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Air-Driven Potassium Iodide-Mediated Oxidative Photocyclization of Stilbene Derivatives

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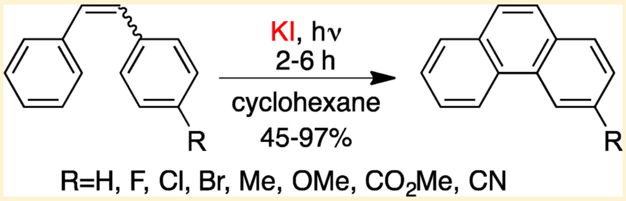
S *Supporting Information*

ABSTRACT: A new method has been developed for the potassium iodide-mediated oxidative photocyclization of stilbene derivatives. Compared with conventional iodine-mediated oxidative photocyclization reactions, this new method requires shorter reaction times and affords cyclized products in yields of 45−97%. This reaction proceeds with a catalytic amount of potassium iodide and works in an air-driven manner without the addition of an external scavenger. The radical-mediated oxidative photocyclization of stilbene derivatives using TEMPO was also investigated.



■ INTRODUCTION

Oxidative photocyclization has been widely used to synthesize various compounds, including phenanthrene derivatives,[1,2] helicenes,[3,4] and a variety of polycyclic aromatic hydrocarbons (PAHs).[1,2,5,6] One of the most popular methods for the oxidative photocyclization of stilbene derivatives is the Mallory reaction, which involves the use of catalytic iodine to oxidize dihydrophenanthrene intermediates.[7,8] Although this procedure has been successfully applied to many substrates, its use has been limited by the formation of several byproducts, including hydrogen peroxide and hydrogen iodide, which can cause undesired side reactions, leading to poor yields. To avoid side reactions, Katz proposed the use of an excess of propylene oxide to trap troublesome byproducts.[9] THF has also been reported to work as a scavenger for hydrogen iodide.[10] According to the conditions reported by Katz, it is necessary to add 1 equiv of iodine because the iodide ions formed during the reaction would be trapped by propylene oxide. The use of increasing amounts of iodine has some drawbacks because iodine itself can have an adverse impact on the oxidative photocyclization. For example, iodine has been reported to quench the excited states of stilbenes.[7,9] Iodine also caused overannulation during the synthesis of helicene, leading to the formation of undesired products.[11]

In this report, we describe the use of potassium iodide instead of iodine to mediate the oxidative photocyclization of stilbene derivatives. The key advantages to this new method over existing procedures include short reaction times and good to excellent yields, as well as operational simplicity.

■ RESULTS AND DISCUSSION

During the course of our recent work toward the synthesis of PAHs[12] and related compounds,[13] we evaluated various reaction conditions in an attempt to improve the oxidative photocyclization of stilbenes in terms of the reaction time, yield, and facile purification process. In this regard, we evaluated several scavengers for hydrogen iodide, which is one of the most harmful byproducts formed in this reaction. When we used potassium carbonate,[14] we noticed that the color of the reaction mixture (i.e., the purple coloration derived from iodine) became deeper in appearance and that the ^{1}H NMR spectrum of the crude mixture was much cleaner than those obtained using the Mallory conditions. Given that hydrogen iodide should react with potassium carbonate to afford potassium iodide, we hypothesized that the potassium iodide could be playing an important role in this reaction. We subsequently investigated the oxidative photocyclization of stilbenes with iodine and/or potassium iodide, and the results revealed that the reaction proceeded well with potassium iodide in the absence of iodine. These findings encouraged us to conduct a full study on the potassium iodide-mediated oxidative photocyclization of stilbenes and styryl heteroarenes.

We initially evaluated five different metal iodides to find the most appropriate inorganic iodide for the oxidative photocyclization of *cis*-stilbene **1a**. These screening reactions were carried out using a 1 mM cyclohexane solution of **1a**. The sample solution was irradiated with a 450 W high-pressure mercury lamp for 1 h, and the efficiency of the reaction was estimated by ^{1}H NMR spectroscopy based on the amount of phenanthrene formed during the reaction. Although all of the metal iodides evaluated in this study afforded phenanthrene, potassium iodide gave the best yield (Table 1).

Table 2 shows our results for the optimization of the reaction conditions with potassium iodide together with the results obtained under the conventional conditions using iodine. The yields of phenanthrene **2a** were estimated by ^{1}H NMR spectroscopy under the same reaction conditions (i.e.,

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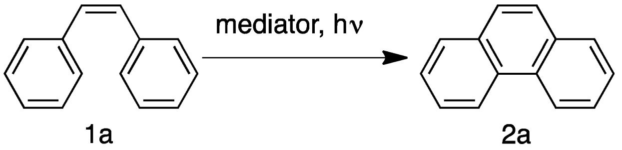
Table 1. Metal Iodide-Mediated Oxidative Photocyclization of *cis*-Stilbene 1a[a]



entry	mediators	yields[b] (%)
1	LiI	22
2	NaI	19
3	KI	51
4	CsI	38
5	CuI	12

[a] A 1 mM solution of **1a** in cyclohexane (10 mL) was irradiated with a 450 W high-pressure mercury lamp for 1 h in the presence of 10 equiv of mediator. [b] Yields were estimated by ^{1}H NMR spectroscopy using dimethyl sulfone as an internal standard.

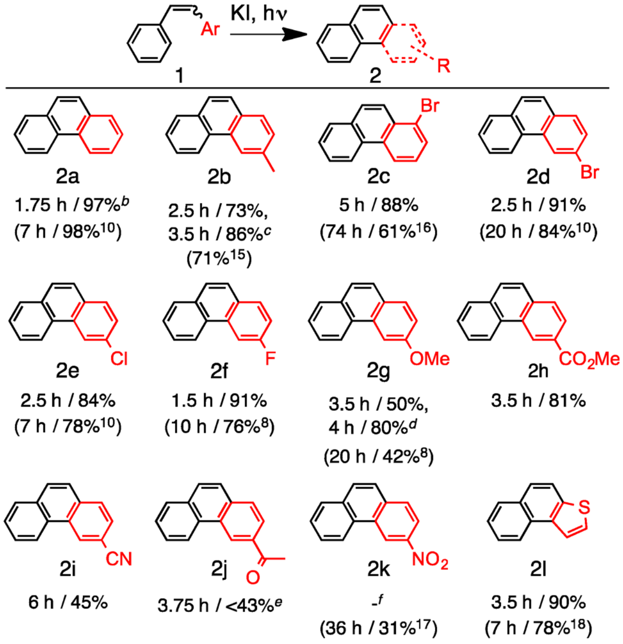
Table 2. Optimization of Potassium Iodide-Mediated Oxidative Photocyclization of *cis*-Stilbene 1a[a]

entry	mediator (equiv)	solvents	yields[b] (%)
1	I_2 (0.03)	cyclohexane	28[c]
2	I_2 (1)	cyclohexane	11[d]
3	KI (100)	cyclohexane	28
4	KI (100)	cyclohexane	–[e]
5	KI (10)	cyclohexane	51
6	KI (1)	cyclohexane	44
7	KI (0.1)	cyclohexane	1
8	KI (0.1)	cyclohexane	37[f]
9	KI (0.01)	cyclohexane	17[f]
10	KI (10)	benzene	27
11	KI (10)	toluene	14

[a] A solution (1 mM) of **1a** in solvent (10 mL) was irradiated with a 450 W high-pressure mercury lamp for 1 h. [b] Yields were estimated by ^{1}H NMR spectroscopy using dimethyl sulfone as an internal standard. [c] In optimized conditions, the yield was reported to be 73%.[1,7,8] [d] Propylene oxide (100 equiv) was used. [e] Degassed solvent was used. [f] Potassium iodide was dissolved in methanol and then evaporated to enlarge the surface area.

irradiation with a 450 W high-pressure mercury lamp for 1 h). The Mallory reaction (Table 2, entry 1) and Katz's conditions (Table 2, entry 2) afforded 28% and 11% yields, respectively. Although the use of a large excess (100 equiv) of potassium iodide afforded phenanthrene in 28% yield (Table 2, entry 3), we did not observe any of the desired target when we used a degassed solvent, indicating that this reaction requires oxygen (Table 2, entry 4). As for the amount of mediator, we found that 10 equiv of potassium iodide gave the best results (Table 2, entries 3 and 5−9). Notably, the direct use of 0.1 equiv of commercially available granular potassium iodide gave a poor yield of **2a** (Table 2, entry 7), whereas the use of the same amount of potassium iodide as a thinly spread film on the inside of the reaction flask gave a much better yield (Table 2, entry 8). This pretreatment process therefore demonstrated that the surface area of the potassium iodide had a considerable impact on the yield of the product. Notably, this result also shows that the potassium iodide was acting as a catalyst, because the yield of the product in the latter of these two cases was almost 4 times higher than it would be if the potassium iodide was being consumed stoichiometrically. This result was further confirmed when the amount of potassium iodide was reduced to 0.01 equiv with the reaction affording a 17% yield of the desired product (Table 2, entry 9). Several solvents were also screened against this reaction, and the results revealed that cyclohexane gave the best results (Table 1, entries 5, 10, and 11).

Table 3. Potassium Iodide-Mediated Oxidative Photocyclization of Stilbenes and Styrylthiophene[a]



[a] A solution (1 mM) of substrate **1** and potassium iodide (1 equiv) in cyclohexane (1300 mL) was irradiated with a 450 W high-pressure mercury lamp. Commercially available granular potassium iodide was used without any pretreatment. Reported reaction times and yields are shown in parentheses. [b] The reaction was almost completed after 1 h irradiation. See ^{1}H NMR spectra of crude product after 1 h irradiation as well as that of purified product in Supporting Information. [c] A solution (1 mM) of stilbene derivative and potassium iodide (5 equiv) in cyclohexane (900 mL) was used. [d] I_2 (1 equiv) with 10 equiv of K_2CO_3 was used. [e] A small amount of impurity remained after chromatographic purification. [f] No target material was observed.

With the optimized conditions in hand for this potassium iodide-mediated oxidative photocyclization, we proceeded to investigate its functional group tolerance using several stilbene derivatives bearing different functional groups, as well as styrylthiophene (Table 3). All of these reactions were monitored periodically by removing a small amount of the reaction mixture and subjecting it to ^{1}H NMR analysis after the evaporation of the solvent. All of these experiments were conducted on a much larger scale (100 times) than those described in Table 2 using the appropriate amount of potassium iodide. From a practical perspective, the use of a smaller amount of potassium iodide would be better. A pilot experiment was conducted using 1 equiv of potassium iodide and afforded an excellent yield of the desired product over a short reaction time of 1 h. Based on this result, we decided to use 1 equiv of potassium iodide in the following experiments. In most cases, the isolated yields were good to excellent, although stilbenes bearing a strong electron withdrawing group afforded poor yields of the cyclized products. The yield for the reaction of compound **1g** bearing a *p*-methoxy phenyl group was worse than expected most likely because of the cleavage of the ether

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bond by the hydrogen iodide byproduct. The yield of **2g** was improved to 80% when iodine was used together with potassium carbonate. This result demonstrated that the use of base would work well for substrates with acid sensitive substituents. These reaction conditions also worked well for the synthesis of naphthothiophene **2l**.

A plausible reaction mechanism for the potassium iodide-mediated oxidative photocyclization of stilbene derivatives is shown in Figure 1. The first step of this reaction would be the oxidative photocyclization of the substrate using the oxygen found in air, as supported by this reactions requirement for oxygen (Table 2, entries 3 and 4). This step would lead to the formation of hydrogen peroxide, which would be used to oxidize potassium iodide to give iodine together with potassium hydroxide. The resulting iodine would then act as an oxidant to afford the phenanthrene derivative and hydrogen iodide, which would react with potassium hydroxide to produce potassium iodide together with water. This reaction cycle would also lead to the formation of potassium iodide for the next cycle. This mechanism is supported by the observation that potassium iodide worked catalytically (Table 2, entries 8 and 9). According to this mechanism, a second molecule of hydrogen peroxide would be derived from oxygen for the next step, suggesting that the catalytic cycle in this reaction is dependent on air. Although the Mallory reaction[7,8] is also air-driven, there are several distinct advantages to our newly developed reaction conditions, including the efficient removal of the troublesome byproducts hydrogen peroxide and hydrogen iodide to reproduce potassium iodide together with water. Compared with Katz's conditions, where a scavenger is required to remove the hydrogen iodide formed during the reaction,[9] this new method does not require the addition of any extra reagents for this purpose because a scavenger (potassium hydroxide in this case) is continuously supplied in catalytic cycle. In terms of its physical appearance, the reaction mixture was initially colorless and gradually became purple, indicating the constant presence of a small amount of iodine in the reaction mixture.

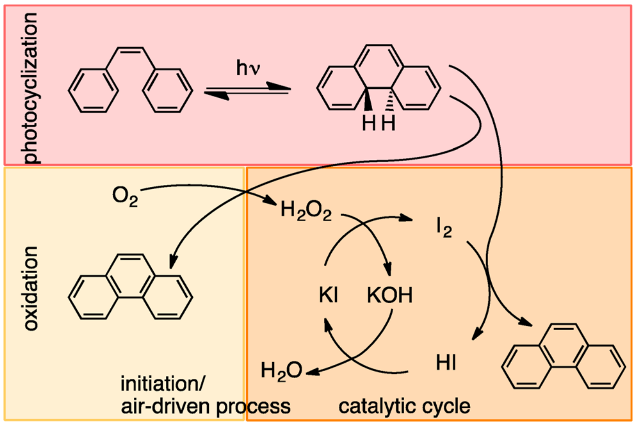


Figure 1. Plausible reaction mechanism for the potassium iodide-mediated oxidative photocyclization of stilbene.

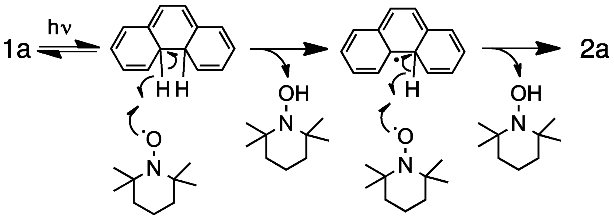
To determine whether this reaction involves the formation of a radical species,[1,7] we investigated the effect of adding TEMPO as a radical scavenger to the potassium iodide-mediated oxidative photocyclization of *cis*-stilbene **1a**. It was envisaged that the addition of TEMPO would lead to a decrease in the yield of target compound because similar examples have been reported in the literature.[19] Surprisingly, however, we found that TEMPO accelerated the reaction. Intrigued by this result, we investigated the effects of several other radical species to determine whether they could be used to oxidize the dihydrophenanthrene intermediate formed during this oxidative photocyclization in the absence of a conventional oxidant (Table 4). These experiments were conducted under the same conditions used for the experiments described in Table 1 except for the addition of a radical-generating species such as BPO, AIBN, or TEMPO. The results revealed that all of these species were capable of promoting the oxidative photocyclization (Table 4, entries 1−3). The TEMPO-mediated photocyclization gave a 97% yield of the cyclized product after 4.5 h of irradiation, which is the same as the isolated yield achieved in the potassium iodide-mediated reaction (**2a** in Table 3). Under these reaction conditions, the radical would most likely abstract a hydrogen atom from the dihydrophenanthrene intermediate. This reaction would therefore be noncatalytic because the radical species would be consumed during this step to give a neutral species (Scheme 1). In sharp contrast to the results observed with the radical-generating species, the addition of the radical scavenger BHT completely suppressed the reaction, with no **2a** being detected (Table 4, entry 4). This result was attributed to the fact that BHT acts as a hydrogen donor in radical reactions. BHT would therefore be unable to abstract hydrogen from the dihydrophenathrene intermediate, which would prevent the reaction from proceeding. Considering the involvement of radicals in the oxidative photocyclization of stilbenes, it is also possible that the oxidation step described in Figure 1 involves a hydrogen abstraction process.

Table 4. Radical Related Compound Mediated Oxidative Photocyclization of *cis*-Stilbene 1a[a]

entry	radical related compounds	yields[b] (%)
1	BPO	18
2	AIBN	32(68[c])
3	TEMPO	25(97[d])
4	BHT	–

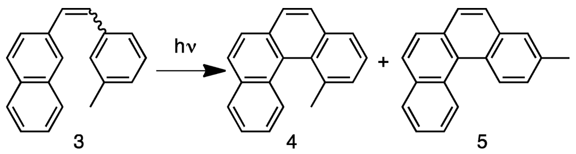
[a] A solution (1 mM) of **1a** in cyclohexane (10 mL) was irradiated with a 450 W high-pressure mercury lamp for 1 h in the presence of 10 equiv of a radical related compound. [b] Yields were estimated by ^{1}H NMR spectroscopy using dimethyl sulfone as an internal standard. [c] Isolated yield after 7.5 h of irradiation with 10 equiv of AIBN. [d] Isolated yield after 4.5 h of irradiation with 10 equiv of TEMPO.

Scheme 1. Plausible Reaction Mechanism for the TEMPO-Mediated Oxidative Photocyclization of Stilbene



Lastly, we investigated the regioselectivity of the oxidative photocyclization using the 2-styrylnaphthalene derivative **3** as a model substrate. This reaction was conducted under the various conditions established in the current study to determine whether they had any impact on the regioselectivity (Table 5). The standard Mallory conditions gave compound **5** as the

Table 5. Photocyclization of the 2-Styrylnaphthalene Derivative 3[a]



entry	mediators (equiv)	ratios (4/5)[b]
1	I_2 (1)	36:64
2	KI (10)	54:43
3	TEMPO (20)[c]	69:31
4	AIBN (20)	49:51

[a] A solution (1 mM) of compound **3** in cyclohexane (10 mL) was irradiated with a 450 W high-pressure mercury lamp for 3 (entry 1) or 2 (entries 2–4) h. [b] Ratios were estimated by ^{1}H NMR analysis of the crude products. Starting material was completely consumed at this point. [c] Degassed solvent was used.

major product, which is consistent with previous reports from the literature.[20] In contrast, the potassium iodide-mediated reaction showed a slight preference for compound **4**. Notably, the TEMPO conditions gave compound **4** as the major product. This change in selectivity therefore suggests that the iodine- and TEMPO-mediated reactions operate via a different reaction mechanism to the Mallory reaction. Further experiments are needed to explain these differences.

■ CONCLUSION

In conclusion, we have demonstrated that potassium iodide is an efficient mediator for the oxidative photocyclization of stilbene derivatives. This reaction proceeds with a catalytic amount of potassium iodide and works in an air-driven manner without the need for an external scavenger to remove any byproducts. In contrast to conventional methods, this new procedure is simple, requires short reaction times, and affords good to excellent yields of the cyclized products. Furthermore, potassium iodide is easy to handle, nontoxic, and environmentally friendly and therefore represents an attractive alternative to conventional oxidants such as iodine. The stable organic radical TEMPO was also found to be a good mediator for the oxidative photocyclization of stilbene derivatives. It is noteworthy that iodine has been used more or less exclusively as an oxidant for oxidative photocyclization reactions to date and very few attempts have been made to seek useful alternatives. Our findings will therefore provide synthetic chemists with an efficient alternative to iodine and provide greater scope for the synthesis of target materials that would otherwise be difficult to access.

■ EXPERIMENTAL SECTION

General Methods. Commercially available granular potassium iodide was used without any pretreatment, except for Table 2, entries 8 and 9. A 450 W high-pressure mercury lamp was used for photoreactions. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on a 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. Silica gel column chromatography was performed using the eluent shown in each experiment.

General Procedure for the Preparation of Stilbene Derivatives 1b–k, Styrylthiophene 1l, and 2-(3-Methylstyryl)-naphthalene (3). *Typical Example: 4-Methylstilbene (**1b**, R = 4-Me).* To a solution of benzyltriphenylphosphonium chloride (2.997 g, 7.71 mmol) and lithium hydroxide monohydrate (0.6559 g, 15.6 mmol) in 2-propanol (90 mL) was added *p*-methylbenzaldehyde (0.8465 g, 7.05 mmol), and the solution was stirred under reflux for 4.5 h. After the solvent was evaporated under reduced pressure, the residue was dissolved in dichloromethane. The solution was washed with brine, dried over magnesium sulfate, and filtered, and the solvent was evaporated under reduced pressure. The residue was separated by column chromatography (SiO_2/hexane) to give 4-methylstilbene (**1b**, 1.255 g, 6.46 mmol, 92%). This compound was obtained in (*E*)/(*Z*) mixture ((*E*)-isomer/(*Z*)-isomer = 1:1) as a white solid and colorless oil. NMR spectral data of product matched those reported in the literature.[21,22]

1b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (m, 2H, (*E*)), 7.43–7.33 (m, 4H, (*E*)), 7.27–7.16 (m, 10H), 7.08 (d, *J* = 1.2 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.55 (s, 2H, (*Z*)), 2.36 (s, 3H, (*E*)), 2.31 (s, 3H, (*Z*)).

*2-Bromostilbene (**1c**, R = 2-Br).* By following the general procedure for the preparation of compound **1b**, the reaction of benzyltriphenylphosphonium chloride (2.997 g, 7.71 mmol) with *o*-bromobenzaldehyde (1.301 g, 7.03 mmol) in the presence of lithium hydroxide monohydrate (0.6511 g, 15.5 mmol) under reflux for 2 h gave 2-bromostilbene (**1c**, 1.729 g, 6.68 mmol, 95%). This compound was obtained in (*E*)/(*Z*) mixture ((*E*)-isomer/(*Z*)-isomer = 0.6:1) as a pale yellow oil. NMR spectral data of product matched those reported in the literature.[23]

1c: ^{1}H NMR (300 MHz $CDCl_3$) δ 7.68 (dd, *J* = 9.0, 3.0 Hz, 0.6H, (*E*)), 7.62–7.54 (m, 2.8H), 7.47 (d, *J* = 18 Hz, 0.6H, (*E*)), 7.40–7.29 (m, 2.4H, (*E*)), 7.12–7.01 (m, 9.2H), 6.69 (d, *J* = 12 Hz, 1H, (*Z*)), 6.61 (d, *J* = 12 Hz, 1H, (*Z*)).

*4-Bromostilbene (**1d**, R = 4-Br).* By following the general procedure for the preparation of compound **1b**, the reaction of benzyltriphenylphosphonium chloride (3.003 g, 7.72 mmol) with *p*-bromobenzaldehyde (1.311 g, 7.09 mmol) in the presence of lithium hydroxide monohydrate (0.6577 g, 15.7 mmol) under reflux for 2 h gave 4-bromostilbene (**1d**, 1.791 g, 6.91 mmol, 97%). This compound was obtained in (*E*)/(*Z*) mixture ((*E*)-isomer/(*Z*)-isomer = 1.1:1) as a white solid. NMR spectral data of product matched those reported in the literature.[24,25]

1d: ^{1}H NMR (300 MHz $CDCl_3$) δ 7.52–7.47 (m, 4.4H, (*E*)), 7.39–7.23 (m, 12.4H), 7.13–6.99 (m, 4.3H), 6.63 (d, *J* = 12 Hz, 1H, (*Z*)), 6.50 (d, *J* = 12 Hz, 1H, (*Z*)).

*4-Chlorostilbene (**1e**, R = 4-Cl).* By following the general procedure for the preparation of compound **1b**, the reaction of benzyltriphenylphosphonium chloride (3.016 g, 7.76 mmol) with *p*-chlorobenzaldehyde (0.9812 g, 6.98 mmol) in the presence of lithium hydroxide monohydrate (0.6525 g, 15.6 mmol) under reflux for 2 h gave 4-chlorostilbene (**1e**, 1.399 g, 6.52 mmol, 93%). This compound was obtained in (*E*)/(*Z*) mixture ((*E*)-isomer/(*Z*)-isomer = 1:1) as a white solid. NMR spectral data of product matched those reported in the literature.[26,27]

1e: ^{1}H NMR(300 MHz $CDCl_3$) δ 7.52–7.17 (m, 18H), 7.07 (s, 2H, (*E*)), 6.63 (d, *J* = 12 Hz, 1H, (*Z*)), 6.52 (d, *J* = 12 Hz, 1H, (*Z*)).

*4-Fluorostilbene (**1f**, R = 4-F).* By following the general procedure for the preparation of compound **1b**, the reaction of benzyltriphenylphosphonium chloride (3.000 g, 7.71 mmol) with *p*-fluorobenzaldehyde (0.8724 g, 7.03 mmol) in the presence of lithium hydroxide monohydrate (0.6570 g, 15.7 mmol) under reflux for 2.5 h gave 4-fluorostilbene (**1f**, 1.122 g, 5.66 mmol, 81%). This compound was obtained in (*E*)/(*Z*) mixture ((*E*)-isomer/(*Z*)-isomer = 0.7:1) as a white solid. NMR spectral data of product matched those reported in the literature.[25,28]

1f: ^{1}H NMR (300 MHz $CDCl_3$) δ 7.51–7.46 (m, 2.8H, (*E*)), 7.39–7.29 (m, 1.4H, (*E*)), 7.24–7.18 (m, 7.7H), 7.11–6.98 (m, 2.8H, (*E*)), 6.93–6.88 (m, 2H, (*Z*)), 6.60 (d, *J* = 12 Hz, 1H, (*Z*)), 6.55 (d, *J* = 12 Hz, 1H, (*Z*)); ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$) δ −114 (s), −115 (s).

*4-Methoxystilbene (**1g**, R = 4-OMe).* By following the general procedure for the preparation of compound **1b**, the reaction of benzyltriphenylphosphonium chloride (2.994 g, 7.70 mmol) with *p*-methoxybenzaldehyde (0.9551 g, 7.02 mmol) in the presence of lithium hydroxide monohydrate (0.6575 g, 15.7 mmol) under reflux for 2 h gave 4-methoxystilbene (**1g**, 1.373 g, 6.53 mmol, 93%). This compound was obtained in (*E*)/(*Z*) mixture ((*E*)-isomer/(*Z*)-isomer

= 1:1) as a white solid. NMR spectral data of product matched those reported in the literature.[29,30]

1g: ^{1}H NMR(300 MHz CDCl$_3$) δ 7.51−7.44 (m, 4H, (*E*)), 7.37−7.32 (m, 2H), 7.29−7.10 (m, 8H), 7.07 (d, *J* = 16.2 Hz, 1H), 6.98 (d, *J* = 17.7 Hz, 1H), 6.92−6.89 (m, 2H), 6.77−6.74 (m, 2H, (*Z*)), 6.56−6.48 (m, 2H, (*Z*)), 3.83 (s, 3H, (*E*)), 3.79 (s, 3H, (*Z*)).

*4-Cyanostilbene (**1i**, R = 4-CN).* By following the general procedure for the preparation of compound **1b**, the reaction of benzyltriphenylphosphonium chloride (2.994 g, 7.70 mmol) with *p*-cyanobenzaldehyde (0.9183 g, 7.00 mmol) in the presence of lithium hydroxide monohydrate (0.6547 g, 15.6 mmol) under reflux for 24 h gave 4-cyanostilbene (**1i**, 1.380 g, 6.72 mmol, 96%). This compound was obtained in (*E*)/(*Z*) mixture ((*E*)-isomer/(*Z*)-isomer = 0.9:1) as a white solid. NMR spectral data of product matched those reported in the literature.[31,32]

1i: ^{1}H NMR(300 MHz CDCl$_3$) δ 7.66−7.48 (m, 7.5H), 7.42−7.30 (m, 5H), 7.25−7.18 (m, 5.5H), 7.09 (d, *J* = 18 Hz, 0.9H, (*E*)), 6.77 (d, *J* = 12.0 Hz, 1H, (*Z*)), 6.57 (d, *J* = 12.0 Hz, 1H, (*Z*)).

*4-Acetylstilbene (**1j**, R = 4-COMe).* By following the general procedure for the preparation of compound **1b**, the reaction of benzyltriphenylphosphonium chloride (2.991 g, 7.70 mmol) with *p*-acetylbenzaldehyde (1.045 g, 7.05 mmol) in the presence of lithium hydroxide monohydrate (0.6521 g, 15.5 mmol) under reflux for 2.5 h gave 4-acetylstilbene (**1j**, 0.9015 g, 4.06 mmol, 58%). This compound was obtained in (*E*)/(*Z*) mixture ((*E*)-isomer/(*Z*)-isomer = 1.2:1) as a white solid. NMR spectral data of product matched those reported in the literature.[33,34]

1j: ^{1}H NMR(300 MHz CDCl$_3$) δ 7.96 (d, *J* = 8.4 Hz, 2.4H, (*E*)), 7.81 (d, *J* = 8.4 Hz, 2H, (*Z*)), 7.61−7.53 (m, 4.8H), 7.40−7.21 (m, 11.8H), 7.13 (d, *J* = 16.2 Hz, 1.2H, (*E*)), 6.73 (d, *J* = 12.3 Hz, 1H, (*Z*)), 6.61 (d, *J* = 12.3 Hz, 1H, (*Z*)), 2.61 (s, 3.6H, (*E*)), 2.57 (s, 3H, (*Z*)).

*4-Nitrostilbene (**1k**, R = 4-NO$_2$).* By following the general procedure for the preparation of compound **1b**, the reaction of benzyltriphenylphosphonium chloride (2.996 g, 7.70 mmol) with *p*-nitrobenzaldehyde (1.058 g, 7.00 mmol) in the presence of lithium hydroxide monohydrate (0.6556 g, 15.6 mmol) under reflux for 2.5 h gave 4-nitrostilbene (**1k**, 1.430 g, 6.35 mmol, 91%). This compound was obtained in (*E*)/(*Z*) mixture ((*E*)-isomer/(*Z*)-isomer = 1.3:1) as a white solid. NMR spectral data of product matched those reported in the literature.[31,35]

1k: ^{1}H NMR(300 MHz CDCl$_3$) δ 8.23 (m, *J* = 7.2 Hz, 2.6H, (*E*)), 8.07 (m, *J* = 8.7 Hz, 2H, (*Z*)), 7.66−7.54 (m, 5.2H), 7.43−7.12 (m, 13.5H), 6.70 (d, *J* = 12.3 Hz, 1H, (*Z*)), 6.58 (d, *J* = 12.3 Hz, 1H, (*Z*)).

*1-Phenyl-2-(2-thienyl)ethene (**1l**).* By following the general procedure for the preparation of compound **1b**, the reaction of benzyltriphenylphosphonium chloride (3.001 g, 7.72 mmol) with 2-thiophenecarboxaldehyde (0.7914 g, 7.06 mmol) in the presence of lithium hydroxide monohydrate (0.6505 g, 15.5 mmol) under reflux for 2 h gave 1-phenyl-2-(2-thienyl)ethene (**1l**, 1.07 g, 5.74 mmol, 81%). This compound was obtained in (*E*)/(*Z*) mixture ((*E*)-isomer/(*Z*)-isomer = 1.6:1) as a white solid. NMR spectral data of product matched those reported in the literature.[36,37]

1l: ^{1}H NMR(300 MHz CDCl$_3$) δ 7.48−7.45 (m, 3.2H, (*E*)), 7.37−7.19 (m, 13.2H), 7.09−6.89 (m, 7.6H), 6.70 (d, *J* = 12 Hz, 1H, (*Z*)), 6.58 (d, *J* = 12 Hz, 1H, (*Z*)).

*1-(4-Methoxycarbonylphenyl)-2-phenylethene (**1h**, R = 4-CO$_2$Me).* A solution of benzyltriphenylphosphonium chloride (5.463 g, 14.0 mmol) and methyl 4-formylbenzoate (2.357 g, 14.4 mmol) in THF (100 mL) was stirred for 30 min at room temperature. To this reaction mixture was added a solution of sodium methoxide (2.272 g, 42.1 mmol) in THF (100 mL), and the solution was stirred for 40.5 h at room temperature and then under reflux for 3.5 h. After the solvent was evaporated under reduced pressure, the residue was dissolved in dichloromethane. The solution was washed with brine, dried over magnesium sulfate, and filtered, and the solvent was evaporated under reduced pressure. The residue was separated by column chromatography (SiO$_2$/chloroform) to give 1-(4-methoxycarbonylphenyl)-2-phenylethene (**1h**, 1.688 g, 7.08 mmol, 50%). This compound was obtained in (*E*)/(*Z*) mixture ((*E*)-isomer/(*Z*)-isomer = 0.5:1) as a white solid and colorless oil. NMR spectral data of product matched those reported in the literature.[34,38]

1h: ^{1}H NMR(300 MHz CDCl$_3$) δ 8.04 (m, 1H, (*E*)), 7.89 (m, 2H, (*Z*)), 7.59−7.53 (m, 2H, (*E*)), 7.41−7.20 (m, 9H), 7.13 (d, *J* = 15 Hz, 0.5H, (*E*)), 6.71 (d, *J* = 12 Hz, 1H, (*Z*)), 6.61 (d, *J* = 12 Hz, 1H, (*Z*)), 3.93 (s, 1.5H, (*E*)), 3.90 (s, 3H, (*Z*)).

*2-(3-Methylstyryl)naphthalene (**3**).* To a solution of 3-methylbenzonitrile (363.0 mg, 3.90 mmol) in dichloromethane (15 mL) was added DIBAL (1 M solution in hexane, 3.0 mL, 3.0 mmol) at −80 °C, and the mixture was stirred for 40 min then for 1.5 h at 0 °C. To the reaction mixture was added 1 M HCl(aq) (30 mL), and the solution was extracted with dichloromethane, dried over magnesium sulfate, and filtered, and the solvent was evaporated under reduced pressure. A solution of crude product, (2-naphthalenylmethyl)-triphenylphosphonium bromide (1.2040 g, 2.49 mmol) and lithium hydroxide monohydrate (215.5 mg, 5.14 mmol) in 2-propanol (50 mL) was stirred under reflux for 3 h. The solvent was evaporated under reduced pressure, and the residue was separated by column chromatography (SiO$_2$/hexane) to give 2-(3-methylstyryl)naphthalene (**3**, 458.3 mg, 1.88 mmol, 75%). This compound was obtained in (*Z*)/(*E*) mixture as a white solid. The structure of the (*E*)-isomer was confirmed because NMR spectral data matched those reported in the literature.[39] (*E*)-isomer: white solid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.85−7.80 (m, 4H), 7.74 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.50−7.41 (m, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.31−7.17 (m, 3H), 7.10 (d, *J* = 7.2 Hz, 1H), 2.40 (s, 3H). (*Z*)-isomer: colorless liquid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.88−7.66 (m, 3H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.44−7.37 (m, 2H), 7.35 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.13−6.97 (m, 4H), 6.72 (d, *J* = 12.0 Hz, 1H), 6.63 (d, *J* = 12.0 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 137.9, 137.3, 135.0, 133.5, 132.6, 130.8, 130.0, 129.8, 128.2, 128.09, 128.06, 128.01, 127.7, 127.4, 127.0, 126.0 (2C), 125.9, 21.4. Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.35; H, 6.52.

Optimization for Reaction Conditions of Oxidative Photocyclization of Diarylethenes by NMR (Tables 1, 2, 4, and 5). A 1 mM solution of starting material (*cis*-stilbene **1a** and compound **3** for Tables 1, 2, 4 and Table 5) in solvent (10 mL) in a 50 mL screw bottle was irradiated at a distance of 10 cm from a 450 W high-pressure mercury lamp in the presence of mediator described in the tables. Reaction conditions are shown in the footnotes of each table. After filtration of reaction mixture, the solvent was evaporated under reduced pressure. Yields were estimated by comparing integrals of products in ^{1}H NMR spectra with dimethylsulfone (0.300 mL of a stock solution of 10 mM dimethylsulfone in CDCl$_3$ was added to the NMR sample before measurement) as an internal standard.

In the oxidative photocyclization of compound **3**, NMR spectral data of product matched those reported in the literature.[40,41] The ratio of products was calculated based on the integrals of methyl proton in ^{1}H NMR spectra.

The yield of each experiment is described in Tables 1, 2, 4, and 5.

Preparative Scale Experiments for the Oxidative Photocyclization of Stilbenes and Styrylthiophene (Table 3). *Typical Example: Phenanthrene (**2a**).* To a 1 mM solution of *cis*-stilbene **1a** in cyclohexane (1300 mL) was added potassium iodide (0.2159 g, 1.30 mmol), and this reaction mixture was irradiated by 450 W high-pressure mercury lamp. Reaction was monitored by ^{1}H NMR spectra: 10 mL of reaction mixture was removed, and ^{1}H NMR spectrum was measured after the solvent was evaporated under reduced pressure. After the starting material was completely consumed (1.75 h), the solvent was evaporated under reduced pressure, and the residue was dissolve in dichloromethane. The solution was washed with aqueous sodium hydrogen sulfite and brine, dried over magnesium sulfate, and filtered, and the solvent was evaporated under reduced pressure. The residue was separated by column chromatography (SiO$_2$/hexane) to give phenanthrene (**2a**, 0.2228 g, 1.25 mmol, 96%) as a white solid. The amount of reaction mixture just before workup was decreased to 1290 mL because 10 mL of the reaction solution was removed for monitoring the reaction. The actual yield should be 97% after correction. NMR spectral data of product matched those reported in the literature.[42]

2a: ^{1}H NMR(300 MHz CDCl$_3$) δ 8.71 (d, J = 9.0 Hz, 2H), 7.90 (dd, J = 9.3, 1.8 Hz, 2H), 7.75 (s, 2H), 7.69−7.57 (m, 4H).

*3-Methylphenanthrene (**2b**).* By following the general procedure for the synthesis of compound **2a**, a 1 mM solution of **1b** in cyclohexane (1300 mL) was irradiated in the presence of potassium iodide (0.2165 g, 1.30 mmol) for 2.5 h to give 3-methylphenanthrene (**2b**, 0.1793 g, 0.933 mmol, 72%) as a white solid. The amount of reaction mixture just before workup was decreased to 1280 mL because 20 mL of reaction solution was removed for monitoring the reaction. The actual yield should be 73% after correction. NMR spectral data of product matched those reported in the literature.[42]

2b: ^{1}H NMR(300 MHz CDCl$_3$) δ 8.68 (d, J = 6.0 Hz, 1H), 8.48 (s, 1H), 7.87 (d, J = 12.0 Hz 1H), 7.79 (d, J = 6.0 Hz, 1H), 7.73−7.55 (m, 4H), 7.44 (d, J = 9.0 Hz, 1H), 2.63 (s, 3H).

*Another Procedure for 3-Methylphenanthrene (**2b**).* By following the general procedure for the synthesis of compound **2a**, a 1 mM solution of **1b** in cyclohexane (900 mL) was irradiated in the presence of potassium iodide (0.7482 g, 4.51 mmol) for 3.5 h to give 3-methylphenanthrene (**2b**, 0.1455 g, 0.757 mmol, 84%) as a white solid. The amount of reaction mixture just before workup was decreased to 1280 mL because 20 mL of reaction solution was removed for monitoring the reaction. The actual yield should be 86% after correction. NMR spectral data of product matched those reported in the literature.[42]

*1-Bromophenanthrene (**2c**).* By following the general procedure for the synthesis of compound **2a**, a 1 mM solution of **1c** in cyclohexane (1300 mL) was irradiated in the presence of potassium iodide (0.2174 g, 1.31 mmol) for 5 h to give 1-bromophenanthrene (**2c**, 0.2890 g, 1.12 mmol, 86%) as a white solid. The amount of reaction mixture just before workup was decreased to 1280 mL because 20 mL of reaction solution was removed for monitoring the reaction. The actual yield should be 88% after correction. NMR spectral data of product matched those reported in the literature.[43]

2c: ^{1}H NMR(300 MHz CDCl$_3$) δ 8.67 (d, J = 6.0 Hz, 2H), 8.22 (d, J = 9.0 Hz, 1H), 7.92−7.84 (m, 3H), 7.67−7.60 (m, 2H), 7.50 (t, J = 7.8 Hz, 1H).

*3-Bromophenanthrene (**2d**).* By following the general procedure for the synthesis of compound **2a**, a 1 mM solution of **1d** in cyclohexane (1300 mL) was irradiated in the presence of potassium iodide (0.2160 g, 1.30 mmol) for 2.5 h to give 3-bromophenanthrene (**2d**, 0.3010 g, 1.17 mmol, 90%) as a white solid. The amount of reaction mixture just before workup was decreased to 1280 mL because 20 mL of reaction solution was removed for monitoring the reaction. The actual yield should be 91% after correction. NMR spectral data of product matched those reported in the literature.[44]

2d: ^{1}H NMR(300 MHz CDCl$_3$) δ 8.62 (s, 1H), 8.61 (d, J = 9.0 Hz, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 9.0 Hz, 2H), 7.70−7.60 (m, 4H).

*3-Chlorophenanthrene (**2e**).* By following the general procedure for the synthesis of compound **2a**, a 1 mM solution of **1e** in cyclohexane (1300 mL) was irradiated in the presence of potassium iodide (0.2165 g, 1.30 mmol) for 2.5 h to give 3-chlorophenanthrene (**2e**, 0.2303 g, 1.08 mmol, 83%) as a white solid. The amount of reaction mixture just before workup was decreased to 1280 mL because 20 mL of reaction solution was removed for monitoring the reaction. The actual yield should be 84% after correction. NMR spectral data of product matched those reported in the literature.[45]

2e: ^{1}H NMR(300 MHz CDCl$_3$) δ 8.65 (s, 1H), 8.61 (d, J = 9.0 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 9.0 Hz, 1H), 7.77−7.60 (m, 4H), 7.59 (dd, J = 9.0, 1.5 Hz, 1H).

*3-Fluorophenanthrene (**2f**).* By following the general procedure for the synthesis of compound **2a**, a 1 mM solution of **1f** in cyclohexane (1300 mL) was irradiated in the presence of potassium iodide (0.2164 g, 1.30 mmol) for 1.5 h to give 3-fluorophenanthrene (**2f**, 0.2286 g, 1.17 mmol, 90%) as a white solid. The amount of reaction mixture just before workup was decreased to 1280 mL because 20 mL of reaction solution was removed for monitoring the reaction. The actual yield should be 91% after correction. NMR spectral data of product matched those reported in the literature.[46]

2f: ^{1}H NMR(300 MHz CDCl$_3$) δ 8.57 (d, J = 9.3 Hz, 1H), 8.30 (dd, J = 12.0, 2.7 Hz, 1H), 7.92−7.85 (m, 2H), 7.75−7.60 (m, 4H), 7.35 (dt, J = 9.0, 2.7 Hz, 1H); ^{19}F{^{1}H} NMR(282 MHz, CDCl$_3$) δ −114 (s).

*3-Methoxyphenanthrene (**2g**).* By following the general procedure for the synthesis of compound **2a**, a 1 mM solution of **1g** in cyclohexane (1300 mL) was irradiated in the presence of potassium iodide (0.2165 g, 1.30 mmol) for 3.5 h to give 3-methoxyphenanthrene (**2g**: 0.1329 g, 0.638 mmol, 49%) as a pale yellow solid. The amount of reaction mixture just before workup was decreased to 1280 mL because 20 mL of reaction solution was removed for monitoring the reaction. The actual yield should be 50% after correction. NMR spectral data of product matched those reported in the literature.[46]

2g: ^{1}H NMR(300 MHz CDCl$_3$) δ 8.61 (d, J = 6.0 Hz, 1H), 8.06 (d, J = 2.4 Hz, 1H), 7.89−7.80 (m, 2H), 7.71−7.60 (m, 4H), 7.27−7.23 (m, 1H), 4.01 (s, 3H).

*3-Methoxyphenanthrene (**2g**) Using Iodine with Potassium Carbonate.* A solution of 4-methoxystilbene (0.265 g, 1.26 mmol), iodine (0.349 g, 1.38 mmol), and potassium carbonate (1.75 g, 12.7 mmol) in cyclohexane (1460 mL) was irradiated by 450 W high-pressure mercury lamp for 4 h. Reaction was monitored by ^{1}H NMR spectra: 10 mL of reaction mixture was removed, and ^{1}H NMR spectrum was measured after the solvent was evaporated under reduced pressure. After the starting material was completely consumed, the solvent was evaporated under reduced pressure, and the residue was dissolve in dichloromethane. The solution was washed with aqueous sodium hydrogen sulfite, dried over sodium sulfate, and filtered, and the solvent was evaporated under reduced pressure. The residue was separated by column chromatography (SiO$_2$/chloroform) to give 3-methoxyphenanthrene (**2g**: 0.209 g, 1.00 mmol, 80%) as a pale yellow solid. NMR spectral data of product matched those reported in the literature.[46]

*3-Methoxycarbonylphenanthrene (**2h**).* By following the general procedure for the synthesis of compound **2a**, a 1 mM solution of **1h** in cyclohexane (1300 mL) was irradiated in the presence of potassium iodide (0.2161 g, 1.30 mmol) for 3.5 h to give 3-methoxycarbonylphenanthrene (**2h**, 0.2449 g, 1.04 mmol, 80%) as a white solid. The amount of reaction mixture just before workup was decreased to 1280 mL because 20 mL of reaction solution was removed for monitoring the reaction. The actual yield should be 81% after correction. NMR spectral data of product matched those reported in the literature.[47]

2h: ^{1}H NMR(300 MHz CDCl$_3$) δ 9.44 (s, 1H), 8.80 (d, J = 8.5 Hz, 1H), 8.21 (dd, J = 9.0, 1.5 Hz, 1H), 7.95−7.61 (m, 6H), 4.03 (s, 3H).

*3-Cyanophenanthrene (**2i**).* By following the general procedure for the synthesis of compound **2a**, a 1 mM solution of **1i** in cyclohexane (1300 mL) was irradiated in the presence of potassium iodide (0.2179 g, 1.31 mmol) for 6 h to give 3-cyanophenanthrene (**2i**, 0.1140 g, 0.561 mmol, 43%) as a white solid. The amount of reaction mixture just before workup was decreased to 1250 mL because 50 mL of reaction solution was removed for monitoring the reaction. The actual yield should be 45% after correction. NMR spectral data of product matched those reported in the literature.[48]

2i: ^{1}H NMR(300 MHz CDCl$_3$) δ 9.03 (s, 1H), 8.66 (d, J = 9.0 Hz, 1H), 7.99−7.90 (m, 3H), 7.80−7.75 (m, 3H), 7.74−7.69 (m, 1H).

*3-Acetylphenanthrene (**2j**).* By following the general procedure for the synthesis of compound **2a**, a 1 mM solution of **1j** in cyclohexane (1300 mL) was irradiated in the presence of potassium iodide (0.2160 g, 1.30 mmol) for 3.75 h to give 3-acetylphenanthrene (**2j**, 0.1216 g, 0.552 mmol, 42%) as a yellow solid. According to the NMR spectra of a product obtained after chromatographic purification, small amount of impurity was contaminated in the product, indicating that the yield is a little below 42%. The amount of reaction mixture just before workup was decreased to 1270 mL because 30 mL of reaction solution was removed for monitoring the reaction. The actual yield should be a little below 43% after correction. NMR spectral data of product matched those reported in the literature.[49]

2j: ^{1}H NMR(300 MHz CDCl$_3$) δ 9.34 (m, 1H), 8.80 (m, 1H), 8.16 (dd, J = 9.0, 1.8 Hz, 1H), 7.97−7.86 (m, 3H), 7.79−7.60 (m, 3H), 2.81 (s, 3H).

*Naphtho[2,1-b]thiophene (**2l**).* By following the general procedure for the synthesis of compound **2a**, a 1 mM solution of **1l** in cyclohexane (1300 mL) was irradiated in the presence of potassium iodide (0.2170 g, 1.31 mmol) for 3.5 h to give naphtho[2,1-*b*]thiophene (**2l**: 0.2093 g, 1.14 mmol, 88%) as a white solid. The amount of reaction mixture just before workup was decreased to 1270 mL because 30 mL of reaction solution was removed for monitoring the reaction. The actual yield should be 90% after correction. NMR spectral data of product matched those reported in the literature.[42]

2l: ^{1}H NMR(300 MHz $CDCl_3$) δ 8.34 (d, J = 8.7 Hz, 1H), 8.01−7.87 (m, 3H), 7.75 (d, J = 9.0 Hz, 1H), 7.64−7.50 (m, 3H).

*Phenanthrene (**2a**): TEMPO Mediated Reaction.* By following the general procedure for the potassium iodide-mediated synthesis of compound **2a**, a 1 mM solution of **1a** in cyclohexane (1300 mL) was irradiated in the presence of TEMPO (2.0340 g, 13.02 mmol) for 4.5 h to give phenanthrene (**2a**, 220.7 mg, 1.24 mmol, 95%) as a white solid. The amount of reaction mixture just before workup was decreased to 1270 mL because 30 mL of reaction solution was removed for monitoring the reaction. The actual yield should be 97% after correction. NMR spectral data of product matched those reported in the literature.[42]

*Phenanthrene (**2a**): AIBN Mediated Reaction.* By following the general procedure for the potassium iodide-mediated synthesis of compound **2a**, a 1 mM solution of **1a** in cyclohexane (1300 mL) was irradiated in the presence of AIBN (2.1419 g, 13.04 mmol) for 7.5 h to give phenanthrene (**2a**, 150.0 mg, 0.84 mmol, 64%) as a white solid. The amount of reaction mixture just before workup was decreased to 1250 mL because 50 mL of reaction solution was removed for monitoring the reaction. The actual yield should be 68% after correction. NMR spectral data of product matched those reported in the literature.[42]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01450.

^{1}H NMR spectra of all compounds and ^{13}C NMR of a new compound (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This work is dedicated to Prof. Takayuki Kawashima on the occasion of his 70th birthday.

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