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Photoinduced [4 + 4], [4 + 2], and [2 + 2] Cycloadditions of *o*-Quinones with Oxazoles: Chemo-, Regio-, and Diastereoselectivity

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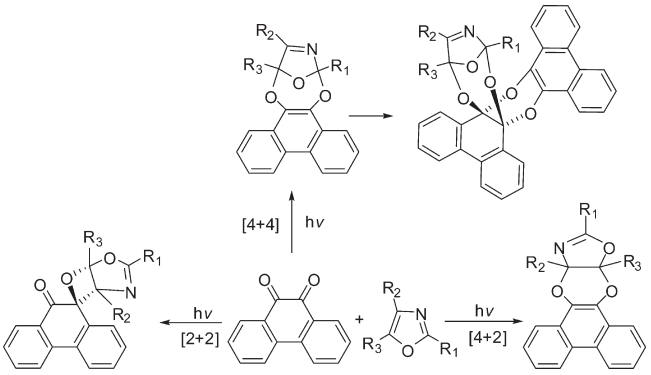

Photoinduced reactions of the 1,2-dicarbonyl compounds phenanthrenequinone (PQ), 1-acetylisatin (IS), and benzil (BZ) with the oxazoles **1a**−**j** have been investigated. In photoreactions of PQ with the oxazoles, in addition to the 1,4-dioxins derived from [4 + 2] cycloaddition and the oxetanes from the Paternó−Büchi [2 + 2] reactions, [4 + 4] cycloaddition products are formed in the reactions with **1a**, **1c**, **1g**, **1i**, and **1j**, with the quinone's dicarbonyl unit (O═C—C═O) and the oxazole's C═N—C═C moiety as two 4π addends. Photoreactions of IS with the oxazoles **1f** and **1g** give the [4 + 4] cycloaddition products exclusively, while in photoreactions of IS with **1a**, **1c**, **1e**, **1h**, and **1i**, [4 + 4] products are formed together with the [2 + 2] products. Reaction pathway partitioning in these photocycloaddtions strongly depends on the substitution pattern on the oxazole ring. The presence of a substituent at the oxazole's C2 atom hampers the [4 + 4] pathway by causing steric hindrance to radical pair recombination in the corresponding 1,7-diradical intermediate to form the [4 + 4] cycloaddition products. A substituent at the C4 atom results in steric hindrance for ring closure of the 1,4-diradicals in the [2 + 2] cycloaddition pathway, therefore favoring the [4 + 4] and [4 + 2] cycloaddition pathways. Regio- and diastereoselectivity in the [2 + 2] and [4 + 4] cycloadditions have been discussed based on the thermodynamic stability of the relevant triplet diradical intermediates and the conformations of these diradicals suitable for the intersystem crossing process. Photoreactions of BZ with the oxazoles afford only [2 + 2] cycloaddition products.

Introduction

Photocycloaddition has been a research focus in organic photochemistry and is considered as one of the fundamental methods to build complex frameworks which are otherwise difficult to make.[1] Study of the chemo-, regio-, and stereoselectivity in the photocycloadditions has contributed greatly to understanding the mechanisms of concerted and nonconcerted reactions as well as to elucidating the structure and reactivity of diradicaloid intermediates involved in these reactions. The most widely investigated photocycloadditions are the [2 + 2]

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photocycloadditions, including the ones between two C=C bonds leading to cyclobutanes[2,3] and the ones between a C=O bond and a C=C bond leading to oxetanes (the Paterno−Büchi reaction).[4,5] Therefore, exploration on novel photocycloadditions along with detailed study on the mechanisms involved is of great interest both synthetically and theoretically.

Several higher order photocycloadditions have been investigated, which has demonstrated important applications in the construction of carbo- and heterocycles with various ring sizes (from five- to eight-membered rings). For example, photocycloaddition of benzene and alkene could proceed in [3 + 2] (meta) or [4 + 2] (para) manner.[6] The [3 + 2] photocycloaddition was able to create a three-ring system with six newly formed chiral carbon atoms and has been successfully applied in the synthesis of many polycyclic natural products. Besides, [5 + 2] photocycloadditions have been found between phathalimide and alkenes.[7] Intramolecular [5 + 2] photocycloadditions of *N*-(ω-vinylalkyl)- and *N*-(ω-iminoalkyl)maleimide derivatives[8] have also been reported, which provided efficient approaches to N-containing seven-membered rings and their annulated derivatives. Photoinduced [4 + 4] reactions represent the highest order photocycloadditions known up to now. [4 + 4] photodimerizations and [4 + 4] photocycloadditions with dienes have been found for naphthalene,[9] anthracene,[10] 2-pyridones,[11,12] and 2-pyrones[13,14] derivatives, some of which have been applied in the synthesis of natural products.[11−14]

1,2-Dicarbonyl compounds constitute another interesting class of substrates in photocycloadditions. They may serve as either 2π or 4π addends to take part in [2 + 2] or [4 + 2] cycloadditions with alkenes. It has been reported that photoexcited benzil,[15] biacetyl,[16] and phenylglyoxylates[17] could react with alkenes to give α-ketooxetanes via [2 + 2] cycloaddition and, less commonly, dihydrodioxins via [4 + 2] cycloaddition. Photoreactions of 1-acetylisatin (IS) with monoalkenes[18] or cyclic dienes[19] (such as furans, indoles) proceed exclusively via [2 + 2] cycloaddition pathway to give α-ketooxetanes. Similarly, photoreactions of 2-methylisoquinoline-1,3,4-trione with alkynes gives products derived from [2 + 2] photocycloaddition.[20] Photoreactions of phenanthrenequinone (PQ) with alkenes afford α-ketooxetanes by [2 + 2] reaction and dihydrodioxins by [4 + 2] reaction.[21]

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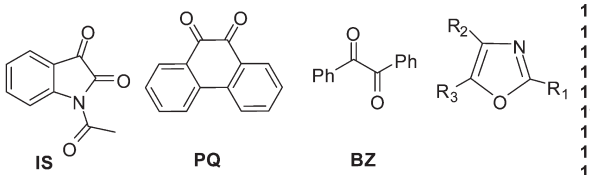
CHART 1



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1d R_1=Ph, R_2=H, R_3=Ph
1e R_1=Me, R_2=H, R_3=EtO
1f R_1=H, R_2=*p*-MeOPh, R_3=H
1g R_1=H, R_2=Ph, R_3=H
1h R_1=H, R_2=p-ClPh, R_3=H
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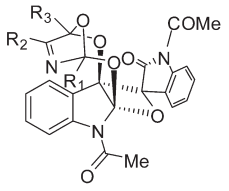
1j R_1=R_2=R3=Me

CHART 2



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2g R_1=H, R_2=Ph, R_3=H
2h R_1=H, R_2=p-ClPh, R_3=H
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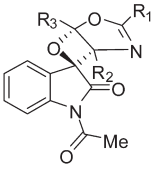

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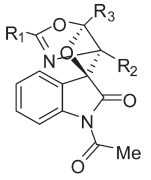

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4b R_1=R_2=Ph, R_3=H
4c R_1=H, R_2=R_3=Ph
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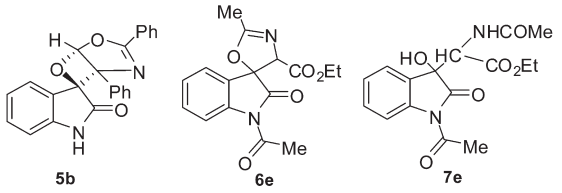
4h R_1=H, R_2=p-ClPh, R_3=H

4j R_1=R_2=R_3=Me



A few years ago, we reported in a preliminary communication the photoinduced [4 + 4] cycloaddition of the *o*-quinones PQ and IS with oxazoles, in which the O=C—C=O moiety in PQ and IS and the C=N—C=C unit in the oxazole serve as the 4π addends.[22] These reactions stand for a new type of [4 + 4] photocycloadditions between two heterodienes. To our knowledge, this is also the first report on photocycloaddition reactions with any azadiene (C=N—C=C) as a 4π addend. Here we report our further investigation on these photoreactions by expanding the oxazoles used to cover a wide range of ring-substitution pattern in search of the reaction scope and the factors affecting reactions pathway ([2 + 2], [4 + 2], and [4 + 4]) competition. Reaction mechanism, regio- and stereoselectivity in these pathways are also discussed based on unambiguous determination of the steric structures of the corresponding products.

Results

Photoinduced cycloadditions of the 1,2-dicarbonyl compounds IS, PQ, and benzil (BZ) with oxazoles have been investigated. The oxazoles used in the photocycloadditions include **1a**−**j** (Chart 1).

1. Photoinduced Reactions of IS with Oxazoles 1a−**j.** The results of photoinduced reactions of IS with the oxazoles **1a**−**j** are given in Chart 2 and Table 1. Irradiation of a benzene solution of IS with **1a** for 24 h resulted in complete conversion of IS and gave the [4 + 4]/[2 + 2] product **2a** in 12% yield and a *trans*-spirooxetane product **3a** (73%). Product **2a** is formed by initial [4 + 4] photocycloaddition of IS with **1a** followed by further [2 + 2] cycloaddition of another excited IS with the primary [4 + 4] product. A small amount of two other diastereoisomeric [4 + 4]/[2 + 2] products and a *cis*-spirooxetane product **4a** were also isolated with a total yield of 4%. Comparison of the spectral data indicated that **2a** has the same configuration as the product **2g** formed from IS and **1g**, whose steric structure was established by an X-ray crystallographic analysis.[22] Similar photolysis of **IS** with 2,4-diphenyloxazole **1b**, on the other hand, afforded only three spirooxetane products: the *trans*-**3b** (27%), the *cis*-**4b** (41%), and an *N*-deacetylated oxetane **5b** (22%). In the photoreactions of **IS** with 4,5-diphenyloxazoles **1c**, the *trans*-oxetane product **3c** (48%)[22] and its cis-isomer **4c** (20%) were formed along with a [4 + 4]/[2 + 2] product **2c** (22%). Photoreactions of **IS** with 2,5-diphenyloxazole **1d** gave two oxetane products: the *trans*-**3d** (22%) and the *cis*- **4d** (48%).[22] For 2-methyl-5-ethoxyoxazole **1e**, reaction with photoexcited **IS** furnished a [4 + 4]/[2 + 2] product **2e** (12%) and two secondary products **6e** (22%) and **7e** (31%) derived from the hydrolysis of the oxetane products. Obviously, **7e** is the primary hydrolysis product, while **6e** is formed by intramolecular condensation of **7e**. Similar to 4-phenyloxazole **1g**, photoreaction of 4-(4-methoxyphenyl)oxazole **1f** with IS gave a [4 + 4]/[2 + 2] product **2f** exclusively in 97% yield.

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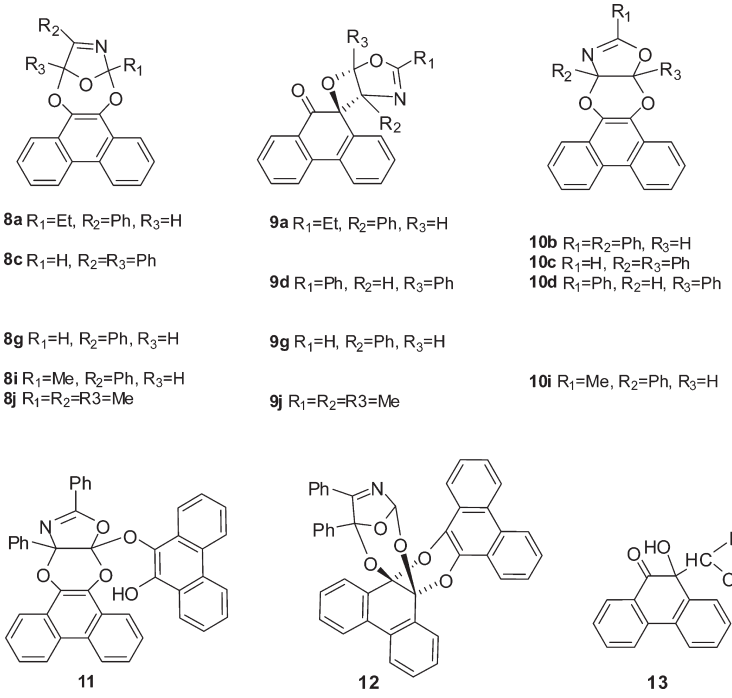
TABLE 1. Photoreactions of IS with Oxazoles 1a−j[a]

				products and yield (%)[b]			
entry	oxazole	irrd. time (h)	conversion (%)	[4 + 4]/[2 + 2]	$[2+2]_{trans}$	$[2+2]_{cis}$	others
1	**1a**	24	100	**2a** (12)	**3a** (73)		
2	**1b**	24	38		**3b** (27)	**4b** (41)	**5b** (22)
3	**1c**	24	100	**2c** (22)	**3c** (48)	**4c** (20)	
4	**1d**	24	100		**3d** (22)	**4d** (48)	
5	**1e**	12	100	**2e** (12)			**6e** (22) **,7e** (31)
6	**1f**	48	100	**2f** (97)			
7	**1g**[c]	24	100	**2g** (97)			
8	**1h**[c]	48	100	**2h** (64)	**3h** (8)	**4h** (13)	
9	**1i**[c]	24	100	**2i** (9)	**3i** (77)		
10	**1j**[c]	24	100		**3j** (54)	**4j** (41)	

[a]All the reactions were run in PhH. [b]Isolated yield. [c]Results for **1g−j** have been reported in ref 22.

CHART 3



The *cis*- and *trans*-spirooxetanes have similar spectral characteristics. X-ray crystallographic analysis of several oxetane products with both trans (**3a**, **3d**, and **3i**) and cis (**4d**) configurations has helped to unambiguously assign their steric structures.[23] On the basis of these crystal structures, we systematically compared the spectral data of the *cis*- and *trans*-oxetanes and found that the following features can be applied as "fingerprint" to distinguish the two isomers. (1) In the ^{1}H NMR spectra, the methyl in the *N*-acetyl groups resonates at significantly higher field at ~2.2 ppm for the cis- but at ~2.7 ppm for the trans-isomers. (2) The aromatic protons of the cis- and trans-isomers absorb in the 7.1−7.7 and 6.8−7.4 ppm region, respectively. (3) In the ^{13}C NMR, the imine carbon for the cis- and trans-isomers resonates at 174−175 and 171−172 ppm, respectively.

2. Photoinduced Reactions of PQ with Oxazoles. The results of photoinduced reactions of PQ with the oxazoles are given in Chart 3 and Table 2. Photoreactions of PQ with 2-ethyl-4-phenyloxazole **1a** in MeCN gave the [4 + 4] product **8a** (20%) and an oxetane product **9a** (69%). The crystal structure of **8a** is shown in Chart 3. Similar reactions of **PQ** with 2,4-diphenyloxazole **1b** gave a [4 + 2] product **10b** and a secondary product **11** (55%) derived from further reaction of **10b** with a second molecule of excited PQ. In the photoreactions of PQ with 4,5-diphenyloxazole **1c**, the [4 + 4] product **8c** (43%) was formed together with a 2:1 product **12** (13%) derived from secondary photo [4 + 2] cycloaddition of the [4 + 4] product with another molecule of PQ. Photolysis of PQ with 2,5-diphenyloxazole **1d** afforded only a *trans*-oxetane product **9d**[22] (45%) and a [4 + 2] product **10d**[22] (32%).

On the basis of the X-ray crystallographic analysis of the [4 + 4] products **8a**, **8c**, and **8i**, and of the [4 + 2] products **10d** and **10i**, we compared the spectral data of the [4 + 4] and the [4 + 2] products and found several main features that help to

(23) **3a** and **4d**: Usman, A.; Fun, H.-K; Wang, L; Zhang, Y.; Xu, J.-H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2003**, *C59*, o305. **3d**: Li, X.-M; Wang, L.; Xu, J.-H.; Zhang, S.-S.; Fun, H.-K. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2003**, *E59*, o1883. **3i**: Usman, A.; Razak, I. A.; Fun, H.-K.; Chantrapromma, S.; Zhang, Y.; Xu, J.-H. *Acta Crystallogr. E: Struct. Rep. Online* **2002**, *E58*, o145.

TABLE 2. Photoreactions of PQ with Oxazoles[a]

				products and yield (100%)[b]			
entry	oxazole	irrd. time (h)	conversion (%)	[4 + 4]	[2 + 2]	[4 + 2]	others
1	**1a**	24	100	**8a** (20)	**9a** (69)		
2	**1b**	24	80			**10b** (25)	**11** (55)
3	**1c**	24	100	**8c** (43)		**10c** (39)	**12** (13)
4	**1d**	24	100		**9d** (45)	**10d** (32)	
5	**1e**	12	100				**13**
6	**1g**[c]	24	100	**8g** (61)	**9g** (30)		
7	**1i**[c]	24	100	**8i** (89)	**9i** (8)		
8	**1j**[c]	24	90	**8j** (89)	**9j** (8)		

[a]All the reactions were run in MeCN except for entry 3, which was carried out in PhH. [b]Isolated yield. [c]Reference 22.

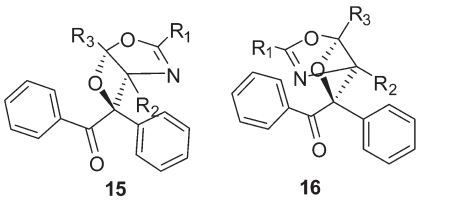
distinguish these two types of products. (1) In the IR, the C−O−C asymmetric stretching band occurs at ~1150 cm^{-1} and is the strongest absorption band for the [4 + 4] product, while the C═N stretching band is at 1628−1659 cm^{-1} and weaker than the 1150 cm^{-1} C−O−C band. In contrast, in the [4 + 2] products, the C−O−C band at 1150 cm^{-1} is never the strongest band in IR, while the C═N stretching band is at ~1657 cm^{-1} with a similar strength as the C−O−C 1150 cm^{-1} band. (2) In MS, the oxazole cation radical is always the base peak for the [4 + 4] products, while other fragmentations gave much weaker peaks. On the other hand, for the [4 + 2] product, the fragment with a m/z 180 derived from the decarbonylation of PQ is always the base peak, while the oxazole cation radical peak is rather weak. (3) In the ^{13}C NMR, the imine carbon atom (C═N) in the [4 + 4] products absorbs at 171−174 ppm, at a field strength 6−9 ppm higher than that of the [4 + 2] product, which resonates at ~165 ppm.

3. Photoinduced Reactions of BZ with Oxazoles. Compared with IS and PQ, BZ showed lower photoreactivity with oxazoles and took a much longer time to reach a similar conversion as in the reactions of IS and PQ. Besides, in contrast to the cyclic IS and PQ, BZ behave only as a 2π addend and gave the [2 + 2] cycloaddition products in photoreactions with the oxazoles **1i** and **1j** (Chart 4 and Table 3).

Discussion

1. Chemoselectivity in the Photocycloadditions. Photocycloadditions of IS and PQ with the oxazoles proceed via the nπ* triplet excited state of the IS[18,19,24] and PQ.[21] With the oxazoles examined, IS takes part in [2 + 2] and [4 + 4] photocycloadditions, while PQ undergoes [2 + 2], [4 + 2], and [4 + 4] cycloadditions. These reactions are proposed to take place via mechanisms shown in Schemes 1 and 2. A different type of biradicals were involved in these photocycloaddition pathways, which was reminiscent of the intramolecular cyclizations reported before.[25] It is rational that no cycloaddition was observed on the C═N bond of the oxazole since the relative stability of the corresponding biradical intermediates is much lower than that of other biradical intermediates as shown in Schemes 1 and 2.

CHART 4



a R_1=Me, R_2=Ph, R_3=H
b R_1=R_2=R_3=Me

a R_1=Me, R_2=Ph, R_3=H

TABLE 3. Photoreactions of BZ with Oxazoles

entry	oxazole	irrd. time (h)	conversion (%)	products and yield (%)[a]
1	**1i**	48	80	**15a** (16), **16a**(81)
2	**1j**	48	70	**15b** (69)

[a]Reactions were run in PhH.

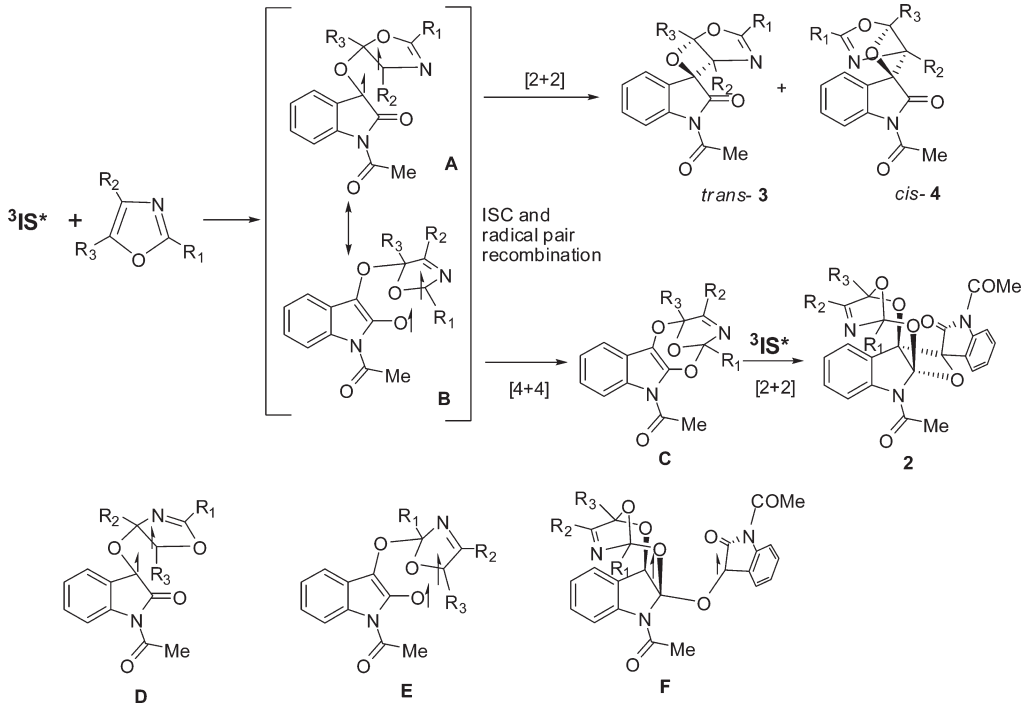
Reactions of triplet excited IS takes place by initial attack of the C3 carbonyl oxygen to the substrate.[18,19,24] The [2 + 2] and [4 + 4] photocycloadditions of IS with the oxazoles proceed via the triplet 1,4-biradical **A** and the 1,7-biradical **B**, respectively. Intersystem crossing (ISC) to the corresponding singlet biradicals followed by radical pair recombination gives the [2 + 2] and [4 + 4] products. The [4 + 4] cycloadduct then acts as an active alkene to undergo a further Paternó−Buchi reaction with a second excited IS to give the [4 + 4]/[2 + 2] product. Similarly, triplet biradicals **G**, **H**, and **I** in Scheme 2 are the precursors of the [2 + 2], [4 + 2], and [4 + 4] cyclization products in the photoreactions of PQ with the oxazoles. After ISC and radical pair recombination, they afforded the corresponding cycloadducts **9**, **10**, and **8**, respectively. As a result, substituents at different positions of the oxazole ring (R1, R2, and R3) may present different steric hindrance to the radical pair recombination process in **A**, **B**, **G**, **H**, and **I**, which leads to the formation of the corresponding [2 + 2], [4 + 4], and [4 + 2] products.

The competition of the different pathways is found to be strongly dependent on the structures of the oxazoles. A general trend can be perceived by inspection of the results shown in Tables 1 and 2. That is, oxazoles without substituents at C2 and C5 showed a strong preference for the formation of the [4 + 4] product over the [2 + 2] and [4 + 2] products. Therefore, photoreactions of IS with the 4-aryloxazoles **1f**, **1g**, and **1h** gave the [4 + 4] product exclusively or predominantly. In the photocycloaddition of PQ with 4-phenyloxazole, the [4 + 4] cycloadduct is also the main product (61%). Introduction of a substituent at C2, or even worse, at both C2 and C5, impedes the formation of [4 + 4] product and favors the formation of [2 + 2] and [4 + 2] products. As a result, in photoreactions of IS with 2-ethyl-4-phenyloxazole **1a** (entry 1 in Table 1), 2-methyl-4-phenyloxazole **1i** (entry 9 in Table 1), and 2-methyl-5-ethoxyoxazole **1e** (entry 5 in Table 1), the [4 + 4] products are minor products with the oxetanes being the major products. Photoreactions of IS with 2,4-diphenyloxazole **1b**, 2,5-diphenyloxazole **1d**, and 2,4,5-trimethyloxazole **1j** gave the oxetane products exclusively. The results of photoreactions of PQ with these 2- and 2,4- or 2,5-substituted oxazoles are parallel with that of IS. Therefore, reactions with **1b** and **1d** gave only [4 + 2] and/or [2 + 2] products without [4 + 4] products. The only exception

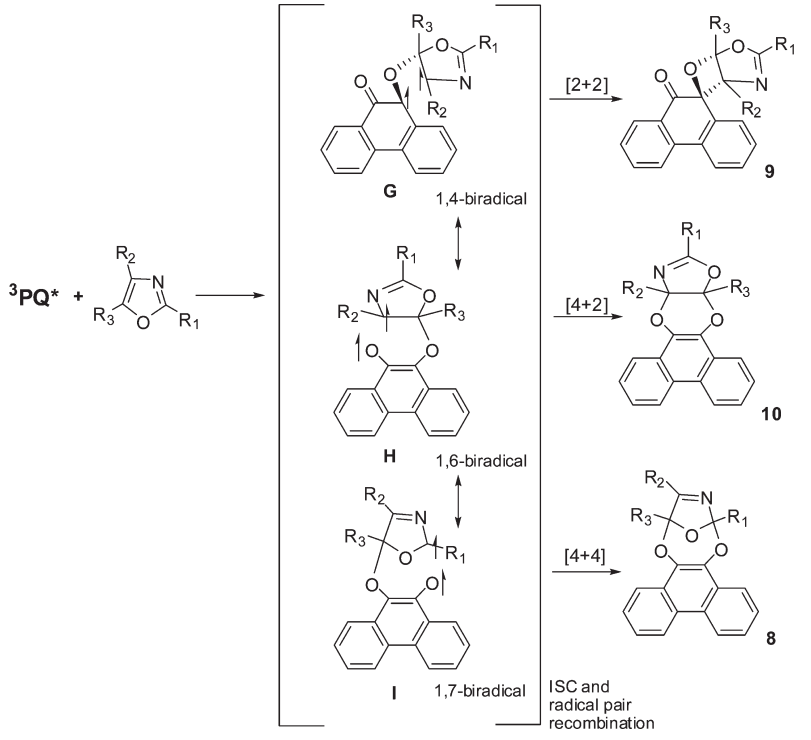
(24) (a) Wang, L.; Zhang, Y.; Hu, H.-Y.; Fun, H.-K; Xu, J.-H. *J. Org. Chem.* **2005**, *70*, 3850. (b) Zhang, Y.; Wang, L.; Zhu, Y.; Xu, J.-H. *Eur. J. Org. Chem.* **2004**, *3*, 527. (c) Xue, J.; Zhang, Y.; Wang, X.-L.; Fun, H.-K.; Xu, J.-H. *Org. Lett.* **2000**, *2*, 2583.

(25) (a) Lewis, F.; Reddy, G. D.; Bassani, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 6468. (b) Lewis, F.; Bassani, D. M.; Reddy, G. D. *J. Org. Chem.* **1993**, *58*, 6390.

SCHEME 1



SCHEME 2



to this trend is in the reaction of PQ with 2,4,5-trimethyloxazole **1j**, which gave the [4 + 4] product in 89% yield together with the oxetane **9j** (8%).

The reaction mechanisms shown in Schemes 1 and 2 reveal that this trend in reaction pathway partitioning is mainly influenced by the steric hindrance toward the intramolecular radical pair recombination. The structures of the biradical intermediates **A**, **B**, **G**, **H**, and **I** indicated that a sterically demanding group at C2 would hamper the [4 + 4] product formation via biradical intermediates **B** and **I** by exerting large steric hindrance for radical pair recombination after the ISC process, leading to the collapse of the singlet

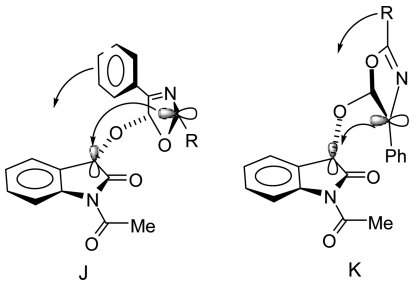
biradical to the starting *o*-quinone and the oxazole because of a large interradicaloid distance (IRD).[26] For the same reason, a bulky group at C4 retards the formation of both [2 + 2] and [4 + 2] products via diradicals **A**, **G**, and **H** at the advantage of [4 + 4] product. The results in Tables 1 and 2 are in perfect agreement with this analysis. The preferential formation of the [4 + 4] product in the photoreaction of PQ with **1j** is probably the result of a balance between the unfavorable steric influence for both the [4 + 4] product and the [2 + 2] (as well as [4 + 2]) product formation.

2. Regio- and Diastereoselectivity in the Photocycloadditions. The [2 + 2] photocycloadditions of IS and PQ with the oxazoles are highly regioselective to give spirooxetanes with an acetal structure. This regioselectivity is similar to that in the [2 + 2] photocycloadditions of the n−π* excited carbonyl compounds with furans,[19] benzofurans,[19] and oxazoles,[27] and is believed to be the result of the intervening of the most stable 1,4-diradical intermediate (the 2-oxabutane-1,4-diyl) in the Paternó−Büchi reaction[4,5] because an allylic type radical as at the oxazole's C4 atom in diradical **A** (Scheme 1) is ∼7 kcal/mol more stable than the alternative α-oxomethylene radical at oxazole's C5 as in **D** (Scheme 1).[28] The [4 + 4] reactions of IS with the oxazoles are also regioselective to give products where the C2 and C5 atoms in the oxazole are linked to the C2 and C3 carbonyl oxygen atoms, respectively.

The secondary [2 + 2] photocycloadditions of IS with the primary [4 + 4] product **C** (Scheme 1) take place with the C3 carbonyl oxygen and carbon atoms of the IS linking to the C2 and C3 atoms of the isatin unit in the [4 + 4] product, respectively. This regioselectivity is the result of the formation of the most stable biradical intermediate **E**, which has two benzylic radical centers.

The diastereoselectivity for the oxetane formation in the photoreactions of IS with the oxazoles is manifested by the relative stability of the triplet diradical conformations suitable for ISC.[29,30] In these active ISC conformers with the two spin-bearing orbitals orthogonal to each other within bond forming distance (∼2−3 Å), steric effect of the oxazole's substituents significantly affects their thermodynamic stability and the ISC process energy barrier. This concept has been successfully applied in the rationalization of the stereoselectivity in the ISC and radical pair recombination of various triplet 1,4-,[30] 1,5-,[31] 1,6-,[32] 1,7-,[33] and 1,8-[34] biradicals. In the case of photoreactions of IS with the oxazoles, for the 2-alkyl-4-phenyloxazoles (**1a** and **1i**), in the ISC conformation for the formation of the *trans*-oxetane (**J** in Scheme 3), there is no significant steric hindrance between the isatin framework and the oxazole's substituents either in the static conformer or in the ISC process by inward rotation of the p orbital at the oxazole's C5 atom. This process, on the contrary, may benefit from the $\pi-\pi$ stacking interaction emerging by the approaching of the phenyl at C4 of the oxazole toward the isatin's benzene ring. In sharp contrast, in the ISC conformation leading to the *cis*-oxetane (**K** in Scheme 3), there is significant steric hindrance between the C4 phenyl of oxazole and the C3 carbonyl of IS. Furthermore, the ISC process would bring the alkyl group to approach the isatin's benzene ring, causing unfavorable steric interaction between them. As a result, the *trans*-oxetanes **3a** and **3i** predominate in the [2 + 2] products. For 2,4-diphenyloxazole, the steric hindrance between the alkyl and the isatin benzene ring during the ISC process is lifted and replaced by a favorable $\pi-\pi$ stacking effect between the two phenyls. This leads to an increased yield of the *cis*-**4c**. For 2,5-diphenyloxazole, the steric hindrance in the ISC conformation and during the ISC process for *cis*-oxetane (see **K** in Scheme 3, with the Ph moved to C5) is removed, allowing the cis-isomer to be the major product.

SCHEME 3. ISC Conformations of the Triplet 1,4-Biradical of IS with 2-Alkyl-4-phenyloxazole



The [4 + 4] cycloadducts of IS with the oxazoles are formed with high regio- and diastereoselectivity. The crystal structure of **2g** and **2i**[22] and the parallelism in the spectral data of the other [4 + 4] products indicated that **2a**, **2e**, **2f**, and **2h** have the same steric configuration as **2g** and **2i**. In all the primary [4 + 4] products (**C** in Scheme 1) the C2 carbonyl oxygen atom in IS is bonded to the oxazole's C2 atom, while the C3 carbonyl oxygen atom is bonded to the C5 atom of the oxazole, and the oxazole ring is *syn* to the isatin framework. To search for the origin of this regio- and diastereoselectivity, with the [4 + 4] product of IS with 4-phenyloxazole **1i** as an example, calculations on the possible ISC conformations of the two regioisomeric triplet biradicals **B** and **E** (Scheme 1) leading to the two regioisomers were carried out with the DFT method at the UB3LYP-6-31G* level.[35] For biradical **B** leading to the experimentally found product **C**,

(26) (a) Ihmels, H.; Scheffer, J. R. *Tetrahedron* **1999**, *55*, 885. (b) Leibovitch, M.; Olovsson, G.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1998**, *120*, 12755. (c) Cheung, E.; Netherton, M. R.; Scheffer, J. R.; Trotter, J. *Org. Lett.* **2000**, *2*, 77. (d) Schmidt-Mende, L.; Kroeze, J. E.; Durrant, J. R.; Nazeeruddin, M. K.; Grätzel, M. *Org. Lett.* **2005**, *7*, 1315. (e) Yang, C.; Xia, W.; Scheffer, J. R.; Botoshansky, M.; Kaftory, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 5087.

(27) (a) Griesbeck, A. G.; Fiege, M.; Lex, J. *Chem. Commun.* **2000**, 589. (b) Griesbeck, A. G.; Bondock, S. *Can. J. Chem.* **2003**, *81*, 555. (c) Griesbeck, A. G.; Bondock, S.; Lex, J. *J. Org. Chem.* **2003**, *68*, 9899. (d) Bondock, S.; Griesbeck, A. G. *Monatsh. Chem.* **2006**, *137*, 765. (e) Griesbeck, A. G.; Bondock, S. *Aust. J. Chem.* **2008**, *61*, 573.

(28) (a) Bordwell, F. G.; Zhang, X. M. *Acc. Chem. Res.* **1993**, *26*, 510 and references cited therein. (b) Leroy, G.; Sana, M.; Wilante, C.; Nemba, R. M. *J. Mol. Struct.* **1989**, *198*, 159.

(29) (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed.* **1972**, *11*, 92. (b) Wirz, J. *Pure Appl. Chem.* **1984**, *56*, 1289. (c) Carlacci, L.; Doubleday, C., Jr.; Furlani, T. R.; King, H. F.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 5323. (d) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165. (e) Kutateladze, A. *J. Am. Chem. Soc.* **2001**, *123*, 9279.

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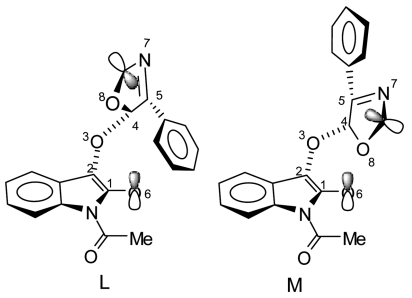
(31) Griesbeck, A. G.; Kramer, W.; Bartoschek, A.; Schmickler, H. *Org. Lett.* **2001**, *3*, 537.

(32) Griesbeck, A. G.; Heckroth, H.; Schmickler, H. *Tetrahedron Lett.* **1999**, *40*, 3137.

(33) Griesbeck, A. G.; Kramer, W.; Lex, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 577.

(34) Shen, Y.-M.; Yang, X.-L.; Chen, D.-Q.; Xue, J.; Zhu, L.; Fun, H.-K.; Hu, H.-W.; Xu, J.-H. *Chem.—Eur. J.* **2010**, *16*, 2873.

SCHEME 4. ISC Conformations of the 1,7-Biradical of IS with 4-Phenyloxazole



two gauche conformations **L** and **M** (Scheme 4) with geometry suitable for ISC were found to be energy minima, with **L** representing the global minimum and **M** as a local minimum with an energy 4 kcal/mol higher than that of **L**. In conformation **L**, the dihedral angle C1−C2−O3−C4 is −37° and that between C2−O3−C4−C5 is 154°. In this geometry, the phenyl group at C5 pointing downward and the two radical centers (O6 and C7) are far apart from each other with an IRD of 5.17 Å. In conformation **M**, the two dihedral angles C1−C2−O3−C4 and C2−O3−C4−C5 are −36° and −41°, respectively, with the phenyl at C5 pointing upward and the two radical centers close to each other (IRD 2.81 Å). In both **L** and **M**, the isatin framework and the oxazole ring are nearly perpendicular to each other, and as a result, the two spin-bearing p orbitals are nearly orthogonal to each other. In these two conformations, one of the 2p orbitals at the O3 atom is parallel with and close to the C4−O8 σ bond, enabling an efficient 2p(O3)−σ*(C4−O8) overlap. This anomeric effect provides stereoelectronic stabilization to the two conformations.

Clearly, the large IRD between the two radical centers (5.17 Å) in **L** means that ISC in this conformation would result in the O3−C4 bond cleavage to give the starting material IS and **1i**. ISC in **M** with a small IRD by inward rotation of the p orbital at C7, on the other hand, leads to the O6−C7 bond formation to give the [4 + 4] product with the actually found *syn*-configuration between the oxazole and the isatin moieties. This ISC process is further benefited by the $\pi-\pi$ stacking interaction between the two benzene rings of the oxazole and the isatin. Meanwhile, the high regioselectivity in the [4 + 4] product formation is accounted for by the fact that in the conformation of **M**, suitable for ISC and bond formation, the regioisomeric biradical **E** (Scheme 1) is 4.3 kcal/mol higher than **M**, resulting in the absence of the regioisomeric [4 + 4] product.

(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision E.01; Gaussian, Inc.: Wallingford, CT, 2004.

Conclusion

In summary, a new type of [4 + 4] photocycloadditions between two heterodienes have been investigated in the photocycloadditions of *o*-quinones (IS and PQ) with oxazoles. The O=C—C=O unit in *o*-quinone and the C=N—C=C part in the oxazole serve as 4π addends in the photocycloadditions, leading to the formation of the [4 + 4] products **2** and **8** with regio- and diastereoselectivity. The [4 + 2] and [2 + 2] photocycloadditions also occurred in competition with the [4 + 4] reaction for some oxazoles. The partitioning between these photocycloaddition pathways is determined by the difference in steric hindrances for radical pair recombination of the biradical intermediates leading to the [4 + 4], [4 + 2], and [2 + 2] products. A substituent at the C4 of oxazole disfavors the [2 + 2] cycloaddition while it favors the [4 + 4] cycloaddition; a substituent at the C2 of oxazole, on the other hand, disfavors the [4 + 4] cycloaddition while it favors the alternative [4 + 2] and [2 + 2] cycloaddition pathways. All the photocycloadditions are highly regioselective. The regioselectivity can be rationalized by the intervening of most stable biradical intermediates in each reaction pathway. Diastereoselectivity in the [4 + 4] and [2 + 2] reactions is dependent on the active conformations suitable for ISC and the ensuing bond formation of the triplet biradical intermediates.

Experimental Section

General Procedures for the Preparative Photolysis of *o*-Quinones with Oxazoles. The light source was a medium-pressure mercury lamp (500 W) in a cooling water jacket that was further surrounded by a layer of filter solution (saturated $NaNO_2$) to cut off light of wavelength shorter than 400 nm. The solution of *o*-quinone and oxazole in dry benzene or acetonitrile was purged with N_2 for 10 min and then 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.

Photolysis of IS with 1a. A solution of **IS** (756 mg, 4 mmol) and **1a** (830 m g, 4.8 mmol) in benzene (80 mL) was irradiated with light of wavelength >400 nm under N_2 atmosphere for 24 h. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **2a** (133 mg, 12%), **3a** (1.06 g, 73%), and **4a** (58 mg, 4%).

2a, (2*R*,3′*S*,5*R*,6a*S*,11a*R*)-1′,11-diacetyl-2,5-dihydro-2-ethyl-4-phenylspiro[2,5-epoxy-11a,6a-(epoxymethano)-11*H*-1,6,3-dioxazocino[8,7-*b*]indole-13,3′-[3*H*]indol]-2′(1′*H*)-one: colorless crystals from acetone−petroleum ether, mp 188−190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (td, 2H, J = 7.9, 1.0 Hz), 8.16 (d, 1H, J = 8.3 Hz), 7.56−7.47 (m, 2H), 7.39 (dd, 2H, J = 7.8, 1.3 Hz), 7.35−7.30 (m, 1H), 7.16 (t, 2H, J = 7.8 Hz), 7.02 (td, 1H, J = 8.0, 1.4 Hz), 6.51 (dd, 1H, J = 7.6, 0.9 Hz), 6.40−6.35 (m, 2H), 2.53 (s, 3H), 2.41 (q, 2H, J = 6.9 Hz), 2.23 (s, 3H), 1.15 (t, 3H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.68, 171.64, 169.92, 169.24, 143.64, 140.50, 132.40, 131.76, 131.36, 128,95, 128.42, 128.33, 128.17, 127.93, 125.44, 123.52, 123.17, 123.08, 122.83, 116.42, 101.46, 29.95, 26.13, 24.96, 7.63; IR (KBr) ν_{max}/cm^{-1} 2982, 2937, 1779, 1717, 1613, 1470, 1377, 1071, 1004, 757; MS m/z (%) 507 (0.1), 405 (0.3), 346 (3), 278 (6), 173 (88), 146 (100), 130 (38), 90 (49); EA found C, 67.24; H, 4.56; N, 7.62, $C_{31}H_{25}N_3O_7$ requires C, 67.51; H, 4.54; N, 7.62.

3a, (1*R*,3′*R*,5*R*)-1′-acetyl-3-ethyl-1-phenylspiro[4,6-dioxa-2-azabicyclo[3.2.0]hept-2-ene-7,3′-[3*H*]indol]-2′(1′*H*)-one: colorless crystals from acetone−petroleum ether, mp 118−120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, 1H, J = 8.2 Hz), 7.24−7.19 (m, 4H), 7.10−7.06 (m, 2H), 6.96 (dd, 1H, J = 7.2, 1.5 Hz), 6.87 (s, 1H), 6.67 (dd, 1H, J = 7.5, 1.1 Hz), 2.71 (s, 3H),

2.67−2.58 (m, 2H), 1.36 (t, 3H, J = 7.6 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 173.02, 172.30, 170.31, 139.56, 133.78, 130.92, 128.75, 128.65, 126.72, 125,67, 124.59, 124.38, 116.32, 94.53, 88.89, 26.43, 22.11, 9.99; IR (KBr) ν_{max}/cm^{-1} 2993, 2947, 1778, 1712, 1658, 1604, 1466, 1277, 950, 752; MS m/z (%) 236 (1), 189 (1), 146 (100), 130 (8), 90 (35), 43 (79); EA found C, 69.52; H, 4.95; N, 7.88, $C_{21}H_{18}N_2O_4$ requires C, 69.61; H, 4.97; N, 7.73.

4a, (1*S*,3′*R*,5*S*)-1′-acetyl-3-ethyl-1-phenylspiro[4,6-dioxa-2-azabicyclo[3.2.0]hept-2-ene-7,3′-[3*H*]indol]-2′(1′*H*)-one: colorless crystals from acetone−petroleum ether, mp 124−126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, 1H, J = 8.2 Hz), 7.57 (dd, 1H, J = 7.4, 1.2 Hz), 7.47 (td, 1H, J = 7.9, 1.4 Hz), 7.34−7.29 (m, 4H), 7.20−7.17 (m, 2H), 7.04 (s, 1H), 2.65 (q, 2H, J = 7.6 Hz), 2.17 (s, 3H), 1.37 (t, 3H, J = 7.5 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 174.95, 171.01, 169.79, 141.59, 134.29, 131.86, 128.85, 128.78, 126.30, 126.08, 125.25, 121.92, 116.75, 105.40, 94.17, 88.61, 25.64, 22.15, 10.04; IR(KBr) ν_{max}/cm^{-1} 2984, 1776, 1703, 1657, 1610, 1458, 1288, 1169, 939, 751; MS m/z (%) 362 (M^+, 0.6), 334 (3), 278 (5), 236 (21), 189 (10), 173 (96), 146 (70), 130 (55), 90 (42), 56 (100); EA found C, 69.63; H, 5.02; N, 7.64, $C_{21}H_{18}N_2O_4$ requires C, 69.61; H, 4.97; N, 7.73.

Photolysis of IS with 1b. A solution of **IS** (400 mg, 2.1 mmol) and **1b** (550 mg, 2.5 mmol) in benzene (40 mL) was irradiated with light of wavelength > 400 nm under N_2 atmosphere for 24 h to reach a 38% conversion of IS. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **3b** (100 mg, 27%), **4b** (150 mg, 41%), **5b** (80 mg, 22%), and recovered **IS** (230 mg).

3b, (1*R*,3′*R*,5*R*)-1′-acetyl-1,3-diphenylspiro[4,6-dioxa-2-azabicyclo[3.2.0]hept-2-ene-7,3′-[3*H*]indol]-2′(1′*H*)-one: colorless crystals from acetone−petroleum ether, mp 126−128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, 1H, J = 8.1 Hz), 8.12 (dt, 2H, J = 7.0, 1.5 Hz), 7.57 (t, 1H, J = 7.2 Hz), 7.48 (t, 2H, J = 7.5 Hz), 7.29−7.15 (m, 6H), 7.06 (s, 1H), 7.02 (d, 1H, J = 7.5 Hz), 6.90 (t, 1H, J = 7.5 Hz), 2.66 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 172.06, 170.41, 167.24, 139.65, 133.84, 132.48, 131.02, 129.03, 128.77, 128.72, 128.56, 126.83, 126.65, 126.22, 125.74, 124.65, 124.40, 116.37, 107.18, 94.49, 89.60, 28.47; IR(KBr) ν_{max}/cm^{-1} 1775, 1712, 1638, 1493, 1372, 1339, 1274, 1171, 957, 747, 697; m/z (%) 382 (1), 221 (100), 193 (61), 165 (10), 146 (49), 105 (13), 90 (46), 63 (16), 43 (30); EA found C, 73.08; H, 4.29; N, 6.76, $C_{25}H_{18}N_2O_4$ requires C, 73.17; H, 4.39; N, 6.83.

4b, (1*S*,3′*R*,5*S*)-1′-acetyl-1,3-diphenylspiro[4,6-dioxa-2-azabicyclo[3.2.0]hept-2-ene-7,3′-[3*H*]indol]-2′(1′*H*)-one: colorless blocks from acetone−petroleum ether, mp 114−116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, 1H, J = 8.4 Hz), 8.15 (dt, 2H, J = 7.0, 1.5 Hz), 7.61 (tt, 1H, J = 7.2, 1.2 Hz), 7.53−7.43 (m, 4H), 7.36−7.27 (m, 5H), 7.22 (s, 1H), 7.20 (td, 1H, J = 7.5, 1.0 Hz), 2.22 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 174.87, 169.84, 165.48, 140.29, 134.40, 132.84, 131.88, 129.32, 129.14, 128.93, 128.82, 128.79, 126.54, 126.40, 126.28, 125.26, 122.04, 116.74, 105.87, 94.59, 89.08, 25.78; IR(KBr) ν_{max}/cm^{-1} 1768, 1711, 1632, 1494, 1374, 1334, 1306, 1281, 1206, 1177, 1015, 938, 780, 693; m/z (%) 221 (19), 193 (13), 189 (16), 146 (100), 119 (7), 90 (32), 76 (2), 63 (10), 43 (50); EA found C, 73.05; H, 4.16; N, 6.97, $C_{25}H_{18}N_2O_4$ requires C, 73.17; H, 4.39; N, 6.83.

5b, (1*R*,3′*R*,5*R*)-1,3-diphenylspiro[4,6-dioxa-2-azabicyclo[3.2.0]-hept-2-ene-7,3′-[3*H*]indol]-2′(1′*H*)-one: colorless needles from acetone−petroleum ether, mp 128−130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, 2H, J = 7.5 Hz), 7.62 (t, 1H, J = 7.5 Hz), 7.53 (t, 3H, J = 7.5 Hz), 7.32−7.35 (m, 6H), 7.23 (s, 1H), 7.15 (s, 1H), 7.05 (t, 1H, J = 7.5 Hz), 6.83 (d, 1H, J = 7.8 Hz); IR (KBr) ν_{max}/cm^{-1} 3208, 1725, 1641, 1621, 1468, 1333, 1276, 1209, 1118, 1048, 1016, 963, 751, 696; m/z (%) 368 (0.1), 340 (2), 221 (100), 193 (66), 165 (11), 147 (26), 119 (43), 105 (8), 89 (48), 77 (10), 62 (26), 51 (10); EA found C, 75.12; H, 4.20; N, 7.48, $C_{23}H_{16}N_2O_3$ requires C, 75.00; H, 4.35; N, 7.61.

Photolysis of IS with 1c. A solution of **IS** (756 mg, 4 mmol) and **1c** (1.768 g, 8 mmol) in benzene (80 mL) was irradiated with light of wavelength > 400 nm under N_2 atmosphere for 24 h. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **2c** (261 mg, 22%), **3c** (787 mg, 48%), and **4c** (326 mg, 20%).

2c, (2*R*,3′*S*,5*R*,6a*S*,11a*R*)-1′,11-diacetyl-2,5-dihydro-4,5-diphenylspiro[2,5-epoxy-11a,6a-(epoxymethano)-11*H*-1,6,3-dioxazocino-[8,7-*b*]indole-13,3′-[3*H*]indol]-2′(1′*H*)-one: colorless crystals from acetone−petroleum ether, mp 224−226 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, 1H, J = 7.8 Hz), 8.21 (d, 1H, J = 6.9 Hz), 8.11 (d, 1H, J = 8.4 Hz), 7.52 (t, 1H, J = 7.8 Hz), 7.42−7.30 (m, 4H), 7.18−7.08 (m, 6H), 7.01−6.90 (m, 3H), 6.61 (d, 1H, J = 7.5 Hz), 6.37 (t, 1H, J = 7.8 Hz), 2.57 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 173.70, 171.65, 170.08, 169.29, 13.49, 140.40, 135.18, 132.09, 132.79, 131.49, 129.92, 129.43, 129.25, 128.82, 128.70, 128.45, 127.89, 127.79, 125.99, 125.47, 123.54, 123.27, 116.76, 116.41, 116.32, 115.86, 115.66, 114.36, 110.81, 26.16, 25.11; IR (KBr) ν_{max}/cm^{-1} 3060, 2974, 1779, 1711, 1690, 1607, 1468, 1371, 1341, 1312, 1279, 1193, 1174, 1079, 785; m/z (%) 555 (0.8), 514 (0.2), 334 (6), 278 (13), 221 (82), 193 (40), 165 (39), 146 (82), 105 (33), 90 (48), 77 (31), 43 (100); EA found C, 70.29; H, 4.08; N, 7.04, $C_{35}H_{25}N_3O_7$ requires C, 70.12; H, 4.17; N, 7.01.

3c, (1*R*,3′*R*,5*R*)-1′-acetyl-1,5-diphenylspiro[4,6-dioxa-2-azabicyclo-[3.2.0]hept-2-ene-7,3′-[3*H*]indol]-2′(1′*H*)-one: colorless crystals from acetone−petroleum ether, mp 122−124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, 1H, J = 8.2 Hz), 7.80−7.76 (m, 2H), 7.68 (s, 1H), 7.63−7.57 (m, 3H), 7.21 (td, 1H, J = 7.9, 1.4 Hz), 7.11 (dd, 1H, J = 7.6, 0.9 Hz), 7.05−6.87 (m, 4H), 6.73−6.70 (m, 2H), 2.75 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 172.43, 170.29, 157.85, 139.91, 134.25, 133.65, 131.01, 130.50, 128.95, 128.16, 128.02, 127.57, 127.37, 126.63, 124.50, 124.34, 116.56, 116.38, 92.80, 89.10, 26.46, IR (KBr) ν_{max}/cm^{-1} 3055, 1777, 1709, 1619, 1497, 1467, 1450, 1372, 1340, 1309, 1272, 1170, 754, 698; m/z (%) 410 (M^+, 0.4), 382 (1), 340 (0.6), 263 (0.4), 221 (94), 193 (77), 165 (84), 146 (100), 90 (60), 77 (27), 43 (84); EA found C, 73.20; H, 4.58; N, 6.71, $C_{25}H_{18}N_2O_4$ requires C, 73.17; H, 4.39; N, 6.83.

4c (1*S*,3′*R*,5*S*)-1′-acetyl-1,5-diphenylspiro[4,6-dioxa-2-azabicyclo[3.2.0]hept-2-ene-7,3′-[3*H*]indol]-2′(1′*H*)-one: colorless crystals from acetone−petroleum ether, mp 128−130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, 1H, J = 8.2 Hz), 7.96−7.93 (m, 2H), 7.67−7.64 (m, 2H), 7.59−7.54 (m, 3H), 7.48 (td, 1H, J = 7.8, 1.5 Hz), 7.34 (td, 1H, J = 7.5, 0.9 Hz), 7.18−7.07 (m, 3H), 6.96−6.92 (m, 2H), 2.05 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 174.32, 169.63, 156.41, 139.84, 133.80, 133.21, 131.77, 130.33, 129.65, 128.58, 128.50, 128.12, 127.24, 126.40, 125.16, 122.22, 117.03, 116.66, 94.53, 87.45, 25.42; IR (KBr) ν_{max}/cm^{-1} 3092, 1784, 1700, 1626, 1492, 1466, 1450, 1344, 1282, 1172, 1127, 940, 698; m/z (%) 410 (M^+, 0.4), 382 (6), 340 (2), 263 (1), 221 (100), 193 (80), 165 (78), 146 (64), 105 (61), 90 (52), 77 (45), 44 (60); EA found C, 72.92; H, 4.44; N, 6.92, $C_{25}H_{18}N_2O_4$ requires C, 73.17; H, 4.39; N, 6.83.

Photolysis of IS with 1d. A solution of **IS** (756 mg, 4 mmol) and **1d** (1.768 g, 8 mmol) in benzene (80 mL) was irradiated with light of wavelength > 400 nm under N_2 atmosphere for 24 h. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **3d** (359 mg, 22%) and **4d** (787 mg, 48%).

3d, (1*R*,3′*R*,5*R*)-1′-acetyl-3,5-diphenylspiro[4,6-dioxa-2-azabicyclo[3.2.0]hept-2-ene-7,3′-[3*H*]indol]-2′(1′*H*)-one: colorless crystals from acetone−petroleum ether, mp 218−220 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, 1H, J = 8.1 Hz), 8.14 (td, 2H, J = 6.9, 1.5 Hz), 7.74−7.71 (m, 2H), 7.64−7.41 (m, 8H), 7.25 (td, 1H, J = 7.5, 0.9 Hz), 5.18 (s, 1H), 2.63 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 171.32, 170.35, 169.80, 139.81, 135.55, 132.64, 131.48, 130.07, 129.03, 128.87, 128.69, 126.63, 126.25, 126.03, 125.78, 124.56, 117.05, 114.76, 86.65, 81.17, 26.54; IR (KBr) ν_{max}/cm^{-1} 3020, 1775, 1711, 1635, 1463, 1336, 1273, 1169, 975, 696; m/z (%)

410 (M^+, 4), 368 (1), 306 (6), 264 (5), 221 (42), 165 (10), 146 (12), 105 (100), 77 (56); EA found C, 73.27; H, 4.63; N, 6.73, $C_{25}H_{18}N_2O_4$ requires C, 73.17; H, 4.39; N, 6.83.

4d, (1*S*,3′*R*,5*S*)-1′-acetyl-3,5-diphenylspiro[4,6-dioxa-2-azabicyclo[3.2.0]hept-2-ene-7,3′-[3*H*]indol]-2′(1′*H*)-one: colorless needles from acetone−petroleum ether, mp 152−154 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, 1H, J = 8.1 Hz), 8.16 (td, 2H, J = 7.2, 1.5 Hz), 7.90−7.81 (m, 2H), 7.69−7.63 (m, 1H), 7.58−7.50 (m, 5H), 7.46−7.37 (m, 2H), 7.13 (td, 1H, J = 7.8, 0.9 Hz), 5.32 (s, 1H), 2.71 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 174.67, 170.15, 168.95, 140.61, 135.05, 133.03, 131.84, 129.97, 129.06, 128.96, 128.47, 126.89, 126.44, 126.31, 125.39, 122.52, 116.85, 115.79, 87.60, 78.20, 26.62; IR (KBr) ν_{max}/cm^{-1} 3063, 1769, 1700, 1632, 1463, 1265, 1172, 759; *m*/*z* (%) 410 (M^+, 1), 306 (4), 264 (2), 221 (100), 165 (29), 146 (34), 105 (79), 77 (41); EA found C, 73.26; H, 4.67; N, 6.81, $C_{25}H_{18}N_2O_4$ requires C, 73.17; H, 4.39; N, 6.83.

Photolysis of IS with 1e. A solution of **IS** (756 mg, 4 mmol) and **1e** (1.016 g, 8 mmol) in benzene (80 mL) was irradiated with light of wavelength >400 nm under N_2 atmosphere for 12 h. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **2e** (120 mg, 12%), **6e** (273 mg, 22%), and **7e** (414 mg, 31%).

2e, (2*R*,3′*S*,5*R*,6a*S*,11a*R*)-1′,11-Diacetyl-2,5-dihydro-2-methyl-5-ethoxyspiro[2,5-epoxy-11a,6a-(epoxymethano)-11*H*-1,6,3-dioxazocino[8,7-*b*]indole-13,3′-[3*H*]indol]-2′(1′*H*)-one: yellow powder from petroleum ether−acetone, mp 254−256 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, 1H, J = 8.3 Hz), 8.27 (d, 1H, J = 8.1 Hz), 7.96 (d, 1H, J = 7.6 Hz), 7.56 (td, 1H, J = 8.1, 1.4 Hz), 7.52 (td, 1H, J = 7.4, 1.7 Hz), 7.40 (td, 1H, J = 7.1, 0.9 Hz), 7.19 (d, 1H, J = 7.5 Hz), 7.14 (td, 1H, J = 6.5, 1.3 Hz), 5.65 (d, 1H, J = 1.8 Hz), 4.36 (ddd, 2H, J = 14.4, 7.8, 0.9 Hz), 2.47 (s, 3H), 2.40 (s, 3H), 1.89 (s, 3H), 1.39 (t, 3H, J = 7.1 Hz); IR (KBr) ν 1761, 1715, 1695, 1607, 1377, 1196, 1010, 759 cm^{-1}; MS *m*/*z* (%) 461 (0.1), 334 (9), 278 (24), 201 (25), 146 (34), 99 (33), 43(100); EA found C, 61.71; H, 4.39; N, 8.43, $C_{26}H_{23}N_3O_8$ requires C, 61.78; H, 4.55; N, 8.32.

6e, ethyl 1-acetyl-2′-methyl-2-oxo-4′*H*-spiro[indoline-3,5′-oxazole]-4′-carboxylate: colorless crystals from petroleum ether−acetone, mp 146−148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, 1H, J = 8.2 Hz), 7.42 (td, 1H, J = 7.8, 1.7 Hz), 7.28−7.19 (m, 2H), 5.17 (s, 1H), 3.87−3.70 (m, 2H), 2.73 (s, 3H), 2.22 (s, 3H), 0.75 (t, 3H, J = 7.1 Hz); IR (KBr) ν 2987, 1747, 1711, 1665, 1608, 1537, 1265, 1017, 766 cm^{-1}; MS *m*/*z* (%) 316 (M^+, 12), 274 (39), 243 (16), 201 (75), 158 (20), 127 (56), 99 (93), 43 (100); EA found C, 60.81; H, 5.01; N, 8.99, $C_{16}H_{16}N_2O_5$ requires C, 60.76; H, 5.06; N, 8.86.

7e, ethyl 2-acetamido-2-(1-acetyl-3-hydroxy-2-oxoindolin-3-yl)-acetate: colorless crystals from petroleum ether−acetone, mp 184−186 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, 1H, J = 8.1 Hz), 7.47 (d, 1H, J = 7.4 Hz), 7.41 (td, 1H, J = 7.3, 1.3 Hz), 7.71 (t, 1H, J = 7.5 Hz), 6.73 (d, 1H, J = 5.7 Hz), 5.36 (d, 1H, J = 6.4 Hz), 3.98−3.86 (m, 2H), 2.73 (s, 3H), 2.22 (s, 3H), 0.97 (t, 3H, J = 7.1 Hz); IR (KBr) ν 2987, 1746, 1710, 1665, 1537, 1469, 1261, 1166, 1131, 1015, 765 cm^{-1}; MS *m*/*z* (%) 334 (M^+, 0.04), 219 (2), 191 (16), 146 (40), 102 (30), 43 (100); EA found C, 57.56; H, 5.56; N, 8.37, $C_{16}H_{18}N_2O_6$ requires C, 57.49; H, 5.39; N, 8.38.

Photolysis of IS with 1f. A solution of **IS** (378 mg, 2 mmol) and **1f** (700 mg, 4 mmol) in benzene (40 mL) was irradiated with light of wavelength >400 nm under N_2 atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **2f** (536 mg, 97%).

2f, (2*R*,3′*S*,5*R*,6a*S*,11a*R*)-1′,11-diacetyl-2,5-dihydro-4-phenylspiro[2,5-epoxy-11a,6a-(epoxymethano)-11*H*-1,6,3-dioxazocino-[8,7-*b*]indole-13,3′-[3*H*]indol]-2′(1′*H*)-one: yellow crystals from petroleum ether−acetone, mp 246−248 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (m, 3H), 7.50 (m, 2H), 7.35 (d, 2H, J = 8.9 Hz), 7.06 (t, 1H, J = 7.3 Hz), 6.98 (s, 1H), 6.66 (d, 2H, J = 8.9 Hz), 6.54 (d, 1H, J = 6.8 Hz), 6.45 (t, 1H, J = 7.4 Hz), 6.33 (s, 1H), 3.81 (s, 3H), 2.54 (s, 3H), 2.29 (s, 3H); IR (KBr) ν 3023, 1780, 1707, 1687, 1608, 1570, 1518, 1264, 1172, 757 cm^{-1}; MS *m*/*z* (%) 364 (1), 278 (1), 189 (20), 175 (59), 146 (100), 90 (59), 63 (27), 43 (95); EA found C, 65.13; H, 4.28; N, 7.57, $C_{30}H_{23}N_3O_8$ requires C, 65.10; H, 4.16; N, 7.59.

Photolysis of PQ with 1a. A solution of **PQ** (832 mg, 4 mmol) and **1a** (1.384 g, 8 mmol) in acetonitrile (80 mL) was irradiated with light of wavelength >400 nm under N_2 atmosphere for 24 h. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **8a** (305 mg, 20%) and **9a** (1.052 g, 69%).

8a, 2,5-dihydro-2-ethyl-4-phenyl-2,5-epoxyphenanthro[9,10-*g*]-1,6,3-dioxazocine: yellow crystals from acetone−petroleum ether, mp 152−154 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, 2H, J = 7.3 Hz), 8.39 (dt, 1H, J = 7.5, 1.2 Hz), 8.30 (dt, 1H, J = 7.5, 1.2 Hz), 7.93 (dd, 2H, J = 7.4, 1.3 Hz), 7.62−7.48 (m, 4H), 7.43−7.32 (m, 3H), 6.83 (s, 1H), 2.78−2.63 (m, 2H), 1.41 (t, 3H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.97, 133.94, 132.71, 132.35, 128.89, 128.29, 128.26, 128.22, 128.16, 128.06, 127.77, 126.97, 126.85, 125.97, 125.75, 123.24, 122.36, 122.24, 122.14, 100.49, 29.57, 8.31; IR (KBr) ν_{max}/cm^{-1} 2975, 1630, 1597, 1454, 1319, 1236, 1118, 966, 757; *m*/*z* (%) 381 (M^+, 1), 297 (0.9), 249 (0.6), 208 (9), 180 (43), 173 (100), 130 (60), 90 (31), 63 (12); EA found C, 78.52; H, 5.04; N, 3.68, $C_{25}H_{19}NO_3$ requires C,78.74; H, 4.99; N, 3.67.

9a, 3-ethyl-1-phenylspiro[4,6-dioxa-2-azabicyclo[3.2.0]hept-2-ene-7,9′(10′*H*)-phenanthren]-10′-one: yellow crystals from acetone−petroleum ether, mp 168−170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80−8.76 (m, 2H), 8.24 (d, 1H, J = 7.7 Hz), 7.79−7.72 (m, 2H), 7.63−7.59 (m, 2H), 7.53−7.47 (m, 3H), 7.41−7.34 (m, 3H), 6.68 (s, 1H), 2.29 (qd, 2H, J = 16.0, 7.7 Hz), 1.06 (t, 3H, J = 7.5 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.33, 173.99, 148.41, 135.91, 131.81, 129.78, 129.48, 129.01, 128.57, 128.29, 128.26, 127.61, 127.16, 126.16, 124.81, 124.35, 124.12, 122.15, 119.90, 115.82, 64.66, 27.73, 9.97; IR (KBr) ν_{max}/cm^{-1} 2978, 1815, 1643, 1534, 1450, 1097, 1008, 755; *m*/*z* (%) 381 (M^+, 42), 353 (5), 297 (100), 252 (10), 165 (14), 104 (5), 57 (14); EA found C, 78.75; H, 5.09; N, 3.63, $C_{25}H_{19}NO_3$ requires C,78.74; H, 4.99; N, 3.67.

Photolysis of PQ with 1b. A solution of **PQ** (832 mg, 4 mmol) and **1b** (1.768 g, 8 mmol) in acetonitrile (80 mL) was irradiated with light of wavelength >400 nm under N_2 atmosphere for 24 h. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **10b** (430 mg, 25%) and **11** (703 mg, 55%).

10b, 9a,12a-dihydro-11,12a-diphenylphenanthro[9′,10′:5,6]-[1,4]dioxino[2,3-*d*]oxazole: yellow blocks from acetone−petroleum ether, mp 148−150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (d, 2H, J = 6.3 Hz), 8.38 (d, 1H, J = 6.9 Hz), 8.28 (d, 1H, J = 7.5 Hz), 7.97 (d, 2H, J = 7.8 Hz), 7.84 (d, 2H, J = 6.6 Hz), 7.66−7.42 (m, 8H), 7.32 (t, 2H, J = 7.2 Hz), 6.49 (s, 1H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 165.92, 140.26, 135.41, 133.56, 132.68, 129.38, 129.02, 128.94, 128.40, 127.99, 127.81, 127.55, 126.96, 126.47, 125.65, 125.87, 125.77, 125.64, 122.69, 122.49, 121.57, 120.75, 105.20, 103.53; IR (KBr) ν_{max}/cm^{-1} 1646, 1450, 1350, 1246, 1140, 1063, 949, 756, 695; *m*/*z* (%) 323 (5), 236 (2), 221 (100), 202 (24), 193 (65), 180 (93), 165 (11), 152 (32), 89 (51), 76 (22), 63 (26), 43 (38); EA found C, 81.19; H, 4.42; N, 3.21, $C_{29}H_{19}NO_3$ requires C, 81.12; H, 4.43; N, 3.26.

11 10-[[(9a*R*,12a*S*)-11,12a-diphenylphenanthro[9′,10′:5,6]-[1,4]dioxino[2,3-*d*]oxazol-9a(12a*H*)-yl]oxy]-9-phenanthrenol: colorless crystals from acetone−petroleum ether, mp 182−184 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71−8.68 (m, 1H), 8.61−8.54 (m, 4H), 8.42−8.39 (m, 1H), 8.19 (td, 2H, J = 6.9, 1.5 Hz), 7.87 (dd, 1H, J = 7.8, 1.5 Hz), 7.76−7.73 (m, 2H), 7.67−7.49 (m, 10H), 7.43−7.39 (m, 2H), 7.36 (s, 1H), 7.28−7.23 (m, 1H), 7.19 (t, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.37, 142.44, 136.42, 136.31, 133.09, 132.68, 129.94, 129.77, 129.43, 129.39, 129.03, 128.51, 128.36, 127.67,

127.42, 127.26, 127.22, 126.95, 126.82, 126.66, 126.47, 126.11, 125.97, 125.88, 25.24, 125.10, 124.50, 124.44, 123.44, 122.72, 122.66, 122.59, 122.43, 122.05, 121.57, 120.43, 105.69; IR (KBr) ν_{max}/cm^{-1} 3489, 1650, 1606, 1500, 1450, 1352, 1334, 1235, 1212, 1056, 925, 881, 723; *m*/*z* (%) 429 (6), 401 (3), 281 (7), 208 (28), 194 (16), 180 (100), 165 (10), 152 (35), 105 (25), 105 (25), 76 (19); EA found C, 81.00; H, 4.09; N, 2.19, $C_{43}H_{27}NO_5$ requires C, 81.00; H, 4.24; N, 2.20.

Photolysis of PQ with 1c. A solution of **PQ** (624 mg, 3 mmol) and **1c** (1.33 g, 6 mmol) in acetonitrile (80 mL) was irradiated with light of wavelength >400 nm under N_2 atmosphere for 24 h. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **8c** (553 mg, 43%), **12** (124 mg, 13%), and **10c** (502 mg, 39%).

8c, 2,5-dihydro-4,5-diphenyl-2,5-epoxyphenanthro[9,10-*g*]-1,6,3-dioxazocine: colorless crystals from acetone−petroleum ether, mp 206−208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57−8.45 (m, 4H), 7.84 (dd, 2H, J = 7.9, 1.7 Hz), 7.70−7.48 (m, 10H), 7.22 (dt, 1H, J = 7.4, 2.2 Hz), 7.13 (t, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.96, 136.04, 133.97, 132.53, 132.50, 130.15, 129.29, 129.08, 128.82, 128.77, 128.72, 128.34, 128.19, 128.18, 127.51, 127.45, 127.06, 126.62, 126.34, 123.59, 122.86, 122.53, 113.62, 109.17; IR (KBr) ν_{max}/cm^{-1} 3070, 1670, 1443, 1315, 1231, 1110, 1012, 753, 688; *m*/*z* (%) 429 (M^+, 4), 297 (4), 221 (100), 193 (45), 180 (44), 165 (51), 152 (26), 105 (16), 77 (24), 63 (9), 44 (2); EA found C,81.08; H, 4.40; N, 3.47, $C_{29}H_{19}NO_3$ requires C, 81.12; H, 4.43; N, 3.26.

12: colorless crystals from acetone−petroleum ether, mp 216−218 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (d, 1H, J = 7.9 Hz), 8.58 (d, 1H, J = 8.1 Hz), 8.49 (d, 1H, J = 7.5 Hz), 8.24 (d, 1H, J = 7.2 Hz), 7.95 (d, 1H, J = 8.4 Hz), 7.83 (dd, 1H, J = 7.7, 1.0 Hz), 7.73−7.62 (m, 5H), 7.51−7.44 (m, 7H), 7.34 (td, 1H, J = 7.8, 1.2 Hz), 7.27−7.16 (m, 6H), 7.02 (t, 2H, J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.28, 136.66, 135.20, 132.84, 132.52, 132.49, 131.90, 131.46, 131.22, 129.90, 129.83, 129.57, 129.24, 128.77, 128.56, 128.29, 127.77, 127.68, 127.60, 127.48, 127.00, 126.80, 126.68, 125.75, 125.46, 125.11, 125.05, 124.56, 122.63, 122.44, 122.36, 121.06, 120.89, 114.91, 109.95; IR (KBr) ν_{max}/cm^{-1} 1709, 1644, 1620, 1451, 1317, 1110, 1061, 1036, 760; *m*/*z* (%) 637 (M^+, 9), 429 (13), 400 (78), 316 (19), 296 (9), 221 (100), 193 (49), 180 (44), 165 (41), 152 (23), 105 (35), 77 (19), 63 (12), 41 (26); EA found C, 81.24; H, 4.31; N, 2.12, $C_{43}H_{27}NO_5$ requires C, 81.00; H, 4.24; N, 2.20.

10c, 9a,12a-dihydro-9a,12a-diphenylphenanthro[9′,10′:5,6]-[1,4]dioxino[2,3-*d*]oxazole: colorless crystals from acetone−petroleum ether, mp 190−192 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72−8.71 (m, 2H), 7.68−7.61 (m, 2H), 7.62−7.67 (m, 4H), 7.45−7.26 (m, 4H), 7.36 (s, 1H), 7.19−7.14 (m, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.11, 137.67, 135.97, 135.53, 135.50, 129.49, 129.01, 128.16, 128.03, 127.90, 127.83, 127.65, 127.05, 126.91, 126.86, 126.21, 125.56, 123.84, 123.76, 121.17, 120.70, 112.79, 108.25; IR (KBr) ν_{max}/cm^{-1} 3068, 1709, 1634, 1606, 1499, 1450, 1353, 1178, 1027, 761; *m*/*z* (%) 429 (M^+, 0.1), 296 (0.4), 221 (85), 208 (26), 193 (51), 180 (100), 165 (60), 152 (41), 77 (24), 51 (14), 43 (10); EA found C, 80.99; H, 4.30; N, 3.15, $C_{29}H_{19}NO_3$ requires C, 81.12; H, 4.43; N, 3.26.

Photolysis of PQ with 1d. A solution of **PQ** (832 mg, 4 mmol) and **1d** (1.768 g, 8 mmol) in acetonitrile (80 mL) was irradiated with light of wavelength >400 nm under N_2 atmosphere for 24 h. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **9d** (776 mg, 45%) and **10d** (541 mg, 32%).

9d, 3,5-diphenylspiro[4,6-dioxa-2-azabicyclo[3.2.0]hept-2-ene-7,9′(10′*H*)-phenanthren]-10′-one: yellow crystals from acetone−petroleum ether, mp 192−194 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01−7.94 (m, 4H), 7.87 (dd, 3H, J = 7.0, 1.4 Hz), 7.77 (d, 1H, J = 7.7 Hz), 7.69 (t, 1H, J = 7.4 Hz), 7.56−7.36 (m, 8H), 7.18 (t, 1H, J = 7.5 Hz), 5.13 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.72, 168.81, 137.53, 136.06, 135.63, 135.17, 132.98, 132.47, 130.61, 129.75, 129.42, 128.68, 128.66, 128.54, 128.51, 128.03, 127.94, 126.92, 126.46, 124.37, 123.66, 114.84, 94.47, 78.43; IR (KBr) ν_{max}/cm^{-1} 3052, 1706, 1449, 1292, 1020, 960, 699; *m*/*z* (%) 429 (M^+, 2), 264 (1), 221 (100), 180 (62), 165 (29), 152 (32), 105 (49), 77 (49); EA found C, 81.10; H, 4.46; N,3.18, $C_{29}H_{19}NO_3$ requires C, 81.12; H, 4.43; N, 3.26.

10d, 9a,12a-dihydro-9a,11-diphenylphenanthro[9′,10′:5,6][1,4]-dioxino[2,3-d]oxazole: colorless crystals from acetone−petroleum ether, mp 144−146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, 2H, J = 7.7 Hz), 8.38−8.35 (m, 1H), 8.31−8.27 (m, 1H), 7.98−7.95 (m, 2H), 7.84−7.82 (m, 2H), 7.67−7.43 (m, 8H), 7.34 (t, 2H, J = 7.5 Hz), 6.57 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.19, 138.47, 134.89, 133.81, 132.75, 129.86, 129.03, 128.96, 128.47, 127.72, 127.59, 127.06, 126.93, 126.43, 125.96, 125.90, 125.84, 125.71, 125.47, 122.68, 122.58, 121.48, 120.84, 108.40, 100.77; IR (KBr) ν_{max}/cm^{-1} 3064, 1648, 1452, 1330, 1140, 990, 760; *m*/*z* (%) 429 (M^+, 0.04), 306 (1), 264 (0.6), 221 (100), 180 (67), 165 (34), 105 (19), 77 (39); EA found C, 81.15; H, 4.34; N,3.41, $C_{29}H_{19}NO_3$ requires C, 81.12; H, 4.43; N, 3.26.

Photolysis of PQ with 1e. A solution of **PQ** (832 mg, 4 mmol) and **1e** (1.016 g, 8 mmol) in acetonitrile (80 mL) was irradiated with light of wavelength >400 nm under N_2 atmosphere for 12 h. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **13** (102 mg).

13: colorless crystals from petroleum ether−acetone, mp 162−164 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (dd, 1H, J = 7.7, 1.2 Hz), 7.97 (d, 1H, J = 7.9 Hz), 7.89 (d, 1H, J = 7.8 Hz), 7.75 (td, 1H, J = 8.0, 1.4 Hz), 7.52−7.40 (m, 3H), 7.36 (td, 1H, J = 7.0, 1.1 Hz), 4.84 (d, 1H, J = 1.2 Hz), 3.70−3.59 (m, 1H), 3.49−3.38 (m, 1H), 2.41 (s, 3H), 0.77 (t, 3H, J = 7.1 Hz); IR (KBr) ν 3358, 2975, 1736, 1706, 1657, 1528, 1206, 1019, 774, 735 cm^{-1}; MS *m*/*z* (%) 335 (15), 294 (54), 235 (20), 221 (100), 180 (47), 152 (29), 99 (51), 71 (29); EA found C, 67.96; H, 5.64; N, 3.84, $C_{20}H_{19}NO_5$ requires C, 67.99; H, 5.38; N, 3.97.

Photolysis of BZ with 1i. A solution of **BZ** (800 mg, 3.8 mmol) and **1i** (1.2 g, 7.5 mmol) in acetonitrile (80 mL) was irradiated with light of wavelength >330 nm under N_2 atmosphere for 48 h to reach a 80% conversation of BZ. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **15a** (180 mg, 16%) and **16a** (910 mg, 81%).

15a, (1*R*,5*R*,7*R*)-7-benzoyl-1,7-diphenyl-3-methyl-4,6-dioxa-2-azabicyclo[3.2.0]hept-2-ene: white powders from acetone−petroleum ether, mp 149−150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (dd, 2H, J = 7.5, 1.5 Hz), 7.53−7.44 (m, 3H), 7.40 (t, 2H, J = 7.5 Hz), 7.30−7.25 (m, 2H), 7.21−7.16 (m, 6H), 6.60 (s, 1H), 2.08 (s, 3H); IR (KBr) ν 3059, 1667, 1597, 1446, 1268, 1013, 959, 860, 739, 694 cm^{-1}; MS *m*/*z* (%) 340 (0.4), 236 (4),167 (4), 159 (100), 131 (29), 105 (79), 77 (60), 51 (18); EA found C, 78.20; H, 5.12; N, 3.50, $C_{24}H_{19}NO_3$ requires C, 78.05; H, 5.15; N, 3.79.

16a, (1*S*,5*S*,7*R*)-7-benzoyl-1,7-diphenyl-3-methyl-4,6-dioxa-2-azabicyclo[3.2.0]hept-2-ene: colorless crystals from acetone−petroleum ether, mp 147−149 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (4H, dd, J = 8.1, 1.5 Hz), 7.53−7.33 (m, 11H), 6.48 (s, 1H), 1.91 (s, 3H); IR (KBr) ν 3054, 1682, 1668, 1598, 1490, 1383, 1259, 1071, 930, 857, 797, 697, 657 cm^{-1}; MS *m*/*z* (%) 298 (1), 236 (4), 178 (2), 159 (100), 105 (82), 77 (69); EA found C, 78.12; H, 5.07; N, 3.52, $C_{24}H_{19}NO_3$ requires C, 78.05; H, 5.15; N, 3.79.

Photolysis of BZ with 1j. A solution of **BZ** (420 mg, 2.0 mmol) and **1j** (0.888 g, 8.0 mmol) in acetonitrile (40 mL) was irradiated with light of wavelength >330 nm under N_2 atmosphere for 48 h to reach a 70% conversation of **BZ**. Solvent was removed under reduced pressure and the residue was separated by flash chromatography to give **15b** (310 mg, 69%).

15b, (1*R*,5*R*,7*R*)-1,3,5-trimethyl-4,6-dioxa-2-azabicyclo-[3.2.0]hept-2-ene: yellow oil from acetone−petroleum ether; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (t, 4H, J = 9.0 Hz), 7.43−7.38 (m, 3H), 7.34−7.29 (m, 3H), 1.89 (s, 3H), 1.61 (s,

3H), 1.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.47, 164.92, 136.61, 135.72, 132.64, 129.31,128.58, 128.35, 128.01, 125.73, 113.61, 98.93, 81.96, 18.92, 17.19, 14.28.

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Supporting Information Available: General experimental information; calculation results on the biradical intermediates **L** and **M**; copies of ^{1}H and ^{13}C NMR spectra for new compounds; and crystal structure and CIF of compound **8a** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.