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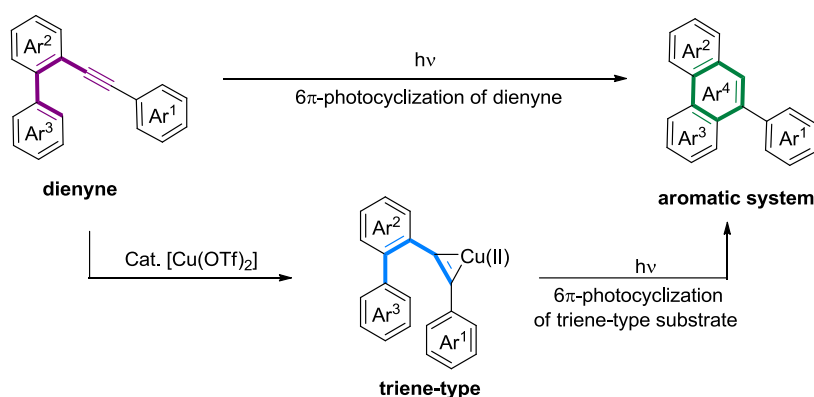
Cu(II)-catalyzed 6 π -photocyclization of dienynes

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Keywords: 6 π -photocyclization, photochemistry, dienyne, alkyne, phenanthrene

ABSTRACT: The first 6 π -photocyclization of dienynes was developed, which provides a new and effective protocol for the synthesis of 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 alkene-type moiety,

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4 which means that the dienyne reactant is converted into a triene-type substrate. Thus,
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7 this reaction proceeds *via* a Cu(II)-catalyzed 6π -photocyclization of triene-type
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10 derivatives.

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15 6π -Photocyclization¹ is a kind of classical photochemical reaction, which is quite
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17 different from thermocyclizations that have been well established by many metal
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19 catalysts² or halonium ions.³ It has a rich history. Since Srimivansan reported the first
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21 example in 1963,⁴ numerous achievements have been reported in this field.⁵ In
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23 modern organic chemistry, such a kind of reactions provide attractive methods for the
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25 preparation of cyclohexa-1,3-diene derivatives, which have been found wide
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27 applications in the synthesis of various medicines,⁶ functionalized materials,⁷ and
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29 building blocks for organic synthesis.⁸ Although it has been studied for quite a long
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31 time, the investigation of 6π -photocyclization is still limited to triene substrates.⁹ To
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33 the best of our knowledge, there are indeed a few photo-induced cyclizations of
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35 dienyynes,¹⁰ however, it has been proved that such reactions did not proceed *via*
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37 6π -photocyclization process.¹⁰ It is well known that the 6π -photocyclization reaction
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39 proceeds *via* two key steps: the formation of a six-membered cyclic transition state
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41 and the following intramolecular 1,5-H shift.^{5a} In a conjugated triene system, it is
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43 quite easy to meet the above requirements (Scheme 1a).⁵ When a dienyne substrate is
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45 irradiated under ultraviolet light, an unstable allene intermediate might be generated
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47 *in situ*.^{10a} Subsequently, it could in principle aromatize *via* 1,5-H shift. However, such
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49 a 1,5-H shift is a high barrier process. Instead, isomerization *via* solvent involved
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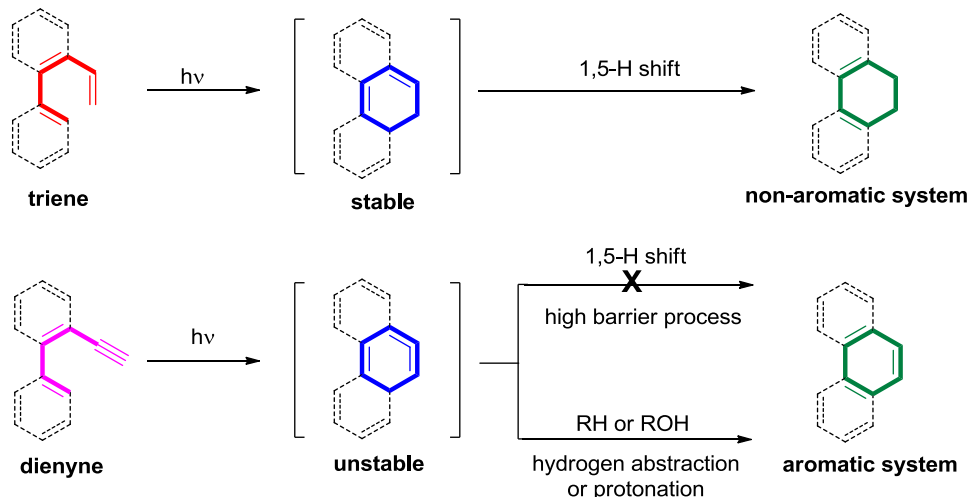
protonation-deprotonation will occur to realize the whole transformation, which is a totally different process from 6π -photocyclization (Scheme 1a).^{10a} Considering that 6π -photocyclization of dienyne will result in the formation of a new phenyl ring, which is totally different from that of trienes and very useful in organic synthesis, development of 6π -photocyclization of dienyne 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 process some C-C double bond properties. Based on this consideration, we questioned that 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 dienyne might proceed *via* triene-type species and afford a new aromatic system as the final product.

In our previous works, we found that the cyclization of 2-((4-methoxyphenyl)ethynyl)-1,1'-biphenyl **1a** could be catalyzed by the merging of $\text{Cu}(\text{OTf})_2$ and Eosin Y *via* visible light-induced single electron transfer (SET) process.¹² In the mechanism explorations, we found that when the single electron transfer mediate 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 wish to report this observation on the $\text{Cu}(\text{II})$ -catalyzed 6π -photocyclization of dienyne, which provides a novel protocol for the synthesis of

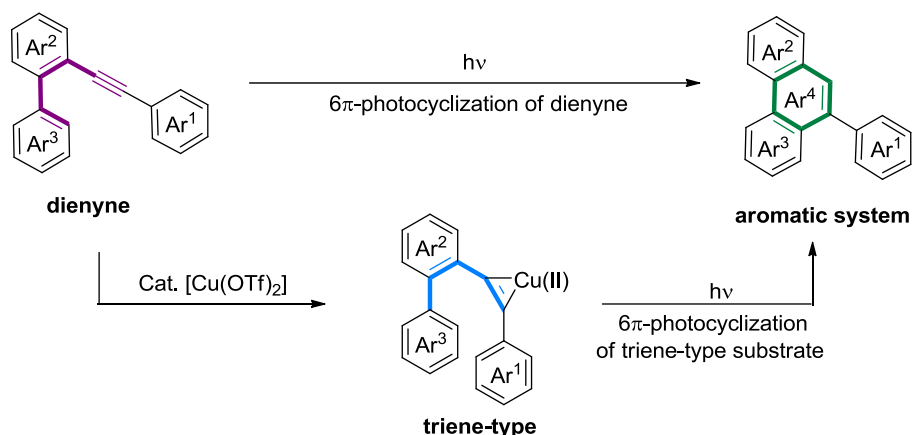
phenyl ring in excellent yields with nice functional group tolerance. (Scheme 1b).

Scheme 1. The 6 π -photocyclizations

(a) 6 π -photocyclization



(b) this work



In the beginning 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 tested (entries 2-5, Table 1). We were delight to see that the desired cyclization occurred in CH₃CN, 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 a 91% NMR yield after irradiated for 2 hours (entry 5, Table 1). Then we 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 photo irradiation energy (entries 10-12, Table 1). The reaction irradiated at $\lambda = 185$ & 254 nm gave **2a** in a slightly lower yield (entry 10, Table 1), but no reaction occurred at $\lambda = 313$ 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, $\lambda = 254$ nm), and rt) was applied in the next studies.

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 ₃ CN	10	254	2	30 (60) ^c

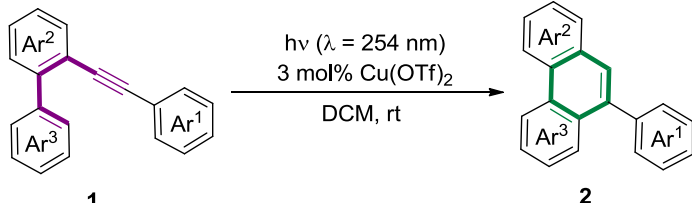
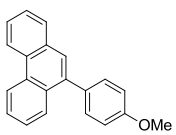
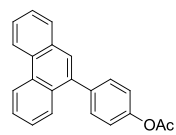
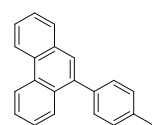
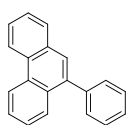
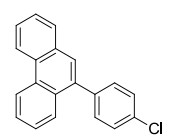
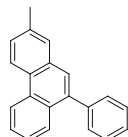
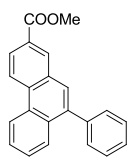
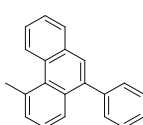
5	DCM	10	254	2	91
6	DCM	5	254	1	91
7	DCM	3	254	0.5	97 (0) ^c (96) ^d
8	DCM	1	254	6	94
9	DCM	0	254	0.5	NR (98) ^c
10	DCM	3	185&254	0.3	93
11	DCM	3	313	0.5	NR (98) ^c
12	DCM	3	365	0.5	NR (>99) ^c
13 ^e	DCM	3	-	0.5	NR (>99) ^c

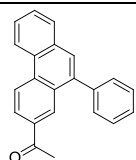
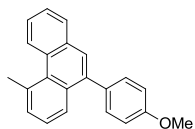
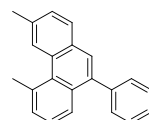
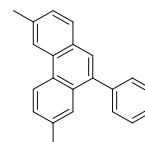
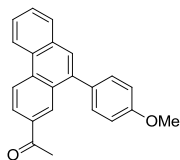
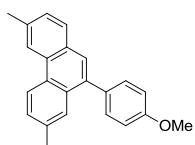
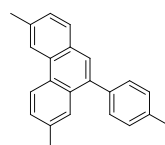
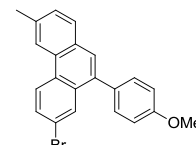
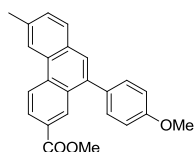
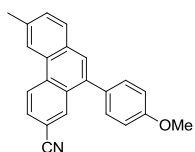
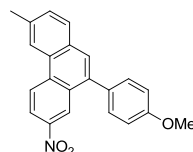
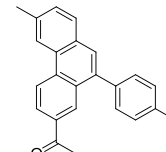
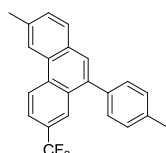
^a All reactions were carried out using **1a** (0.2 mmol) and Cu(OTf)₂ in anhydrous solvent (5 mL) in a quartz reaction flask irradiated by ultraviolet lamps (30 W) at rt under argon atmosphere. ^b The yield was determined by ¹H NMR analysis (400 MHz) of the crude reaction mixture employing CH₂Br₂ (0.2 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.

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

atom), and strong electron-withdrawing group (methoxycarbonyl, acetyl, nitrile, nitro, or trifluoromethyl) into the diyne 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 photo cyclization at all. Further explorations focused on the influence of the substituent position on Ar¹, Ar², or Ar³ gave a conclusion that there was no clear influence on the reactivity (**2c**, **2f**, and **2h**). Importantly, diynes 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 multi-substituted phenanthrenes might be found wide applications in organic synthesis.

Table 2. The 6 π -photocyclization of different diynes 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%

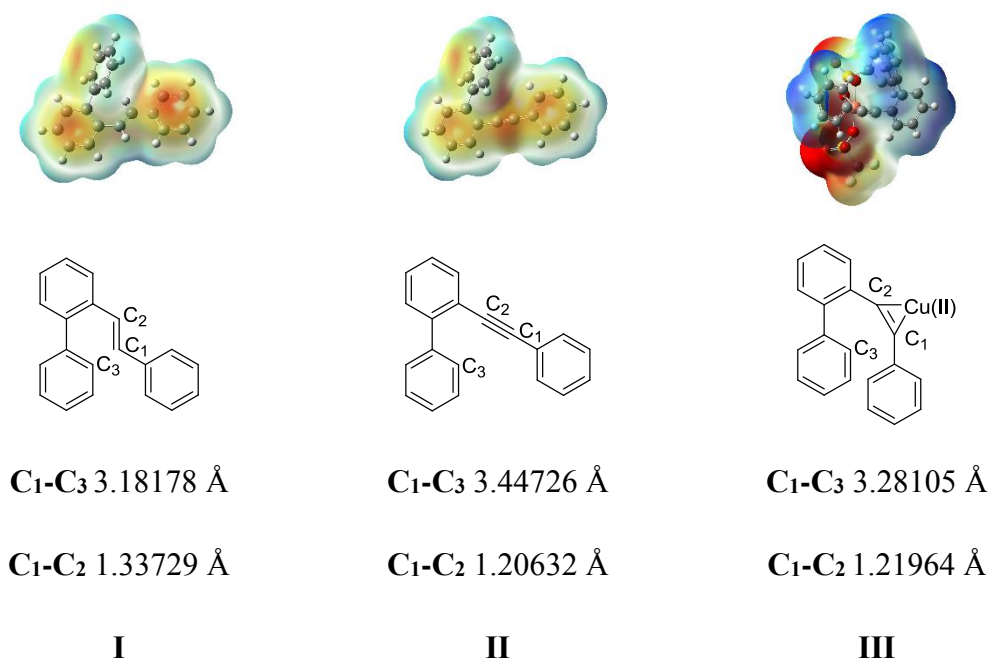
**2i**, 18.5 h, 85%**2j**, 1 h, 95%**2k**, 1 h, 96%**2l**, 50 min, 95%**2m**, 50 min, 94%**2n**, 30 min, 98%**2o**, 30 min, 93%**2p**, 5 h, 84%**2q**, 6 h, 91%**2r**, 6 h, 92%**2s**, 6 h, 91%**2t**, 8.5 h, 88%**2u**, 10.5 h, 84%

^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, $\lambda = 254$ nm) at rt under argon atmosphere. Isolated yield was reported.

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 M06-2X level. The distance between C₁ and C₃ is 3.18 Å in **I** and 3.45 Å in **II**. While 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 C₁-C₂ is 1.34 Å in **I** and 1.21 Å in **II**. While 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 6 π -photocyclization of dienyne turned into 6 π -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.

Scheme 2. The interaction of Lewis acid catalysis and C-C triple bond

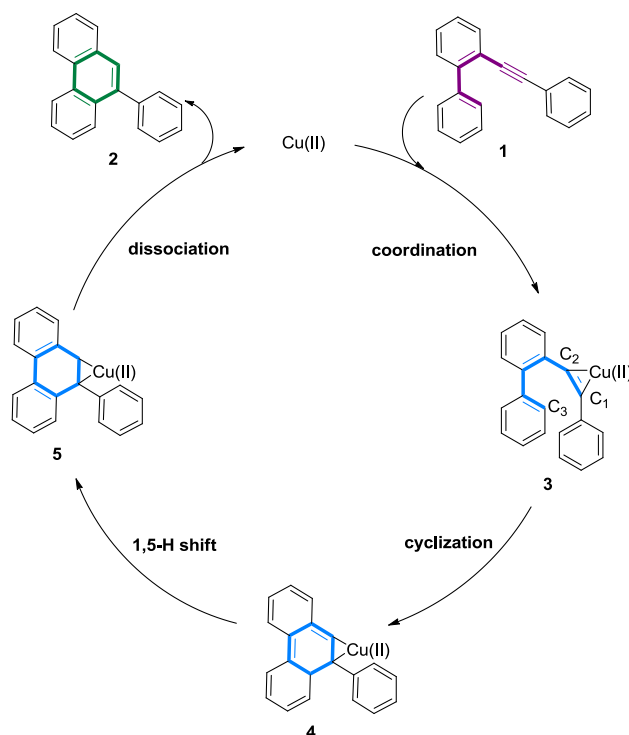


The computer calculation indicated that the coordination of Cu(II) with alkynes rendered changes of the spatial configuration of the dienyne. On the other hand, it was likely that this coordination could also influence the efficiency of UV absorption. Hence, we monitored the UV absorption of **1a** as well as a mixture of **1a** and Cu(OTf)₂ (**1a**:Cu(OTf)₂ = 1:1) at λ = 254 nm (Figures S5 and S6, in the Supporting

Information). The molar absorption coefficient was $2.88 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $3.15 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. Obviously, the UV absorption increased when $\text{Cu}(\text{OTf})_2$ was added, which might suggest that the reactivity could be improved in the presence of $\text{Cu}(\text{OTf})_2$.

Based on the above experimental evidence and literature reports,¹³ a possible mechanism was proposed as showed in Scheme 3. The coordination of $\text{Cu}(\text{II})$ 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 $\text{Cu}(\text{II})$ -alkyne complex **3** was irradiated by ultraviolet light, the six-membered ring intermediate **4** could be formed. In this species, the $\text{Cu}(\text{II})$ -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 $\text{Cu}(\text{II})$ -alkene complex **5**. Finally, the $\text{Cu}(\text{II})$ 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 $\text{Cu}(\text{OTf})_2$ -catalyzed 6π -photocyclization of dienynes, which 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 condition, 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 M06-2X level. Anhydrous DCM was distilled with CaH_2 . **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-1u** (0.20 mmol),

Cu(OTf)₂ (0.006 mmol), and anhydrous DCM (5 mL) were added subsequently into a 25 mL of 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-2u**.

9-(4-methoxyphenyl)phenanthrene (2a).¹² Liquid (55 mg, 96%); ¹H NMR (400 MHz, CDCl₃) 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-Acetoxyphenyl)phenanthrene (2b).¹² Liquid (58 mg, 93%); ¹H NMR (400 MHz, CDCl₃) 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%); ¹H NMR (400 MHz, CDCl₃) 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%); ¹H NMR (400 MHz, CDCl₃) 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%); ¹H NMR (400 MHz, CDCl₃) 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%); ¹H NMR (400 MHz, CDCl₃) 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%); ¹H NMR (400 MHz, CDCl₃) 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%); ¹H NMR (400 MHz, CDCl₃) 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%); ¹H NMR (400 MHz, CDCl₃) 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%); ¹H NMR (400 MHz, CDCl₃) 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%); ¹H NMR (400 MHz, CDCl₃) 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).

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4 *2,6-Dimethyl-10-phenylphenanthrene (2l)*.¹⁷ Liquid (54 mg, 95%); ¹H NMR (400
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6 MHz, CDCl₃) 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
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8 (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).

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11 *10-(4-Methoxyphenyl)-2-acetylphenanthrene (2m)*.¹⁶ Solid (61 mg, 94%); ¹H NMR
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13 (400 MHz, CDCl₃) δ 8.83 (d, *J* = 8.4 Hz, 1 H), 8.74 (d, *J* = 8.8 Hz, 1 H), 8.58 (s, 1 H),
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15 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* =
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17 8.8 Hz, 2 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 3.94 (s, 3 H), 2.62 (s, 3 H).

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20 *10-(4-Methoxyphenyl)-2,6-dimethylphenanthrene (2n)*.¹⁶ Solid (62 mg, 98%); ¹H
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22 NMR (400 MHz, CDCl₃) δ 8.63 (d, *J* = 8.4 Hz, 1 H), 8.45 (s, 1 H), 7.74 (d, *J* = 8.0 Hz,
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24 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,
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26 *J* = 8.4 Hz, 2 H), 3.90 (s, 3 H), 2.62 (s, 3 H), 2.46 (s, 3 H).

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29 *2,6-Dimethyl-10-(p-tolyl)phenanthrene (2o)*.¹² Liquid (55 mg, 93%); ¹H NMR (400
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31 MHz, CDCl₃) 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
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33 (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),
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35 2.48 (s, 3 H), 2.46 (s, 3 H).

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38 *2-Bromo-10-(4-methoxyphenyl)-6-methylphenanthrene (2p)*.¹⁶ Solid (64 mg, 84%);
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40 ¹H NMR (400 MHz, CDCl₃) δ 8.60 (d, *J* = 8.8 Hz, 1 H), 8.43 (s, 1 H), 8.04 (s, 1 H),
41
42 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
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44 H), 7.06 (d, *J* = 8.8 Hz, 2 H), 3.92 (s, 3 H), 2.64 (s, 3 H).

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47 *10-(4-Methoxyphenyl)-6-methyl-2-methoxycarbonylphenanthrene (2q)*.¹⁶ Solid (65
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49 mg, 91%); ¹H NMR (400 MHz, CDCl₃) δ 8.80 (d, *J* = 8.8 Hz, 1 H), 8.67 (s, 1 H), 8.52
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51 (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
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(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%);
¹H NMR (400 MHz, CDCl₃) 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%);
¹H NMR (400 MHz, CDCl₃) 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%); ¹H
NMR (400 MHz, CDCl₃) 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%); ¹H NMR (400 MHz, CDCl₃) 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

Spectral distribution of irradiance density for the UV lamps.

Molar absorption coefficients.

The computer simulations and calculations.

¹H NMR spectra of all the products.

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Notes

The authors declare no competing financial interest.

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