] Reaction of **1** with BCP proceeded smoothly in anhydrous benzene under irradiation with light of wavelengths longer than 400 nm (500 W medium-pressure mercury lamp was used with 20% aqueous sodium nitrite as filter solution to cut off light of wavelength shorter than 400 nm). After irradiation for 7 h, complete conversion of **1** was achieved and two products **1a** and **1b** were obtained. As shown in Table 2, the major product, **1a**, is a spirooxetane with two spiro-fused cyclopropane rings, formed in the Paterno−Büchi reaction.[17] Product **1b** is a spirocyclopropanated spiro[4.5]decadienedione. Control experiments show that **1b** is a secondary product derived from **1a** under irradiation. Therefore, independent irradiation of **1a** under the same photolysis conditions resulted in smooth and clean conversion of **1a** to **1b**. Also, in the photoreactions of **1** with BCP, **1b** can be made the sole product in 98% yield simply by lengthening the irradiation time to 24 h (Table 2). The proposed mechanism for transformation of **1a** to **1b** is shown in Scheme 1. Homolytic scission of the C−O bond in the highly strained oxetane ring in **1a** followed by cyclopropane ring-opening leads to the 1,5-diradical **I**. Subsequent radical pair recombination after intersystem crossing in **I** furnishes the product.

Photoreactions of 2,6-dimethylbenzoquinone (**2**) and 2,6-dichlorpbenzoquinone (**5**) with BCP, respectively, similarly gave the spirooxetane (**2a** and **5a**) and the spiro[4.5]-decadienedione (**2b** and **5b**) together when the irradiation was stopped after a complete conversion of the quinone was reached as indicated by TLC monitoring, while lengthy irradiation resulted in the conversion of the spirooxetane to spiro[4.5]decadienedione and gave **2b** and **5b** as the only product in high yield (Table 2). These photocycloadditions are regioselective, taking place at the 4-carbonyl group because 1-carbonyl was blocked by two chlorine atoms or the two methyl groups. The structures of **2a** and **5a** were confirmed by ^{1}H−^{1}H NOESY measurements, which showed the steric proximity of the cyclopropane protons with the dienone protons. The structure of **5a** was further unambiguously established by an X-ray crystallographic analysis (Figure S1, Supporting Information). Meanwhile, irradiation of 2-chlorobenzoquinone (**4**) with BCP for 25 h afforded **4b** in 68% yield. The regioselectivity in **4b** was also proved by a ^{1}H−^{1}H NOESY measurement. In contrast, duroquinone (**3**) could not take part in photoreactions with BCP under the same conditions, probably because of the $\pi\pi^*$ nature of its excited triplet state[18] and the steric hindrance of the two methyl groups, which impedes the [2 + 2] reaction leading to cyclobutane product.[12d,19]

It is noteworthy that the high-yielding formation of **1b−5b** provides a direct and convenient pathway for the construction of the spiro[4,5]decane core structure commonly found in a large variety of sesquiterpene natural products, such as in acorane, spirovetivane, spirolaurane, spiroaxane and the vitrine family of sesquiterpenes,[20] and the spiro[4.5]deca-6,9-diene-2,8-dione structures in **1b−5b** are themselves important synthetic intermediates for the synthesis of several spiro[4,5]-decane sesquiterpenes.[21]

Photoreaction of Naphthoquinones 6−13 with BCP. For naphthoquinone, nπ^* and $\pi\pi^*$ triplet states are close in energy and are both accessible to take part in reactions with olefins.[12d,22] In accord with this, irradiation of 1,4-naphthoquinone (**6**) with BCP in benzene with light of $\lambda > 400$ nm for 24 h led to a complete conversion of **6** to afford the cyclobutane product **6a** (for crystal structure, see: Figure S2, Supporting Information) and the benzannulated spiro[4.5]deca-6,9-diene-2,8-dione **6b** derived from the primary spirooxetane product (Table 3). At the same time, 2-methylnaphthoquinone (**7**) afforded the cyclobutane **7a** as main product, reflecting an increased involvement of the $\pi\pi^*$ excited state.[23] The regioselectivity in **7b** was also determined by an ^{1}H−^{1}H NOESY measurement.

Irradiation of 2-chloronaphthoquinone (**8**) and 2,3-dichloronaphthoquinone (**9**) with BCP in benzene, respectively, gave the cyclobutanes **8a** and **9a** respectively in high yield without

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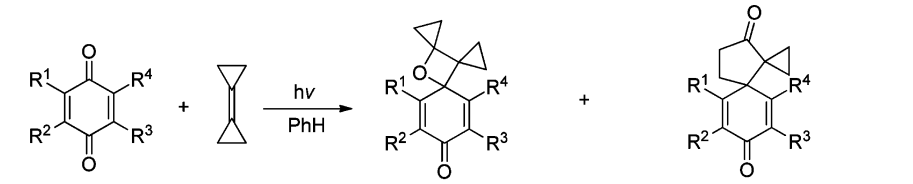
Table 2. Summary of the Photoreaction Products of Benzoquinones with BCP



1: $R^1 = R^2 = R^3 = R^4 = H$
2: $R^1 = R^4 = H$, $R^2 = R^3 = Me$
3: $R^1 = R^2 = R^3 = R^4 = Me$
4: $R^1 = R^3 = R^4 = H$, $R^2 = Cl$
5: $R^1 = R^4 = H$, $R^2 = R^3 = Cl$

1a: $R^1 = R^2 = R^3 = R^4 = H$
2a: $R^1 = R^4 = H$, $R^2 = R^3 = Me$
5a: $R^1 = R^4 = H$, $R^2 = R^3 = Cl$

1b: $R^1 = R^2 = R^3 = R^4 = H$
2b: $R^1 = R^4 = H$, $R^2 = R^3 = Me$
4b: $R^1 = R^3 = R^4 = H$, $R^2 = Cl$
5b: $R^1 = R^4 = H$, $R^2 = R^3 = Cl$

entry	quinone	irrad. time (h)	products, yields (%)[a]	irrad. time (h)	products, yields (%)[a]
1	**1**	7	**1a** (53), **1b** (42)	24	**1b** (98)
2	**2**	10	**2a** (53), **2b** (36)	24	**2b** (95)
3	**3**	48	no reaction	–	–
4	**4**	–	–	25	**4b** (68)
5	**5**	24	**5a** (57), **5b** (32)	48	**5b** (83)

[a]Isolated yield.

Scheme 1. Proposed Mechanism for Transformation of 1a to 1b

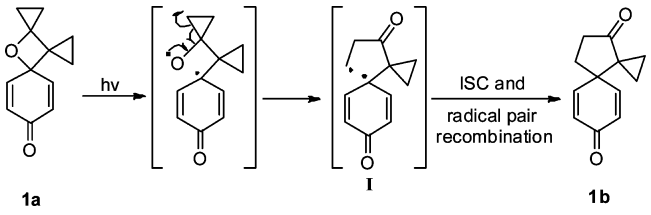
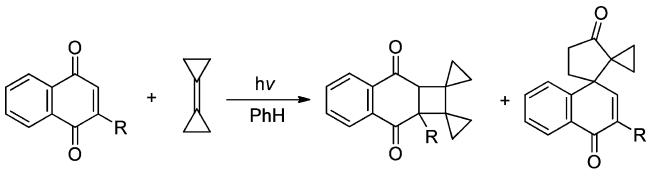


Table 3. Summary on the Photoreaction Products of Naphthoquinones with BCP



6: R = H
7: R = Me

6a: R = H
7a: R = Me

6b: R = H
7b: R = Me

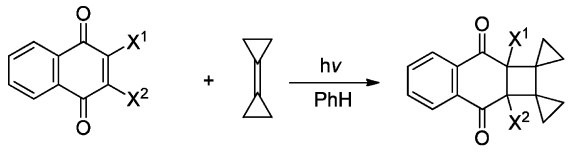
entry	naphthoquinone	irrad. time (h)	products, yields (%)[a]
1	**6**	24	**6a** (36), **6b** (58)
2	**7**	24	**7a** (88), **7b** (8)

[a]Isolated yield.

the formation of any spirooxetane product (Table 4). This is in accord with the previous finding that **8**[24] and **9**[12a,b,25] afford cyclobutane product with common olefins in photocycloadditions without single electron transfer (SET) process involvement.

The cyclobutane product **8a** can be converted to the cyclobutene **8b**[26] via elimination of hydrogen chloride by treatment with a base. The optimized reaction condition for this is treating **8a** in acetonitrile with potassium carbonate. In this case, **8b** is obtained in nearly quantitative yield. An attempt to induce thermal cyclobutene ring-opening in **8b** to give the quinodimethane intermediate II (Scheme 2) by refluxing in xylene and trapping it with such dienophiles as maleimide, maleic anhydride, diethyl maleate and diethyl fumarate failed. This is in sharp contrast with the facile cyclobutene ring-

Table 4. Summary on the Photoreaction Products of Chloronaphthoquinones with BCP



8: $X^1 = Cl$, $X^2 = H$
9: $X^1 = X^2 = Cl$

8a: $X^1 = Cl$, $X^2 = H$
9a: $X^1 = X^2 = Cl$

entry	naphthoquinone	irrad. time (h)	products, yields (%)[a]
1	**8**	24	**8a** (87)
2	**9**	24	**9a** (80)

[a]Isolated yeld.

opening in refluxing xylene for similar 1,2-dihydrocyclobuta-[*b*]naphthalene-3,8-diones formed in photocycloadditions of **8** with simple alkenes followed by elimination of hydrogen chloride. We believe that the electrocyclic ring-opening in **8b** is sterically hindered by the two spiro-fused cyclopropane rings. Meanwhile, **8b** behaves as an electron-deficient olefin and serves as a dienophile in Diels–Alder reaction with isoprene and 1,3-cyclohexadiene, giving **8c** and **8d** (for crystal structure, see: Figure S3, Supporting Information), respectively (Scheme 2).

Introduction of an electron-donating alkoxy group at C2 atom in naphthoquinone raises the energy of the $n\pi^*$ excited state,[27] and the 2-alkoxy naphthoquines show reactivity of typical $\pi\pi^*$ excited state to give cyclobutane as primary product exclusively.[12d,19,22a] Indeed, photoreaction of 2-phenoxynaphthoquinone (**10**) with BCP proceeds quickly and gives the cyclobutane **10a** in 87% yield upon the completion of the reaction after 3 h irradiation (Table 5). Similarly, facile photoreactions of 2-methoxynaphthoquinone (**11**), 2-ethoxynaphthoquinone (**12**) and 2-isopropoxynaphthoquinone (**13**) with BCP afforded the corresponding cyclobutane **11a**, **12a** and **13a** in high yield, respectively, if the irradiation was stopped shortly after the starting quinone was completely consumed. However, lengthy irradiation resulted in secondary intramolecular hydrogen abstraction reaction in the primary product and resulted in the formation of the cyclobutane-oxetane

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Scheme 2. Thermal Transformation of Compound 8a and 8b

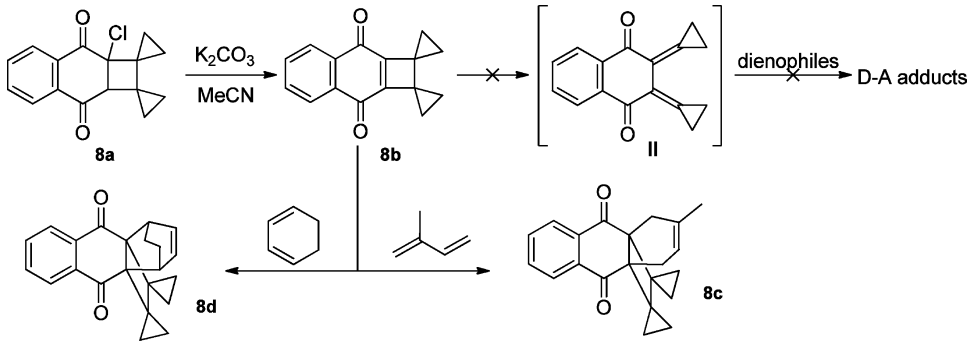
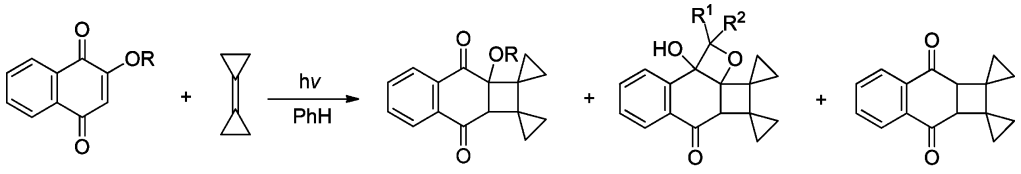


Table 5. Summary on the Photoreaction Products of Alkoxy Naphthoquinones with BCP



10: R = Ph
11: R = Me
12: R = Et
13: R = ^{i}Pr

10a: R = Ph
11a: R = Me
12a: R = Et
13a: R = ^{i}Pr

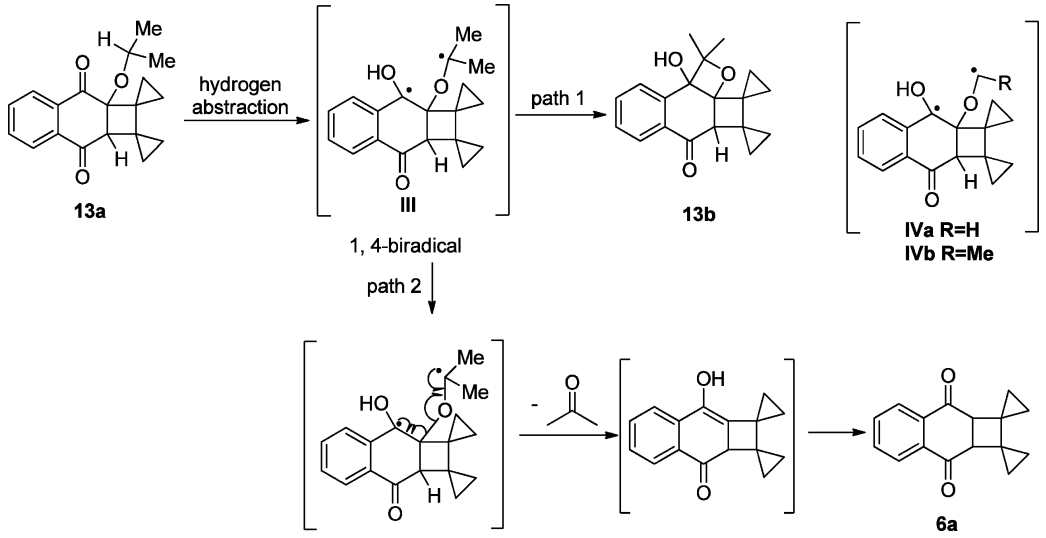
11b: $R^1 = R^2$ = H
12b: R^1 = Me, R^2 = H
13b: $R^1 = R^2$ = Me

6a

entry	naphthoquinone	irrad. time (h)	products, yields (%)[a]	irrad. time (h)	products, yields (%)[a]
1	**10**	3	**10a** (87)	–	–
2	**11**	3	**11a** (87)	24	**11b** (85)
3	**12**	3	**12a** (85)	24	**12b** (88)
4	**13**	4	**13a** (88)	48	**13a** (6), **13b** (54), **6a** (25)

[a]Isolated yield.

Scheme 3. Proposed Mechanism for Transformation of Compound 13a to 13b and 6a



products **11b**, **12b** and **13b** (for crystal structure, see: Figure S4, Supporting Information).[12d,22a] Therefore, either the cyclobutane or the cyclobutane-oxetane can be made the main or even the sole product in high yield simply by monitoring the reaction course.

In the reaction of **13** with BCP, an additional product **6a** was also formed in significant amount. Possible mechanism for the formation of **13b** and **6a** is shown in Scheme 3. In the 1,4-diradical **III** formed by intramolecular hydrogen abstraction in excited **13a**, radical pair recombination furnishes **13b**, while hemolysis of the C2–O bond leads to the elimination of an acetone to give **6a**. The two germinal methyl groups at the alkoxycarbinyl radical center in **III** cause serious steric hindrance toward the radical pair recombination leading to **13b**, enabling the C2–O bond homolysis to compete effectively with the former process, resulting in the simulta-

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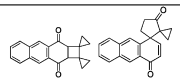
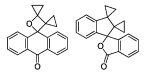
neous formation of **13b** and **6a**. In the intramolecular hydrogen abstraction reactions in **11a** and **12a**, on the contrary, radical pair recombination in the diradical intermediates **IVa** and **IVb** (Scheme 3) meets no significant steric hindrance.

Photoreaction of 1,4-Anthraquinone (14) and 9,10-Anthraquinone (15) with BCP. 1,4-Anthraquinone (**14**) has a $\pi\pi^*$ T_1 state in thermal equilibrium with a slightly higher $n\pi^*$ T_2 state at room temperature.[28] To our knowledge, there is only one previous report on photocycloaddition reactions of **14** with olefins where cyclobutanes are exclusively formed.[28] In our work, photoreactions of **14** with BCP in benzene gave rise to the cyclobutane **14a** and the spirocyclopentanone **14b** concomitantly (Table 6), in line with the participation of the thermally equilibrated $\pi\pi^*$ and $n\pi^*$ triplet states. At the same time, photocycloadditions of 9,10-anthraquinone (**15**) having a distinct $\pi\pi^*$ T_1 state[29] have been widely investigated and found to invariably give spirooxetane product exclusively. However, we found that in photoreactions of 9,10-anthraquinone with BCP in benzene, the spirooxetane **15a** (55% yield) was formed along with an unexpected spiro[indan-1,1′-phthalan]-3′-one product **15b** (41% yield) (Table 6). The structure of **15b** was established by X-ray crystallographic analysis (Figure S5, Supporting Information).

Table 6. Summary on the Photoreaction Products of Anthraquinones with BCP

Entry	Anthraquinone	Irrad. Time (h)	Products & yields (%)[a]
1	 **14**	10	 **14a** (78), **14b** (15)
2	 **15**	12	 **15a** (55), **15b** (41)

[a]Isolated yield.

Control experiments showed that **15a** was photostable under the reaction conditions, and upon prolonged irradiation of pure **15a** in benzene, little consumption of the starting material was observed, and no transformation to **15b** even in a trace amount could be detected. This indicates that **15a** and **15b** are both primary products in the photoreactions of **15** with BCP. The proposed mechanism for the formation of **15a** and **15b** is shown in Scheme 4. Radical pair recombination following intersystem crossing in the triplet 1,4-diradical **V** furnishes the spirooxetane **15a**. However, in diradical intermediate **V**, the specific conformation for efficient intersystem crossing (ISC)[30] and the ISC process from this conformation are both significantly impeded by the unfavorable steric hindrance between the bulky cyclopropyl at the radical center and the benzene ring at either side of it. This enables an alternative pathway to be operative via a transannular attack of the cyclopropyl radical toward the C10 carbonyl, leading to the 1,6-diradical **VI**, from which diradical **VII** is derived by homolytic scission of the C−O bond α- to the alkoxycarbinyl center in **VI**. Another transannular attack of the alkoxy radical in **VII** to the C9 carbonyl inducing a α-cleavage at the latter, furnishing the rearranged product **15b**. The formation of the unusual product **15b** represents an unprecedented reaction pathway in the Paterno−Büchi reaction of anthraquinone. Since the driving force for this alternative pathway leading to **15b** is the severe steric hindrance to the radical pair recombination induced by the interaction between the bulky substituents at the C4 radical center in the 1,4-diradical and the neighboring benzene ring, this pathway may also be operative in the Paterno−Büchi reaction of *para*-quinones in cases where the structures of the quinone and the alkene are suitable to lead to serious steric hindrance for the oxetane ring formation in the 1,4-diradical intermediate, similar to that seen in the intermediate **V**.

Photoreaction of Naphtho[2,3-*b*]furan-4,9-diones 16−19 with BCP. Photoinduced reactions of the avicequinone B (Naphtho[2,3-*b*]furan-4,9-dione) derivatives **16**−**19** with BCP were also investigated. Quinones **16** and **17** with an ester group at C3 atom showed a typical $\pi\pi^*$ excited state reactivity to give the cyclobutane products **16a** and **17a** (for crystal structure, see: Figure S6, Supporting Information) in high yields (Table 7). However, similar irradiation of **18** and **19** with an acyl group at C3 atom resulted in the unexpected formation of the spirocyclopropane and spirofuranone annulated 1*H*-benz[*f*]inden-9-one products **18b** and **19b** (Table 7). The structure of **19b** was unequivocally established by X-ray crystallographic analysis (Figure S7, Supporting Information).

Scheme 4. Proposed Mechanism for Formation of Compound 15a and 15b

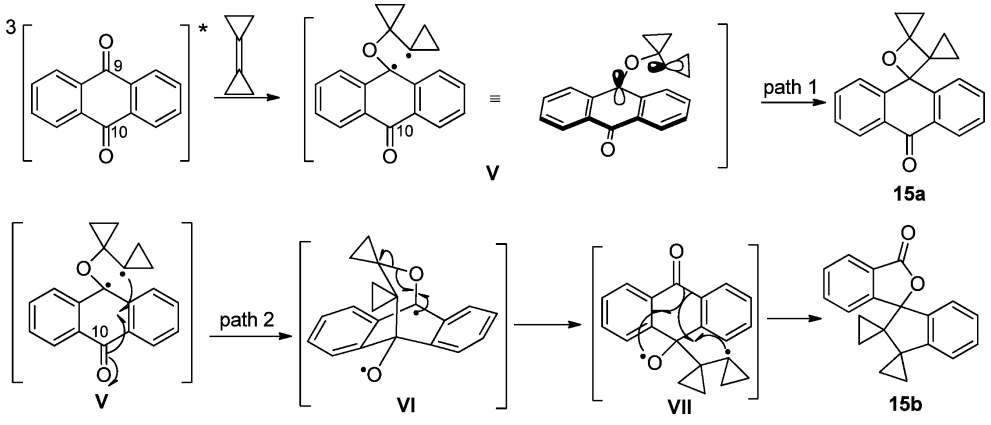


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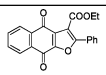
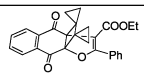
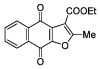
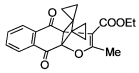
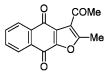
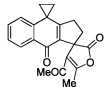
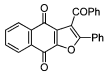
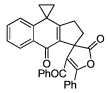
Table 7. Summary on the Photoreaction Products of Naphtho[2,3-*b*]furan-4,9-diones with BCP

Entry	Naphtho[2,3-*b*]furan-4,9-dione	Irrad. Time (h)	Products & yields (%)[a]
1	 **16**	24	 **16a** (88)
2	 **17**	24	 **17a** (98)
3	 **18**	24	 **18b** (68)
4	 **19**	24	 **19b** (69)

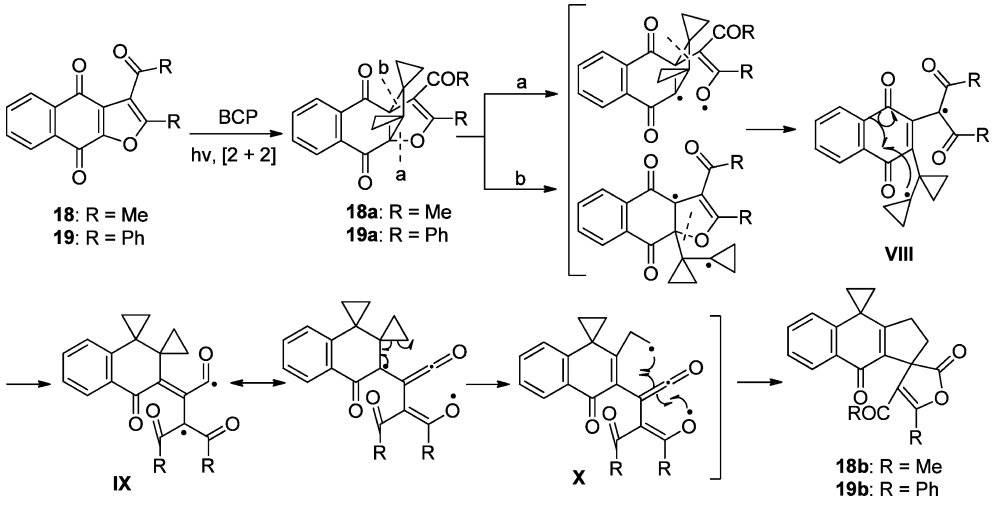
[a]Isolated yield.

Although no primary products were isolated, we suggest that **18b** and **19b** are derived from secondary photoreactions of the primary cyclobutane products (**18a** and **19a**), and a possible mechanism is proposed in Scheme 5. Homolytic scission of the C−O bond in the furan ring and the ensuing cleavage of one of the C−C bonds between two quarternary carbon atoms in the cyclobutane ring lead to the diradical **VIII** (pathway a). Alternatively, initial C−C bond homolysis in the cyclobutane ring followed by C−O bond cleavage in the furan ring also leads to the diradical **VIII** (pathway b). Attack of the cyclopropyl radical to the C4′ atom in the benzene ring furnishes **IX**. Ring-opening of one of the cyclopropyls in **IX** via a cyclopropylcarbinyl to allylcarbinyl radical transformation affords the diradical **X**, where a 5-*exo*-*trig* cyclization followed by radical pair recombination gives the deeply rearranged addition product **18b** and **19b**. At this time, we have no definite explanation on why products **16a** and **17a** are stable while **18a** and **19a** are so labile as to be too elusive to be isolated from the reaction mixture, although it is speculated that the stronger absorption in the long wavelength region used for the photolysis and the heavier steric congestion of the acyl substituted **18a** and **19a** than the ethoxycarbonyl substituted **16a** and **17a** may contribute to the stability difference.

CONCLUSION

In summary, photoreactions of BCP with various substituted *p*-quinones proceeded cleanly and resulted in distinct product distribution from the photoreactions of *p*-quinones with common alkenes. The special structural features of BCP have shown profound influences on reaction modes and the formation of special secondary products. The high steric hindrance of the cyclopropyl radical in the Paterno−Büchi 1,4-diradical intermediate toward ring closure by radical pair recombination may hamper the spirooxetane formation and open new reaction channels. Along with the spirooxetanes and cyclobutanes that resulted from common photocycloaddition via nπ^* and $\pi\pi^*$ triplet of quinones, secondary products such as the spiro[4.5]deca-6,9-diene-2,8-diones with the spiro[4.5]-decane core that presents in many natural products were obtained in the photoreactions of BCP with benzoquinones, naphthoquinone and 1,4-anthraquinone. In the case of 9,10-anthraquinone, an unprecedented reaction pathway was observed via the Paterno−Büchi 1,4-diradical intermediate, enforcing a transannular attack of the C4 carbinyl radical to the *para*-carbonyl group and leading to the formation of the novel addition-rearrangement product **15b**. In photocycloadditions of the acyl substituted furanonaphthoquinones (**18** and **19**) with BCP, steric congestion caused by the two spiro-fused cyclopropyls in the primary cyclobutane product led to the

Scheme 5. Proposed Mechanism for the Formation of Compound 18b and 19b



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formation of deeply rearranged cycloadducts (**18b** and **19b**). The photoreactions of BCP with *p*-quinones therefore provided facile approach to a range of novel polycyclic framework with one or two spiro-fused cyclopropane rings via known or new reaction pathways.

EXPERIMENTAL SECTION

General Methods. Commercial reagents were used as supplied or purified by standard techniques when necessary. Benzene was distilled from Na and benzophenone. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300 or 400 MHz spectrometer in $CDCl_3$ using TMS as an internal standard. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). *J* = coupling constant in hertz. NOESY spectra were recorded on a 400 MHz spectrometer. IR spectra were with an FT-IR spectrophotometer and are reported as cm^{-1}. HRMS analyses were carried out on an electrospray ionization apparatus using time-of-flight mass spectrometry. Melting points are uncorrected.

General Procedures for the Preparative Photoreactions. The light source for the photolysis was a medium-pressure mercury lamp (500 W) in a cooling water jacket that was further surrounded by a layer of filter solution (1 cm thick, 20% aqueous sodium nitrite) to cut off light of wavelength shorter than 400 nm. The solution of *para*-quinone and an excess amount of BCP in anhydrous benzene was irradiated under continuous nitrogen purging. The reaction course was monitored by TLC. At the end of the reaction, the solvent was removed under reduced pressure, and the residue was separated by flash chromatography on a silica gel column.

Photolysis of 1 with BCP in Anhydrous Benzene. A solution of **1** (216 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 7 h to reach a complete conversion of **1**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **1a** (199 mg, 53%) and **1b** (158 mg, 42%). Photolysis for 24 h gave **1b** (368 mg, 98%) only.

1a: 13-Oxatrispiro[2.0.2.0.5.1]trideca-8,11-diene-10-one, white powder, mp 76−78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 10.3 Hz, 2H), 6.17 (d, *J* = 10.3 Hz, 2H), 0.94−0.89 (m, 2H), 0.54−0.43 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.4, 147.1, 128.6, 79.2, 71.7, 31.3, 7.8, 5.7; IR (ATR, neat) 3068, 3044, 2996, 1661, 1625, 1599, 1402, 1377, 1296, 1245, 1223, 1170, 1151, 1080, 1054, 1023, 996, 957, 925, 853, 778, 715, 681 cm^{-1}; MS (ESI+) *m*/*z* 189 [M + H]$^+$; HRMS (ESI) *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{13}O_2$ 189.0916, found 189.0906.

1b: Dispiro[2.0.5.3]dodeca-5,8-diene-7,12-dione, white powder, mp 80−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86−6.82 (m, 2H), 6.29−6.25 (m, 2H), 2.64 (t, *J* = 7.9 Hz, 2H), 2.29 (t, *J* = 7.9 Hz, 2H), 1.21−1.18 (m, 2H), 0.81−0.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.2, 185.3, 150.9, 128.5, 46.0, 35.9, 35.7, 32.0, 15.7; IR (ATR, neat) 3071, 1806, 1707, 1639, 1598, 1480, 1444, 1347, 1308, 1295, 1262, 1208, 1198, 1090, 1087, 1023, 1008, 966, 941, 890, 856, 837, 774, 751, 737, 707, 695, 657 cm^{-1}; MS (ESI+) *m*/*z* 189 [M + H]$^+$; HRMS (ESI) *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{13}O_2$ 189.0916, found 189.0909.

Photolysis of 2 with BCP in Anhydrous Benzene. A solution of **2** (272 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 10 h to reach a complete conversion of **2**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **2a** (229 mg, 53%) and **2b** (156 mg, 36%). Photolysis for 24 h gave **2b** (410 mg, 95%) only.

2a: 9,11-Dimethyl-13-oxatrispiro[2.0.2.0.5.1]trideca-8,11-diene-10-one, colorless crystal, mp 100−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 2H), 1.90 (s, 6H), 0.90−0.86 (m, 2H), 0.50−0.40 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 142.1, 135.5, 79.2, 71.0, 31.2, 15.8, 7.8, 5.8; IR (ATR, neat) 3068, 1806, 1639, 1598, 1483, 1447, 1347, 1314, 1292, 1256, 1211, 1196, 1096, 1078, 1008, 966, 941, 891, 856, 838, 774, 751, 737, 707, 695, 657 cm^{-1}; MS (ESI+) *m*/*z* 217 [M + H]$^+$. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.61; H, 7.42.

2b: 6,8-Dimethyldispiro[2.0.5.3]dodeca-5,8-diene-7,12-dione, white powder, mp 114−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (s, 2H), 2.61 (t, *J* = 7.9 Hz, 2H), 2.21 (t, *J* = 7.9 Hz, 2H), 1.90 (s, 6H), 1.16−1.13 (m, 2H), 0.75−0.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.2, 186.7, 145.9, 134.7, 45.4, 36.2, 35.9, 32.5, 16.2, 15.8; IR (ATR, neat) 2966, 2944, 2929, 1717, 1670, 1636, 1456, 1435, 1414, 1399, 1373, 1359, 1310, 1255, 1226, 1203, 1090, 1059, 1028, 982, 935, 921, 904, 845, 816, 774, 754, 661 cm^{-1}; MS (ESI+) *m*/*z* 217 [M + H]$^+$; HRMS (ESI) *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{16}O_2Na$ 239.1048, found 239.1044.

Photolysis of 3 with BCP in Anhydrous Benzene. A solution of **3** (328 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 48 h, and TLC analysis showed no conversion of **3**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents only recovered **3**.

Photolysis of 4 with BCP in Anhydrous Benzene. A solution of **4** (285 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 25 h to reach a complete conversion of **4**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **4b** (302 mg, 68%).

4b: 6-Chlorodispiro[2.0.5.3]dodeca-5,8-diene-7,12-dione, colorless crystal, mp 92−94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 2.9 Hz, 1H), 6.87 (dd, *J* = 10.0, 2.9 Hz, 1H), 6.35 (d, *J* = 10.0 Hz, 1H), 2.65 (t, *J* = 7.9 Hz, 2H), 2.33 (t, *J* = 7.9 Hz, 2H), 1.26−1.19 (m, 2H), 0.86−0.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.4, 178.4, 150.8, 146.6, 132.7, 127.7, 48.7, 36.0, 35.7, 32.2, 16.0, 16.0; IR (ATR, neat) 3050, 3002, 2975, 2923, 1722, 1660, 1592, 1414, 1354, 1314, 1230, 1138, 1088, 1053, 1033, 976, 899, 838, 824, 813, 760, 718, 672, 606 cm^{-1}; MS (ESI+) *m*/*z* 223 [M + H]$^+$, 245 [M + Na]$^+$; HRMS (ESI) *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{11}ClO_2Na$ 245.0345, found 245.0339.

Photolysis of 5 with BCP in Anhydrous Benzene. A solution of **5** (354 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 24 h to reach a complete conversion of **5**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **5a** (292 mg, 57%) and **5b** (164 mg, 32%). Photolysis for 48 h gave **5b** (425 mg, 83%) only.

5a: 9,11-Dichloro-13-oxatrispiro[2.0.2.0.5.1]trideca-8,11-diene-10-one, white powder, mp 92−94 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (s, 2H), 0.96−0.91 (m, 2H), 0.64−0.51 (m, 4H), 0.50−0.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 143.2, 131.6, 80.8, 72.2, 31.7, 7.8, 6.1; IR (ATR, neat) 3071, 3047, 1806, 1686, 1639, 1599, 1480, 1448, 1347, 1296, 1263, 1211, 1154, 1029, 1007, 941, 890, 855, 837, 771, 751, 737, 695, 656, 611 cm^{-1}; MS (ESI+) *m*/*z* 257 [M + H]$^+$. Anal. Calcd for $C_{12}H_{10}O_2Cl_2$: C, 56.06; H, 3.92. Found: C, 56.07; H, 3.99.

5b: 6,8-Dichlorodispiro[2.0.5.3]dodeca-5,8-diene-7,12-dione, white powder, mp 134−136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (s, 2H), 2.67 (t, *J* = 7.9 Hz, 2H), 2.38 (t, *J* = 7.9 Hz, 2H), 1.29−1.25 (m, 2H), 0.88−0.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.5, 172.2, 146.9, 131.5, 49.5, 36.0, 35.5, 32.2, 16.1; IR (ATR, neat) 3041, 2941, 2914, 1724, 1667, 1595, 1453, 1417, 1353, 1315, 1287, 1253, 1088, 977, 887, 838, 771, 729, 705, 670 cm^{-1}; MS (ESI+) *m*/*z* 257 [M + H]$^+$. Anal. Calcd for $C_{12}H_{10}O_2Cl_2$: C, 56.06; H, 3.92. Found: C, 56.13; H, 4.01.

Photolysis of 6 with BCP in Anhydrous Benzene. A solution of **6** (316 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 24 h to reach a complete conversion of **6**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **6a** (171 mg, 36%) and **6b** (276 mg, 58%).

6a: 1′,2′,2′a,8′a-Tetrahydrodispiro[cyclopropane-1,1′-cyclobuta[*b*]-naphthalene-2′,11″-cyclopropane]-3′,8′-dione, white powder, mp 136−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16−8.12 (m, 2H), 7.81−7.77 (m, 2H), 3.75 (s, 2H), 0.70−0.65 (m, 2H), 0.50−0.40 (m, 4H), 0.08−0.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 135.2, 134.3, 127.3, 47.5, 27.9, 9.4, 6.6; IR (ATR, neat) 3069, 3053,

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1666, 1587, 1429, 1318, 1289, 1272, 1257, 1212, 1196, 1154, 1118, 1054, 1033, 1019, 955, 924, 889, 871, 791, 776, 753, 722, 679 cm^{-1}; MS (ESI+) m/z 239 $[M + H]^+$; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{14}O_2Na$ 261.0891, found 261.0886.

6b: Dispiro[cyclopropane-1,1′-cyclopentane-2′,11″-(4″*H*)-naphthalene]-4″,5′-dione, white powder, mp 158−160 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, J = 8.1, 1.4 Hz, 1H), 7.62 (td, J = 7.8, 1.5 Hz, 1H), 7.45−7.41 (m, 2H), 7.04 (d, J = 10.4 Hz, 1H), 6.43 (d, J = 10.4 Hz, 1H), 2.85−2.70 (m, 2H), 2.62−2.46 (m, 2H), 1.36−1.26 (m, 2H), 0.74−0.70 (m, 1H), 0.55−0.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.5, 184.3, 151.7, 146.0, 132.6, 131.6, 128.2, 127.4, 126.7, 126.4, 47.0, 38.5, 36.1, 35.6, 20.1, 18.5; IR (ATR, neat) 3074, 3029, 3005, 2963, 1710, 1661, 1600, 1452, 1417, 1396, 1316, 1299, 1171, 1093, 1072, 1033, 986, 972, 906, 838, 781, 764, 733, 691, 641 cm^{-1}; MS (ESI+) m/z 239 $[M + H]^+$; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{14}O_2Na$ 261.0891, found 261.0889.

Photolysis of 7 with BCP in Anhydrous Benzene. A solution of **7** (344 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 24 h to reach a complete conversion of **7**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **7a** (444 mg, 88%) and **7b** (40 mg, 8%).

7a: 2′a-Methyl-1′,2′,2′a,8′a-tetrahydrodispiro[cyclopropane-1,1′-cyclobuta[*b*]naphthalene-2′,1″-cyclopropane]-3′,8′-dione, white powder, mp 115−116 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.15−8.10 (m, 2H), 7.80−7.75 (m, 2H), 3.36 (s, 1H), 1.52 (s, 3H), 0.70−0.60 (m, 2H), 0.46−0.33 (m, 3H), 0.19 (ddd, J = 10.3, 6.9, 5.4 Hz, 1H), 0.07 (ddd, J = 10.2, 6.9, 5.2 Hz, 1H), 0.03 to −0.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 195.5, 135.3, 135.1, 134.2, 134.0, 127.5, 126.9, 55.3, 48.2, 32.8, 25.9, 20.9, 9.5, 8.0, 5.9, 5.7; IR (ATR, neat) 3068, 3035, 2990, 2932, 1711, 1663, 1591, 1450, 1420, 1396, 1371, 1286, 1256, 1171, 1154, 1129, 1094, 1069, 1027, 986, 912, 836, 801, 782, 765, 733, 694, 636 cm^{-1}; MS (ESI+) m/z 253 $[M + H]^+$. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.89; H, 6.43.

7b: 3″-Methyldispiro[cyclopropane-1,1′-cyclopentane-2′,1″-(4″*H*)-naphthalene]-4″,5′-dione, white powder, mp 136−138 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 7.8, 1.8 Hz, 1H), 7.59 (td, J = 7.8, 1.4 Hz, 1H), 7.43−7.39 (m, 2H), 6.83 (q, J = 1.4 Hz, 1H), 2.79−2.74 (m, 2H), 2.58−2.42 (m, 2H), 2.04 (d, J = 1.4, 3H), 1.30−1.27 (m, 2H), 0.71−0.67 (m, 1H), 0.53−0.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.0, 184.9, 147.4, 146.2, 132.7, 132.2, 131.5, 128.0, 127.3, 126.9, 46.6, 38.7, 36.2, 35.8, 20.1, 18.5, 16.3; IR (ATR, neat) 3077, 1794, 1709, 1653, 1632, 1602, 1459, 1383, 1370, 1314, 1286, 1235, 1196, 1175, 1093, 1018, 952, 934, 893, 790, 777, 757, 718, 670 cm^{-1}; MS (ESI+) m/z 253 $[M + H]^+$; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}O_2Na$ 275.1048, found 275.1044.

Photolysis of 8 with BCP in Anhydrous Benzene. A solution of **8** (385 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 24 h to reach a complete conversion of **8**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **8a** (473 mg, 87%).

8a: 2′a-Chloro-1′,2′,2′a,8′a-tetrahydrodispiro[cyclopropane-1,1′-cyclobuta[*b*]naphthalene-2′,11″-cyclopropane]-3′,8′-dione, white powder, mp 122−124 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25−8.20 (m, 1H), 8.16−8.12 (m, 1H), 7.86−7.81 (m, 2H), 4.04 (s, 1H), 1.10 (ddd, J = 10.6, 7.7, 5.7 Hz, 1H), 0.77 (ddd, J = 10.6, 7.2, 5.7 Hz, 2H), 0.60 (ddd, J = 10.2, 7.2, 5.7 Hz, 1H), 0.51 (ddd, J = 10.2, 6.6, 5.7 Hz, 1H), 0.41 (ddd, J = 10.3, 6.6, 5.7 Hz, 1H), 0.30 (ddd, J = 10.3, 7.7, 5.7 Hz, 1H), 0.10 (ddd, J = 10.2, 7.2, 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 189.6, 134.9, 134.8, 134.7, 133.5, 128.5, 127.3, 68.5, 59.4, 35.0, 26.1, 10.6, 10.2, 8.8, 6.1; IR (ATR, neat) 3074, 2999, 1710, 1680, 1585, 1456, 1399, 1302, 1274, 1244, 1094, 1026, 970, 927, 814, 798, 783, 766, 749, 726, 691, 606 cm^{-1}; MS (ESI+) m/z 273 $[M + H]^+$. Anal. Calcd for $C_{16}H_{13}O_2Cl$: C, 70.46; H, 4.80. Found: C, 70.23; H, 4.92.

Photolysis of 9 with BCP in Anhydrous Benzene. A solution of **9** (454 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 24 h to reach a complete conversion of **9**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **9a** (490 mg, 80%).

9a: 2′a,8′a-Dichloro-1′,2′,2′a,8′a-tetrahydrodispiro[cyclopropane-1,1′-cyclobuta[*b*]naphthalene-2′,11″-cyclopropane]-3′,8′-dione, white powder, mp 163−164 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24−8.19 (m, 2H), 7.89−7.85 (m, 2H), 1.11 (ddd, J = 10.7, 7.6, 5.8 Hz, 2H), 0.74 (ddd, J = 10.7, 7.2, 5.8 Hz, 2H), 0.61 (ddd, J = 10.2, 7.2, 5.8 Hz, 2H), 0.33 (ddd, J = 10.2, 7.6, 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7, 135.3, 133.2, 128.5, 76.8, 34.5, 9.9, 9.8; IR (ATR, neat) 3068, 3029, 2993, 1710, 1695, 1662, 1580, 1450, 1417, 1390, 1299, 1257, 1223, 1175, 1126, 1099, 1069, 1039, 1017, 966, 936, 842, 802, 780, 766, 725, 688, 636, 612 cm^{-1}; MS (ESI+) m/z 307 $[M + H]^+$; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{12}O_2Cl_2Na$ 329.0112, found 329.0117.

Photolysis of 10 with BCP in Anhydrous Benzene. A solution of **10** (500 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 3 h to reach a complete conversion of **10**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **10a** (574 mg, 87%).

10a: 2′a-Phenoxy-1′,2′,2′a,8′a-tetrahydrodispiro[cyclopropane-1,1′-cyclobuta[*b*]naphthalene-2′,11″-cyclopropane]-3′,8′-dione, white powder, mp 156−157 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22−8.18 (m, 2H), 7.89−7.82 (m, 2H), 7.17−7.12 (m, 2H), 6.92−6.88 (m, 1H), 6.66−6.62 (m, 2H), 3.84 (s, 1H), 1.41−1.33 (m, 1H), 0.73−0.67 (m, 1H), 0.56−0.50 (m, 3H), 0.41−0.35 (m, 1H), 0.29−0.21 (m, 1H), 0.13−0.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 192.3, 154.7, 135.2, 134.9, 134.6, 134.0, 129.7, 128.1, 127.5, 121.7, 116.0, 80.8, 55.5, 31.7, 24.8, 9.4, 9.3, 7.2, 6.8; IR (ATR, neat) 3071, 2993, 2947, 2914, 1806, 1639, 1598, 1480, 1448, 1347, 1295, 1258, 1211, 1198, 1094, 1008, 966, 941, 891, 856, 837, 773, 751, 737, 722, 707, 695, 657 cm^{-1}; MS (ESI+) m/z 331 $[M + H]^+$, 353 $[M + Na]^+$; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{22}H_{18}O_3Na$ 353.1154, found 353.1152.

Photolysis of 11 with BCP in Anhydrous Benzene. A solution of **11** (376 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 3 h to reach a complete conversion of **11**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **11a** (468 mg, 87%). Photolysis for 24 h gave **11b** (457 mg, 85%).

11a: 2′a-Methoxy-1′,2′,2′a,8′a-tetrahydrodispiro[cyclopropane-1,1′-cyclobuta[*b*]naphthalene-2′,11″-cyclopropane]-3′,8′-dione, white powder, mp 159−161 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21−8.19 (m, 1H), 8.11−8.08 (m, 1H), 7.84−7.79 (m, 2H), 3.80 (s, 1H), 3.35 (s, 3H), 1.12 (ddd, J = 10.3, 5.0, 3.3 Hz, 1H), 0.69 (ddd, J = 10.3, 7.2, 5.8 Hz, 1H), 0.48−0.39 (m, 3H), 0.33 (ddd, J = 10.3, 7.0, 5.5, 1H), 0.18−0.13 (m, 1H), 0.06 (ddd, J = 10.3, 7.0, 5.5, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 194.3, 135.5, 134.9, 134.7, 134.2, 127.7, 127.1, 82.2, 54.1, 52.8, 31.5, 24.3, 8.7, 8.5, 7.0, 6.9; IR (ATR, neat) 3068, 3038, 2947, 2914, 1724, 1663, 1595, 1456, 1441, 1353, 1315, 1290, 1253, 1226, 1088, 1051, 977, 838, 728, 705, 667 cm^{-1}; MS (ESI+) m/z 269 $[M + H]^+$; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}O_3Na$ 291.0997, found 291.0992.

11b: white powder, mp 169−171 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 7.9 Hz, 1H), 7.70−7.65 (m, 2H), 7.52−7.47 (m, 1H), 4.61−4.54 (m, 2H), 3.75 (s, 1H), 2.65 (s, 1H), 1.20−1.03 (m, 2H), 0.58−0.48 (m, 2H), 0.37−0.29 (m, 2H), 0.25−0.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.4, 144.1, 134.8, 129.9, 128.8, 127.1, 127.0, 89.1, 81.8, 72.9, 54.1, 30.9, 24.4, 6.3, 4.6, 4.2, 4.1; IR (ATR, neat) 3377, 3062, 3002, 2953, 2875, 1662, 1598, 1447, 1383, 1318, 1297, 1278, 1262, 1194, 1160, 1096, 1066, 1020, 1004, 956, 930, 869, 812, 770, 752, 725, 687, 628 cm^{-1}; MS (ESI+) m/z 269 $[M + H]^+$; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}O_3Na$ 291.0997, found 291.0993.

Photolysis of 12 with BCP in Anhydrous Benzene. A solution of **12** (404 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 3 h to reach a complete conversion of **12**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents

afforded **12a** (479 mg, 85%). Photolysis for 24 h gave **12b** (496 mg, 88%).

12a: 2′a-Ethoxy-1′,2′,2′a,8′a-tetrahydrodispiro[cyclopropane-1,1′-cyclobuta[*b*]naphthalene-2′,11″-cyclopropane]-3′,8′-dione, white powder, mp 159−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21−8.18 (m, 1H), 8.09−8.07 (m, 1H), 7.82−7.78 (m, 2H), 3.80 (s, 1H), 3.52 (dq, J = 8.7, 7.0 Hz, 1H), 3.41 (dq, J = 8.7, 7.0 Hz, 1H), 1.26 (t, J = 7.0, 3H), 1.19−1.14 (m, 1H), 0.69−0.63 (m, 1H), 0.50−0.40 (m, 3H), 0.32−0.26 (m, 1H), 0.15−0.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 194.5, 135.5, 134.9, 134.6, 134.2, 127.7, 127.0, 81.5, 61.0, 55.0, 31.8, 24.3, 15.5, 8.4, 8.3, 7.2, 7.0; IR (ATR, neat) 3071, 2987, 2941, 2905, 1806, 1713, 1639, 1595, 1574, 1483, 1441, 1420, 1347, 1308, 1295, 1257, 1208, 1193, 1093, 1008, 966, 941, 891, 856, 838, 774, 752, 737, 707, 695, 657 cm^{-1}; MS (ESI+) m/z 283 [M + H]$^+$; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{18}H_{18}O_3Na$ 305.1154, found 305.1159.

12b: white powder (with photolysis for 24 h), mp 155−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.06 (m, 1H), 7.69−7.65 (m, 1H), 7.56−7.54 (m, 1H), 7.49−7.45 (m, 1H), 4.67 (t, J = 6.3 Hz, 1H), 3.73 (s, 1H), 2.57 (s, 1H), 1.35 (d, J = 6.3 Hz, 3H), 1.09−0.98 (m, 2H), 0.55−0.46 (m, 2H), 0.34−0.27 (m, 2H), 0.22−0.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 145.1, 134.8, 129.7, 128.6, 127.1, 126.5, 86.5, 85.5, 73.1, 54.3, 30.5, 24.5, 15.8, 6.3, 4.4, 4.2, 3.8; IR (ATR, neat) 3401, 3083, 2984, 2947, 2908, 1806, 1653, 1638, 1595, 1574, 1477, 1447, 1348, 1314, 1295, 1259, 1211, 1198, 1099, 1081, 1108, 966, 941, 891, 856, 838, 773, 752, 737, 707, 695, 657 cm^{-1}; MS (ESI+) m/z 283 [M + H]$^+$; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{18}H_{18}O_3Na$ 305.1154, found 305.1150.

Photolysis of 13 with BCP in Anhydrous Benzene. A solution of **13** (432 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 3 h to reach a complete conversion of **13**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **13a** (521 mg, 88%). Photolysis for 48 h gave **13a** (36 mg, 6%), **13b** (320 mg, 54%) and **6a** (257 mg, 25%).

13a: 2′a-Isopropoxy-1′,2′,2′a,8′a-tetrahydrodispiro[cyclopropane-1,1′-cyclobuta[*b*]naphthalene-2′,11″-cyclopropane]-3′,8′-dione, white powder, mp 158−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.19 (m, 1H), 8.10−8.05 (m, 1H), 7.82−7.78 (m, 2H), 3.89 (s, 1H), 3.80 (m, 1H), 1.20 (ddd, J = 9.8, 6.9, 4.4 Hz, 1H), 1.18 (d, J = 6.1 Hz, 3H), 1.13 (d, J = 6.1 Hz, 3H), 0.60 (ddd, J = 10.3, 7.1, 5.7, 1H), 0.52−0.35 (m, 3H), 0.23 (ddd, J = 10.3, 6.6, 5.6 Hz, 1H), 0.12−0.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 194.7, 135.4, 134.6, 134.6, 134.1, 127.8, 127.0, 80.5, 69.2, 56.7, 33.0, 24.4, 23.8, 23.7, 8.0, 7.7, 7.6, 7.3; IR (ATR, neat) 3068, 2987, 2938, 2902, 1806, 1707, 1639, 1595, 1477, 1447, 1347, 1307, 1291, 1257, 1211, 1198, 1095, 1081, 1008, 966, 941, 891, 856, 837, 774, 752, 722, 707, 695, 657 cm^{-1}; MS (ESI+) m/z 297 [M + H]$^+$, 319 [M + Na]$^+$; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{19}H_{20}O_3Na$ 319.1310, found 319.1313.

13b: white powder, mp 147−149 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10−8.07 (m, 1H), 7.69−7.63 (m, 1H), 7.56−7.53 (m, 1H), 7.49−7.44 (m, 1H), 3.68 (s, 1H), 2.68 (s, 1H), 1.41 (s, 3H), 1.12−0.96 (m, 2H), 0.94 (s, 3H), 0.53−0.44 (m, 2H), 0.32−0.11 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6, 143.4, 134.4, 130.8, 128.5, 127.4, 126.8, 88.3, 83.8, 75.4, 54.5, 30.7, 27.4, 24.8, 23.7, 6.5, 4.3, 4.1, 3.8; IR (ATR, neat) 3413, 3368, 3074, 2999, 1807, 1695, 1639, 1598, 1574, 1480, 1444, 1348, 1314, 1293, 1208, 1193, 1033, 1007, 941, 890, 856, 837, 770, 752, 737, 721, 707, 695, 657 cm^{-1}; MS (ESI+) m/z 297 [M + H]$^+$. Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.92; H, 6.82.

Photolysis of 14 with BCP in Anhydrous Benzene. A solution of **14** (416 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 10 h to reach a complete conversion of **14**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **14a** (451 mg, 78%) and **14b** (146 mg, 15%).

14a: 1′,2′,2′a,10′a-Tetrahydrodispiro[cyclopropane-1,1′-cyclobuta-[*b*]anthracene-2′,11″-cyclobutane]-3′,10′-dione, white powder, mp 176−178 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (s, 2H), 8.12−8.07 (m, 2H), 7.73−7.67 (m, 2H), 3.82 (s, 2H), 0.75−0.68 (m, 2H), 0.54−0.41 (m, 4H), 0.08 to −0.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.1, 135.3, 131.2, 130.0, 129.4, 129.3, 47.9, 28.1, 9.5, 6.7; IR (ATR, neat) 3080, 2987, 2947, 2911, 1806, 1639, 1595, 1480, 1447, 1423, 1348, 1295, 1258, 1211, 1197, 1096, 1060, 1008, 966, 941, 891, 856, 838, 774, 752, 737, 724, 707, 695, 657 cm^{-1}; MS (ESI+) m/z 289 [M + H]$^+$; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{20}H_{16}O_2Na$ 311.1048, found 311.1043.

14b: Dispiro[cyclopropane-1,1′-cyclopentane-2′,1″-(4″*H*)-anthracene]-4″,5′-dione, white powder, mp 172−174 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.85 (s, 1H), 7.65−7.53 (m, 2H), 7.09 (d, J = 10.3 Hz, 1H), 6.51 (d, J = 10.3 Hz, 1H), 2.95−2.52 (m, 4H), 1.42−1.31 (m, 2H), 0.84−0.79 (m, 1H), 0.61−0.55 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.8, 184.6, 151.9, 141.4, 135.0, 131.6, 129.6, 129.1, 128.7, 128.3, 127.7, 127.5, 126.9, 126.9, 47.0, 39.7, 36.7, 36.1, 20.1, 18.8; IR (ATR, neat) 3087, 3071, 2990, 2947, 1711, 1665, 1621, 1591, 1447, 1401, 1309, 1278, 1272, 1218, 1160, 1092, 1075, 1033, 979, 895, 834, 821, 756, 665, 642 cm^{-1}; MS (ESI+) m/z 289 [M + H]$^+$; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{17}O_2$ 289.1229, found 289.1256.

Photolysis of 15 with BCP in Anhydrous Benzene. A solution of **15** (416 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (200 mL) was photolyzed with nitrogen bubbling for 12 h to reach a complete conversion of **15**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **15a** (317 mg, 55%) and **15b** (236 mg, 41%).

15a: Trispiro[biscyclopropane-1,2″:1′,3″-oxetane-4″,9‴-(10‴*H*)-anthracene]-10‴-one, white powder, mp 156−158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (dd, J = 7.9, 1.3 Hz, 2H), 8.21 (dd, J = 7.9, 1.5 Hz, 2H), 7.79 (td, J = 7.9, 1.5 Hz, 2H), 7.52 (td, J = 7.9, 1.3 Hz, 2H), 1.29−1.24 (m, 2H), 0.67−0.62 (m, 2H), 0.35−0.31 (m, 2H), 0.00 to −0.04 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.5, 143.9, 133.9, 130.3, 128.5, 127.6, 126.6, 83.2, 71.9, 39.9, 8.6, 8.5; IR (ATR, neat) 3065, 3035, 2999, 1659, 1599, 1459, 1318, 1283, 1195, 1175, 1151, 1114, 1019, 1003, 966, 957, 930, 864, 817, 768, 751, 733, 686, 628 cm^{-1}; MS (ESI+) m/z 289 [M + H]$^+$; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{20}H_{16}O_2Na$ 311.1048, found 311.1042.

15b: white powder, mp 154−156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (dt, J = 7.6, 1.1 Hz, 1H), 7.64 (td, J = 7.4, 1.1 Hz, 1H), 7.54 (td, J = 7.5, 1.1 Hz, 1H), 7.37−7.31 (m, 2H), 7.15 (td, J = 7.5, 1.2 Hz, 1H), 6.91 (dt, J = 7.6, 0.9 Hz, 1H), 6.82 (dt, J = 7.6, 0.9 Hz, 1H), 1.07−0.98 (m, 2H), 0.92−0.87 (m, 1H), 0.79−0.63 (m, 2H), 0.50−0.33 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 150.0, 148.9, 140.7, 134.1, 130.1, 129.4, 126.8, 126.5, 125.2, 123.8, 123.4, 119.0, 96.0, 33.9, 29.9, 13.9, 11.7, 9.1, 6.3; IR (ATR, neat) 3074, 3038, 3008, 1744, 1704, 1610, 1466, 1417, 1338, 1284, 1236, 1187, 1157, 1113, 1090, 1020, 940, 916, 900, 820, 757, 751, 724, 691, 662, 650 cm^{-1}; MS (ESI+) m/z 289 [M + H]$^+$, 311 [M + Na]$^+$. Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.06; H, 5.60.

Photolysis of 16 with BCP in Anhydrous Benzene. A solution of **16** (693 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 24 h to reach a complete conversion of **16**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **16a** (750 mg, 88%).

16a: yellow powder, mp 130−131 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20−8.17 (m, 1H), 8.10−8.07 (m, 1H), 7.89−7.79 (m, 2H), 7.76−7.73 (m, 2H), 7.47−7.37 (m, 3H), 4.26−4.16 (m, 2H), 1.48−1.43 (m, 1H), 1.26−1.18 (m, 1H), 1.21 (t, J = 7.2 Hz, 3H), 0.69−0.53 (m, 3H), 0.29−0.18 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9, 189.6, 166.2, 164.7, 136.8, 135.3, 134.1, 133.6, 130.6, 129.6, 129.2, 127.7, 127.5, 106.0, 87.8, 64.5, 60.4, 33.6, 33.4, 29.7, 13.9, 9.5, 7.9, 7.8, 6.2; IR (ATR, neat) 3071, 1794, 1708, 1632, 1602, 1480, 1453, 1414, 1371, 1337, 1315, 1269, 1235, 1094, 1062, 1030, 950, 934, 866, 840, 777, 758, 748, 719, 704, 671, 622 cm^{-1}; MS (ESI+) m/z 427 [M + H]$^+$, 449 [M + Na]$^+$; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{27}H_{22}O_5Na$ 449.1365, found 449.1358.

Photolysis of 17 with BCP in Anhydrous Benzene. A solution of **17** (468 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 24 h to reach a complete conversion of **17**. Flash column chromatography on

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300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **17a** (713 mg, 98%).

17a: white powder, mp 175−177 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16−8.13 (m, 1H), 8.05−8.02 (m, 1H), 7.87−7.77 (m, 2H), 4.28 (q, J = 7.2 Hz, 2H), 2.36 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H), 1.30−1.25 (m, 1H), 1.12 (ddd, J = 9.8, 6.8, 4.8 Hz, 1H), 0.64−0.48 (m, 3H), 0.22−0.11 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9, 189.7, 170.5, 165.1, 137.2, 135.3, 133.9, 133.3, 127.6, 127.3, 105.9, 88.3, 62.8, 60.0, 33.3, 32.7, 14.9, 14.3, 9.4, 7.8, 7.6, 5.8; IR (ATR, neat) 3065, 2984, 2950, 2905, 1806, 1639, 1594, 1483, 1453, 1414, 1347, 1299, 1258, 1210, 1198, 1087, 1059, 1008, 966, 941, 891, 856, 838, 774, 751, 722, 695, 657, 639 cm^{-1}; MS (ESI+) m/z 365 $[M + H]^+$, 387 $[M + Na]^+$; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{22}H_{20}O_5Na$ 387.1208, found 387.1240.

Photolysis of 18 with BCP in Anhydrous Benzene. A solution of **18** (508 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 24 h to reach a complete conversion of **18**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **18b** (454 mg, 68%).

18b: white powder, mp 162−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 7.9, 1.5 Hz, 1H), 7.51 (ddd, J = 8.1, 7.1, 1.5 Hz, 1H), 7.35 (ddd, J = 7.9, 7.1, 1.0 Hz, 1H), 6.93 (dd, J = 8.1, 1.0 Hz, 1H), 3.11 (ddd, J = 16.3, 9.0, 7.3 Hz, 1H), 2.66 (ddd, J = 12.4, 9.4, 3.1 Hz, 1H), 2.54 (s, 3H), 2.46 (ddd, J = 14.1, 9.4, 7.3 Hz, 1H), 2.37−2.31 (m, 1H), 2.30 (s, 3H), 2.03−1.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 181.1, 178.4, 169.8, 161.9, 146.4, 136.2, 133.0, 132.3, 126.3, 126.0, 122.7, 121.1, 59.8, 33.8, 33.0, 30.3, 25.4, 24.2, 23.7, 15.5; IR (ATR, neat) 3068, 1794, 1654, 1632, 1603, 1477, 1459, 1411, 1378, 1336, 1300, 1272, 1231, 1197, 1120, 1023, 972, 949, 933, 839, 790, 747, 727, 709, 680 cm^{-1}; MS (ESI+) m/z 335 $[M + H]^+$, 357$[M + Na]^+$; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{21}H_{18}O_4Na$ 357.1103, found 357.1099.

Photolysis of 19 with BCP in Anhydrous Benzene. A solution of **19** (757 mg, 2 mmol) and BCP (320 mg, 4 mmol) in anhydrous benzene (100 mL) was photolyzed with nitrogen bubbling for 24 h to reach a complete conversion of **19**. Flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded **19b** (632 mg, 69%).

19b: white powder, mp 234−236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.1, 1.5 Hz, 1H), 7.60−7.57 (m, 2H), 7.48 (ddd, J = 8.1, 7.2, 1.5 Hz, 1H), 7.39−7.37 (m, 2H), 7.33 (ddd, J = 8.1, 7.2, 1.2 Hz, 1H), 7.24−7.19 (m, 2H), 7.14−7.05 (m, 4H), 6.89 (dd, J = 8.1, 1.2 Hz, 1H), 3.23−3.14 (m, 1H), 3.01−2.94 (m, 1H), 2.75−2.64 (m, 2H), 2.01−1.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 181.3, 178.5, 170.4, 158.0, 146.3, 137.8, 135.8, 133.1, 132.4, 132.3, 130.7, 129.5, 129.2, 128.1, 127.9, 127.9, 126.5, 126.1, 121.0, 119.4, 62.6, 35.0, 32.9, 25.4, 24.5, 23.7; IR (ATR, neat) 3074, 1805, 1710, 1662, 1639, 1594, 1483, 1448, 1417, 1396, 1347, 1297, 1281, 1253, 1208, 1196, 1094, 1008, 966, 940, 891, 855, 837, 773, 751, 737, 695, 656 cm^{-1}; MS (ESI+) m/z 459 $[M + H]^+$, 481 $[M + Na]^+$; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{31}H_{23}O_4$ 459.1596, found 459.1590.

Synthesis of 8b. To a solution of **8a** (272 mg, 1 mmol) in CH_3CN (10 mL) was added K_2CO_3 (166 mg, 1.2 mmol). The mixture was stirred at room temperature overnight. TLC analysis showed complete conversion of **8a**; the reaction mixture was filtered. The filtrate was evaporated under a vacuum, and the crude product was separated by flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents to give the final product **8b** (231 mg, 98%).

8b: 1′,2′-Dihydrodispiro[cyclopropane-1,1′-cyclobuta[*b*]-naphthalene-2′,1″-cyclopropane]-3′,8′-dione, yellow powder, mp 104−106 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02−7.99 (m, 2H), 7.68−7.65 (m, 2H), 1.43−1.39 (m, 4H), 0.86−0.82 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 157.6, 133.9, 133.0, 126.3, 36.4, 9.2; IR (ATR, neat) 3068, 1806, 1639, 1595, 1483, 1444, 1347, 1287, 1210, 1193, 1096, 1084, 1008, 941, 891, 855, 838, 774, 751, 737, 722, 707, 695, 657 cm^{-1}; MS (ESI+) m/z 237 $[M + H]^+$. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.25; H, 5.18.

Synthesis of 8c. To a solution of **8b** (236 mg, 1 mmol) in xylene (10 mL) was added isoprene (82 mg, 1.2 mmol). The mixture was heated at 130 °C overnight. TLC monitoring showed complete conversion of **8b**. The reaction mixture was cooled, the solvent was evaporated under a vacuum, and the crude product was separated by flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents to give the final product **8c** (283 mg, 93%).

8c: white powder, mp 144−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13−8.09 (m, 2H), 7.79−7.75 (m, 2H), 5.76−5.72 (m, 1H), 2.45−2.22 (m, 4H), 1.88 (s, 3H), 0.52−0.46 (m, 2H), 0.30−0.23 (m, 2H), 0.17−0.09 (m, 2H), 0.05 to −0.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 196.9, 135.3, 135.2, 135.2, 134.0, 133.9, 127.2, 120.1, 53.1, 52.4, 32.0, 29.4, 29.3, 27.1, 24.0, 9.0, 8.6, 6.4, 5.8; IR (ATR, neat) 3071, 2917, 2845, 1713, 1668, 1625, 1590, 1444, 1308, 1272, 1163, 1093, 1022, 1002, 948, 939, 859, 836, 794, 763, 724, 708, 670, 621 cm^{-1}; MS (ESI+) m/z 305 $[M + H]^+$; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{21}O_2$ 305.1542, found 305.1568.

Synthesis of 8d. To a solution of **8b** (236 mg, 1 mmol) in xylene (10 mL) was added 1,3-cyclohexadiene (96 mg, 1.2 mmol). The mixture was heated at 130 °C overnight. TLC analysis showed complete conversion of **8b**. The reaction mixture was cooled, the solvent was evaporated under a vacuum, and the crude product was separated by flash column chromatography on 300−400 mesh silica gel with petroleum ether/ethyl acetate as eluents to give the final product **8d** (272 mg, 86%).

8d: white powder; mp 217−220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.05 (m, 2H), 7.74 - 7.71 (m, 2H), 6.32−6.30 (m, 2H), 3.25 (ddd, J = 4.5, 3.0, 1.5 Hz, 2H), 2.58−2.53 (m, 2H), 1.30−1.26 (m, 2H), 0.77−0.73 (m, 2H), 0.54−0.49 (m, 2H), 0.28−0.24 (m, 2H), 0.01 to −0.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 135.5, 135.4, 133.8, 127.2, 56.7, 33.6, 25.6, 19.6, 8.8, 8.3; IR (ATR, neat) 3068, 3038, 2944, 2914, 1723, 1662, 1596, 1450, 1417, 1359, 1315, 1260, 1223, 1087, 1054, 976, 838, 827, 809, 722, 695, 672, 625 cm^{-1}; MS (ESI+) m/z 317 $[M + H]^+$; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{22}H_{20}O_2Na$ 339.1361, found 339.1341.

CCDC 932973−932979 contain the supplementary crystallographic data for compounds **5a**, **6a**, **8d**, **13b**, **15b**, **17a**, and **19b** in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

Crystal structure of compounds **5a**, **6a**, **8d**, **13b**, **15b**, **17a**, and **19b**. NMR spectra of all compounds. CIF files of **5a**, **6a**, **8d**, **13b**, **15b**, **17a**, and **19b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to the memory of Professor Howard E. Zimmerman.

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