Tetrahedron 70 (2014) 1748–1762

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Construction of polyaromatics via photocyclization of 2-(fur-3-yl) ethenylarenes, using a 3-furyl group as an isopropenyl equivalent synthon

Ying-Zhe Chen, Ching-Wen Ni, Fu-Lin Teng, Yi-Shun Ding, Tunng-Hsien Lee, Jinn-Hsuan Ho *

Department of Chemical Engineering, National Taiwan University of Science and Technology, No. 43, Sec. 4, Keelung Road, Taipei 10607, Taiwan

ARTICLE INFO

Article history:
Received 8 September 2013
Received in revised form 4 January 2014
Accepted 20 January 2014
Available online 25 January 2014

Keywords:
3-Furyl
Furan
Synthon
Photorearrangement
Polyaromatics

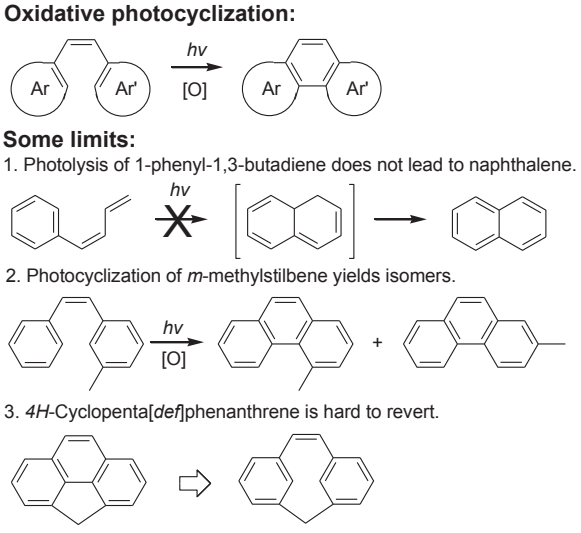
ABSTRACT

The construction of different types of substituted arenes was demonstrated through the photocyclization of 2-(fur-3-yl)ethenylarenes using a 3-furyl group as an isopropenyl equivalent synthon in the photocyclization reaction. The furan portion of the photocyclization intermediate could be fragmented via a base-induced elimination reaction to yield a series of substituted polyaromatics, including naphthalene, benzofuran, benzothiophene, phenanthrene, phenalene, acenaphthene, and triphenylene. Using different reagents, this method made it possible to introduce methyl or 2-hydroxyethyl groups as substituents at specific positions in these arenes.

1. Introduction

Compounds with polyaromatic skeletons are widely used in optoelectronic materials, and the development of methodologies for the synthesis of derivatives from these compounds has received considerable attention for the past several decades. Although direct functionalization of arenes appears to be a straightforward method for synthesizing substituted arenes, it is only feasible for certain specific substituted arenes because of regioselectivity. Instead, many different synthetic methodologies have been designed for individual polyaromatics, including naphthalenes,[1] benzofurans,[2] benzothiophenes,[3] phenanthrenes,[4] phenalenes,[5] acenaphthenes,[6] and triphenylenes.[7]

Among the methodologies for the synthesis of polyaromatics, oxidative photocyclization of stilbene-type compounds[8] is a well-known technique for synthesizing different kinds of arenes (Scheme 1), including phenanthrenes, naphthoheterocycles, and arenes containing multiple fused benzene or heterocyclic rings. Additionally, oxidative photocyclization remains a popular way to synthesize some aromatic compounds for optoelectronic materials.[9] However, oxidative photocyclization shows some limitations.



Scheme 1. Oxidative photocyclization of stilbene-type compounds and its limits.

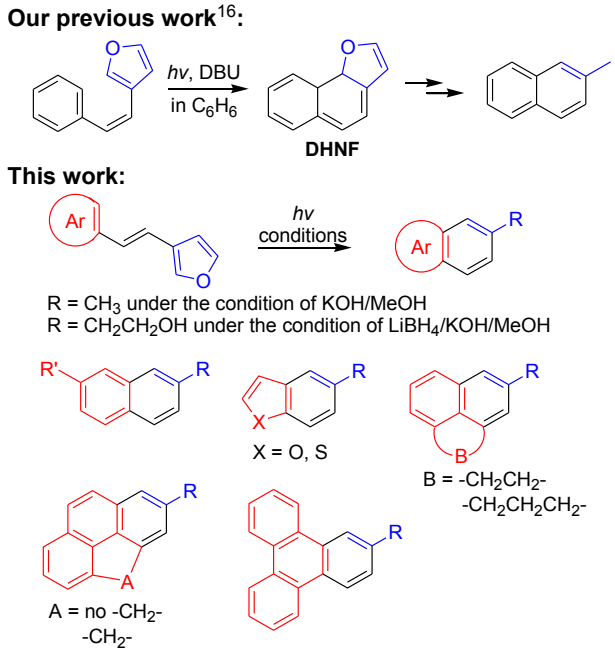
First, photolysis of 1-phenyl-1,3-butadiene in the presence of oxidants does not lead to oxidative photocyclization,[10] instead resulting in a variety of photoadditions and four-π-electron cyclization reactions. Second, the photocyclization of substituted

* Corresponding author. Tel.: +886 2 2737 6642; fax: +886 2 2737 6644; e-mail address: jhho@mail.ntust.edu.tw (J.-H. Ho).

0040-4020/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2014.01.035

stilbene-type compounds sometimes transforms both desired and undesired regio-isomers; for example, the irradiation of *m*-methylstilbene can generate a mixture of 2-methylphenanthrene and 4-methylphenanthrene. Third, arenes with cycloalkyl chains, such as 4*H*-cyclopenta[*def*]phenanthrene, are difficult to revert back to stilbene-type compounds.[11] Therefore, developing a new synthetic strategy that can overcome these difficulties would represent a significant improvement.

Furan is a useful synthon that can be converted into different functional groups,[12] such as 1,4-diketones,[13] benzene rings,[14] and penta-2,4-dienals.[15] Recently, we reported[16] a base-induced photorearrangement of 3-styrylfurans to yield 2-methyl-7-substituted naphthalenes in the presence of DBU/EtOH/C_6H_6. (Scheme 2). This photorearrangement led to a new transformation of furan. The furan portion of the photocyclization intermediate of 3-styrylfurans is fragmented to generate 2-methylnaphthalenes, which is the theoretical result of oxidative photocyclization of 1-ary-3-methyl-1,3-butadienes. Thus, in six-electron photocyclization, the 3-furyl group can be regarded as an isopropenyl equivalent synthon to construct a simple benzene ring. We hypothesized that this base-induced photorearrangement would not only solve the previous difficulties inherent in synthesizing substituted polyaromatics, but also provide a new method for synthesizing several different polyaromatics.



Scheme 2. Photorearrangement with a 3-furyl group as an isopropenyl equivalent synthon.

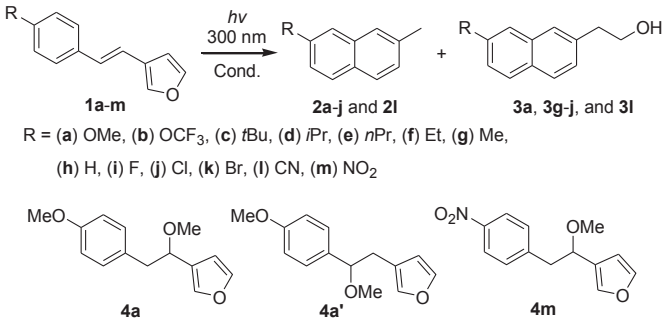
In addition to using benzene as solvent, we determined that this photorearrangement occurs in the presence of KOH/MeOH, making it more environmentally friendly. We also discovered that using the strong reducing agent $LiBH_4$ leads to the formation of the reductive products and higher yields. Therefore, we report this synthetic methodology for synthesizing a series of naphthalenes, benzofurans, benzothiophenes, phenanthrenes, phenalenes, acenaphthenes, and triphenylenes.

2. Results and discussion

2.1. Synthesis of 2,7-disubstituted naphthalenes

As the starting materials for the photochemical synthesis of 2,7-disubstituted naphthalenes, 3-(4-substituted styryl)furans **1a**–**m** were synthesized, and preparation of **1a**–**m** was carried out via the Wittig Reaction[17] using the appropriate 4-substituted benzyl halide, triphenylphosphine, and furan-3-carboxaldehyde. The applied synthetic procedures and yields are described in the experimental section.

Photolysis of **1a**–**m** generated 2-methyl-7-substituted naphthalenes or 2-(7-substituednaphthalen-2-yl)ethanols as the major products. The results are shown in Scheme 3. The photoreaction yields in the presence of 10% $KOH_{(aq)}$/MeOH are reported in Table 1, and the yields in the presence of $LiBH_4/KOH_{(aq)}$/MeOH are reported in Table 2.



Scheme 3. Photolysis of 3-styrylfurans.

Table 1
Photolysis of 3-styrylfurans in the presence of 10% $KOH_{(aq)}$/MeOH for 3 h

Entry	Reactant	Conversion (%)	Product	Yield (%)	Yield (%)[a] from Ref. 16
1	**1a**	95	**4a**+**4a′**[b]	40	41 (**2a**)
2	**1b**	98	**2b**	19	—
3	**1c**	75	**2c**	43	—
4	**1d**	81	**2d**	48	61
5	**1e**	93	**2e**	45	—
6	**1f**	90	**2f**	42	46
7	**1g**	93	**2g**	40	58
8	**1h**	100	**2h**	20	42
9	**1i**	94	**2i**	34	35
10	**1j**	100	**2h**+**2j**[c]	21	—
11	**1k**	100	**2h**	22	—
12	**1l**	76	**2l**	52	15
13	**1m**	97	**4m**	24	—

[a] Irradiation was carried out in the presence of DBU/EtOH/C_6H_6.[16]
[b] The ratio of **4a** and **4a′** was 1:5.
[c] The ratio of **2h** and **2j** was 2:1.

Table 2
Photolysis of 3-styrylfurans in the presence of $LiBH_4/KOH_{(aq)}$/MeOH for 3 h

En.	React.	Conver. (%)	Prod. **2** (Yield, %)	Prod. **3** (Yield, %)	Total yield (%)
1	**1a**	100	**2a** (27)	**3a** (43)	70
2	**1g**	100	**2g** (31)	**3g** (41)	72
3	**1h**	100	**2h** (30)	**3h** (7)	37
4	**1i**	100	**2i** (28)	**3i** (12)	40
5	**1j**	100	**2h**+**2j** (15)[a]	**3h**+**3j** (12)[a]	27
6	**1l**	100	**2l** (6)	**3l** (3)	9

[a] The ratio of **2h** and **2j** was 1:1, and that of **3h** and **3j** was 1:0.9.

In the presence of 10% $KOH_{(aq)}$/MeOH (Table 1), the photolysis of **1b**–**i** and **1l** generated the 2-methyl-7-substituted naphthalenes **2b**–**i** and **2l** as the major products (19–52% yields) and a small amount of side products with a complicated structure (examined via thin-layer-chromatography (TLC) and crude ^{1}H NMR spectrum

analyses). The best photoreaction results (40–52% yields) were obtained using 3-styrylfurans with alkyl groups (**1c**–**g**, entries 3–7) and a cyano group (**1l**, entry 12), while 3-stytylfuran (**1h**, entry 8) and 3-(4-fluorostyryl)furan (**1i**, entry 9) generated poor results (20 and 34% yields, respectively). Irradiation of 3-(4-chlorostyryl)furan (**1j**, entry 10) and 3-(4-bromostyryl)furan (**1k**, entry 11) led to dehalogenated **2h** as the major product. The reason for this result is expected to be the same as the results of photo-debromination of bromonaphthalene with potassium hydroxide.[18] However, this photorearrangement did not proceed in some cases. Photolysis of **1a** only generated the methanol addition products **4a** and **4a′** at a total yield of 40%; this photoaddition of methanol to stilbene-type compounds has been reported for methoxystilbenes[19] and 2-(4-methoxystyryl)naphthalene.[20] Alternative reaction conditions for the formation of 2-methoxy-2-methylnaphthalene **2a** involve the irradiation of **1a** and DBU in benzene.[16] Photolysis of **1m** also generated the methanol addition product **4m**, as a nitro group would retard the process of photocyclization to produce a photorearrangement product.[21]

Compared with the results of photorearrangement in methanol, photolysis of most 3-styrylfurans (**1a**, **1d**, **1f**–**g**, entries 1, 4, 6–8) in the presence of DBU/EtOH/C_6H_6 produced higher yields,[16] perhaps due to avoiding the photoaddition of methanol. However, photolysis of 3-(4-cyanostyryl)furan (**1l**, entry 12) with DBU in benzene may lead to a charge transfer reaction, resulting in a low yield of the photorearrangement product **2l**. This difficulty was overcome using the reagents KOH/MeOH, resulting in a significantly higher yield.

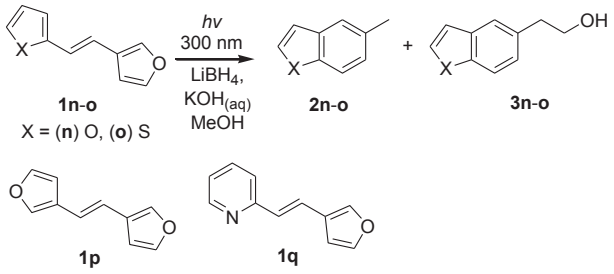
In the presence of $LiBH_4$/$KOH_{(aq)}$/MeOH (Table 2), photolysis of **1a** generated the products **2a** and **3a**, and similar results were obtained for irradiation of **1g**–**j** and **1l**. The total yields of **2** and **3** in these cases were in the range of 9–72%. 3-Styrylfurans with electron-donating groups, methoxy (**1a**, entry 1) and methyl groups (**1g**, entry 2) underwent photorearrangement to yield the best results (70–72% yields). 3-Styrylfurans without functional groups (**1h**, entry 3) or with halides (**1i**–**1j**, entries 4–5) generated the poorest results (27–40% yields). The extremely low yield obtained for **1l** may be due to the lability of cyano groups in the presence of $LiBH_4$.

Most of these photoreactions showed low yields (Tables 1 and 2). To confirm the causes of these low yields, two individual experiments were performed, in which the *trans* and *cis* forms of 3-(4-methylstyryl)furan (*trans* and *cis*-**1g**) were maintained at 40 °C in the presence of $KOH_{(aq)}$/MeOH without irradiation. The results showed that *trans*-**1g** was recovered with a 98% yield, whereas *cis*-**1g** was recovered with only a 78% yield. The low yields may have resulted from the stability of *cis*-styryfurans, which contain a more acidic hydrogen at the C-2 position in the furan ring.[22]

2.2. Synthesis of benzoheterocycles

The 1-heterocyclic-2-(fur-3-yl)ethenes **1n**–**q** were synthesized as starting materials for the photochemical synthesis of 5-substitued-benzoheterocycles. The preparation of **1n**–**p** was carried out through multiple procedures, including the reduction of heterocyclic-carboxaldehyde into heterocyclic-methanol, chlorination to synthesize heterocyclic-methyl chloride, and the Wittig Reaction with triphenylphosphine and furan-3-carboxaldehyde. The preparation of **1q** was carried out via the condensation of 2-picoline and furan-3-carboxaldehyde in acetic anhydride.[23] The synthetic procedures and yields are described in the experimental section.

Photolysis of **1n**–**q** in the presence of 10% $KOH_{(aq)}$/MeOH did not lead to photorearrangement, and most of the starting materials were decomposed. 5-Substitued-benzoheterocycles can only be obtained in the presence of $LiBH_4$/$KOH_{(aq)}$/MeOH following irradiation. The photoreaction results are shown in Scheme 4 and Table 3.



Scheme 4. Photolysis of 1-heterocyclic-2-(fur-3-yl)ethenes.

Table 3
Photolysis of 1-heterocyclic-2-(fur-3-yl)ethenes in the presence of $LiBH_4$/$KOH_{(aq)}$/MeOH for 3 h

En.	React.	Conver. (%)	Prod. **2** (Yield, %)	Prod. **3** (Yield, %)	Total yield (%)
1	**1n**	100	**2n** (0)	**3n** (29)	29
2	**1o**	100	**2o** (5)	**3o** (84)	89
3	**1p**	100	0	0	0
4	**1q**	83	0	0	0

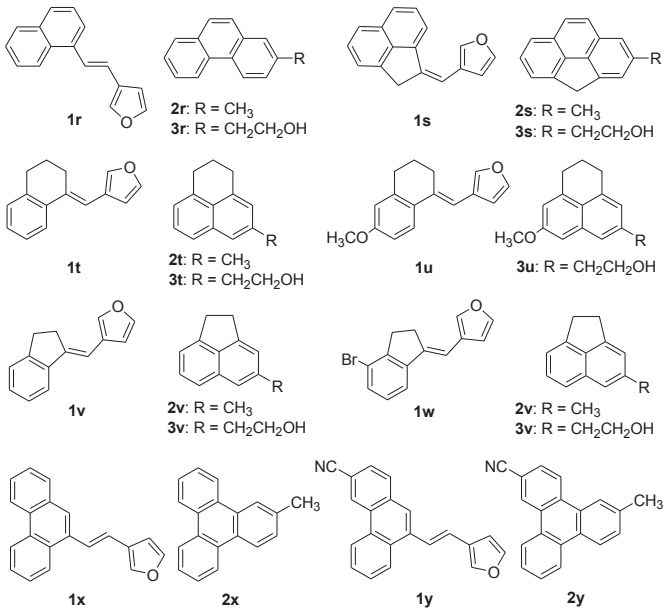
Photolysis of **1n** in the presence of $LiBH_4$/$KOH_{(aq)}$/MeOH (Table 3) only generated the product **3n** at a 29% yield, while photolysis of **1o** generated the products **2o** and **3o** at a total yield of 89%. However, irradiation of **1p** and **1q** did not generate any photorearrangement products. 1,2-Di(fur-3-yl)ethene **1p** contains two unstable 3-furyl groups, which may cause the compound to decompose very quickly. The compound *cis*-**1q** exhibits a lower quantum yield from photocyclization because of the presence of a 2-pyridinyl group (the quantum yield of the photocyclization of *cis*-2-styrylpyridine is 0.014,[24] while that for *cis*-stilbene is 0.1[25]), so that the rate of photorearrangement may be too slow to compete with the decompositions.

2.3. Synthesis of polyaromatics

The 1-aryl-2-(fur-3-yl)ethenes **1r**–**y** were synthesized as the starting materials for the photochemical synthesis of substituted arenes. The preparation of **1r**–**w** was initiated by synthesizing the appropriate arylmethyl halide via NBS-bromination or $SOCl_2$-chlorination, followed by the Wittig Reaction. The preparation of **1x**–**y** was initiated by preparing 9-methylphenanthrenes via oxidative photocyclization of the appropriate stilbenes, followed by NBS-bromination and the Wittig Reaction. The synthetic procedures and yields are described in experimental section.

Photolysis of **1r**–**w** in the presence of 10% $KOH_{(aq)}$/MeOH and $LiBH_4$/$KOH_{(aq)}$/MeOH led to the photorearrangement products **2r**–**w** and **3r**–**w**. However, due to the solubility of **1x**–**y**, only photolysis of **1x**–**y** in the presence of DBU/EtOH/C_6H_6 was able to generate the photorearrangement products **2x**–**y**. The structures of **1r**–**y**, **2r**–**y**, and **3r**–**w** are shown in Scheme 5. The photoreaction results are reported in Tables 4 and 5.

Photolysis of **1r**–**t** and **1v** in the presence of 10% $KOH_{(aq)}$/MeOH and photolysis of **1r** and **1x**–**y** in the presence of DBU/EtOH/C_6H_6 successfully generated the methylarenes **2r**–**t**, **2v**, and **2x**–**y** (20–38% yields) (Table 4). Photolysis of **1u** (entry 5) did not yield **2u**, possibly because the methoxy group increases the rate of the photoaddition of methanol.[19] Photolysis of **1w** (entry 7) led to formation of the product **2v**, which may have resulted from the photo-dehalogenation of **2w** with potassium hydroxide.[18] Photolysis of **1r** in benzene (entry 1) resulted in a higher yield than when carried out in methanol (entry 2) due to avoiding the photoaddition of methanol.



Scheme 5. Structures of 1-aryl-2-(fur-3-yl)ethenes and their photorearrangement products.

Table 4
Photolysis of 1-aryl-2-(fur-3-yl)ethenes in the presence of 10% $KOH_{(aq)}$/MeOH for 6 h

Entry	Reactant	Conversion (%)	Prod. **2** (%)	Yield (%)
1[a]	**1r**	100	**2r**	38
2	**1r**	100	**2r**	29
3	**1s**	100	**2s**	25
4	**1t**	100	**2t**	27
5	**1u**	100	**2u**	0
6	**1v**	100	**2v**	26
7	**1w**	100	**2v**	21
8[a]	**1x**	100	**2x**	32
9[a]	**1y**	100	**2y**	20

[a] The reaction was carried out in the presence of DBU/EtOH/C_6H_6.

Table 5
Photolysis of 1-aryl-2-(fur-3-yl)ethenes in the presence of $LiBH_4$/$KOH_{(aq)}$/MeOH for 6 h

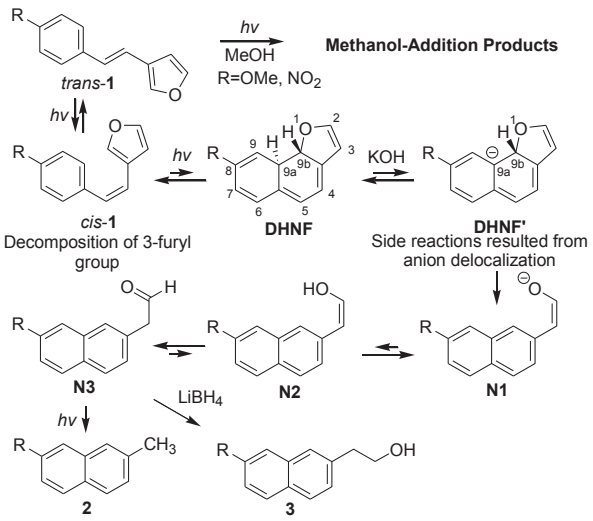
En.	React.	Conver. (%)	Prod. **2** (Yield, %)	Prod. **3** (Yield, %)	Total yield (%)
1	**1r**	100	**2r** (5)	**3r** (44)	49
2	**1s**	100	**2s** (20)	**3s** (40)	60
3	**1t**	100	**2t** (8)	**3t** (68)	76
4	**1u**	100	**2u** (0)	**3u** (26)	26
5	**1v**	100	**2v** (15)	**3v** (48)	63
6	**1w**	100	**2v** (15)	**3v** (26)	41

Photolysis of **1r**–**w** in the presence of $LiBH_4$/$KOH_{(aq)}$/MeOH generated the products **2r**–**t**, **2v**, and **3r**–**v**; the total yields of **2** and **3** were in the moderate range of 26–76% (Table 5). The poor results of the irradiation of **1u** may have been caused by the methoxy group enhancing the photoaddition of methanol,[19] and the generation of the products **2v** and **3v** from the photolysis of **1w** may have resulted from the photo-dehalogenation of **2w** and **3w** with potassium hydroxide.[18]

There were some unique results of synthesizing different substituted arenes using this methodology, including the acquisition of 2-substituted phenanthrene (**2r** and **3r**) without regioisomers via a photochemical reaction; the direct photochemical formation of 2-substituted-4*H*-cyclopenta[*def*]phenanthrene (**2s** and **3s**); the first synthesis of 5-sustituted-2,3-dihydro-1*H*-phenalenes (**2t** and **3t**), 5,8-disustituted-2,3-dihydro-1*H*-phenalene (**3u**), and 4-substituted acenaphthenes (**2v** and **3v**); and the development of a feasible technique for synthesizing a 2-methyl-10-substitutedtriphenylene, such as the compound **2y**.

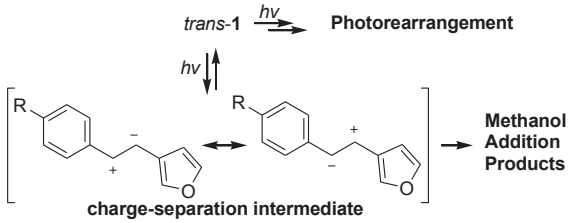
2.4. Mechanism

A proposed mechanism for this photoreaction is shown in Scheme 6. The reaction steps include the *trans*–*cis* isomerization of *trans*-**1**, photocyclization of *cis*-**1**, the E1cB (unimolecular elimination of conjugate base) reaction of **DHNF** and **DHNF′**, the protonation of **N1**, the tautomerization of **N2**, the Norrish-type 1 photoreaction[26] of **N3** to generate compound **2**, and the reduction of the aldehyde group of **N3** to yield compound **3**. The side reaction consisting of the photoaddition of methanol, and the possible decomposition pathways are also included. Based on this proposed mechanism, we can discuss the following issues: 1. the substitution effect of the photoaddition of methanol; 2. the fact that the arylethenolate anion of **N1** is a leaving group; 3. the increase of yields using a reducing agent; 4. the E1cB reaction; and 5. the presence of the intermediate **N3**.



Scheme 6. A proposed mechanism.

2.4.1. Substitution effect of the photoaddition of methanol. The photoaddition of methanol to stilbene-type compounds has been reported for compounds with a methoxy group.[16] The key step in this addition is the formation of a charge separation intermediate (Scheme 7). This charge separation intermediate can be stabilized by electron-donating or electron-withdrawing groups to enhance the rate of photoaddition, resulting in regioselectivity. In the irradiation of **1a**, we found that a methoxy group stabilized the cation to enhance the rate of photoaddition and generated the methanol addition products **4a** and **4a′** as the only type of products, with



Scheme 7. The charge separation intermediate for methanol addition products.

good regioselectivity (Table 1, entry 1, **4a**:**4a**′=1:5). When a trifluoromethoxy substituent (**1b**, Table 1, entry 2) was used to decrease the cation stabilization ability, photorearrangement became the major reaction pathway. In the irradiation of **1m** (Table 1, entry 13), a nitro group not only retarded the process of photocyclization but also stabilized the charge separation intermediate, such that irradiation of **1m** led to the methanol addition product **4m** as the major product (but with a low yield). In the irradiation of **1g** with a methyl group (weak electron-donating group), photorearrangement was the major reaction pathway, while photoaddition was a minor reaction. A time-tracking analysis of the photolysis of **1g** showed that the methanol addition products (**4g** and **4g**′ in this case) were not stable under irradiation and silica gel chromatography.[27]

*2.4.2. The arylethenolate anion of **N1** as a good leaving group.* The elimination reaction from **DHNF** to **N1** employs the arylethenolate anion of **N1** as the leaving group. Typically strong bases, such as alkoxide (pK_a of alkanols are 16–17), are inferior leaving groups, whereas the phenolate anion (the pK_a of phenol is approximately 10) is a weaker base than alkoxide and can be used the leaving group in some photoreactions.[28] According to the findings of Kresge,[29] the pK_a of phenylethenol is 9.45, which is similar to the pK_a of phenol, and the arylethenolate anion can therefore also be employed as a leaving group in this photorearrangement. Similar results have been reported for other heterocycles, including benzofuran and oxadiazole.[30]

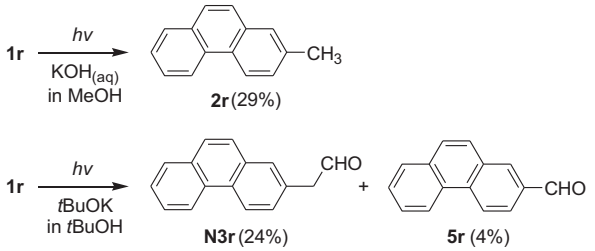
2.4.3. Increased yields using a reducing agent. To understand the effect of the base and reducing agent, different bases (KOH, NaOH, LiOH, and ^{t}BuOK) and reducing agents ($LiBH_4$, $NaBH_4$, and KBH_4) were used in the photorearrangement procedure. The effects of the bases were estimated by irradiating **1r** with the different bases, and the photorearrangement results are shown in Table 6 and Scheme 8. According to the experimental results, the photolysis of **1r** without a base in the presence of $LiBH_{4(aq)}$/MeOH did not lead to any photorearrangement (Table 6, entry 1). When **1r** was irradiated with the different bases under these conditions, the total yields of the photorearrangements were not markedly different (Table 6, entries 2–4). Even when **1r** was irradiated in the presence of ^{t}BuOK/^{t}BuOH, the total yields of **N3r** and **5r** were very close to the yields obtained from the photolysis of **1r** in the presence of $KOH_{(aq)}$/MeOH (Scheme 8). These results indicate that the base is necessary for this photorearrangement to occur, but different bases do not significantly affect the photorearrangement.

Table 6
Photolysis of 1-(naphthen-1-yl)-2-(fur-3-yl)ethenes **1r** with different bases in $LiBH_{4(aq)}$/MeOH for 3 h

Entry	Reagent	Conversion (%)	Prod. **2r** (%)	Prod. **3r** (%)	Total yield (%)
1[a]	None	—	0	0	0
2[b]	LiOH	100	Trace	47	47
3[b]	NaOH	100	3	42	45
4[b]	KOH	100	5	44	49

[a] The results were determined based on the ^{1}H NMR spectrum of the crude sample.
[b] Isolated yields.

The effect of the reducing agents was estimated by irradiating **1g** with the different reducing agents, and the photorearrangement results are shown in Table 7. Compared to the results of photorearrangement in the absence of reducing agents, the photolysis of **1g** with different reducing agents led to the production of compounds **2g** and **3g** at better yields[31] (Table 7, entries 2–4). Additionally, the use of a stronger reducing agent, $LiBH_4$, led to the best



Scheme 8. Comparison of the photolysis of **1r** in the presence of ^{t}BuOK/^{t}BuOH and KOH/MeOH.

Table 7
Photolysis of 3-(4-methylstyryl)furan **1g** with different reducing agents in $KOH_{(aq)}$/MeOH for 3 h

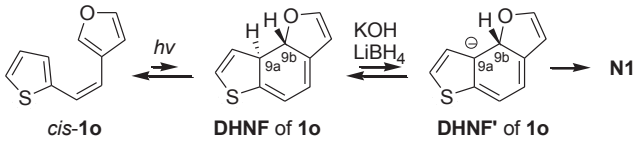
Entry	Reagent	Conversion (%)	Prod. **2g** (%)	Prod. **3g** (%)	Total yield (%)
1	None	93	40	0	40
2	KBH_4	100	18	23	41
3	$NaBH_4$	100	17	31	48
4	$LiBH_4$	100	31	41	72

reaction yield (entry 4) because the stronger reducing agent could efficiently trap the unstable aldehyde **N3g** to prevent the formation of unstable radical intermediates in the Norrish-type 1 photoreaction. However, the reaction rate of the Norrish-type 1 photoreaction for **N3** is expected to be very close to that of the reduction of the aldehyde group of **N3**; thus, this photorearrangement only produced a mixture of **2g** and **3g**.

2.4.4. E1cB (unimolecular elimination conjugated base) reaction. In accordance with the theory of six-π-electron cyclization, the photocyclization of stilbene-type compounds leads to conrotatory ring closure. This leaves the hydrogens on carbon 9a and 9b of **DHNF** in a *trans* configuration[8b] and the leaving oxygen-1 and the hydrogen on carbon 9a in a *cis* configuration (Scheme 6), such that in the elimination reaction from **DHNF** to **N1**, the E2 reaction cannot occur directly. A possible reaction pathway was hypothesized to be E1cB elimination. Hence, the hydrogen on carbon 9a was first deprotonated with a base to form an anion on carbon 9a of **DHNF**′, and the fragmentation of oxygen-1 from carbon 9b of **DHNF**′ was then driven by the negative charge of carbon 9a to generate the naphthalene ring of **N1**. When electron-withdrawing groups on carbon 8, heterocycles or polyaromatics increased the stability of the intermediate **DHNF**′, reducing the rate of the reaction from **DHNF**′ to **N1**,[28,32] the photolysis of **1b** (trifluoromethoxy), **1i** (fluoro), **1j** (chloro), **1k** (bromo), **1q** (pyridin-2-yl), and **1r**–**y** (polyaromatics) led to poor results. However, when electron-releasing groups on carbon 8 decreased the stability of **DHNF**′, the formation rate of **N1** was increased, causing the photolysis of **1a** (methoxy) and **1g** (methyl) to occur with better results.

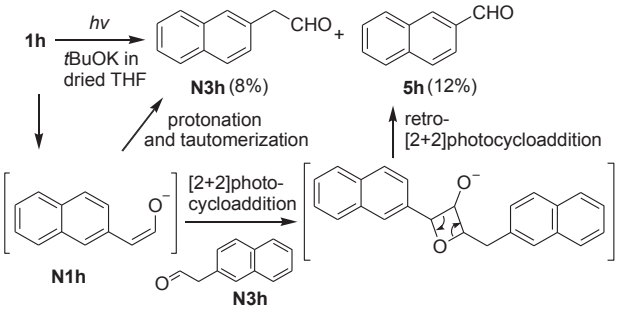
It is worth mentioning that photorearrangement of **1o** leads to a good result (89% total yield). A possible reason for this finding is that the thiophene of *cis*-**1o** presents a lower resonance energy, making photocyclization more efficient, and the sulfur atom of **DHNF**′ has an electron-releasing effect in the case of **1o**, to increase the transformation from **DHNF**′ to **N1** (Scheme 9).

*2.4.5. The presence of the intermediate **N3**.* To confirm the presence of the intermediate **N3**, harsh conditions (potassium *tert*-butoxide in *tert*-butyl alcohol and dried THF) were used to prevent the **N1** protonation step. In addition to the isolation of **N3r** (Scheme 8), the photolysis of **1h** in the presence of ^{t}BuOK/dried THF generated a mixture of **N3h**, **5h**, and some uncharacterized side products



Scheme 9. Intermediates of the photolysis of **1o**.

(Scheme 10). Because of the influence of the side products, further TLC purification was performed to achieve acceptable purity of the products. The isolation of **N3h** and **N3r** confirmed the presence of the intermediate **N3**. However, the formation of **5h** and **5r** was unexpected. The mechanism of **5h** formation probably included the [2+2]photocycloaddition of the double bond of **N1h** and carbonyl group of **N3h** to form oxetane, followed by the retro-[2+2] photocycloaddition of oxetane to generate **5h**.[33]



Scheme 10. Possible mechanism for the formation of **N3h** and **5h**.

3. Conclusion

A new synthetic methodology for the synthesis of substituted polyaromatics is reported here. Using a 3-furyl group as an isopropenyl equivalent synthon provides an alternative approach for constructing aromatic rings through photocyclization. We have successfully demonstrated the synthesis of a series of substituted naphthalenes, substituted benzofurans, substituted benzothiophenes, substituted phenanthrenes, substituted phenalenes, substituted acenaphthenes, and substituted triphenylenes through this photorearrangement process under different conditions. In these photorearrangements, the use of $LiBH_4/KOH_{(aq)}$/MeOH provides acceptable total yields (**2** and **3**) from the photolysis of **1a**, **1g**–**j**, **1l**, **1n**–**o**, and **1r**–**w**. The mechanism is also discussed in this report. The intermediates **N3h** and **N3r** can be obtained by the irradiation of **1h** and **1r**, respectively, with a stronger base, ^{t}BuOK. This new photochemical synthetic methodology provides several advantages, including the ability to easily synthesize naphthalenes, to synthesize some complicated substituted arenes without regioisomers, and to synthesize different polyaromatics using a single method.

4. Experimental section

4.1. Materials and methods

A photochemical reactor produced by a local company was equipped with a merry-go-round apparatus and 16 monochromic light tubes (300 nm). The quartz tubes for photolysis were 1.5 cm in diameter and 20 cm in length. NMR spectra were measured on a Bruker AVIII-500 MHz FT-NMR spectrometer, with chloroform-d_1 as the standard. Mass spectra were recorded on a Finnigan MAT95S spectrometer. Column chromatography was conducted using silica gel with a 60–120 mesh via gravity. Tetrahydrofuran was dried using a liquid chromatography solvent purification system. All other solvents were employed as received, and all commercial reagents were used without purification.

4.2. General procedure for the synthesis of 3-styrylfurans 1a–m

Preparation of 3-styrylfurans was carried out via the Wittig Reaction using the appropriate 4-substituted benzyl halide as the starting material. The general experimental procedures were as follows. A mixture of triphenylphosphine (42 mmol), 4-substituted benzyl halide (35 mmol) and benzene (20 mL) was refluxed overnight. The mixture was then cooled to room temperature, and the precipitant (triphenylphosphonium salt) was collected via suction filtration. Next, triphenylphosphonium salt (24 mmol), 3-fural (22 mmol), and 18-crown-6 (3 mmol) were dissolved in dichloromethane (55 mL), and a 50% potassium carbonate aqueous solution (24 mL) was added to the dichloromethane mixture. The mixture was stirred vigorously overnight. Then, the reaction was extracted with ethyl acetate several times, and the organic layers were combined and subsequently dried using anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator and the products, *cis*- and *trans*-3-styrylfurans, were purified via gravity chromatography using hexane/ethyl acetate for elution. The total yields of the *cis* and *trans* forms are reported below.

*4.2.1. trans-3-(4-Methoxystyryl)furan trans-**1a**.*[34] 56 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.35 (m, 1H), 7.33 (d, J=8.7 Hz, 2H), 6.83 (d, J=8.7 Hz, 1H), 6.79 (d, J=16.3 Hz, 1H), 6.72 (d, J=16.3 Hz, 1H), 6.60 (d, J=1.9 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.05, 143.58, 140.43, 130.17, 127.94, 127.27, 124.70, 116.32, 114.08, 107.34, 55.27; MS (EI, 70 eV) m/z 200 (M^+, 100), 171 (73), 169 (4), 128 (28); HRMS ($C_{13}H_{12}O_2$) calcd: 200.0837, found: 200.0840.

*4.2.2. trans-3-(4-Trifluoromethoxystyryl)furan trans-**1b**.* 44 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.46 (d, J=8.3 Hz, 2H), 7.44 (s, 1H), 7.20 (d, J=8.3 Hz, 2H), 6.96 (d, J=16.3 Hz, 1H), 6.80 (d, J=16.3 Hz, 1H), 6.67 (d, J=1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.27, 148.26, 143.80, 141.23, 136.17, 127.24, 126.80, 124.28, 121.54, 121.12, 119.50, 119.43, 107.27; MS (EI, 70 eV) m/z 255 (M^++1, 8), 254 (M^+, 97), 226 (12), 225 (97), 169 (14), 141 (18), 128 (17); HRMS ($C_{13}H_9F_3$) calcd: 254.0555, found: 254.0560.

*4.2.3. trans-3-(4-tert-Butylstyryl)furan trans-**1c**.* 76 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.42 (s, 1H), 7.40 (d, J=9.2 Hz, 2H), 7.37 (d, J=8.7 Hz, 2H), 6.94 (d, J=16.2 Hz, 1H), 6.81 (d, J=16.2 Hz, 1H), 6.67 (d, J=1.4 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.45, 143.62, 140.71, 134.58, 128.22, 125.83, 125.56, 124.68, 117.60, 107.40, 34.60, 31.30; MS (EI, 70 eV) m/z 227 (M^++1, 3), 226 (M^+, 38), 211 (100), 170 (16), 141 (8), 128 (3); HRMS ($C_{16}H_{18}O$) calcd: 226.1358, found: 226.1350.

*4.2.4. trans-3-(4-Isopropylstyryl)furan trans-**1d**.* 82 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (s, 1H), 7.42 (s, 1H), 7.40 (d, J=8.2 Hz, 2H), 7.22 (d, J=8.2 Hz, 2H), 6.95 (d, J=16.2 Hz, 1H), 6.82 (d, J=16.2 Hz, 1H), 6.67 (s, 1H), 2.93 (heptet, J=6.9 Hz, 1H), 1.25 (d, J=6.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.21, 143.61, 140.69, 134.97, 128.33, 126.70, 126.09, 124.66, 117.48, 107.38, 33.86, 23.92; MS (EI, 70 eV) m/z 213 (M^++1, 5), 212 (M^+, 100), 197 (87), 170 (42), 169 (32), 141 (47), 128 (3); HRMS ($C_{15}H_{16}O$) calcd: 212.1201, found: 212.1201.

*4.2.5. trans-3-(4-Propylstyryl)furan trans-**1e**.* 74 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.41 (t, J=1.3 Hz, 1H), 7.38 (d, J=7.9 Hz, 2H), 7.16 (d, J=7.9 Hz, 2H), 6.94 (d, J=16.1 Hz, 1H), 6.81 (d,

J=16.1 Hz, 1H), 6.66 (d, J=1.9 Hz, 1H), 2.59 (t, J=7.7 Hz, 2H), 1.66 (sextet, J=7.5 Hz, 2H), 0.97 (t, J=7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.59, 142.02, 140.66, 134.80, 128.73, 128.36, 125.98, 124.65, 117.41, 107.37, 37.76, 24.47, 13.81; MS (EI, 70 eV) m/z 213 (M^++1, 4), 212 (M^+, 70), 183 (100), 169 (17), 155 (17), 141 (13), 128 (3); HRMS ($C_{15}H_{16}O$) calcd: 212.1201, found: 212.1197.

*4.2.6. trans-3-(4-Ethylstyryl)furan trans-**1f**.* 50 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.41 (s, 1H), 7.37 (d, J=7.9 Hz, 2H), 7.17 (d, J=7.9 Hz, 2H), 6.93 (d, J=16.4 Hz, 1H), 6.80 (d, J=16.4 Hz, 1H), 6.66 (d, J=1.9 Hz, 1H), 2.65 (q, J=7.7 Hz, 2H), 1.24 (t, J=7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.62, 140.69, 134.83, 128.37, 128.15, 126.10, 124.67, 117.46, 107.39, 28.61, 15.51; MS (EI, 70 eV) m/z 199 (M^++1, 5), 198 (M^+, 100), 183 (39), 169 (68), 155 (9), 141 (37), 128 (3); HRMS ($C_{14}H_{14}O$) calcd: 198.1045, found: 198.1047.

*4.2.7. trans-3-(4-Methylstyryl)furan trans-**1g**.*[34] 81 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.40 (s, 1H), 7.34 (d, J=8.1 Hz, 2H), 7.14 (d, J=7.9 Hz, 2H), 6.92 (d, J=16.2 Hz, 1H), 6.79 (d, J=16.2 Hz, 1H), 6.65 (d, J=1.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.61, 140.67, 137.16, 134.58, 129.33, 128.37, 126.02, 124.66, 117.41, 107.39, 21.18; MS (EI, 70 eV) m/z 185 (M^++1, 4), 184 (M^+, 78), 155 (100), 141 (22), 70 (16), 61 (17); HRMS ($C_{13}H_{12}O$) calcd: 184.0888, found: 184.0887.

*4.2.8. trans-3-Styrylfuran trans-**1h**.*[34] 84 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.51 (d, J=8.0 Hz, 2H), 7.47 (s, 1H), 7.40 (t, J=7.7 Hz, 2H), 7.30 (t, J=7.8 Hz, 1H), 7.03 (d, J=16.4 Hz, 1H), 6.88 (d, J=16.4 Hz, 1H), 6.72 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.63, 140.89, 137.30, 128.58, 128.36, 127.27, 126.07, 124.50, 118.34, 107.34; MS (EI, 70 eV) m/z 171 (M^++1, 4), 170 (M^+, 84), 141 (100), 115 (34), 70 (18), 61 (14); HRMS ($C_{12}H_{10}O$) calcd: 170.0732, found: 170.0731.

*4.2.9. trans-3-(4-Fluorostyryl)furan trans-**1i**.*[34] 57 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.41 (s, 1H), 7.40 (dd, J=8.6, 5.5 Hz, 2H), 7.03 (t, J=8.7 Hz, 2H), 6.88 (d, J=16.2 Hz, 1H), 6.78 (d, J=16.2 Hz, 1H), 6.65 (d, J=1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.14 (d, J_{C-F}=245.3 Hz), 143.74, 140.91, 133.53 (d, J_{C-F}=3.1 Hz), 127.58, 127.36 (d, J_{C-F}=39.9 Hz), 124.39, 118.19 (d, J_{C-F}=2.5 Hz), 115.55 (d, J_{C-F}=21.5 Hz), 107.28; MS (EI, 70 eV) m/z 189 (M^++1, 3), 188 (M^+, 76), 160 (24), 159 (100), 133 (25), 70 (20), 61 (16); HRMS ($C_{12}H_9FO$) calcd: 188.0637, found: 188.0640.

*4.2.10. trans-3-(4-Chlorostyryl)furan trans-**1j**.*[34] 39 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.43 (s, 1H), 7.38 (d, J=8.7 Hz, 2H), 7.31 (d, J=8.7 Hz, 2H), 7.27 (s, 1H), 6.95 (d, J=16.2 Hz, 1H), 6.77 (d, J=16.2 Hz, 1H), 6.66 (d, J=1.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.80, 141.15, 135.86, 130.90, 129.45, 128.77, 127.24, 127.07, 119.03, 107.27; MS (EI, 70 eV) m/z 206 (M^++2, 15), 204 (M^+, 63), 175 (39), 169 (30), 141 (100), 139 (23), 70 (25); HRMS ($C_{12}H_9ClO$) calcd: 204.0342, found: 204.0344.

*4.2.11. trans-3-(4-Bromostyryl)furan trans-**1k**.*[34] 75 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.46 (d, J=8.5 Hz, 2H), 7.43 (s, 1H), 7.32 (d, J=8.5 Hz, 2H), 6.97 (d, J=16.2 Hz, 1H), 6.75 (d, J=16.2 Hz, 1H), 6.65 (d, J=1.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.82, 141.20, 136.31, 131.71, 127.58, 127.11, 124.30, 120.94, 119.15, 107.26; MS (EI, 70 eV) m/z 250 (M^++2, 25), 248 (M^+, 27), 169 (24), 141 (100), 139 (22); HRMS ($C_{12}H_9BrO$) calcd: 247.9837, found: 247.9843.

*4.2.12. trans-3-(4-Cyanostyryl)furan trans-**1l**.*[34] 64 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J=8.5 Hz, 2H), 7.59 (s, 1H), 7.50 (d, J=8.5 Hz, 2H), 7.44 (s, 1H), 7.08 (d, J=16.1 Hz, 1H), 6.79 (d, J=16.1 Hz, 1H), 6.66 (d, J=1.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.04, 142.06, 141.85, 132.39, 126.40, 123.94, 122.13, 119.01, 110.17, 107.14; MS (EI, 70 eV) m/z 196 (M^++1, 3), 195 (M^+, 62), 166 (100), 155 (3), 140 (16); HRMS ($C_{13}H_9NO$) calcd: 195.0684, found: 195.0689.

*4.2.13. trans-3-(4-Nitrostyryl)furan trans-**1m**.*[34] 56 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, J=8.8 Hz, 2H), 7.61 (s, 1H), 7.55 (d, J=8.8 Hz, 2H), 7.45 (s, 1H), 7.14 (d, J=16.1 Hz, 1H), 6.84 (d, J=16.1 Hz, 1H), 6.68 (d, J=1.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.46, 144.13, 143.91, 142.37, 126.37, 125.94, 124.06, 123.96, 123.08, 107.12; MS (EI, 70 eV) m/z 216 (M^++1, 8), 215 (M^+, 100), 198 (9), 185 (14), 169 (17), 168 (28), 156 (13), 141 (36), 139 (25), 128 (11); HRMS ($C_{12}H_9NO_3$) calcd: 215.0582, found: 215.0581.

4.3. Synthesis of 1-heterocyclic-2-(fur-3-yl)ethenes 1n–q

*4.3.1. 1-(Fur-2-yl)-2-(fur-3-yl)ethene **1n**.* Preparation of 1-(fur-2-yl)-2-(fur-3-yl)ethene was carried out via multiple procedures, including the reduction of furan-2-carboxaldehyde to (fur-2-yl) methanol, the chlorination of (fur-2-yl)methanol to (fur-2-yl) methyl chloride, and the Wittig Reaction to generate **1n**. The experimental details are described as follows: *Reduction of furan-2-carboxaldehyde*: A solution of furan-2-carboxaldehyde (0.02 mol) and methanol (20 mL) was held in 10 °C water bath, and a solution of 2 M $NaOH_{(aq)}$ (0.4 mL), $NaBH_4$ (0.28 g) and water (3.6 mL) was added to the methanol solution with a dropping funnel. The mixture was then stirred for an additional thirty minutes and subsequently neutralized with an acidic aqueous solution. The reaction mixture was extracted with ethyl acetate several times, after which the organic layers were combined and dried using anhydrous $MgSO_4$, and the organic solvent was removed with a rotary evaporator, followed by purification of the residue via silica gel chromatography. The reduction compound, (fur-2-yl)-methanol, was obtained at a 92% yield. *Chlorination of (fur-2-yl)methanol*: A solution of (fur-2-yl)methanol (0.01 mol), triethylamine (0.01 mol), and dichloromethane (20 mL) was prepared and transferred to a 50-mL double-neck flask equipped with a condenser and a dropping funnel. A solution of thionyl chloride (1 mL) and dichloromethane (10 mL) was then added to the flask with a dropping funnel while the flask was held in a 15 °C water bath under a nitrogen atmosphere. Next, the mixture was stirred at 20 °C for thirty minutes and at 40 °C for another thirty minutes. Subsequently, the reaction was quenched with crushed ice and water, and the solution was neutralized with $NaOH_{(aq)}$. Next, the reaction mixture was extracted with ethyl acetate, and the organic layers were collected and dried using anhydrous $MgSO_4$. After removing the organic solvent with a rotary evaporator, the product, (fur-2-yl)methyl chloride, was used for the Wittig Reaction directly, without characterization. *Wittig Reaction*: A mixture of triphenylphosphine (24 mmol), (fur-2-yl)methyl chloride (20 mmol) and benzene (15 mL) was refluxed overnight. The mixture was cooled to room temperature, and the precipitate (triphenylphosphonium salt) was collected via suction filtration. Subsequently, the triphenylphosphonium salt (10 mmol), 3-fural (11 mmol), and 18-crown-6 (1.5 mmol) were dissolved in 25 mL dichloromethane, and a 50% potassium carbonate aqueous solution (12 mL) was added to the dichloromethane mixture. The mixture was subsequently stirred vigorously for 2 days, and then extracted with ethyl acetate several times. The organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator and the product, *trans*-1-(fur-2-yl)-2-(fur-3-yl)ethene **1n**, was purified via silica gel chromatography using hexane for elution. The yield was 31%.

4.3.1.1. (Fur-2-yl)-methanol.[35] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (dd, J=1.8, 0.7 Hz, 1H), 6.34 (dd, J=3.2, 1.8 Hz, 1H), 6.29 (d, J=3.2 Hz, 1H), 4.60 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.96, 142.55, 110.33, 107.73, 57.42.

*4.3.1.2. trans-1-(Fur-2-yl)-2-(fur-3-yl)ethene trans-**1n**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.40 (s, 1H), 7.37 (d, J=1.5 Hz, 1H), 6.89 (d, J=16.3 Hz, 1H), 6.61 (d, J=16.3 Hz, 1H), 6.60 (s, 1H), 6.40 (dd, J=3.4, 1.7 Hz, 1H), 6.27 (d, J=3.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.16, 143.69, 141.80, 140.67, 124.26, 117.08, 116.51, 111.46, 107.60, 107.17.

*4.3.2. 1-(Fur-3-yl)-2-(thiophen-2-yl)ethene **1o**.* Preparation of 1-(fur-3-yl)-2-(thiophen-2-yl)ethene was carried out via procedures similar to those used for the preparation of **1n**, and all of the experimental procedures are summarized as follows: *Reduction of thiophene-2-carboxaldehyde*: 0.02 mol of thiophene-2-carboxal dehyde was used as the starting material to synthesize (thiophen-2-yl)methanol (97% yield). *Chlorination of (thiophen-2-yl) methanol*: 0.01 mol of (thiophen-2-yl)methanol was used as the starting material to synthesize (thiophen-2-yl)methyl chloride, without characterization. *Wittig Reaction*: 24 mmol of triphenylphosphine and 20 mmol of (thiophen-2-yl)methyl chloride were used to synthesize triphenylphosphonium salt. Then, 10 mmol of the triphenylphosphonium salt, 11 mmol of 3-fural, and all of the other necessary reagents were used to synthesize *cis*- and *trans*-1-(fur-3-yl)-2-(thiophen-2-yl)ethene **1o**, obtaining a total yield 62%. The *cis* and *trans* forms were purified via silica gel chromatography using hexane for characterization.

4.3.2.1. (Thiophen-2-yl)methanol.[36] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (d, J=5.3 Hz, 1H), 7.11 (d, J=3.3 Hz, 1H), 6.98 (dd, J=5.3, 3.3 Hz, 1H), 4.83 (s, 2H).

*4.3.2.2. trans-1-(Fur-3-yl)-2-(thiophen-2-yl)ethene trans-**1o**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.41 (s, H), 7.16 (d, J=5.0 Hz, 1H), 7.01–6.98 (m, 2H), 6.95 (d, J=16.0 Hz, 1H), 6.80 (d, J=16.0 Hz, 1H), 6.61 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.70, 142.79, 140.81, 127.49, 125.32, 124.16, 123.83, 121.58, 118.19, 107.23.

*4.3.3. 1,2-Di(Fur-3-yl)ethene **1p**.* Preparation of 1,2-di(fur-3-yl) was carried out via procedures similar to those used for the preparation of **1n**, and all of the experimental procedures are summarized as follows: *Reduction of furan-3-carboxaldehyde*: 0.02 mol of furan-3-carboxaldehyde was used as the starting material to synthesize (fur-3-yl)-methanol (92% yield). *Chlorination of (fur-3-yl)methanol*: 0.01 mol of (fur-3-yl)methanol was used as the starting material to synthesize (fur-3-yl)methyl chloride, without characterization. *Wittig Reaction*: 24 mmol of triphenylphosphine and 20 mmol of (fur-3-yl)methyl chloride were used to synthesize triphenylphosphonium salt. Then, 10 mmol of the triphenylphosphonium salt, 11 mmol of 3-fural, and all of the other necessary reagents were used to synthesize *cis*- and *trans*-1,2-di(fur-3-yl)ethene **1p**, obtaining a total yield 32%. The *cis* and *trans* forms were purified via silica gel chromatography using hexane for characterization.

4.3.3.1. (Fur-3-yl)methanol.[37] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (s, 2H), 6.34 (s, 1H), 4.40 (s, 2H).

*4.3.3.2. trans-1,2-Di(fur-3-yl)ethene trans-**1p**.*[38] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (s, 2H), 7.37 (s, 2H), 6.66 (s, 2H), 6.58 (s, 2H).

*4.3.4. 1-(Fur-3-yl)-2-(pyridin-2-yl)ethene **1q**.* A mixture of furan-3-carbaldehyde (2.0 mL, 0.02 mol), 4-picoline (2.0 mL, 0.02 mol), and acetic anhydride (30 mL) was refluxed for 24 h. Then, the reaction was poured into an ice/water mixture and neutralized with sodium carbonate. The solution was extracted with ethyl acetate several times. The organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the product **1q** was purified via silica gel chromatography using ethyl acetate and hexane for elution. The yield was 18%.

*4.3.4.1. trans-1-(Fur-3-yl)-2-(pyridin-2-yl)ethene trans-**1q**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.57 (dq, J=4.7, 0.8 Hz, 1H), 7.63 (td, J=7.7, 1.8 Hz, 1H), 7.59 (s, 1H), 7.50 (d, J=15.9 Hz, 1H), 7.42 (s, 1H), 7.31 (d, J=7.9 Hz, 1H), 7.12 (ddd, J=7.4, 4.9, 1.0 Hz, 1H), 6.88 (d, J=15.9 Hz, 1H), 6.68 (d, J=1.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.61, 149.52, 143.86, 142.21, 136.53, 127.63, 124.10, 122.69, 121.80, 121.57, 107.45; MS (EI, 70 eV) m/z 171 (M^+, 87), 170 (M^+-1, 100), 143 (88), 142 (72), 141 (70); HRMS ($C_{11}H_9NO$) calcd: 171.0679, found: 171.0676.

4.4. Synthesis of 1-aryl-2-(fur-3-yl)ethenes 1r–y

*4.4.1. 1-(Fur-3-yl)-2-(naphthalen-1-yl)ethene **1r**.* A mixture of 1-(chloromethyl)naphthalene (2 g, 11.3 mmol), triphenylphosphine (3.56 g, 13.6 mmol) and ethyl acetate (23 mL) was refluxed overnight. Then, the mixture was cooled to room temperature, and a precipitate (triphenylphosphonium salt) was formed and collected via suction filtration. Subsequently, the triphenylphosphonium salt, 3-furaldehyde (1.03 g, 10.7 mmol) and 18-crown-6 (0.42 g) were dissolved in dichloromethane (30 mL), and a 50% potassium carbonate aqueous solution (15 mL) was added. The mixture was stirred vigorously overnight, followed by extraction with ethyl acetate several times. The organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the residue was purified via chromatography using hexanes to generate *cis*- and *trans*-1-(fur-3-yl)-2-(naphthalen-1-yl)ethene **1r** (2.13 g, 85%).

*4.4.1.1. cis-1-(Fur-3-yl)-2-(naphthalen-1-yl)ethene cis-**1r**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (dd, J=8.0, 1.0 Hz, 1H), 7.86 (d, J=7.8 Hz, 1H), 7,80 (dd, J=7.1, 2.3 Hz, 1H), 7.51–7.41 (m, 4H), 7.23 (s, 1H), 7.06 (t, J=1.6 Hz, 1H), 6.90 (d, J=11.9 Hz, 1H), 6.66 (d, J=11.9 Hz, 1H), 5.72 (d, J=1.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.40, 142.19, 135.62, 133.54, 131.41, 128.28, 127.60, 127.07, 126.28, 125.95, 125.90, 125.40, 125.09, 122.46, 121.94, 109.97.

*4.4.1.2. trans-1-(Fur-3-yl)-2-(naphthalen-1-yl)ethene trans-**1r**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, J=8.4 Hz, 1H), 7.85 (dd, J=7.9, 1.6 Hz, 1H), 7.77 (d, J=8.2 Hz, 1H), 7.67 (d, J=7.2 Hz, 1H), 7.59–7.44 (m, 6H), 7.00 (d, J=16.0 Hz 1H), 6.77 (t, J=0.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.78, 141.14, 134.99, 133.71, 131.19, 128.58, 127.78, 126.00, 125.79, 125.67, 125.40, 124.86, 123.72, 123.31, 121.41, 107.50; MS (EI, 70 eV) m/z 220 (M^+, 100), 219 (M^+-1, 17), 191 (87); HRMS ($C_{16}H_{12}O$) calcd: 220.0888, found: 220.0886.

*4.4.2. 3-(2H-Acenaphthylen-1-ylidenemethyl)furan **1s**.* The preparation of 3-(2*H*-acenaphthylen-1-ylidenemethyl)furan began with the NBS-bromination of acenaphthene to generate 1-bromo acenaphthene, which was then subjected to the Wittig Reaction to synthesize **1s**. A carbon tetrachloride solution (45 mL) of acenaphthene (1 g, 6.48 mmol), *N*-bromosuccinimide (1.05 g, 5.90 mmol) and dibenzoylperoxide (0.03 g, 0.12 mmol) was refluxed for 8 h. The reaction mixture was then cooled to room temperature, filtered and evaporated to dryness. Next, the crude product and triphenylphosphine (1.7 g, 6.48 mmol) were dissolved in ethyl acetate (13 mL), and the ethyl acetate solution was refluxed overnight. The mixture was subsequently cooled to room temperature, and the precipitate (triphenylphosphonium salt) was collected via suction filtration. This salt, 3-furaldehyde (0.4 g, 4.2 mmol) and 18-crown-6 (0.22 g) were dissolved in

dichloromethane (7 mL), and a 50% potassium carbonate aqueous solution (3.5 mL) was added. The mixture was stirred vigorously overnight. Then, the reaction mixture was extracted with ethyl acetate several times. The organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the residue was purified via chromatography with hexanes to generate 3-(2*H*-acenaphthylen-1-ylidenemethyl)furan **1s** (0.47 g, 32%).

*4.4.2.1. 3-(2H-Acenaphthylen-1-ylidenemethyl)furan **1s**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.63 (dd, J=8.0, 3.1 Hz, 2H), 7.58 (d, J=7.0 Hz, 1H), 7.52–7.45 (m, 3H), 7.33 (d, J=6.7 Hz, 1H), 7.07 (s, 1H), 6.69 (s, 1H), 4.11 (s, 2H); MS (EI, 70 eV) m/z 232 (M^+, 100), 203 (59); HRMS ($C_{17}H_{12}O$) calcd: 232.0888, found: 232.0882.

*4.4.3. 3-(3,4-Dihydro-2H-naphthalen-1-ylidenemethyl)furan **1t**.* The preparation of 3-(3,4-dihydro-2*H*-naphthalen-1-ylidene methyl)furan began with the NBS-bromination of 1,2,3,4-tetrahydronaphthalene to generate 1-bromo-1,2,3,4-tetrahydrona phthalene, which was then subjected to the Wittig Reaction to synthesize **1t**. An ethyl acetate solution (200 mL) of 1,2,3,4-tetrahydronaphthalene (10 g, 75.6 mmol), *N*-bromosuccinimide (12.8 g, 72 mmol) and dibenzoylperoxide (0.37 g, 1.53 mmol) was refluxed for 4 h. Next, triphenylphosphine (23.8 g, 90.7 mmol) was added to the mixture, followed by refluxing overnight. Subsequently, the mixture was cooled to room temperature, and the precipitate (triphenylphosphonium salt)was collected via suction filtration. This salt, 3-furaldehyde (2.33 g, 24.3 mmol) and 18-crown-6 (0.83 g) were dissolved in dichloromethane (58 mL), and a 50% potassium carbonate aqueous solution (28 mL) was added. The mixture was stirred vigorously overnight and then extracted with ethyl acetate several times. The organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the residue was purified via chromatography using hexane for elution to generate 3-(3,4-dihydro-2*H*-naphthalen-1-ylidenemethyl)furan **1t** (0.48 g, 3%).

*4.4.3.1. 3-(3,4-Dihydro-2H-naphthalen-1-ylidenemethyl)furan **1t**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (dd, J=7.7, 0.9 Hz, 1H), 7.36 (d, J=0.6 Hz, 1H), 7.25 (t, J=1.7 Hz, 1H), 7.16–7.09 (m, 2H), 6.99 (tm, J=7.0 Hz, 1H), 6.24 (d, J=1.8 Hz, 1H), 6.16 (s, 1H), 2.83 (t, J=6.7 Hz, 2H), 2.47 (td, J=6.5, 1.4 Hz, 2H), 1.94 (quintet, J=6.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.33, 141.17, 138.74, 137.89, 135.53, 128.49, 128.47, 127.51, 124.61, 122.94, 113.84, 110.63, 34.71, 29.35, 23.89; MS (EI, 70 eV) m/z 210 (M^+, 100), 181 (75), 165 (59); HRMS ($C_{15}H_{14}O$) calcd: 210.1045, found: 210.1043.

*4.4.4. 3-((6-Methoxy-3,4-dihydronaphthalen-1(2H)-ylidene)methyl) furan **1u**.* Sodium borohydride (0.43 g, 11.37 mmol) was added to a methanol solution (15 mL) of 6-methoxyl-1-tetralone (1.0 g, 5.68 mmol). The reaction mixture was stirred at room temperature for 1 h and subsequently diluted with water and extracted with ethyl acetate. The organic phase was dried over anhydrous magnesium sulfate, and the solvent was evaporated. The resulting alcohol and triphenylphosphonium bromide (1.95 g, 5.68 mmol) were suspended in benzene (10 mL) and refluxed for 12 h. The precipitate collected through filtration and dried. The obtained salt (2.32 g, 4.61 mmol), 3-furaldehyde (0.44 g, 4.58 mmol) and 18-crown-6 (0.15 g) were dissolved in dichloromethane (10 mL), and a 50% potassium carbonate aqueous solution (5 mL) was added. The reaction mixture was stirred vigorously overnight and then extracted with ethyl acetate several times. The organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the residue was purified via chromatography using hexane for elution to generate 3-(3,4-dihydro-2*H*-naphthalen-1-ylidenemethyl)furan **1u** (0.26 g, 21%).

*4.4.4.1. 3-((6-Methoxy-3,4-dihydronaphthalen-1(2H)-ylidene) methyl)-furan **1u**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J=8.8 Hz, 1H), 7.52 (t, J=0.8 Hz, 1H), 7.41 (t, J=1.8 Hz, 1H), 6.76 (dd, J=8.8, 2.8 Hz, 1H), 6.67 (s, 1H), 6.64 (d, J=2.8 Hz, 1H), 6.52 (dd, J=1.8, 0.8 Hz, 1H), 3.80 (s, 3H), 2.73 (t, J=6.5 Hz, 2H), 2.69 (td, J=6.5, 2.1 Hz, 2H), 1.85 (quintet, J=6.3 Hz, 2H).

*4.4.5. 3-Indan-1-ylidenemethylfuran **1v**.* The preparation of 3-indan-1-ylidenemethylfuran began with the chlorination of 1-indanol to generate 1-chloroindane, which was then subjected to the Wittig Reaction to synthesize **1v**. A sealed 250 mL double-neck flask was charged with 1-indanol (8.28 g, 61.7 mmol) and triethylamine (6.25 g, 61.7 mmol) and filled with nitrogen. Dry dichloromethane (120 mL) was added with a syringe. A dry dichloromethane solution (12 mL) of thionyl chloride (8.0 g, 67.2 mmol) was added dropwise to the reaction mixture in a 0 °C ice water bath over a period of 10 min. Then, the solution was stirred at 0 °C for 30 min and refluxed at 40 °C for another 40 min. After cooling to room temperature, ice and a 10% sodium bicarbonate aqueous solution were added to the mixture, and the organic and aqueous layers were separated. The aqueous layer was extracted with dichloromethane, and the organic layers were collected. The organic layers were dried over magnesium sulfate and concentrated under vacuum to obtain a yellow residue. The residue and triphenylphosphine (16.2 g, 61.7 mmol) were dissolved in ethyl acetate (130 mL), and the resulting solution was refluxed overnight. Then, the mixture was cooled to room temperature, and the precipitate (triphenylphosphonium salt) was collected via suction filtration. The obtained salt (1.79 g, 4.3 mmol), 3-furaldehyde (0.4 g, 4.2 mmol) and 18-crown-6 (0.14 g) were dissolved in dichloromethane (10 mL), and a 50% potassium carbonate aqueous solution (5 mL) was added. The reaction mixture was stirred vigorously overnight, followed by extraction with ethyl acetate several times. The organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator and purified via chromatography with hexanes to generate *cis*- and *trans*-3-indan-1-ylidenemethylfuran **1v** (0.52 g, 4%).

*4.4.5.1. (Z)-3-Indan-1-ylidenemethylfuran (Z)-**1v**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, J=7.9 Hz, 1H), 7.44–7.41 (m, 2H), 7.25 (d, J=7.6 Hz, 1H), 7.16 (td, J=7.4, 1.1 Hz, 1H), 7.05 (t, J=7.4 Hz, 1H), 6.48 (d, J=1.3 Hz, 1H), 6.28 (s, 1H), 2.97–2.94 (m, 2H), 2.87–2.83 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.61, 144.29, 142.62, 140.24, 139.71, 128.07, 125.87, 125.24, 124.26, 122.05, 111.14, 110.71, 34.30, 30.11.

*4.4.5.2. (E)-3-Indan-1-ylidenemethylfuran (E)-**1v**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 2H), 7.52 (dd, J=6.3, 2.0 Hz, 1H), 7.42 (t, J=1.6 Hz, 1H), 7.26 (dd, J=6.3, 2.0 Hz, 1H), 7.22–7.17 (m, 2H), 6.75 (t, J=2.6 Hz, 1H), 6.57 (d, J=1.3 Hz, 1H), 3.11–3.08 (m, 2H), 2.94–2.90 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.99, 143.03, 142.86, 141.96, 140.58, 127.78, 126.55, 125.26, 123.98, 119.90, 110.59, 108.47, 30.53, 30.46; MS (EI, 70 eV) m/z 197 (M^++1, 40), 196 (M^+, 79), 167 (100); HRMS ($C_{14}H_{12}O$) calcd: 196.0888, found: 196.0885.

*4.4.6. 3-(4-Bromo-indan-1-ylidenemethyl)furan **1w**.* Sodium borohydride (0.36 g, 9.52 mmol) was added to a methanol solution (15 mL) of 4-bromo-1-indanone (1.0 g, 4.74 mmol). The mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with water, and extracted with ethyl acetate. The organic phase was dried over anhydrous magnesium sulfate, and the solvent was evaporated. The resulting alcohol and triphenylphosphonium bromide (1.63 g, 4.74 mmol) were suspended in benzene

(10 mL) and refluxed for 12 h. The precipitate was collected by filtration and dried. The obtained salt (0.68 g, 1.26 mmol), 3-furaldehyde (0.12 g, 1.25 mmol) and 18-crown-6 (0.04 g) were dissolved in dichloromethane (3 mL), and a 50% potassium carbonate aqueous solution (1.4 mL) was added. The mixture was stirred vigorously overnight. Then, the reaction was extracted with ethyl acetate several times. The organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the residue was purified via chromatography using hexane for elution to generate 3-(4-bromo-indan-1-ylidenemethyl)furan (0.26 g, 20% yield).

*4.4.6.1. (Z)-3-(4-Bromo-indan-1-ylidenemethyl)furan (Z)-**1w**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, J=7.8 Hz, 1H), 7.42 (t, J=1.7 Hz, 1H), 7.41 (s, 1H), 7.31 (d, J=7.8 Hz, 1H), 6.92 (t, J=7.8 Hz, 1H), 6.42 (d, J=1.7 Hz, 1H), 6.28 (d, J=1.0 Hz, 1H), 2.97–2.93 (m, 2H), 2.88–2.85 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.96, 143.97, 143.05, 142.62, 140.98, 130.46, 128.40, 123.60, 120.81, 118.65, 110.49, 110.23, 32.15, 29.75.

*4.4.6.2. (E)-3-(4-Bromo-indan-1-ylidenemethyl)furan (E)-**1w**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.44–7.42 (m, 2H), 7.33 (d, J=7.8 Hz, 1H), 7.07 (t, J=7.8 Hz, 1H), 6.73 (t, J=2.7 Hz, 1H), 6.56 (d, J=1.1 Hz, 1H), 3.09–3.05 (m, 2H), 2.94–2.92 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.43, 144.12, 142.82, 141.73, 140.36, 130.92, 127.73, 123.05, 121.62, 120.66, 112.54, 111.01, 33.22, 31.55.

*4.4.7. 3-(2-(Phenanthren-9-yl)vinyl)furan **1x**.* 3-(2-(Phenanthren-9-yl)vinyl)furan was synthesized through multiple steps, which included the Wittig Reaction to synthesize 1,2-diphenylpropene, the oxidative photocyclization of 1,2-diphenylpropene, and the NBS-bromination of 9-methylphenanthrene, which was then subjected to the Wittig Reaction to synthesize **1x**. The experimental details are described as follows: *Synthesis of 1,2-diphenylpropene via the Wittig Reaction*: A mixture of 1-(bromoethyl)benzene (3.7 g, 20 mmol), triphenylphosphine (6.3 g, 24 mmol) and ethyl acetate (16 mL) was refluxed for 3 days. Then, the mixture was cooled to room temperature, and a precipitate (triphenylphosphonium salt) was formed and collected via suction filtration. Subsequently, the triphenylphosphonium salt (4.0 g, 9 mmol) and potassium *tert*-butoxide (1.5 g, 13.5 mmol) were transferred to a 100 mL flask, which was sealed and maintained under a nitrogen atmosphere. Dry tetrahydrofuran (21 mL) and benzaldehyde (0.87 g, 8.2 mmol) were then added to the mixture with a syringe, followed by stirring for 5 h. Next, the reaction was extracted with ethyl acetate several times. The organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the residue was purified via chromatography with hexane to produce *cis*- and *trans*-1,2-diphenylpropene (0.94 g, 59%). *Oxidative photocyclization*: A mixture of 1,2-diphenylpropene (0.1 g), iodine (0.02 g), and hexane (50 mL) was prepared and divided into five quartz tubes. The tubes were sealed with septa and irradiated under 300 nm UV light at ambient temperature (approximately 40 °C). After irradiation, the reaction was quenched with an aqueous sodium hydroxide solution, and the mixture was extracted with ethyl acetate. The organic layers were collected and dried, and the organic solvent was removed. A yellow-brown solid, 9-methylphenanthrene, was obtained at a 98% yield. *NBS-bromination and the Wittig Reaction*: An ethyl acetate solution (25 mL) of 9-methylphenanthrene (0.69 g, 3.57 mmol), *N*-bromosuccinimide (0.66 g, 3.72 mmol) and dibenzoylperoxide (0.02 g, 0.076 mmol) was refluxed for 2 h. The reaction mixture was cooled to room temperature, and triphenylphosphine (0.80 g, 3.05 mmol) was added to the previous reaction. The reaction was refluxed for 3 days. Then, the mixture was cooled to room temperature, and the precipitate, triphenylphosphonium salt (0.96 g, 71% yield), was collected via suction filtration. The obtained salt (1.60 g, 3 mmol), 3-furaldehyde (0.26 g, 2.73 mmol) and 18-crown-6 (0.10 g, 0.67 mmol) were dissolved in dichloromethane (7 mL), and a 50% potassium carbonate aqueous solution (4 mL) was added. The mixture was stirred vigorously at room temperature for 2 days. Then, the reaction was extracted with ethyl acetate several times. The organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the residue was purified via chromatography with hexane and ethyl acetate to generate a yellow solid, *cis*- and *trans*-3-(2-(phenanthren-9-yl)vinyl)furan **1x** (0.66 g, 70% yield).

4.4.7.1. 9-Methylphenanthrene.[39] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.74 (dd, J=7.3, 2.1 Hz, 1H), 8.67 (d, J=7.9 Hz, 1H), 8.07 (dd, J=7.3, 2.1 Hz, 1H), 7.82 (dd, J=7.3, 1.7 Hz, 1H), 7.69 (td, J=6.7, 1.7 Hz, 1H), 7.66 (td, J=7.2, 1.5 Hz, 1H), 7.61 (td, J=7.2, 1.5 Hz, 1H), 7.60 (s, 1H), 7.58 (td, J=7.2, 1.4 Hz, 1H), 2.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.47, 132.08, 132.01, 130.37, 129.66, 127.81, 126.72, 126.56, 126.50, 126.19, 125.79, 124.64, 122.99, 122.44, 20.01.

*4.4.7.2. trans-3-(2-(Phenanthren-9-yl)vinyl)furan trans-**1x**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.75 (dd, J=7.9, 1.3 Hz, 1H), 8.67 (d, J=8.1 Hz, 1H), 8.24 (dd, J=7.9, 1.3 Hz, 1H), 7.92 (s, 1H), 7.90 (dd, J=7.7, 1.5 Hz, 1H), 7.69 (td, J=7.4, 1.5 Hz, 1H), 7.66 (td, J=7.4, 1.5 Hz, 1H), 7.63 (td, J=7.7, 1.5 Hz, 1H), 7.62 (s, 1H), 7.60 (td, J=7.3, 1.3 Hz, 1H), 7.58 (d, J=15.8 Hz, 1H), 7.49 (s, 1H), 7.10 (d, J=15.8 Hz, 1H), 6.81 (d, J=1.7 Hz, 1H).

*4.4.8. 3-(2-(3-Cyanophenanthren-9-yl)vinyl)furan **1y**.* The preparation of (*Z*)-3-(2-(3-cyanophenanthren-9-yl)vinyl)furan was performed following the same procedures used for the compound **1x**. *Synthesis of 1-(4-cyanophenyl)-2-phenylpropene via the Wittig Reaction*: Using 1-(bromoethyl)benzene (3.7 g, 20 mmol), triphenylphosphine (6.3 g, 24 mmol), and ethyl acetate (16 mL), triphenyl phosphonium salt (8.74 g, 19.5 mmol) was synthesized. Then, using the triphenylphosphonium salt (4.02 g, 9 mmol), potassium *tert*-butoxide (1.5 g, 13.5 mmol), dry tetrahydrofuran (21 mL), and 4-cyanobenzaldehyde (1.07 g, 8.2 mmol), (*Z*)- and (*E*)-1-(4-cyanophenyl)-2-phenylpropene **1y** were synthesized (1.10 g, 60%). *Oxidative photocyclization*: Using (*Z*)- and (*E*)-1-cyanophenyl-2-phenylpropene (0.1 g), iodine (0.02 g), and hexane (50 mL), 3-cyano-9-methylphenanthrene was synthesized (99% yield). *NBS-bromination and the Wittig Reaction*: Using 3-cyano-9-methyl phenanthrene (0.44 g, 2.04 mmol), *N*-bromosuccinimide (0.38 g, 2.12 mmol), dibenzoylperoxide (0.01 g, 0.043 mmol), and ethyl acetate (20 mL), 3-cyano-9-(bromomethyl)phenanthrene was synthesized. Then, triphenylphosphine (0.64 g, 2.44 mmol) was added to the previous reaction directly to produce triphenylphosphonium salt (0.45 g, 40% yield). Subsequently, the triphenylphosphonium salt (0.6 g, 1.0 mmol), 3-furaldehyde (0.09 g, 0.98 mmol), 18-crown-6 (0.03 g, 0.13 mmol), dichloromethane (3 mL), and a50% potassium carbonate aqueous solution (4 mL) were employed to synthesize *cis*- and *trans*-3-(2-(3-cyano phenanthren-9-yl)vinyl)furan **1y** (0.17 g, 54% yield).

4.4.8.1. 3-Cyano-9-methylphenanthrene. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.67 (dd, J=6.7, 2.5 Hz, 1H), 8.11 (dd, J=7.3, 1.8 Hz, 1H), 7.87 (d, J=8.5 Hz, 1H), 7.76 (td, J=7.3, 1.2 Hz, 1H), 7.74 (td, J=7.6, 1.8 Hz, 1H), 7.74 (d, J=6.7 Hz, 1H), 7.61 (s, 1H), 2.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.69, 134.27, 132.31, 129.37, 129.34, 128.71, 128.04, 127.78, 127.35, 125.97, 124.97, 122.93, 119.76, 108.93, 20.26.

*4.4.8.2. trans-3-(2-(3-Cyanophenanthren-9-yl)vinyl)furan trans-**1y**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.98 (s, 1H), 8.69 (d, J=8.3 Hz, 1H),

8.27 (d, J=7.7 Hz, 1H), 7.95 (dd, J=8.3, 2.2 Hz, 1H), 7.91 (d, J=2.2 Hz, 1H), 7.80–7.72 (m, 3H), 7.65 (s, 1H), 7.55 (d, J=16.0 Hz, 1H), 7.50 (s, 1H), 7.15 (d, J=16.0 Hz, 1H), 6.80 (d, J=1.7 Hz, 1H).

4.5. Procedures for photorearrangement of compound 1

4.5.1. General procedures for irradiation in the presence of 10% KOH$_{(aq)}$/MeOH. Here, the irradiation of 3-(2-naphthalen-1-ylvinyl) furan **1r** is employed as an example to describe the general experimental procedures, as follows: A total of five identical samples were prepared, each of which contained 1r (20 mg), methanol (19 mL), and 10% KOH$_{(aq)}$ (1 mL) in a quartz tube (1.5×20 cm). The tubes were sealed with septa and subjected to sonication to dissolve all of the components. Then, the solution was bubbled with nitrogen gas for 20 min to remove dissolved oxygen. The sample was irradiated with 300 nm UV light at ambient temperature (approximately 40 °C) for 6 h. After irradiation, the five samples were combined, and 500 mL of water was added to the solution. The resulting solution was extracted with ethyl acetate several times, and the organic layers were then combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the products were purified via chromatography using hexane for elution. Following chromatography, 26.5 mg of **2r** was obtained, and the yield was 29%.

4.5.2. General procedures for irradiation in the presence of lithium borohydride in methanol. Here, the irradiation of 3-(2-naphthalen-1-ylvinyl)furan **1r** is used as an example to describe the general experimental procedures, as follows: A total of five identical samples were prepared, each of which contained **1r** (20 mg), methanol (18 mL), 50% KOH$_{(aq)}$ (2 mL), and lithium borohydride (40 mg) (*CAUTION: the addition of lithium borohydride sometimes causes flames for a short while*) in a quartz tube (1.5×20 cm). The tubes were sealed with septa and subjected to sonication to dissolve all of the components. Then, the solution was bubbled with nitrogen gas for 20 min to remove dissolved oxygen. The sample was irradiated with 300 nm UV light at ambient temperature (approximately 40 °C) for a certain time. After irradiation, the five samples were combined, and 500 mL of water was added to the solution. The resulting solution was extracted with ethyl acetate several times, and the organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the products were purified via chromatography using a mixed solvent of hexane and ethyl acetate (4:1) for elution. Following chromatography, 4.5 mg of **2r** and 44.6 mg of **3r** were obtained, and the yields were 5% and 44%, respectively.

4.5.3. General procedures for irradiation in the presence of DBU in benzene. Here, the irradiation of 3-(2-naphthalen-1-ylvinyl)furan **1r** is employed as an example to describe the general experimental procedures, as follows: A total of five identical samples were prepared, each of which contained **1r** (20 mg, 0.37 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 70 mg), ethanol (2 drops), and benzene (20 mL) in a quartz tube (1.5×20 cm). The tubes were sealed with septa and subjected to sonication to dissolve all of the components. Then, the solution was bubbled with nitrogen gas for 20 min to remove dissolved oxygen. The sample was irradiated with 300 nm UV light at ambient temperature (approximately 40 °C) for a certain time. After irradiation, the five samples were combined, and 500 mL of water was added to the solution. The resulting solution was extracted with ethyl acetate several times, and the organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the products were purified via chromatography using hexane for elution. Following chromatography, 34.3 mg of **2r** was obtained, and the yield was 37.5%.

*4.5.4. Spectral data of compound **2a**–**j**, **2l**, **2o**, **2r**–**t**, and **2v**–**y**. 2-Methoxy-7-methylnaphthalene* **2a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J=8.5 Hz, 1H), 7.69 (d, J=8.5 Hz, 1H), 7.54 (s, 1H), 7.20 (d, J=8.8 Hz, 1H), 7.11 (d, J=8.8 Hz, 1H), 7.09 (s, 1H), 3.93 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.69, 136.01, 134.79, 129.06, 127.43, 125.85, 125.81, 117.65, 105.30, 54.23, 21.71; MS (EI, 70 eV) m/z 173 (M^++1, 6), 172 (M^+, 100), 155 (12), 129 (30); HRMS ($C_{12}H_{12}O$) calcd: 172.0883, found: 172.0887.

4.5.4.1. 2-Methyl-7-trifluoromethoxynaphthalene **2b**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, J=8.9 Hz, 1H), 7.77 (d, J=8.4 Hz, 1H), 7.61 (s, 1H), 7.59 (s, 1H), 7.36 (dd, J=8.4, 1.4 Hz, 1H), 7.28 (d, J=8.9 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.98, 146.97, 136.93, 133.81, 129.99, 129.65, 128.62, 127.55, 126.73, 121.69, 119.64, 119.15, 117.49, 21.67; MS (EI, 70 eV) m/z 227 (M^++1, 13), 226 (M^+, 100), 225 (M^+−1, 42), 141 (40), 129 (17); HRMS ($C_{12}H_9F_3O$) calcd: 226.0605, found: 226.0608.

4.5.4.2. 2-tert-Butyl-7-methylnaphthalene **2c**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J=8.5 Hz, 1H), 7.72 (d, J=8.2 Hz, 1H), 7.71 (s, 1H), 7.61 (s, 1H), 7.52 (dd, J=8.5, 1.9 Hz, 1H), 7.28 (dd, J=8.2, 1.3 Hz, 1H), 2.52 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.48, 135.29, 133.58, 129.85, 127.44, 127.20, 127.11, 126.88, 123.84, 122.21, 34.79, 31.25, 21.71; MS (EI, 70 eV) m/z 199 (M^++1, 3), 198 (M^+, 44), 183 (100), 155 (18); HRMS ($C_{15}H_{18}$) calcd: 198.1409, found: 198.1409.

4.5.4.3. 2-Isopropyl-7-methylnaphthalene **2d**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, J=8.5 Hz, 1H), 7.74 (d, J=8.2 Hz, 1H), 7.61 (s, 2H), 7.37 (dd, J=8.5, 1.6 Hz, 1H), 7.30 (dd, J=8.2, 1.3 Hz, 1H), 3.10 (heptet, J=6.9 Hz, 1H), 2.55 (s, 3H), 1.39 (d, J=6.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.31, 135.33, 133.85, 130.30, 127.50, 127.33, 127.29, 126.55, 124.82, 123.43, 34.22, 23.94, 21.70; MS (EI, 70 eV) m/z 185 (M^++1, 3), 184 (M^+, 74), 169 (100), 154 (31); HRMS ($C_{14}H_{16}$) calcd: 184.1252, found: 184.1253.

4.5.4.4. 2-Methyl-7-propylnaphthalene **2e**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J=7.6 Hz, 1H), 7.73 (d, J=7.6 Hz, 1H), 7.58 (s, 1H), 7.56 (s, 1H), 7.29 (dd, J=8.5, 1.6 Hz, 1H), 7.28 (dd, J=8.5, 1.3 Hz, 1H), 2.77 (t, J=7.5 Hz, 2H), 2.53 (s, 3H), 1.77 (sextet, J=7.4 Hz, 2H), 1.01 (t, J=7.5 Hz, 3H).

4.5.4.5. 2-Ethyl-7-methylnaphthalene **2f**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J=8.8 Hz, 1H), 7.72 (d, J=8.5 Hz, 1H), 7.57 (s, 1H), 7.56 (s, 1H), 7.30 (dd, J=8.5, 1.9 Hz, 1H), 7.27 (dd, J=8.5, 1.6 Hz, 1H), 2.82 (q, J=7.5 Hz, 2H), 2.52 (s, 3H), 1.34 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.76, 135.37, 133.90, 130.14, 127.47, 127.37, 127.25, 126.38, 126.16, 124.89, 29.05, 21.71, 15.54; MS (EI, 70 eV) m/z 171 (M^++1, 10), 170 (M^+, 96), 155 (100); HRMS ($C_{13}H_{14}$) calcd: 170.1096, found: 170.1097.

4.5.4.6. 2,7-Dimethylnaphthalene **2g**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J=8.3 Hz, 2H), 7.55 (s, 2H), 7.27 (d, J=8.3 Hz, 2H), 2.53 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.41, 133.89, 129.93, 127.38, 127.20, 126.20, 21.70; MS (EI, 70 eV) m/z 157 (M^++1, 5), 156 (M^+, 100), 142 (25), 141 (90); HRMS ($C_{12}H_{12}$) calcd: 156.0939, found: 156.0939.

4.5.4.7. 2-Methylnaphthalene **2h**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J=8.0 Hz, 1H), 7.78 (d, J=8.0 Hz, 1H), 7.77 (d, J=8.2 Hz, 1H), 7.64 (s, 1H), 7.47–7.43 (m, 2H), 7.34 (dd, J=8.5, 1.3 Hz, 1H), 2.54 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.41, 133.65, 131.69, 128.08, 127.66, 127.57, 127.20, 126.81, 125.83, 124.92, 21.68; MS (EI, 70 eV)

m/*z* 142 (M^+, 100), 141 (M^+-1, 90), 115 (13); HRMS ($C_{12}H_{12}$) calcd: 142.0783, found: 142.0780.

4.5.4.8. 2-Fluoro-7-methylnaphthalene ***2i***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (dd, *J*=9.0, 3.3 Hz, 1H), 7.74 (d, *J*=8.4 Hz, 1H), 7.57 (s, 1H), 7.38 (dd, *J*=10.1, 2.6 Hz, 1H), 7.29 (d, *J*=8.6, 1.4 Hz, 1H), 7.20 (td, *J*=8.7, 2.6 Hz, 1H), 2.53 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.77 (d, J_{C-F}=242.5 Hz), 136.67, 134.41 (d, J_{C-F}=10.0 Hz), 129.91 (d, J_{C-F}=8.8 Hz), 128.67, 127.64, 127.38 (d, J_{C-F}=2.5 Hz), 126.24 (d, J_{C-F}=5.0 Hz), 115.25 (d, J_{C-F}=26.3 Hz), 110.21 (d, J_{C-F}=20.0 Hz), 21.68; MS (EI, 70 eV) *m*/*z* 160 (M^+, 100), 159 (M^+-1, 95), 70 (59), 61 (65); HRMS ($C_{11}H_9F$) calcd: 160.0688, found: 160.0686.

4.5.4.9. 2-Chloro-7-methylnaphthalene ***2j***.[40] (Record the spectral data from the mixture of **2h** and **2j**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.73 (d, *J*=8.5 Hz, 1H), 7.72 (d, *J*=8.5 Hz, 1H), 7.53 (s, 1H), 7.38–7.33 (m, 2H), 2.52 (s, 3H); MS (EI, 70 eV) *m*/*z* 178 (M^++2, 24), 176 (M^+, 63), 141 (100), 139 (25), 115 (25); HRMS ($C_{11}H_9Cl$) calcd: 176.0393, found: 176.0395.

4.5.4.10. 2-Cyano-7-methylnaphthalene ***2l***.[41] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.86 (d, *J*=8.5 Hz, 1H), 7.79 (d, *J*=8.5 Hz, 1H), 7.66 (s, 1H), 7.54 (d, *J*=8.5 Hz, 1H), 7.48 (d, *J*=8.5 Hz, 1H), 2.55 (s, 1H); MS (EI, 70 eV) *m*/*z* 168 (M^++1, 8), 167 (M^+, 100), 166 (M^+-1, 50), 140 (14), 131 (60); HRMS ($C_{12}H_9N$) calcd: 167.0735, found: 167.0734.

4.5.4.11. 5-Methylbenzothiophene ***2o***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, *J*=8.2 Hz, 1H), 7.63 (s, 1H), 7.41 (d, *J*=5.4 Hz, 1H), 7.26 (dd, *J*=5.4, 0.7 Hz, 1H), 7.18 (dd, *J*=8.2, 1.7 Hz, 1H), 2.48 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.93, 136.87, 133.83, 126.35, 125.96, 123.50, 123.46, 122.05, 21.34; MS (EI, 70 eV) *m*/*z* 148 (M^+, 71), 147 (M^+-1, 100), 121 (2); HRMS (C_9H_8S) calcd: 148.0341, found: 148.0341.

4.5.4.12. 2-Methylphenanthrene ***2r***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (d, *J*=8.3 Hz, 1H), 8.58 (d, *J*=8.4 Hz, 1H), 7.88 (d, *J*=7.9 Hz, 1H), 7.72 (d, *J*=8.9 Hz, 1H), 7.69–7.72 (m, 3H), 7.60–7.56 (m, 1H), 7.49 (d, *J*=8.4 Hz, 1H), 2.57 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.27, 132.18, 131.71, 130,34, 128.49, 128.30, 128.11, 126.88, 126.65, 126.45, 126.08, 122.53, 122.43, 21.43; MS (EI, 70 eV) *m*/*z* 192 (M^+, 79), 105 (46), 57 (100); HRMS ($C_{15}H_{12}$) calcd: 192.0939, found: 192.0935.

4.5.4.13. 2-Methyl-4H-cyclopenta[def]phenanthrene ***2s***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, *J*=8.6 Hz, 2H), 7.77 (d, *J*=8.9 Hz, 1H), 7.67 (d, *J*=7.0 Hz, 1H), 7.63 (s, 1H), 7.61 (d, *J*=7.0 Hz, 1H), 7.54 (s, 1H), 4.30 (s, 2H), 2.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.85, 141.68, 138.33, 137.26, 136.48, 127.79, 127.53, 126.74, 125.24, 124.97, 122.99, 122.50, 122.25, 121.12, 37.26, 29.70, 22.76; MS (EI, 70 eV) *m*/*z* 205 (M^++1, 20), 204 (M^+, 100), 189 (61); HRMS ($C_{16}H_{12}$) calcd: 204.0939, found: 204.0938.

4.5.4.14. 5-Methyl-2,3-dihydro-1H-phenalene ***2t***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J*=8.2 Hz, 1H), 7.43 (s, 1H), 7.31 (t, *J*=8.2 Hz, 1H), 7.13 (d, *J*=6.9 Hz, 1H), 7.06 (s, 1H), 3.08 (t, *J*=6.1 Hz, 2H), 3.06 (t, *J*=6.1 Hz, 2H), 2.46 (s, 3H), 2.06 (quintet, *J*=6.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.25, 136.17, 134.92, 133.97, 128.29, 126.03, 125.46, 125.13, 124.79, 122.93, 31.22, 31.19, 23.18, 21.64; MS (EI, 70 eV) *m*/*z* 182 (M^+, 11), 183 (M^+-1, 12), 134 (68), 57 (100); HRMS ($C_{14}H_{14}$) calcd: 182.1096, found: 182.1095.

4.5.4.15. 4-Methylacenaphthene ***2v***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J*=8.2 Hz, 1H), 7.39 (t, *J*=7.5 Hz, 1H), 7.36 (s, 1H), 7.20 (d, *J*=6.8 Hz, 1H), 7.12 (s, 1H), 3.40–3.34 (m, 4H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.99, 145.64, 137.75, 131.58, 127.86, 121.52, 121.37, 121.30, 118.27, 30.49, 30.11, 22.38; MS (EI, 70 eV) *m*/*z* 168 (M^+, 57), 153 (58), 57 (100); HRMS ($C_{13}H_{12}$) calcd: 168.0939, found: 168.0940.

4.5.4.16. 2-Methyltriphenylene ***2x***.[42] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.68–8.60 (m, 4H), 8.55 (d, *J*=8.6 Hz, 1H), 8.45 (s, 1H), 7.67–7.61 (m, 4H), 7.49 (dd, *J*=8.4, 1.2 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 129.89, 129.75, 129.69, 129.40, 128.68, 127.47, 127.14, 127.07, 127.06, 126.76, 123.30, 123.28, 123.24, 123.06, 21.83.

4.5.4.17. 2-Methyl-10-cyanotriphenylene ***2y***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.94 (s, 1H), 8.70 (d, *J*=8.5 Hz, 1H), 8.63 (d, *J*=8.3 Hz, 1H), 8.57 (d, *J*=8.0 Hz, 1H), 8.56 (d, *J*=8.4 Hz, 1H), 8.41 (s, 1H), 7.83 (d, *J*=8.4 Hz, 1H), 7.72 (td, *J*=7.8, 1.5 Hz, 1H), 7.69 (td, *J*=7.8, 1.4 Hz, 1H), 7.58 (dd, *J*=8.4, 1.2 Hz, 1H), 2.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.57, 132.87, 130.39, 130.24, 130.10, 128.84, 128.53, 128.40, 128.37, 128.34, 127.84, 127.44, 124.29, 123.91, 123.49, 123.27, 123.24, 119.42, 110.41, 29.69.

4.5.5. Spectral data of compound ***3a***, ***3g–j***, ***3l***, ***3n–o***, *and* ***3r–w***

4.5.5.1. 2-(7-Methoxynaphthalen-2-yl)ethanol ***3a***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J*=8.4 Hz, 1H), 7.71 (d, *J*=8.7 Hz, 1H), 7.58 (s, 1H), 7.21 (dd, *J*=8.4, 1.0 Hz, 1H), 7.12 (dd, *J*=8.9, 2.5 Hz, 1H), 7.10 (d, *J*=2.2 Hz, 1H), 3.92 (t, *J*=6.5 Hz, 2H), 3.91 (s, 3H), 3.00 (t, *J*=6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.79, 136.51, 134.70, 129.08, 127.93, 127.70, 126.40, 125.05, 118.21, 105.43, 63.46, 55.22, 39.30; MS (EI, 70 eV) *m*/*z* 202 (M^+, 16), 171 (100), 128 (4); HRMS ($C_{13}H_{14}O_2$) calcd: 202.0994, found: 202.0992.

4.5.5.2. 2-(7-Methylnaphthalen-2-yl)ethanol ***3g***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J*=8.3 Hz, 1H), 7.71 (d, *J*=8.3 Hz, 1H), 7.59 (s, 1H), 7.56 (s, 1H), 7.28 (dt, *J*=8.2, 2.3 Hz, 2H), 3.94 (t, *J*=6.5 Hz, 2H), 3.02 (t, *J*=6.5 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.90, 135.71, 133.77, 130.49, 127.93, 127.72, 127.41, 126.82, 126.45, 126.41, 63.50, 39.33, 21.68.

4.5.5.3. 2-(Naphthalen-2-yl)ethanol ***3h***.[43] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84–7.78 (m, 3H), 7.69 (s, 1H), 7.48 (td, *J*=7.5, 1.3 Hz, 1H), 7.45 (td, *J*=7.5, 1.3 Hz, 1H), 7.37 (dd, *J*=8.6, 1.5 Hz, 1H), 3.96 (t, *J*=6.5 Hz, 2H), 3.04 (t, *J*=6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.92, 133.56, 132.27, 128.27, 127.64, 127.47, 127.37, 126.09, 125.47, 63.52, 39.32; MS (EI, 70 eV) *m*/*z* 173 (M^++1, 2), 172 (M^+, 32), 142 (21), 141 (100), 115 (13); HRMS ($C_{12}H_{12}O$) calcd: 172.0888, found: 172.0888.

4.5.5.4. 2-(7-Fluoronaphthalen-2-yl)ethanol ***3i***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (dd, *J*=8.9, 5.9 Hz, 1H), 7.79 (d, *J*=8.6 Hz, 1H), 7.62 (s, 1H), 7.40 (dd, *J*=9.9, 2.3 Hz, 1H), 7.32 (dd, *J*=8.4, 1.5 Hz, 1H), 7.22 (td, *J*=8.8, 2.5 Hz, 1H), 3.95 (t, *J*=6.5 Hz, 2H), 3.03 (t, *J*=6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.82 (d, J_{C-F}=244.1 Hz), 137.24, 134.33 (d, J_{C-F}=8.9 Hz), 130.00 (d, J_{C-F}=8.7 Hz), 129.23, 128.19, 126.83 (d, J_{C-F}=5.1 Hz), 126.67 (d, J_{C-F}=2.4 Hz), 115.80 (d, J_{C-F}=25.0 Hz), 110.48 (d, J_{C-F}=20.4 Hz), 63.41, 39.25; MS (EI, 70 eV) *m*/*z* 191 (M^++1, 3), 190 (M^+, 71), 160 (71), 159 (100), 133 (53); HRMS ($C_{12}H_{11}FO$) calcd: 190.0794, found: 190.0793.

4.5.5.5. 2-(7-Chloronaphthalen-2-yl)ethanol ***3j***. (Record the spectral data from the mixture of **3h** and **3j**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.4 Hz, 1H), 7.77 (d, *J*=2.0 Hz, 1H), 7.75 (d, *J*=8.7 Hz, 1H), 7.60 (s, 1H), 7.37 (d, *J*=8.2 Hz, 2H), 3.95 (t, *J*=6.5 Hz, 2H), 3.03 (t, *J*=6.5 Hz, 2H); MS (EI, 70 eV) *m*/*z* 208 (M^++2, 17), 206 (M^+, 41), 174 (47), 170 (92), 141 (100).

4.5.5.6. 2-(7-Cyanonaphthalen-2-yl)ethanol ***3l***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.89 (d, *J*=8.5 Hz, 1H), 7.85 (d,

J=8.4 Hz, 1H), 7.74 (s, 1H), 7.57 (dd, J=8.4, 1.7 Hz, 1H), 7.55 (dd, J=8.4, 1.7 Hz, 1H), 3.98 (t, J=6.5 Hz, 2H), 3.07 (t, J=6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.43, 133.71, 133.48, 130.69, 128.92, 128.29, 127.84, 127.00, 125.97, 119.27, 109.53, 63.22, 39.11; MS (EI, 70 eV) m/z 198 (M^++1, 2), 197 (M^+, 11), 167 (48), 166 (100), 140 (18); HRMS ($C_{13}H_{11}NO$) calcd: 197.0841, found: 197.0829.

4.5.5.7. 2-Benzofuran-5-ylethanol ***3n***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, J=2.2 Hz, 1H), 7.46–7.42 (m, 2H), 7.15 (dd, J=8.6, 1.7 Hz, 1H), 6.73 (dd, J=2.2, 1.0 Hz, 1H), 3.88 (t, J=6.5 Hz, 2H), 2.96 (t, J=6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.93, 145.28, 132.82, 127.74, 125.28, 111.34, 106.35, 64.02, 39.03; MS (EI, 70 eV) m/z 162 (M^+, 10), 132 (4), 131 (100), 103 (2), 77 (3); HRMS ($C_{10}H_{10}O_2$) calcd: 162.0675, found: 162.0678.

4.5.5.8. 2-Benzothiophen-5-ylethanol ***3o***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, J=8.2 Hz, 1H), 7.68 (d, J=0.8 Hz, 1H), 7.44 (dd, J=5.5, 0.3 Hz, 1H), 7.30 (dd, J=5.5, 0.7 Hz, 1H), 7.22 (dd, J=8.2, 1.5 Hz, 1H), 3.89 (t, J=6.5 Hz, 1H), 2.98 (t, J=6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.91, 137.83, 134.48, 126.67, 125.48, 123.70, 123.49, 122.43, 63.69, 38.96; MS (EI, 70 eV) m/z 178 (M^+, 10), 148 (4), 147 (100), 131 (3); HRMS ($C_{10}H_{10}OS$) calcd: 178.0447, found: 178.0453.

4.5.5.9. 2-Phenanthren-2-ylethanol ***3r***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.64 (d, J=8.3 Hz, 1H), 8.62 (d, J=8.5 Hz, 1H), 7.87 (dd, J=7.8, 1.0 Hz, 1H), 7.74–7.71 (m, 2H), 7.68 (d, J=8.9 Hz, 1H), 7.63 (t, J=8.3 Hz, 1H), 7.57 (t, J=8.3 Hz, 1H), 7.52 (dd, J=1.7, 8.4 Hz, 1H), 3.97 (t, J=6.5 Hz, 2H), 3.07 (t, J=6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.83, 132.24, 131.85, 130.21, 128.95, 128.55, 128.47, 127.78, 127.18, 126.64, 126.59, 126.38, 123.04, 122.51, 63.63, 39.11; MS (EI, 70 eV) m/z 223 (M^++1, 9), 222 (M^+, 52), 191 (100), 189 (50); HRMS ($C_{16}H_{14}O$) calcd: 222.1045, found: 222.1046.

4.5.5.10. 2-(4H-Cyclopenta[def]phenanthren-2-yl)ethanol ***3s***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J=8.9 Hz, 1H), 7.80 (d, J=7.4 Hz, 1H), 7.77 (d, J=8.9 Hz, 1H), 7.67 (d, J=7.4 Hz, 1H), 7.66 (s, 1H), 7.61 (t, J=7.4 Hz, 1H), 7.57 (s, 1H), 4.32 (s, 2H), 3.98 (t, J=6.5 Hz, 2H), 3.15 (t, J=6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.33, 141.70, 138.20, 137.81, 137.27, 127.83, 127.72, 127.06, 125.56, 124.97, 122.87, 122.64, 122.59, 121.28, 64.26, 40.43, 37.37; MS (EI, 70 eV) m/z 235 (M^++1, 13), 234 (M^+, 64), 203 (100), 202 (92), 189 (18); HRMS ($C_{17}H_{14}O$) calcd: 234.1045, found: 234.1043.

4.5.5.11. 2-(5,6-Dihydro-4H-phenalen-2-yl)ethanol ***3t***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J=8.2 Hz, 1H), 7.49 (s, 1H), 7.34 (t, J=7.0 Hz, 1H), 7.17 (dd, J=6.9, 0.9 Hz, 1H), 7.09 (s, 1H), 3.92 (t, J=6.5 Hz, 2H), 3.08 (t, J=6.1 Hz, 4H), 2.97 (t, J=6.5 Hz, 2H), 2.06 (quintet, J=6.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.87, 136.33, 135.33, 133.85, 128.92, 125.71, 125.43, 125.38, 125.27, 123.44, 63.52, 39.30, 31.24, 31.17, 23.09; MS (EI, 70 eV) m/z 213 (M^++1, 14), 212 (M^+, 83), 181 (100), 165 (51); HRMS ($C_{15}H_{16}O$) calcd: 212.1201, found: 212.1202.

4.5.5.12. 2-(8-Methoxy-5,6-dihydro-4H-phenalen-2-yl)ethanol ***3u***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (s, 1H), 6.94 (d, J=1.2 Hz, 1H), 6.92 (d, J=2.5 Hz, 1H), 6.85 (dt, J=2.5, 1.2 Hz, 1H), 3.90 (t, J=6.5 Hz, 2H), 3.87 (s, 3H), 3.05–3.01 (m, 4H), 2.94 (t, J=6.5 Hz, 2H), 2.03 (quintet, J=6.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.41, 138.21, 136.89, 136.10, 135.26, 124.55, 124.41, 123.17, 115.68, 103.55, 63.51, 55.12, 39.33, 31.13, 31.05, 23.09; MS (EI, 70 eV) m/z 242 (M^+, 100), 211 (73), 165 (28).

4.5.5.13. 2-Acenaphthen-4-ylethanol ***3v***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, J=8.2 Hz, 1H), 7.42–7.38 (m, 2H), 7.22 (d, J=6.8 Hz, 1H), 7.15 (s, 1H), 3.92 (t, J=6.5 Hz, 2H), 3.37 (s, 4H), 3.01 (t, J=6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.7, 145.8, 138.4, 138.2, 131.5, 128.1, 122.1, 121.8, 120.7, 118.8, 63.8, 40.0, 30.5, 30.2; MS (EI, 70 eV) m/z 198 (M^+, 38), 167 (100), 152 (30); HRMS ($C_{14}H_{14}O$) calcd: 198.1045, found: 198.1047.

4.5.6. Spectral data of methanol addition compounds

4.5.6.1. 3-(1-Methoxy-2-(4-methoxyphenyl)ethyl)furan ***4a***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.23 (s, 1H), 7.05 (d, J=8.7 Hz, 2H), 6.80 (d, J=8.7 Hz, 2H), 6.36 (s, 1H), 4.29 (t, J=6.8 Hz, 1H), 3.79 (s, 3H), 3.23 (s, 3H), 3.08 (dd, J=13.8, 6.8 Hz, 1H), 2.73 (dd, J=13.8, 6.7 Hz, 1H).

4.5.6.2. 3-(2-Methoxy-2-(4-methoxyphenyl)ethyl)furan ***4a′***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (s, 1H), 7.20 (d, J=8.6 Hz, 2H), 7.15 (s, 1H), 6.89 (d, J=8.6 Hz, 2H), 6.17 (s, 1H), 4.22 (t, J=6.7 Hz, 1H), 3.82 (s, 3H), 3.22 (s, 3H), 2.93 (dd, J=14.6, 7.3 Hz, 1H), 2.73 (dd, J=14.6, 6.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.14, 142.25, 139.95, 133.52, 127.97, 121.30, 113.66, 111.60, 83.62, 56.37, 55.17, 33.62; MS(EI, 70 eV) m/z 232 (M^+, 2), 201 (2), 185 (3), 173 (4), 151 (100); HRMS ($C_{14}H_{16}O_3$) calcd: 232.1099, found: 232.1101.

4.5.6.3. 3-(1-Methoxy-2-(4-nitrophenyl)ethyl)furan ***4m***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, J=8.8 Hz, 2H), 7.41 (d, J=8.8 Hz, 2H), 7.31 (t, J=1.6 Hz, 1H), 7.12 (dd, J=1.6, 0.6 Hz, 1H), 6.16 (d, J=0.9 Hz, 1H), 4.38 (t, J=6.5 Hz, 1H), 3.27 (s, 3H), 2.92 (dd, J=14.8, 6.9 Hz, 1H), 2.75 (dd, J=14.8, 6.0 Hz, 1H).

4.6. Synthesis of the N3h and N3r intermediates

4.6.1. Photolysis of ***1h*** *in the presence of ^{t}BuOK/dried THF.* A total of five identical samples were prepared, each of which contained **1h** (20 mg), ^{t}BuOK (0.5 g), and dried THF (20 mL) in a quartz tube (1.5×20 cm). The tubes were sealed with septa and sonicated and shaken to suspend the undissolved particles. Then, the solution was bubbled with nitrogen gas for 20 min to remove dissolved oxygen. The sample was irradiated with 300 nm UV light at ambient temperature (approximately 40 °C) for 3 h. After irradiation, the five samples were combined, and 500 mL of water was added to the solution. The resulting solution was extracted with ethyl acetate several times, and the organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the products were purified via chromatography using a mixed solution of ethyl acetate and hexane (1:10) for elution. Further purification was conducted via thin-layer-chromatography (TLC) to achieve an acceptable purity, 8.3 mg (8% yield) of **N3h** and 10.8 mg (12% yield) of **5h** were obtained.

4.6.1.1. Naphthalen-2-yl-acetaldehyde ***N3h***.[44] ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.84 (t, J=2.4 Hz, 1H), 7.91–7.81 (m, 3H), 7.71 (s, 1H), 7.53–7.47 (m, 2H), 7.34 (dd, J=8.4, 1.8 Hz, 1H), 3.86 (d, J=2.4 Hz, 1H).

4.6.1.2. Naphthalene-2-carbaldehyde ***5h***.[45] ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.18 (s, 1H), 8.02 (d, J=8.2 Hz, 1H), 7.97 (dd, J=8.6, 1.5 Hz, 1H), 7.95 (d, J=8.6 Hz, 2H), 7.92 (d, J=8.2 Hz, 1H), 7.66 (td, J=8.2, 1.3 Hz, 1H), 7.60 (td, J=8.2, 1.2 Hz, 1H).

4.6.2. Photolysis of ***1r*** *in the presence of ^{t}BuOK/^{t}BuOH.* A total of five identical samples were prepared, each of which contained **1r** (20 mg), *tert*-butyl alcohol (20 mL), and potassium *tert*-butoxide (0.1 g) in a quartz tube (1.5×20 cm). The tubes were sealed with septa and subjected to sonication to dissolve all of the components. Then, the solution was bubbled with nitrogen gas for 20 min to remove dissolved oxygen. The sample was irradiated with 300 nm UV light at ambient temperature (approximately 40 °C) for 6 h. After irradiation, the five samples were combined, and 500 mL of

water was added to the solution. The resulting solution was extracted with ethyl acetate several times, and the organic layers were combined and dried with anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator, and the products were purified via chromatography using hexane and ethyl acetate (10:1) for elution. Following chromatography, 3.3 mg (4% yield) of **5r** and 24.3 mg (24% yield) of **N3r** were obtained.

*4.6.2.1. Phenanthren-2-yl-acetaldehyde **N3r**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.84 (t, J=2.4 Hz, 1H), 8.67–8.64 (m, 2H), 7.88 (dd, J=7.8, 1.3 Hz, 1H), 7.76–7.57 (m, 4H), 7.47 (dd, J=8.5, 1.9 Hz, 1H), 3.87 (d, J=2.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.25, 132.37, 131.99, 130.03, 130.01, 129.47, 129.26, 128.59, 127.92, 127.54, 126.74, 126.68, 126.45, 123.47, 122.59, 50.43; MS (EI, 70 eV) m/z 221 (M^++1, 15), 220 (M^+, 85), 191 (100); HRMS ($C_{16}H_{12}O$) calcd: 220.0888, found: 220.0886.

*4.6.2.2. Phenanthrene-2-carbaldehyde **5r**.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.21 (s, 1H), 8.79 (d, J=8.6 Hz, 1H), 8.72 (dd, J=7.6, 1.5 Hz, 1H), 8.37 (d, J=1.7 Hz, 1H), 8.13 (dd, J=8.6, 1.7 Hz, 1H), 7.92 (dd, J=7.2, 1.8 Hz, 1H), 7.85 (d, J=8.9 Hz, 1H), 7.82 (d, J=8.9 Hz, 1H), 7.71 (td, J=7.1, 1.6 Hz, 1H), 7.68 (td, J=7.1, 1.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.15 (d), 134.48, 134.35, 133.24, 133.00, 131.68, 129.73, 128.81, 128.28, 128.10, 127.20, 127.06, 124.77, 123.72, 123.50; MS (EI, 70 eV) m/z 206 (M^+, 100), 205 (M^+−1, 59), 176 (54); HRMS ($C_{15}H_{10}O$) calcd: 206.0732, found: 206.0730.

Acknowledgements

We are grateful to National Science Council of the Republic of China (Taiwan) for financial support (NSC 98-2113-M-011-004-MY2).

Supplementary data

^{1}H and ^{13}C NMR spectra of the compounds are available. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.01.035.

References and notes

1. Selected papers: (a) de Koning, C. B.; Rousseaub, A. L.; van Otterloa, W. A. L. *Tetrahedron* **2003**, *59*, 7; (b) Mal, D.; Pahari, P. *Chem. Rev.* **2007**, *107*, 1892; (c) van Otterlo, W. A. L.; de Koning, C. B. *Chem. Rev.* **2009**, *109*, 3743; (d) Linghu, X.; McLaughlin, M.; Chen, C.-Y.; Reamer, R. A.; Dimichele, L.; Davies, I. W. *Tetrahedron Lett.* **2012**, *53*, 1550; (e) Zhang, X.; Jia, X.; Liu, N.; Guo, X.; Song, Y.; Fan, X. *Tetrahedron* **2013**, *69*, 5374.
2. Selected papers: (a) Zhao, B.; Lu, X. *Org. Lett.* **2006**, *8*, 5987; (b) Huang, X.-C.; Liu, Y.-L.; Liang, Y.; Pi, S.-F.; Wang, F.; Li, J.-H. *Org. Lett.* **2008**, *10*, 1525; (c) Zhou, L.; Shi, Y.; Xiao, Q.; Liu, Y.; Ye, F.; Zhang, Y.; Wang, J. *Org. Lett.* **2011**, *13*, 968; (d) Ghosh, S.; Das, J. *Tetrahedron Lett.* **2011**, *52*, 1112; (e) Chen, P.-Y.; Wang, T.-P.; Huang, K.-S.; Kao, C.-L.; Tsai, J.-C.; Wang, E.-C. *Tetrahedron* **2011**, *67*, 9291; (f) Markina, N. A.; Chen, Y.; Larock, R. C. *Tetrahedron* **2013**, *69*, 2701.
3. Selected papers: (a) Syu, S.-E.; Lee, Y.-T.; Jang, Y.-J.; Lin, W. *Org. Lett.* **2011**, *13*, 2970; (b) Guilarte, V.; Fernández-Rodríguez, M. A.; García-García, P.; Hernando, E.; Sanz, R. *Org. Lett.* **2011**, *13*, 5100; (c) Sun, L.-L.; Deng, C.-L.; Tang, R.-Y.; Zhang, X.-G. *J. Org. Chem.* **2011**, *76*, 7546; (d) Wanga, Z.; Geng, W.; Wang, H.; Zhang, S.; Zhang, W.-X.; Xi, Z. *Tetrahedron Lett.* **2011**, *52*, 6997; (e) Toguem, S.-M. T.; Malik, I.; Hussain, M.; Iqbal, J.; Villinger, A.; Langer, P. *Tetrahedron* **2013**, *69*, 160; (f) Kim, S.; Dahal, N.; Kesharwani, T. *Tetrahedron Lett.* **2013**, *54*, 1112.
4. Selected papers: (a) Rochais, C.; Yougnia, R.; Dallemagne, P.; Rault, S. *Tetrahedron Lett.* **2009**, *50*, 5704; (b) Yougnia, R.; Rochais, C.; Santos, J. S. O.; Dallemagne, P.; Rault, S. *Tetrahedron* **2010**, *66*, 2803; (c) Bera, K.; Sarkar, S.; Jalal, S.; Jana, U. *J. Org. Chem.* **2012**, *77*, 8780; (d) Lin, Y.-D.; Cho, C.-L.; Ko, C.-W.; Pulte, A.; Wu, Y.-T. *J. Org. Chem.* **2012**, *77*, 9979; (e) Kwon, Y.; Cho, H.; Kim, S. *Org. Lett.* **2013**, *15*, 920.
5. Selected papers: (a) Reid, D. H. *Q. Rev. Chem. Soc.* **1965**, *19*, 274; (b) Paskovich, D. H.; Das, N. C. *Chem. Commun. (London)* **1967**, 39; (c) Piers, E.; Friesen, R. W.; Kao, P.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1993**, *71*, 1463; (d) Patti, R. K.; Duan, S.; Wang, Z.; Herndon, J. W. *Tetrahedron Lett.* **2011**, *52*, 4182.
6. Selected papers: (a) Bosch, A.; Brown, R. K. *Can. J. Chem.* **1968**, *46*, 715; (b) Haddad, N.; Abu-Shqara, E. *J. Org. Chem.* **1994**, *59*, 6090; (c) Chan, S.-C.; Jang, J.-P.; Cherng, Y.-J. *Tetrahedron* **2009**, *65*, 1977.
7. Selected papers: (a) Pérez, D.; Guitián, E. *Chem. Soc. Rev.* **2004**, *33*, 274; (b) Cant, A. A.; Roberts, L.; Greaney, M. F. *Chem. Commun.* **2010**, 8671; (c) Xu, L.; Yu, R.; Wang, Y.; Chen, J.; Yang, Z. *J. Org. Chem.* **2013**, *78*, 5744; (d) Liu, Z.; Larock, R. C. *J. Org. Chem.* **2007**, *72*, 223.
8. (a) Jørgensen, K. B. *Molecules* **2010**, *15*, 4334; (b) Mallory, F. B.; Mallory, C. W. *Org. React.* **1984**, *30*, 1; (c) Laarhoven, W. H. *Pure Appl. Chem.* **1984**, *56*, 1225.
9. (a) Shi, L.; Liu, Z.; Dong, G.; Duan, L.; Qiu, Y.; Jia, J.; Guo, W.; Zhao, D.; Cui, D.; Tao, X. *Chem.—Eur. J.* **2012**, *18*, 8092; (b) Braiek, M. B.; Aloui, F.; Moussa, S.; Tounsi, M.; Marrot, J.; Hassine, B. B. *Tetrahedron Lett.* **2013**, *54*, 5421; (c) Zhao, Z.; Zhang, Y.; Xiao, Y. *J. Org. Chem.* **2013**, *78*, 5544; (d) Lei, T.; Pei, J. *J. Mater. Chem.* **2012**, *22*, 785; (e) Toyoshima, T.; Yoshida, S.; Watanabe, S. *Tetrahedron* **2013**, *69*, 1904.
10. (a) Baldry, P. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 805; (b) Pomerantz, M.; Gruber, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 6615; (c) Baldry, P. J. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1913; (d) Olsen, R. J.; Minniear, J. C.; Overton, W. M.; Sherrick, J. M. *J. Org. Chem.* **1991**, *56*, 989.
11. According to our survey, there is no literature reporting about synthesizing 4*H*-cyclopenta[*def*]phenanthrene by oxidative photocyclization of a stilbene-type precursor. Instead, the synthesis of 4*H*-cyclopenta[*def*]phenanthrene can be accomplished by multi-step syntheses from acenaphthene, fluorene derivative or 1-naphthylacetic acid, or the reduction of cyclopenta[*def*]-phenanthren-4-one. (a) Bachmann, W. E.; Sheehan, J. C. *J. Am. Chem. Soc.* **1941**, *63*, 204; (b) Yoshida, M.; Minabe, M.; Suzuki, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2179; (c) Kim, J.; Song, S.; Suh, H.; Jin, Y.; Kim, I. *Chem. Lett.* **2009**, *38*, 1008; (d) Medenwald, H. *Chem. Ber.* **1953**, *86*, 287 By contrast, 4,5-dihydropyrene can be synthesized by oxidative photocyclization of stilbene-type precursor; (e) Blaschke, H.; Ramey, C. E.; Calder, I.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3675 Other cases of oxidative photocyclization of macrocyclic stilbene derivatives: (f) Ben, I.; Castedo, L.; Saá, J. M.; Seijas, J. A.; Suau, R.; Tojo, G. *J. Org. Chem.* **1985**, *50*, 2236; (g) Dyker, G.; Körning, J.; Stirner, W. *Eur. J. Org. Chem.* **1998**, 149.
12. (a) Wright, D. L. In *Progress in Heterocyclic Chemistry*; Gribble, G. W., Joule, J. A., Eds.; Elsevier: Oxford, UK, 2005; Vol 17, Chapter 1; (b) Cermola, F.; Temussi, F.; Iesce, M. R. *Tetrahedron Lett.* **2011**, *52*, 7058.
13. Pilipenko, A. S.; Melćhin, V. V.; Trushkov, I. V.; Cheshkov, D. A.; Butin, A. V. *Tetrahedron* **2012**, *68*, 619.
14. Kikaš, I.; Škorić, I.; Marinić, Ž.; Šindler-Kulyk, M. *Tetrahedron* **2010**, *66*, 9405.
15. Ouairy, C.; Michel, P.; Delpech, B.; Crich, D.; Marazano, C. *J. Org. Chem.* **2010**, *75*, 4311.
16. Ho, J.-H.; Lee, T.-H.; Lo, C.-K.; Chuang, C.-L. *Tetrahedron Lett.* **2011**, *52*, 7199.
17. Maercker, A. *Org. React.* **1965**, *14*, 270.
18. Yoshimi, Y.; Ishise, A.; Oda, H.; Moriguchi, Y.; Kanezaki, H.; Nakaya, Y.; Katsuno, K.; Itou, T.; Inagaki, S.; Morita, T.; Hatanaka, M. *Tetrahedron Lett.* **2008**, *49*, 3400.
19. (a) Woning, J.; Oudenampsen, A.; Laarhoven, W. H. *J. Chem. Soc., Perkin Trans. 2* **1989**, 2147; (b) Roberts, J. C.; Pincock, J. A. *J. Org. Chem.* **2004**, *69*, 4279; (c) Roberts, J. C.; Pincock, J. A. *J. Org. Chem.* **2006**, *71*, 7480.
20. Lewis, F. D.; Yang, J.-S. *J. Am. Chem. Soc.* **1997**, *119*, 3834.
21. Bent, D. V.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1974**, *78*, 446.
22. Tofi, M.; Georgiou, T.; Montagnon, T.; Vassilikogiannakis, G. *Org. Lett.* **2005**, *7*, 3347.
23. Efange, S. M. N.; Michelson, R. H.; Remmel, R. P.; Boudreau, R. J.; Dutta, A. K.; Freshler, A. *J. Med. Chem.* **1990**, *33*, 3133.
24. Lewis, F. D.; Kalgutkar, R. S.; Yang, J.-S. *J. Am. Chem. Soc.* **2001**, *123*, 3878.
25. Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415.
26. Schaffner, K.; Wolf, H.; Rosenfeld, S. M.; Lawler, R. G.; Ward, H. R. *J. Am. Chem. Soc.* **1972**, *94*, 6553.
27. Photolysis of **1g** under the condition of KOH/MeOH with different irradiation times afforded different amount of **2g** and **4g**+**4g′**. The results were recorded in the format of (time: **2g**, **4g**+**4g′**) and described below: (1 h: 9 %, 14 %), (2 h: 25 %, 11 %), (3 h: 37%, 5%). The decreasing amount of **4g**+**4g′** may represent that the methanol addition products are not stable under irradiation.
28. (a) Sarker, M.; Shahrin, T.; Steinmetz, M. G. *Org. Lett.* **2011**, *13*, 872; (b) Jia, J.; Sarker, M.; Steinmetz, M. G.; Shukla, R.; Rathore, R. *J. Org. Chem.* **2008**, *73*, 8867; (c) Jia, J.; Steinmetz, M. G.; Shukla, R.; Rathore, R. *Tetrahedron Lett.* **2008**, *49*, 4621.
29. Chiang, Y.; Kresge, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 2355.
30. (a) Auzias, M.; Häussinger, D.; Neuburger, M.; Wegner, H. A. *Org. Lett.* **2011**, *13*, 474; (b) Buscemi, S.; Cusmano, G.; Gruttadauria, M. *J. Heterocycl. Chem.* **1990**, *27*, 861.
31. Tedaldi, L. M.; Baker, J. R. *Org. Lett.* **2009**, *11*, 811.
32. Neo, A. G.; López, C.; Romero, V.; Antelo, B.; Delamano, J.; Pérez, A.; Fernández, D.; Almeida, J. F.; Castedo, L.; Tojo, G. *J. Org. Chem.* **2010**, *75*, 6764.
33. In accordance with our proposed mechanism for the formation of **5h**, (3-naphthen-2-yl)-propionaldehyde and longer alkyl chain aldehyde should be obtained as the side products. These side products have similar polarity and were hard to separate from **N3h** and **5h**. So many small peaks of uncharacterized impurities could be seen in ^{1}H NMR spectra of **N3h** and **5h**.
34. Aun, C. E.; Clarkson, T. J.; Happer, D. A. R. *J. Chem. Soc., Perkin Trans. 2* **1990**, 635.
35. Ambre, R.; Yu, C.-Y.; Mane, S. B.; Yao, C.-F.; Hung, C.-H. *Tetrahedron* **2011**, *67*, 4680.
36. Shaikh, N. S.; Junge, K.; Beller, M. *Org. Lett.* **2007**, *9*, 5429.
37. Montana, Á. M.; Grima, P. M.; Castellví, M.; Batalla, C.; Font-Bardia, M. *Tetrahedron* **2012**, *68*, 9982.
38. Castedo, L.; Cid, M. M.; Dominguez, R.; Seijas, J. A.; Villaverde, M. C. *Heterocycles* **1990**, *31*, 1271.
39. Yu, D.-G.; Wang, X.; Zhu, R.-Y.; Luo, S.; Zhang, X.-B.; Wang, B.-Q.; Wang, L.; Shi, Z.-J. *J. Am. Chem. Soc.* **2012**, *134*, 14638.

40. Terfort, A.; Goerls, H.; Brunner, H. *Synthesis* **1997**, 79.
41. Koshio, H.; Ishihara, T.; Yamada, H.; Hirayama, F.; Matsumoto, Y.; Yanagisawa, I. *Chem. Pharm. Bull.* **2005**, *53*, 4482.
42. Liu, Z.; Zhang, X.; Larock, R. C. *J. Am. Chem. Soc.* **2005**, *127*, 15717.
43. Gómez, C.; Maciá, B.; Lillo, V. J.; Yus, M. *Tetrahedron* **2006**, *62*, 9832.
44. Ertürk, E.; Göllü, M.; Demir, A. S. *Tetrahedron* **2010**, *66*, 2373.
45. Kirihara, M.; Noguchi, T.; Okajima, N.; Naito, S.; Ishizuka, Y.; Harano, A.; Tsukiji, H.; Takizawa, R. *Tetrahedron* **2012**, *68*, 1515.