JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

Cu(II)-Catalyzed 6π-Photocyclization of Dienynes

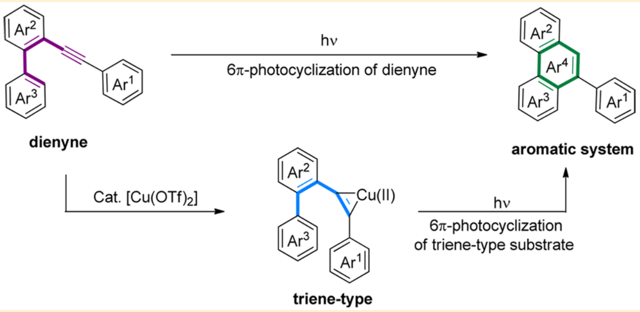
Ruiwen Jin,[†] Jinjin Chen,[‡] Yiyong Chen,[†] Wangsheng Liu,[†] Dawen Xu,[†] Yawei Li,[†] Aishun Ding,[†] and Hao Guo*,[†]

[†]Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, P. R. China

[‡]Department of Child Health Care, Shanghai Children's Hospital Affiliated to Shanghai Jiao Tong University, 1400 Beijing Xi Road, Shanghai 200040, P. R. China

Supporting Information

ABSTRACT: The first 6π-photocyclization of dienynes was developed, which provides a new and effective protocol for the synthesis of the phenyl ring in excellent yields with nice functional group tolerance. In this transformation, the $Cu(OTf)_2$ catalyst plays a key role in the conversion of alkyne moiety into an alkene-type moiety, which means that the dienyne reactant is converted into a triene-type substrate. Thus, this reaction proceeds via a Cu(II)-catalyzed 6π-photocyclization of triene-type derivatives.



6π-Photocyclization[1] is a kind of classical photochemical reaction, which is quite different from thermocyclizations that have been well established by many metal catalysts[2] or halonium ions.[3] It has a rich history. Since Srimivansan reported the first example in 1963,[4] numerous achievements have been reported in this field.[5] In modern organic chemistry, such reactions provide attractive methods for the preparation of cyclohexa-1,3-diene derivatives, which have found wide applications in the synthesis of various medicines,[6] functionalized materials,[7] and building blocks for organic synthesis.[8] Although it has been studied for quite a long time, the investigation of 6π-photocyclization is still limited to triene substrates.[9] To the best of our knowledge, there are indeed a few photoinduced cyclizations of dienynes;[10] however, it has been proven that such reactions did not proceed via a 6π-photocyclization process.[10] It is well-known that the 6π-photocyclization reaction proceeds via two key steps: the formation of a six-membered cyclic transition state and the following intramolecular 1,5-H shift.[5a] In a conjugated triene system, it is quite easy to meet the above requirements (Scheme 1a).[5] When a dienyne substrate is irradiated under ultraviolet light, an unstable allene intermediate might be generated in situ.[10a] Subsequently, it could in principle aromatize via a 1,5-H shift. However, such a 1,5-H shift is a high barrier process. Instead, isomerization via solvent-involved protonation−deprotonation will occur to realize the whole transformation, which is a totally different process from 6π-photocyclization (Scheme 1a).[10a] Considering that 6π-photocyclization of dienynes will result in the formation of a new phenyl ring, which is totally different from that of trienes and very useful in organic synthesis, development of 6π-photocyclization of dienynes is highly desired. It is well-known that Lewis acid could coordinate with an alkyne moiety. As described by the standard Dewar−Chatt−Duncanson model,[11] electrons in one filled π orbital of the alkyne will fill into an empty orbital of the metal center. Thus, in the resulting metal−alkyne complex, the C−C triple bond will possess some C−C double-bond properties. Based on this consideration, we questioned whether it is possible to convert the dienyne derivatives into triene-type substrates under the catalysis of a proper Lewis acid. If this idea works, the 6π-photocyclization of dienynes might proceed via triene-type species and afford a new aromatic system as the final product.

In our previous studies, we found that the cyclization of 2-((4-methoxyphenyl)ethynyl)-1,1′-biphenyl **1a** could be catalyzed by the merging of $Cu(OTf)_2$ and Eosin Y via a visible light-induced single-electron transfer (SET) process.[12] In the mechanism explorations, we found that when the single electron transfer mediated Eosin Y was removed from the catalysts system, the same cyclization could also take place under high energy UV irradiation.[12] Such a transformation must proceed via a totally different mechanism. Thus, we further studied this UV-induced photocyclization. Herein, we report this observation on the Cu(II)-catalyzed 6π-photocyclization of dienynes, which provides a novel protocol for the synthesis of phenyl ring in excellent yields with nice functional group tolerance (Scheme 1b).

At the start of our research, 2-((4-methoxyphenyl)ethynyl)-1,1′-biphenyl **1a** was chosen as the model substrate. Initially, a solution of **1a** (0.2 mmol) and $Cu(OTf)_2$ (10 mol %) in DMF (5 mL) was irradiated by ultraviolet lamps (30 W, $\lambda = 254$ nm) at rt under argon atmosphere. Disappointingly, no reaction took place (entry 1, Table 1). Then some other solvents were

Received: October 18, 2016
Published: November 16, 2016

DOI: 10.1021/acs.joc.6b02537
J. Org. Chem. 2016, 81, 12553−12558

Scheme 1. 6π-Photocyclizations

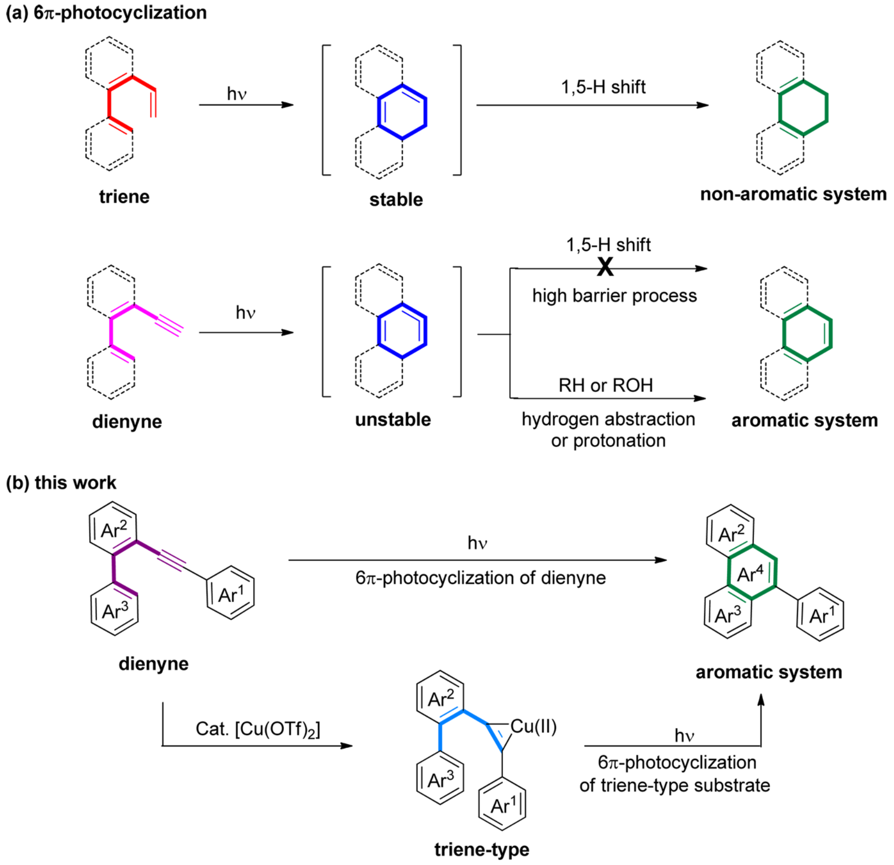
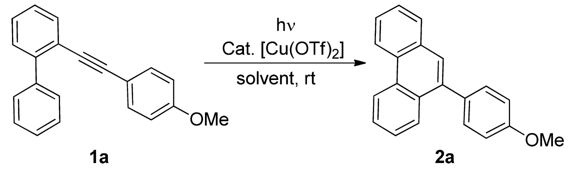


Table 1. Optimization of Reaction Conditions[a]



entry	solvent	$Cu(OTf)_2$ (mol %)	λ (nm)	time (h)	NMR yield[b] (%)
1	DMF	10	254	2	NR (93)[c]
2	MeOH	10	254	2	NR (99)[c]
3	acetone	10	254	2	NR (98)[c]
4	CH_3CN	10	254	2	30 (60)[c]
5	DCM	10	254	2	91
6	DCM	5	254	1	91
7	DCM	3	254	0.5	97 (0)[c] (96)[d]
8	DCM	1	254	6	94
9	DCM	0	254	0.5	NR (98)[c]
10	DCM	3	185&254	0.3	93
11	DCM	3	313	0.5	NR (98)[c]
12	DCM	3	365	0.5	NR (>99)[c]
13[e]	DCM	3		0.5	NR (>99)[c]

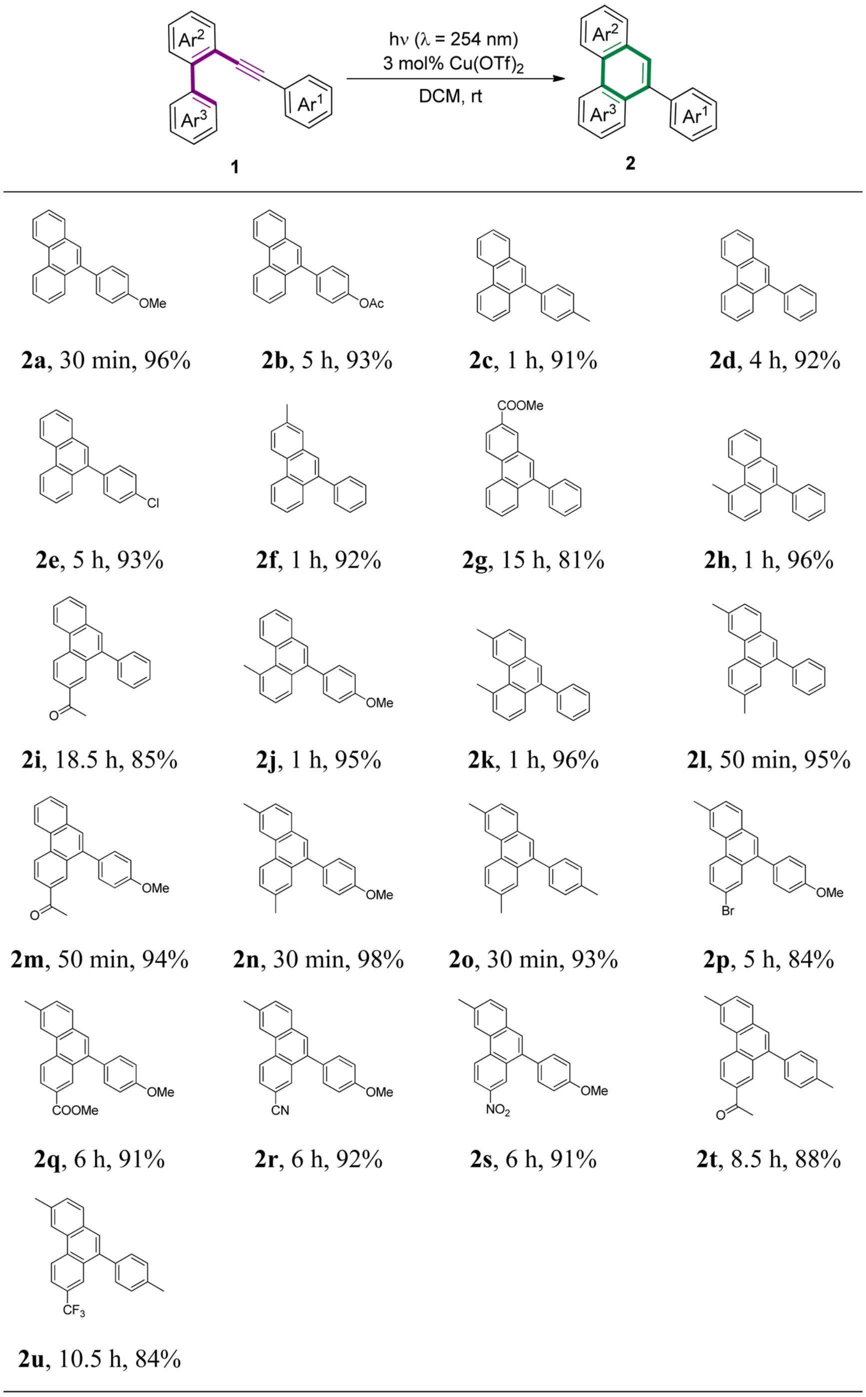
[a] All reactions were carried out using **1a** (0.2 mmol) and $Cu(OTf)_2$ in anhydrous solvent (5 mL) in a quartz reaction flask irradiated by ultraviolet lamps (30 W) at rt under argon atmosphere. [b] The yield was determined by ^1H NMR analysis (400 MHz) of the crude reaction mixture employing CH_2Br_2 (0.2 mmol) as the internal standard. [c] Recovered yield of **1a**. [d] Isolated yield of **2a**. [e] The reaction was carried out under reflux without UV irradiation.

tested (entries 2−5, Table 1). We were delight to see that the desired cyclization occurred in CH_3CN, although the reaction speed was low (entry 4, Table 1). The best result was observed when DCM was used as the solvent, affording **2a** in 91% NMR yield after being irradiated for 2 h (entry 5, Table 1). We then tried to decrease the catalyst loading (entries 6−8, Table 1). The results indicated that the highest yield was afforded in the presence of 3 mol % of $Cu(OTf)_2$ (entry 7, Table 1). Notably, no reaction occurred in the absence of $Cu(OTf)_2$ (entry 9, Table 1), which indicated that $Cu(OTf)_2$ was a key factor in this reaction. Finally, we examined the influence of the photoirradiation energy (entries 10−12, Table 1). The reaction irradiated at λ = 185&254 nm gave **2a** in a slightly lower yield (entry 10, Table 1), but no reaction occurred at λ = 313 or 365 nm (entries 11 and 12, Table 1). Considering the thermal effect caused by UV irradiation, the reaction was carried out under reflux without light. The results indicated that no reaction took place at all (entry 13, Table 1), which clearly showed that high energy UV irradiation was necessary for this transformation. Thus, Condition A (**1a** (0.2 mmol), $Cu(OTf)_2$ (3 mol %), DCM (5 mL), UV (30 W, λ = 254 nm), and rt) was applied in the next studies.

With the optimized reaction conditions in hand, the scope of this 6π-photocyclization with different dienynes was examined carefully. Some typical results are summarized in Table 2. In general, mono-, di-, or trisubstituted dienynes were all reactive in this reaction, which meant that a series of multisubstituted phenanthrene derivatives would be synthesized by this method. The electron effect was studied carefully by introducing strong electron-donating groups (methoxy or acetoxy), weak electron-donating groups (methyl), weak electron-withdrawing groups

DOI: 10.1021/acs.joc.6b02537
J. Org. Chem. 2016, 81, 12553−12558

Table 2. 6π-Photocyclization of Different Dienynes under Condition A[a]



2a, 30 min, 96% **2b**, 5 h, 93% **2c**, 1 h, 91% **2d**, 4 h, 92%

2e, 5 h, 93% **2f**, 1 h, 92% **2g**, 15 h, 81% **2h**, 1 h, 96%

2i, 18.5 h, 85% **2j**, 1 h, 95% **2k**, 1 h, 96% **2l**, 50 min, 95%

2m, 50 min, 94% **2n**, 30 min, 98% **2o**, 30 min, 93% **2p**, 5 h, 84%

2q, 6 h, 91% **2r**, 6 h, 92% **2s**, 6 h, 91% **2t**, 8.5 h, 88%

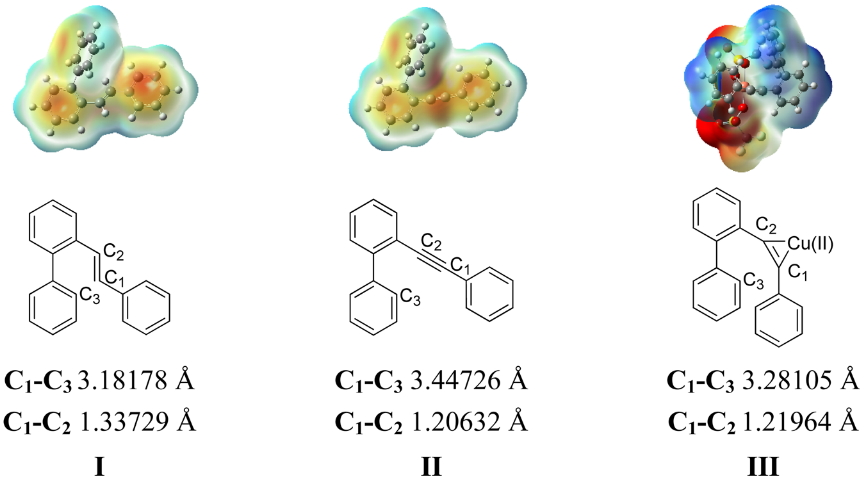
2u, 10.5 h, 84%

[a] All reactions were carried out using **1** (0.2 mmol) and Cu(OTf)$_2$ (3 mol %) in anhydrous DCM (5 mL) in a quartz reaction flask irradiated by ultraviolet lamps (30 W, λ = 254 nm) at rt under argon atmosphere. Isolated yield was reported.

(chloro or bromo atom), and strong electron-withdrawing groups (methoxycarbonyl, acetyl, nitrile, nitro, or trifluoromethyl) into the dienyne substrates. The corresponding phenanthrene products were formed in excellent yields from both electron-rich and electron-deficient reactants. These results indicated that the electron effect did not affect this photocyclization at all. Further explorations focused on the influence of the substituent position on Ar^1, Ar^2, or Ar^3 gave the conclusion that there was no clear influence on the reactivity (**2c**, **2f**, and **2h**). Importantly, dienynes with a series of functional groups, such as methoxy, methyl, acetoxy, halogen atom, methoxycarbonyl, acetyl, nitrile, nitro, and trifluoromethyl, were all highly reactive, showing nice functional group tolerance. These data demonstrated that this method for the preparation of multisubstituted phenanthrenes might find wide applications in organic synthesis.

To get a better understanding of the mechanism, we studied the molecular configurations of the key model intermediates triene **I**, dienyne **II**, and Cu(II) dienyne **III** by computer simulations (Scheme 2). The calculations were performed by using the basis sets 6-311G(d,p) for all species at the M06-2X level. The distance between C$_1$ and C$_3$ is 3.18 Å in **I** and 3.45 Å

Scheme 2. Interaction of Lewis Acid Catalysis and C−C Triple Bond

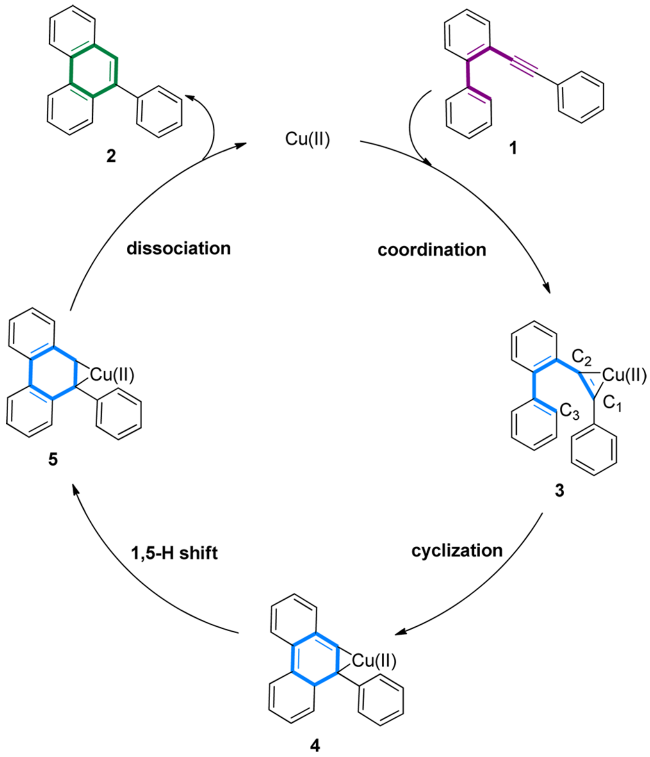


in **II**. For **III**, this value is 3.28 Å, which is still a little longer than that of **I** but much shorter than that of **II**. Thus, the formation of the required six-membered cyclic transition state from **III** is easier on the spatial configuration as compared to **II**. The bond length of C_1-C_2 is 1.34 Å in **I** and 1.21 Å in **II**. For **III**, this value is 1.22 Å, which is shorter than the C−C double bond but longer than the C−C triple bond. These data might indicate that the Cu(II)-coordinated C−C triple bond processed some double-bond properties. In such a model, the 6π-photocyclization of dienynes turned into 6π-photocyclization of triene-type substrates, which meant that the formation of the required six-membered cyclic transition state is easier and the barrier of the following intramolecular 1,5-H shift is lower.

The computer calculation indicated that the coordination of Cu(II) with alkynes rendered changes of the spatial configuration of the dienyne. On the other hand, it was likely that this coordination could also influence the efficiency of UV absorption. Hence, we monitored the UV absorption of **1a** as well as a mixture of **1a** and $Cu(OTf)_2$ (**1a**/$Cu(OTf)_2$ = 1:1) at $\lambda = 254$ nm (Figures S5 and S6, Supporting Information). The molar absorption coefficients were 2.88×10^4 and 3.15×10^4 M^{-1} cm^{-1}, respectively. Obviously, the UV absorption increased when $Cu(OTf)_2$ was added, which might suggest that the reactivity could be improved in the presence of $Cu(OTf)_2$.

Based on the above experimental evidence and literature reports,[13] a possible mechanism was proposed as showed in Scheme 3. The coordination of Cu(II) with dienyne **1** led to the formation of a three-membered ring complex **3**,[14] in which the original linear geometry of the C−C triple bond was twisted to a certain extent. Thus, the distance between C_1 and C_3 turned to be closer and the formation of the required six-membered cyclic transition state became easier. More importantly, the coordinated C−C triple bond possessed some double bond properties, which turned the dienyne system into a triene-type system. This also made the formation of the required six-membered transition state easier. When the Cu(II)-alkyne complex **3** was irradiated by ultraviolet light, the six-membered ring intermediate **4** could be formed. In this species, the Cu(II)-coordinated C−C double bond possessed some single bond properties. Thus, its following 1,5-H shift proceeded more easily to form a new aromatic ring in Cu(II)−alkene complex **5**. Finally, the Cu(II) catalyst would dissociate from **5** to form the final phenanthren product **2** and coordinate to **1** again to start the next catalytic cycle.

Scheme 3. Proposed Mechanism



In conclusion, we have developed a UV-induced $Cu(OTf)_2$-catalyzed 6π-photocyclization of dienynes that provides a new and effective protocol for the synthesis of phenyl ring. The whole transformation might proceed via the classic 6π-photocyclization of a triene-type substrate. Under the standard reaction conditions, a series of phenanthrene derivatives were prepared from dienynes.

■ EXPERIMENTAL SECTION

General Methods. All reactions were irradiated by ultraviolet lamps (30 W). ^1H NMR spectra were obtained at 400 MHz in $CDCl_3$. The computer simulations and calculations were performed by using the basis sets 6-311G(d,p) for all species at the M06-2X level. Anhydrous DCM was distilled with CaH_2. Compounds **1a**,[15] **1b**,[12]

1c,[15] **1d**,[15] **1e**,[15] **1f**,[12] **1g**,[15] **1h**,[15] **1i**,[15] **1j**,[15] **1k**,[12] **1l**,[12] **1m**,[16] **1n**,[15] **1o**,[16] **1p**,[15] **1q**,[16] **1r**,[16] **1s**,[16] **1t**,[12] and **1u**[12] were synthesized according to literature procedures.

General Procedure for the 6π-Photocyclization. Dienynes **1a−u** (0.20 mmol), Cu(OTf)$_2$ (0.006 mmol), and anhydrous DCM (5 mL) were added subsequently into a 25 mL dry quartz reaction flask. The mixture was irradiated by ultraviolet lamps (30 W) at rt under argon atmosphere. The photoreaction was completed as monitored by TLC. The solvent was removed, and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether) to afford **2a−u**.

*9-(4-Methoxyphenyl)phenanthrene (**2a**):*[12] liquid (55 mg, 96%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.77 (d, J = 8.0 Hz, 1 H), 8.71 (d, J = 8.0 Hz, 1 H), 7.94 (d, J = 8.0 Hz, 1 H), 7.88 (d, J = 8.0 Hz, 1 H), 7.69−7.44 (m, 7 H), 7.05 (d, J = 8.8 Hz, 2 H), 3.91 (s, 3 H).

*9-(4-Acetoxylphenyl)phenanthrene (**2b**):*[12] liquid (58 mg, 93%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.77 (d, J = 8.4 Hz, 1 H), 8.72 (d, J = 8.4 Hz, 1 H), 7.92 (d, J = 7.6 Hz, 1 H), 7.89 (d, J = 8.8 Hz, 1 H), 7.70−7.50 (m, 7 H), 7.24 (d, J = 8.8 Hz, 2 H), 2.37 (s, 3 H).

*9-(p-Tolyl)phenanthrene (**2c**):*[16] solid (49 mg, 91%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.77 (d, J = 8.4 Hz, 1 H), 8.72 (d, J = 8.0 Hz, 1 H), 7.94 (d, J = 8.0 Hz, 1 H), 7.89 (d, J = 8.0 Hz, 1 H), 7.70−7.49 (m, 5 H), 7.44 (d, J = 7.6 Hz, 2 H), 7.33 (d, J = 8.0 Hz, 2 H), 2.48 (s, 3 H).

*9-Phenylphenanthrene (**2d**):*[16] solid (47 mg, 92%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.78 (d, J = 8.4 Hz, 1 H), 8.73 (d, J = 8.4 Hz, 1 H), 7.95−7.85 (m, 2 H), 7.72−7.58 (m, 4 H), 7.57−7.42 (m, 6 H).

*9-(4-Chlorophenyl)phenanthrene (**2e**):*[17] solid (54 mg, 93%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.81 (d, J = 8.4 Hz, 1 H), 8.75 (d, J = 8.4 Hz, 1 H), 7.92 (d, J = 8.0 Hz, 1 H), 7.88 (d, J = 8.4 Hz, 1 H), 7.75−7.62 (m, 4 H), 7.61−7.46 (m, 5 H).

*2-Methyl-9-phenylphenanthrene (**2f**):*[12] liquid (50 mg, 92%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.74 (d, J = 8.4 Hz, 1 H), 8.61 (d, J = 8.8 Hz, 1 H), 7.89 (d, J = 8.4 Hz, 1 H), 7.70−7.59 (m, 3 H), 7.57−7.40 (m, 7 H), 2.57 (s, 3 H).

*2-Methoxycarbonyl-9-phenylphenanthrene (**2g**):*[12] liquid (51 mg, 81%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.76 (d, J = 8.4 Hz, 1 H), 8.72 (d, J = 8.8 Hz, 1 H), 8.59 (s, 1 H), 8.24 (d, J = 8.8 Hz, 1 H), 7.93 (d, J = 8.0 Hz, 1 H), 7.75−7.63 (m, 2 H), 7.61−7.42 (m, 6 H), 3.99 (s, 3 H).

*4-Methyl-10-phenylphenanthrene (**2h**):*[16] liquid (52 mg, 96%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.90 (d, J = 8.0 Hz, 1 H), 7.90 (d, J = 6.8 Hz, 1 H), 7.77 (d, J = 8.0 Hz, 1 H), 7.67−7.58 (m, 3 H), 7.55−7.38 (m, 7 H), 3.19 (s, 3 H).

*10-Phenyl-2-acetylphenanthrene (**2i**):*[12] liquid (50 mg, 85%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.83 (d, J = 8.8 Hz, 1 H), 8.75 (d, J = 8.0 Hz, 1 H), 8.55 (s, 1 H), 8.23 (d, J = 8.8 Hz, 1 H), 7.93 (d, J = 8.8 Hz, 1 H), 7.79−7.63 (m, 3 H), 7.59−7.43 (m, 5 H), 2.60 (s, 3 H).

*10-(4-Methoxyphenyl)-4-methylphenanthrene (**2j**):*[16] solid (57 mg, 95%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.89 (d, J = 8.8 Hz, 1 H), 7.90 (d, J = 9.2 Hz, 1 H), 7.81 (d, J = 8.0 Hz, 1 H), 7.65−7.57 (m, 3 H), 7.55−7.48 (m, 1 H), 7.46−7.36 (m, 3 H), 7.04 (d, J = 8.4 Hz, 2 H), 3.91 (s, 3 H), 3.19 (s, 3 H).

*3,5-Dimethyl-9-phenylphenanthrene (**2k**):*[12] liquid (55 mg, 96%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.69 (s, 1 H), 7.80 (d, J = 8.0 Hz, 1 H), 7.76 (d, J = 8.0 Hz, 1 H), 7.61 (s, 1 H), 7.52−7.34 (m, 8 H), 3.19 (s, 3 H), 2.64 (s, 3 H).

*2,6-Dimethyl-10-phenylphenanthrene (**2l**):*[17] liquid (54 mg, 95%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.65 (d, J = 8.4 Hz, 1 H), 8.47 (s, 1 H), 7.76 (d, J = 8.4 Hz, 1 H), 7.67 (s, 1 H), 7.61 (s, 1 H), 7.57−7.37 (m, 7 H), 2.63 (s, 3 H), 2.46 (s, 3 H).

*10-(4-Methoxyphenyl)-2-acetylphenanthrene (**2m**):.*[16] solid (61 mg, 94%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.83 (d, J = 8.4 Hz, 1 H), 8.74 (d, J = 8.8 Hz, 1 H), 8.58 (s, 1 H), 8.23 (d, J = 8.4 Hz, 1 H), 7.92 (d, J = 8.8 Hz, 1 H), 7.75−7.64 (m, 3 H), 7.49 (d, J = 8.8 Hz, 2 H), 7.09 (d, J = 8.4 Hz, 2 H), 3.94 (s, 3 H), 2.62 (s, 3 H).

*10-(4-Methoxyphenyl)-2,6-dimethylphenanthrene (**2n**):*[16] solid (62 mg, 98%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.63 (d, J = 8.4 Hz, 1 H), 8.45 (s, 1 H), 7.74 (d, J = 8.0 Hz, 1 H), 7.69 (s, 1 H), 7.58 (s, 1 H), 7.48−7.42 (m, 3 H), 7.39 (d, J = 8.0 Hz, 1 H), 7.04 (d, J = 8.4 Hz, 2 H), 3.90 (s, 3 H), 2.62 (s, 3 H), 2.46 (s, 3 H).

*2,6-Dimethyl-10-(p-tolyl)phenanthrene (**2o**):*[12] liquid (55 mg, 93%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.64 (d, J = 8.4 Hz, 1 H), 8.46 (s, 1 H), 7.75 (d, J = 8.0 Hz, 1 H), 7.69 (s, 1 H), 7.59 (s, 1 H), 7.49−7.36 (m, 4 H), 7.32 (d, J = 7.6 Hz, 1 H), 2.62 (s, 3 H), 2.48 (s, 3 H), 2.46 (s, 3 H).

*2-Bromo-10-(4-methoxyphenyl)-6-methylphenanthrene (**2p**):*[16] solid (64 mg, 84%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.60 (d, J = 8.8 Hz, 1 H), 8.43 (s, 1 H), 8.04 (s, 1 H), 7.78 (d, J = 8.0 Hz, 1 H), 7.72 (dd, J = 8.8, 2.0 Hz, 1 H), 7.64 (s, 1 H), 7.49−7.40 (m, 3 H), 7.06 (d, J = 8.8 Hz, 2 H), 3.92 (s, 3 H), 2.64 (s, 3 H).

*10-(4-Methoxyphenyl)-6-methyl-2-methoxycarbonylphenanthrene (**2q**):*[16] solid (65 mg, 91%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.80 (d, J = 8.8 Hz, 1 H), 8.67 (s, 1 H), 8.52 (s, 1 H), 8.24 (d, J = 10.0 Hz, 1 H), 7.80 (d, J = 8.0 Hz, 1 H), 7.68 (s, 1 H), 7.53−7.44 (m, 3 H), 7.08 (d, J = 8.4 Hz, 2 H), 3.93 (s, 6 H), 2.65 (s, 3 H).

*10-(4-Methoxyphenyl)-6-methyl-2-cyanophenanthrene (**2r**):*[16] solid (60 mg, 92%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.81 (d, J = 8.8 Hz, 1 H), 8.48 (s, 1 H), 8.27 (s, 1 H), 7.84−7.77 (m, 2 H), 7.73 (s, 1 H), 7.54 (d, J = 8.4 Hz, 1 H), 7.41 (d, J = 8.4 Hz, 2 H), 7.07 (d, J = 8.4 Hz, 2 H), 3.93 (s, 3 H), 2.66 (s, 3 H).

*10-(4-Methoxyphenyl)-6-methyl-2-nitrophenanthrene (**2s**):*[16] solid (63 mg, 91%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.87−8.81 (m, 2 H), 8.50 (s, 1 H), 8.40 (dd, J = 9.2, 2.4 Hz, 1 H), 7.83 (d, J = 8.4 Hz, 1 H), 7.76 (s, 1 H), 7.56 (d, J = 8.0 Hz, 1 H), 7.45 (d, J = 8.4 Hz, 2 H), 7.09 (d, J = 8.4 Hz, 2 H), 3.93 (s, 3 H), 2.66 (s, 3 H).

*10-(4-Methylphenyl)-6-methyl-2-acetylphenanthrene (**2t**):*[12] solid (57 mg, 88%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.81 (d, J = 8.8 Hz, 1 H), 8.57 (s, 1 H), 8.52 (s, 1 H), 8.20 (d, J = 8.8 Hz, 1 H), 7.81 (d, J = 8.4 Hz, 1 H), 7.70 (s, 1 H), 7.51 (d, J = 8.0 Hz, 1 H), 7.45 (d, J = 7.6 Hz, 2 H), 7.35 (d, J = 7.6 Hz, 2 H), 2.66 (s, 3 H), 2.60 (s, 3 H), 2.49 (s, 3 H).

*10-(4-Methylphenyl)-6-methyl-2-trifluoromethylphenanthrene (**2u**):*[12] solid (59 mg, 84%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.82 (d, J = 8.4 Hz, 1 H), 8.48 (s, 1 H), 8.23 (s, 1 H), 7.80 (t, J = 8.0 Hz, 2 H), 7.70 (s, 1 H), 7.48 (d, J = 8.4 Hz, 1 H), 7.40 (d, J = 8.0 Hz, 2 H), 7.33 (d, J = 7.6 Hz, 2 H), 2.63 (s, 3 H), 2.47 (s, 3 H).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02537.

- Spectral distribution of irradiance density for the UV lamps; molar absorption coefficients; computer simulations and calculations; ^{1}H NMR spectra of all products (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hao_guo@fudan.edu.cn.

ORCID

Hao Guo: 0000-0003-3314-4564

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge financial support from the International Science & Technology Cooperation Program of China (2014DFE40130) and theNational Nature Science Foundation of China (21274023).

■ REFERENCES

(1) (a) Clay, A.; Kumarasamy, E.; Ayitou, A. J. L.; Sivaguru, J. *Chem. Lett.* **2014**, *43*, 1816. (b) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (c) Blackburn, E. V.; Timmons, C. J. *Q. Rev., Chem. Soc.* **1969**, *23*, 482.

(2) (a) Wang, Y.; Zhang, W.; Dai, J.; Feng, Y.; Xu, H. *RSC Adv.* **2014**, *4*, 61706. (b) Lim, W.; Rhee, Y. H. *Eur. J. Org. Chem.* **2013**, *2013*, 460.

(c) Mamane, V.; Hannen, P.; Fürstner, A. *Chem. - Eur. J.* **2004**, *10*, 4556.

(3) (a) Dillard, R. D.; Pavey, D. E.; Benslay, D. N. *J. Med. Chem.* **1973**, *16*, 251. (b) Yao, T.; Campo, M. A.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 3511.

(4) (a) Srinivasan, R. *J. Chem. Phys.* **1963**, *38*, 1039. (b) Seelam, N.; Shrivastava, S. P.; S, P.; Gupta, S. *J. Saudi Chem. Soc.* **2016**, *20*, 411.

(5) (a) Fornier de Violet, Ph.; Bonneau, R.; Lapouyade, R.; Koussini, R.; Ware, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 6683. (b) Alabugin, I. V.; Manoharan, M.; Breiner, B.; Lewis, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 9329. (c) Shah, A.; Raj, D. *J. Saudi Chem. Soc.* **2015**, *19*, 73.

(6) Leutbecher, H.; Conrad, J. R.; Klaiber, I.; Beifuss, U. *QSAR Comb. Sci.* **2004**, *23*, 895.

(7) (a) Akritopoulou-Zanze, I.; Whitehead, A.; Waters, J. E.; Henry, R. F.; Djuric, S. W. *Tetrahedron Lett.* **2007**, *48*, 3549. (b) Yamada, S.; Okuda, M.; Yamamoto, N. *Tetrahedron Lett.* **2015**, *56*, 2098.

(8) Sydorenko, N.; Hsung, R. P.; Vera, E. L. *Org. Lett.* **2006**, *8*, 2611.

(9) (a) Lewis, F. D.; Zuo, X.; Gevorgyan, V.; Rubin, M. *J. Am. Chem. Soc.* **2002**, *124*, 13664. (b) Sajimon, M. C.; Lewis, F. D. *Photochem. & Photobio. Sci.* **2005**, *4*, 789. (c) Lewis, F. D.; Zuo, X. *Photochem. Photobiol. Sci.* **2003**, *2*, 1059.

(10) (a) Lewis, F. D.; Karagiannis, P. C.; Sajimon, M. C.; Lovejoy, K. S.; Zuo, X.; Rubin, M.; Gevorgyan, V. *Photochem. & Photobio. Sci.* **2006**, *5*, 369. (b) op den Brouw, P. M.; Laarhoven, W. H. *J. Chem. Soc., Perkin Trans. 2* **1982**, *2*, 795. (c) Sajimon, M. C.; Lewis, F. D. *Photochem. & Photobio. Sci.* **2005**, *4*, 629.

(11) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, 71. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, *52*, 2939.

(12) Jin, R.; Chen, Y.; Liu, W.; Xu, D.; Li, Y.; Ding, A.; Guo, H. *Chem. Commun.* **2016**, *52*, 9909−9912.

(13) (a) Zuccaccia, D.; Belpassi, L.; Macchioni, A.; Tarantelli, F. *Eur. J. Inorg. Chem.* **2013**, *2013*, 4121. (b) Debrouwer, W.; Heugebaert, T. S. A.; Roman, B. I.; Stevens, C. V. *Adv. Synth. Catal.* **2015**, *357*, 2975. (c) Abu Sohel, S. M.; Liu, R. *Chem. Soc. Rev.* **2009**, *38*, 2269.

(14) (a) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939. (b) Braunschweig, H.; Damme, A.; Dewhurst, R. D. *Nat. Chem.* **2012**, *5*, 115.

(15) Liu, W.; Chen, J.; Jin, R.; Xu, D.; Li, Y.; Ba, F.; Gu, G.; Kuang, Y.; Guo, H. *Org. Chem. Front.* **2016**, *3*, 852−855.

(16) Xu, D.; Jin, R.; Liu, W.; Ba, F.; Li, Y.; Ding, A.; Guo, H. *Tetrahedron Lett.* **2016**, *57*, 3235−3238.

(17) García-Cuadrado, D.; de Mendoza, P.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2007**, *129*, 6880−6886.