

# Cycloaddition Reaction of Vinylphenylfurans and Dimethyl Acetylenedicarboxylate to [8 + 2] Isomers via Tandem [4 + 2]/Diradical Alkene–Alkene Coupling/[1,3]-H Shift Reactions: Experimental Exploration and DFT Understanding of Reaction Mechanisms

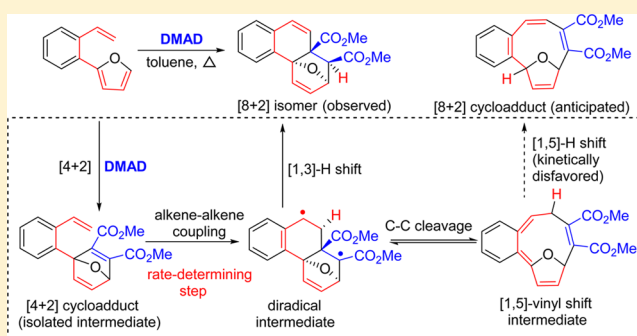
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## S Supporting Information

**ABSTRACT:** An experimental test of designed [8 + 2] reaction of vinylphenylfuran and dimethyl acetylenedicarboxylate (DMAD) has been carried out, showing that the reaction gave unexpected addition products under different conditions. When the reaction was conducted under thermal conditions in toluene, exoxyphenanthrene, which was named as a [8 + 2] isomer, was generated. The scope of this reaction has been investigated in the present study. In addition, experiments and DFT calculations have been conducted to investigate how the reaction between vinylphenylfuran and DMAD took place. Surprisingly, the reaction did not involve the expected [8 + 2] intermediate, *o*-quinodimethane. Instead, the reaction starts from intermolecular Diels–Alder reactions between DMAD and the furan moiety of vinylphenylfuran, followed by unexpected intramolecular alkene–alkene coupling. This step generates a diradical species, which then undergoes [1,3]-H shift to give the experimentally observed exoxyphenanthrene. DFT calculations revealed that, the [8 + 2] cycloadduct cannot be obtained because the [1,5]-H shift process from the [1,5]-vinyl shift intermediate is disfavored kinetically compared to the [1,3]-H shift to the [8 + 2] isomer.

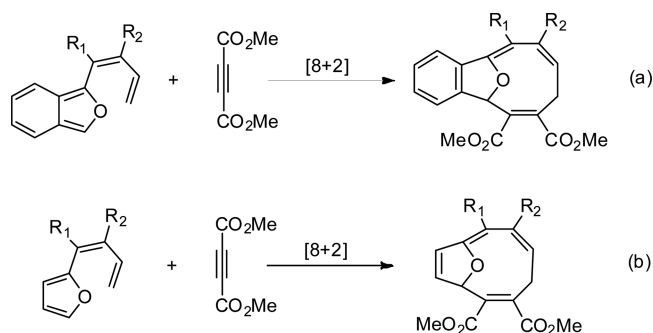


## 1. INTRODUCTION

The [8 + 2]-cycloaddition reaction can provide a straightforward approach for the synthesis of 10-membered ring compounds.<sup>1</sup> However, before 2003, all reported [8 + 2] reactions were limited to using geometrically constrained tetraenes as the 8 $\pi$  components (such as heptafulvenes,<sup>1b</sup> tropones,<sup>2</sup> and indolizines<sup>3</sup>), in which carbons 1 and 8 are rigidly held in close proximity. In 2003, Herndon and co-workers reported the first successful [8 + 2]-cycloaddition reaction between conformationally flexible tetraene (dienylisobenzofurans) and tetraenophile [dimethyl acetylenedicarboxylate (DMAD)], as shown in Scheme 1a, which provided an incredibly simple entry into furan-bridged 10-membered rings.<sup>4</sup> In their following study, it was found that simple furandienes could also be excellent tetraene substrates for a [8 + 2] reaction with DMAD (Scheme 1b).<sup>5</sup> These [8 + 2] cycloadditions provide a potentially powerful method to synthesize the skeleton of a variety of biologically active coral-derived natural products.<sup>6</sup>

Computational organic chemistry has become an important tool to facilitate a mechanistic understanding of chemical

## Scheme 1. Cycloadditions of Dienylfurans and DMAD Reported by Herndon and Co-workers<sup>4,5</sup>

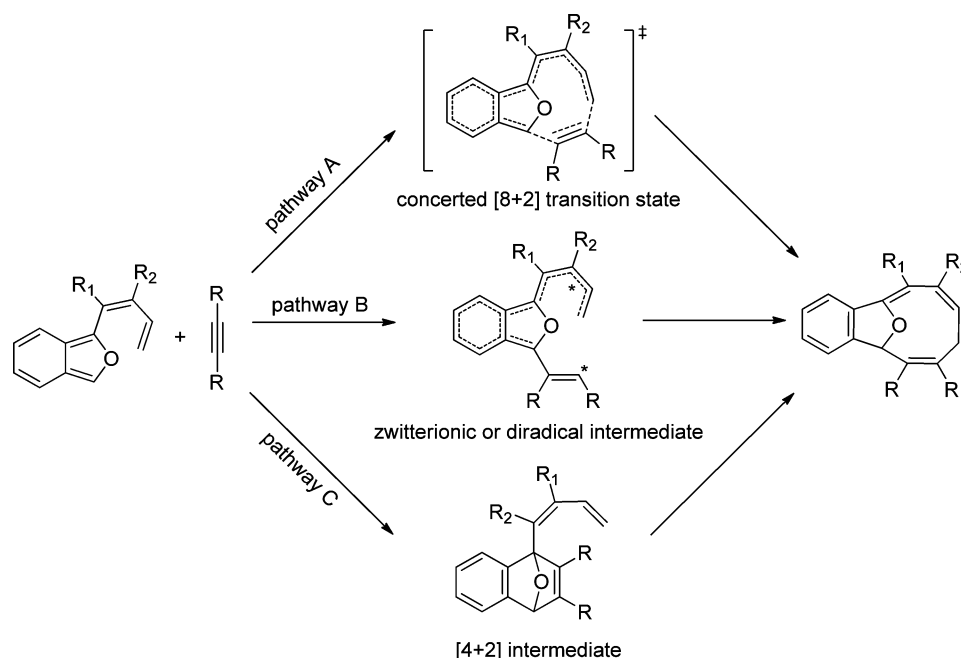
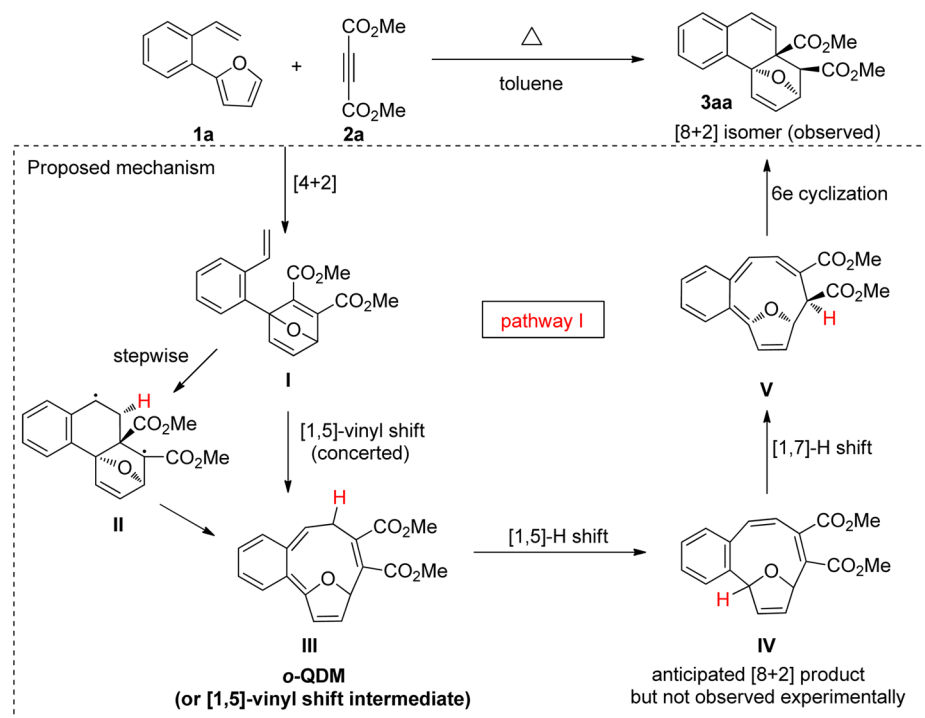


reactions.<sup>7</sup> In 2007, Yu and co-workers carried out density functional theory (DFT) calculations to investigate the mechanism of the [8 + 2] cycloaddition shown in Scheme

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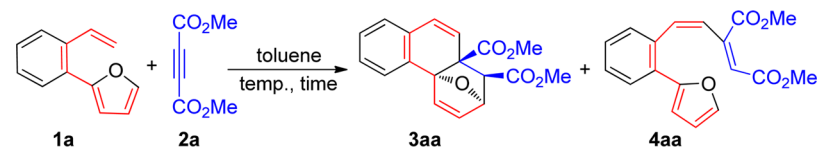
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Scheme 2. Three Pathways for Dienylisobenzofuran-alkyne  $[8 + 2]$  Cycloaddition Proposed by Yu and Co-workers<sup>8</sup>Scheme 3. Design and Experimental Finding of the  $[8 + 2]$  Reaction between Enylfuran and DMAD

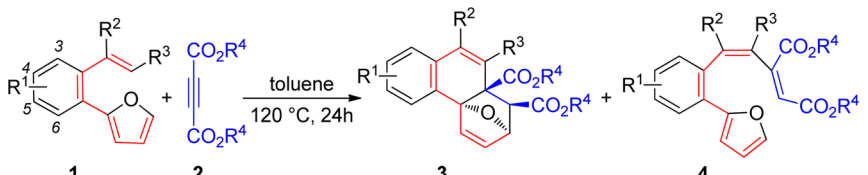
1a.<sup>8</sup> It was suggested that the concerted  $[8 + 2]$  pathway (Scheme 2, pathway A) was not favored because the two terminal carbons of the tetraenes are far away from each other, and this geometry did not allow simultaneous frontier orbital overlap between HOMO of tetraenes and LUMO of dienophiles. In contrast, these reactions were proposed to proceed through a stepwise pathway, which starts from Diels–Alder  $[4 + 2]$  cycloaddition, followed by a  $[1,5]$ -vinyl shift to afford the observed  $[8 + 2]$  product (Scheme 2, pathway C). When there is an electron-donating group (such as a methoxy group) in the dienyl moiety of dienylisobenzofurans, a stepwise

reaction pathway involving formation of a zwitterionic or diradical intermediate becomes very competitive (Scheme 2, pathway B), especially in solution, due to the stabilization effect of electron-donating group to the transition state, which contains positive charge on its tetraene moiety. These theoretical studies helped chemists to understand the mechanisms of these  $[8 + 2]$  cycloadditions and provided insights and guides for the future design of new  $[8 + 2]$  cycloaddition reactions and other higher order  $[m + n]$  cycloadditions.<sup>9</sup>

Table 1. Optimization of Reaction Conditions<sup>a</sup>


entry	2a (eq)	temp. (°C) <sup>b</sup>	time (h)	yield (%) <sup>c</sup>		
				total	3aa	4aa
1	1.0	85	12	14 <sup>d</sup>	11 <sup>d</sup>	3 <sup>d</sup>
2	1.0	110	24	65	38	27
3	1.0	120	24	77	43	34
4	1.5	120	24	86	45	41

<sup>a</sup>Unless otherwise noted, the reaction was carried out using sealed tubes in toluene under N<sub>2</sub>. <sup>b</sup>The oil bath temperature. <sup>c</sup>Isolated yield. <sup>d</sup>Yield determined by <sup>1</sup>H NMR spectroscopy.

Table 2. Substrate Scope of the Reaction of Vinylphenylfuran and Alkyne in Toluene<sup>a</sup>


entry	1	2	yield (%) <sup>b</sup>		
			total	3	4
1	1a (R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H)	2a (R <sup>4</sup> = Me)	86	45 (3aa)	41 (4aa)
2	1a (R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H)	2b (R <sup>4</sup> = Et)	86	45 (3ab)	41 (4ab)
3	1b (R <sup>1</sup> = 5-Me; R <sup>2</sup> , R <sup>3</sup> = H)	2a (R <sup>4</sup> = Me)	87	52 (3ba)	35 (4ba)
4	1c (R <sup>1</sup> = 4-OMe; R <sup>2</sup> , R <sup>3</sup> = H)	2a (R <sup>4</sup> = Me)	88	52 (3ca)	36 (4ca)
5	1d (R <sup>1</sup> = 4-CF <sub>3</sub> ; R <sup>2</sup> , R <sup>3</sup> = H)	2a (R <sup>4</sup> = Me)	63	33 (3da)	30 (4da)
6	1e (R <sup>1</sup> = 4-F; R <sup>2</sup> , R <sup>3</sup> = H)	2a (R <sup>4</sup> = Me)	71	43 (3ea)	28 (4ea)
7	1f (R <sup>1</sup> , R <sup>3</sup> = H; R <sup>2</sup> = Me)	2a (R <sup>4</sup> = Me)	65	26 (3fa)	39 (4fa)
8	1g (R <sup>1</sup> , R <sup>3</sup> = H; R <sup>2</sup> = CO <sub>2</sub> Me)	2a (R <sup>4</sup> = Me)			
9	1h (R <sup>1</sup> , R <sup>2</sup> = H; R <sup>3</sup> = Me)	2a (R <sup>4</sup> = Me)			

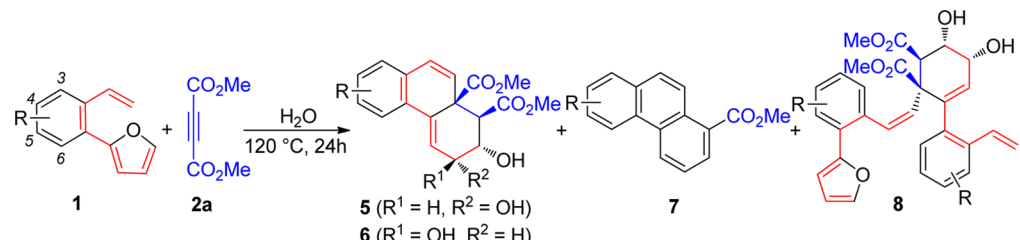
<sup>a</sup>The reaction was carried out using sealed tubes in toluene under N<sub>2</sub> for 24 h. The molar ratio of 1/2 = 1:1.5. The oil bath temperature was set at 120 °C. <sup>b</sup>Yield of isolated product.

*o*-Quinodimethane (*o*-QDM), a transient and highly reactive species, has attracted much attention of both theoretical and synthetic chemists over the past four decades.<sup>10</sup> As part of our continuing efforts to develop *o*-QDM chemistry,<sup>11</sup> together with our interests to develop new [8 + 2] reactions, we envisioned that vinylphenylfuran (1a) can act as 8e tetraene and react with DMAD to generate *o*-QDM III, via the [4 + 2]/vinyl shift process (Scheme 3). Intermediate III here was also labeled as a [1,5]-vinyl shift intermediate. The vinyl shift could also occur in a stepwise fashion via diradical intermediate II, which was formed by coupling the two alkene parts in intermediate I, followed by C–C bond cleavage to give intermediate III. Intermediate III is regarded as an [8 + 2] cycloadduct, but we thought direct [8 + 2] is not allowed geometrically, as found previously in Herndon's system. We then envisioned that, III is not stable and can undergo [1,5]-H shift to give IV as the final product. We expected that this transformation from III to IV should be easy due to the restoration of aromaticity in this process, but to our surprise, we did not obtain product IV when we carried out the designed reaction (see Scheme 3 and later on the Results and Discussion section). Instead, we obtained product 3aa, which was named as the [8 + 2] isomer and its *retro*-Diels–Alder reaction product (not shown in Scheme 3 and will be discussed later on the

Results and Discussion section). We then hypothesized that IV, generated through [4 + 2]/[1,5]-vinyl and H shifts, underwent [1,7]-H shift to give V. Then, V underwent 6e cyclization to furnish product 3aa (pathway I). Here, we report our discovery of the synthesis of 3aa, the computational and experimental exploration of whether 3aa is generated via the pathway I described in Scheme 3, and the reason why the expected [8 + 2] cycloadduct IV was not observed.

## 2. RESULTS AND DISCUSSION

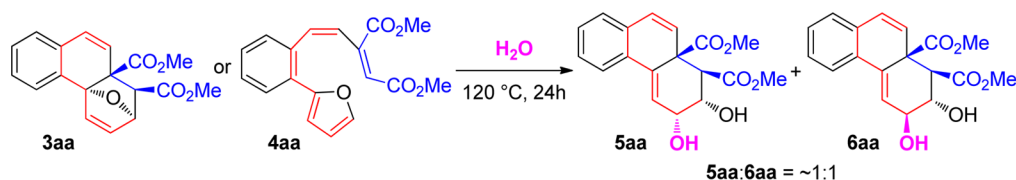
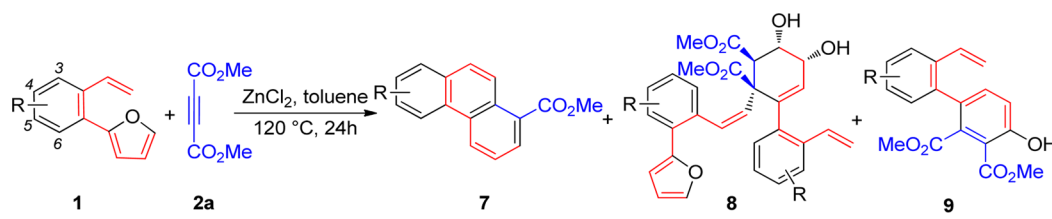
**2.1. Reaction of Vinylphenylfurans and DMAD.** Initial efforts were made to systematically investigate various reaction conditions for the designed [8 + 2] reaction of vinylphenylfuran 1a and DMAD 2a.<sup>12</sup> Following the conditions reported in previous work,<sup>4,8</sup> the reaction was conducted in anhydrous toluene at 85 °C for 12 h. In this case, product 3aa, which was named as a [8 + 2] isomer, and its *retro*-Diels–Alder product 4aa were obtained in only 14% yield, as determined by <sup>1</sup>H NMR spectroscopy (Table 1, entry 1). The combined yield of 3aa and 4aa could be enhanced to 65% when the reaction was conducted at 110 °C for 24 h (entry 2). Marginal improvement of the reaction yield was observed when the reaction temperature was raised to 120 °C (entry 3). The reaction yields cannot be substantially improved by using other solvents

Table 3. Reaction of Vinylphenylfuran and Alkyne in Water<sup>a</sup>


entry	1	5	6	7	8	yield <sup>b</sup>
1	1a (R = H)	5aa (22%)	6aa (24%)	7aa (14%)	8aa (5%)	65%
2	1b (R = 5-Me)	5ba (46%)	6ba (28%)	7ba (7%)	8ba (4%)	85%
3	1d (R = 4-CF <sub>3</sub> )	5da (29%)	6da (8%)	7da (8%)	8da (—)	45%
4	1e (R = 4-F)	5ea (15%)	6ea (21%)	7ea (13%)	8ea (13%)	62%

<sup>a</sup>The reaction was carried out using sealed tubes in water for 24 h under N<sub>2</sub>. The molar ratio of 1/2 = 1:1. The oil bath temperature was set at 120 °C. <sup>b</sup>Yield of isolated product.

## Scheme 4. Control Reaction

Table 4. Reaction of Vinylphenylfuran and Alkyne in Toluene with the Zinc Catalyst<sup>a</sup>


entry	1	7	8	9	yield <sup>b</sup>
1	1a (R = H)	7aa (7%)	8aa (45%)	9aa (30%)	82%
2	1b (R = 5-Me)	7ba (31%)	8ba (16%)	9ba (34%)	81%
3	1c (R = 4-OMe)	7ca (—)	8ca (—)	9ca (100%)	100%
4	1d (R = 4-CF <sub>3</sub> )	7da (17%)	8da (21%)	9da (—)	38%
5	1e (R = 4-F)	7ea (6%)	8ea (39%)	9ea (28%)	73%

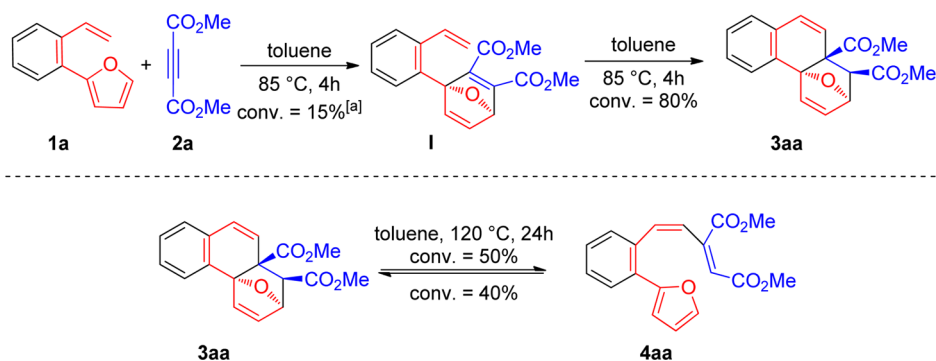
<sup>a</sup>The reaction was carried out using sealed tubes in toluene for 24 h using 5 mol % ZnCl<sub>2</sub> under N<sub>2</sub>. The molar ratio of 1/2 = 1:1. The oil bath temperature was set at 120 °C. <sup>b</sup>Yield of isolated product.

(see SI for detail). Interestingly, it was found that the reaction in water gave different results from those in toluene (see later discussion). The reaction yield was further improved to 86% when 1.5 equiv DMAD was applied (entry 4). The structure of 3aa was confirmed by X-ray diffraction analysis (see SI), where the two ester groups are in *cis*-position, and the bridge oxygen is in *trans*-position to the ester groups. The vicinal proton coupling constant of the bridgehead CH to CHCO<sub>2</sub>Me in 3aa is about 4.2 Hz, which is also consistent with the dihedral angle of these two protons in the crystal structure according to the Karplus equation.<sup>13</sup>

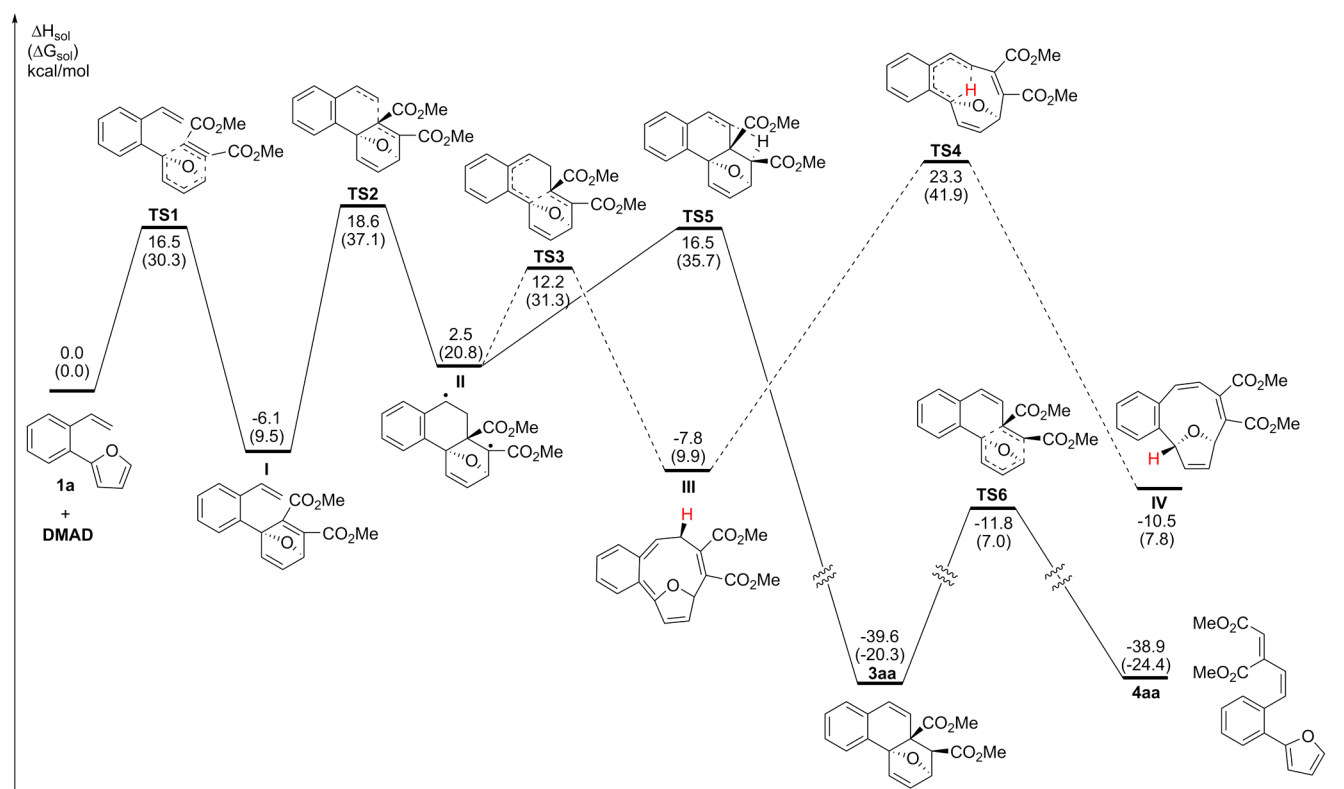
With the optimized reaction conditions (Table 1, entry 4) in hand, the substrate scope was then examined. When diethyl acetylenedicarboxylate (DEAD, 2b) was used as the 2π component, the desired products 3ab and 4ab could be produced in 45% and 41%, respectively (Table 2, entry 2). For substituents in the phenyl moiety of 1, the electron-donating group (-Me or -OMe) was more favorable than the electron-

withdrawing group (-F or -CF<sub>3</sub>) (Table 2, entries 3–6). Such a reactivity difference may be attributed to the fact that the electron-rich tetraenes 1 have higher HOMO energies than electron-poor ones. Similar electronic effects and reactivity trends had also been observed in the [8 + 2] of dienylobenzofurans with dienophiles reported previously by Yu and Herndon.<sup>4,5,8</sup> Substituents in the alkene moiety of 1 was explored as well, and a methyl group at R<sup>2</sup> could be tolerated, affording the desired products 3fa and 4fa in yields of 26% and 39%, respectively. However, an electron-withdrawing group (-CO<sub>2</sub>Me) at R<sup>2</sup> or internal alkene was ineffective for this transformation, as neither 3 nor 4 was obtained experimentally.

As mentioned above, when the reaction was conducted in water at 120 °C for 24 h, four different products 5, 6, 7, and 8 were isolated. Compounds 5 and 6 were two diastereomers, which should come from the nucleophilic ring-opening of 3 by water (6aa was confirmed by X-ray diffraction analysis, see SI).<sup>14</sup> Product 7 was generated possibly from a decarboxylative

Scheme 5. Interconversion of Products in Toluene<sup>a</sup>

<sup>a</sup>The yield of I/3aa/4aa = 6%:8%:2%. The molar ratio was determined by <sup>1</sup>H NMR spectroscopy.



**Figure 1.** Computed potential energy surfaces for pathways I and II at the (U)B3LYP/6-31+G(d) level in toluene.

aromatization of 3. Intermolecular Diels–Alder reaction of compounds 4 with 1, followed by ring-opening led to the generation of product 8. In all cases, 5 and its diastereomers 6 were the major products (Table 3).

To further understand the water mediated process, a control reaction was then conducted (Scheme 4). When the aqueous solution of 3aa or 4aa was refluxed for 24 h, a mixture of 5aa and 6aa was produced in about 1:1 ratio. This control experiment showed clearly that 5aa and 6aa came from the nucleophilic ring-opening of 3 by water.

When catalytic amount of Lewis acid, such as ZnCl<sub>2</sub> or FeCl<sub>3</sub>, was used as catalyst for this transformation in toluene, a different distribution of products was observed. Taking the ZnCl<sub>2</sub>-catalyzed system as an example, in addition to products 7 and 8, which were found in the water reaction system, another product 4-phenylphenol derivative 9 was observed (Table 4). The product distributions were sensitive to the

electronic properties of tetraenes 1. For example, the reaction of vinylphenylfuran 1a with DMAD gave products 7aa, 8aa, and 9aa in 7%, 45%, and 30% yields, respectively (Table 4, entry 1). Vinylphenylfurans with electron-donating groups (Table 4, entries 2–3) performed much better than those with electron-withdrawing groups (Table 4, entries 4–5). Interestingly, 4-phenylphenol derivative 9ca was obtained in quantitative yield when electron-rich substrate 1c was applied (Table 4, entry 3). While for electron-deficient substrate 1d, only 7da and 8da were detected (Table 4, entry 4).

**2.2. Understanding the Mechanism from Experimental Observations and DFT Calculations.** In this part, we will report our understanding of the reaction mechanism for the thermal reaction of 1a and 2a using DFT calculations and experiments.

**Experimental Study.** We proposed pathway I for the formation of the final product 3aa in Scheme 3.<sup>8,15</sup> It was



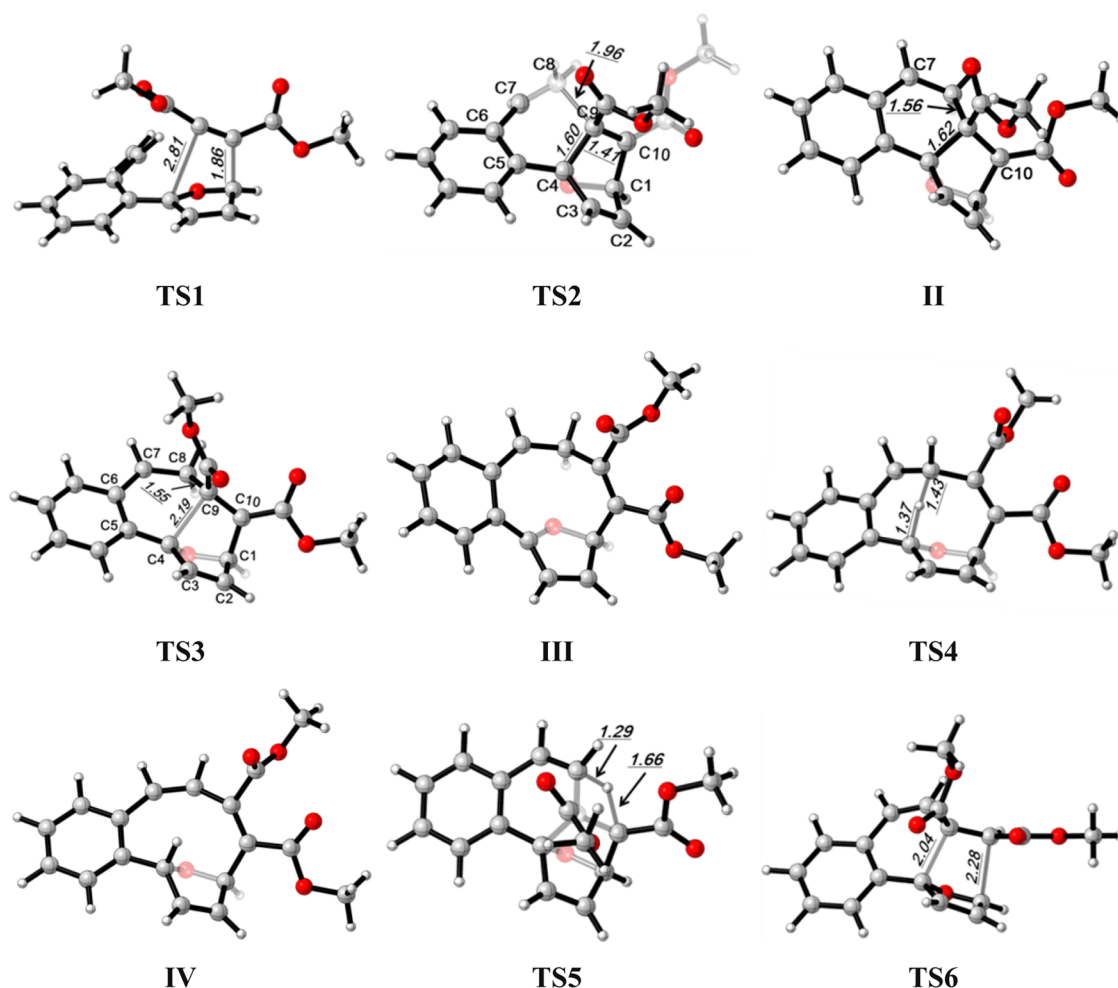


Figure 2. Optimized geometries of key transition states and intermediates. Bond distances are in Å.

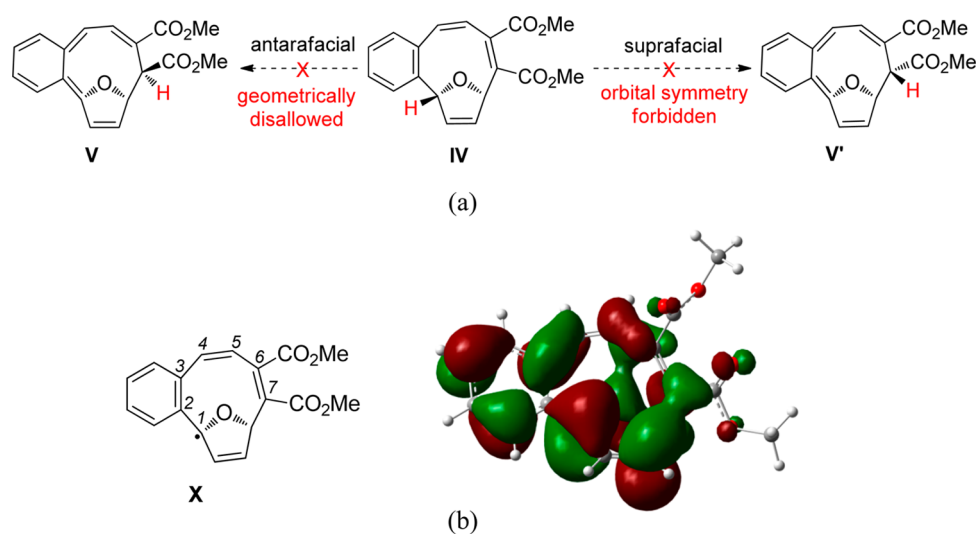


Figure 3. (a) Antarafacial or suprafacial [1,7]-H shift from IV to V (or V'). (b) The SOMO of X.

expected that the [4 + 2] cycloadduct **I** should be a stable and isolable intermediate if milder reaction conditions were applied. With this hypothesis, we then carried out the reaction of vinylphenylfuran and DMAD in toluene at 85 °C (not the original 120 °C) for 4 h. To our delight, the expected [4 + 2] cycloadduct **I** was successfully obtained (Scheme 5). This [4 +

2] cycloadduct **I** can be further converted into **3aa** in 80% yield at 85 °C for additional heating of 4 h. It was found that **3aa** and **4aa** could be converted into each other at 120 °C in toluene (the ratio of **3aa** to **4aa** was close to 1:1), implying that **4aa** or **3aa** could be formed from its counterpart through Diels–Alder or *retro*-Diels–Alder reaction (Scheme 5).<sup>16</sup>

**Pathway I.** On the basis of these experimental observations, DFT calculations were then performed to help understand the reaction mechanism. As shown in Figure 1, the [4 + 2] via TS1 (with an activation enthalpy of 16.5 kcal/mol) is easy and exothermic (by 6.1 kcal/mol). This step is concerted but asynchronous, as evidenced by the large difference between the two forming C–C bond distances in transition structure TS1 (2.81 vs 1.86 Å, Figure 2). To our surprise, we found that the [1,5]-vinyl shift is stepwise. The first step is to form the C8–C9 bond via a diradical transition state TS2. The resulting intermediate II is a diradical species with a computed  $\langle S^2 \rangle$  of 1.03, and the spin densities are mostly distributed on atoms C7 (0.87) and C10 (–0.74) (see Supporting Information (SI)), both of which could be stabilized by the conjugated phenyl group and ester group, respectively. Then, the C4–C9 bond breaks via TS3 to give intermediate III, the vinyl shift product from I. The forming bond in TS2 is about 1.96 Å in length, and the breaking bond in TS3 is about 2.19 Å. We can locate a closed-shell one-step concerted vinyl shift transition state, which is very similar to TS3, but its wave function is not stable, and such a transition state is an artificial one. The difficult step of the stepwise [1,5]-vinyl shift is the C–C bond formation step with an activation enthalpy of 24.7 kcal/mol, and this step is endothermic. The C–C bond breaking step in the [1,5]-vinyl shift requires an activation enthalpy of 9.7 kcal/mol, and this step is exothermic.

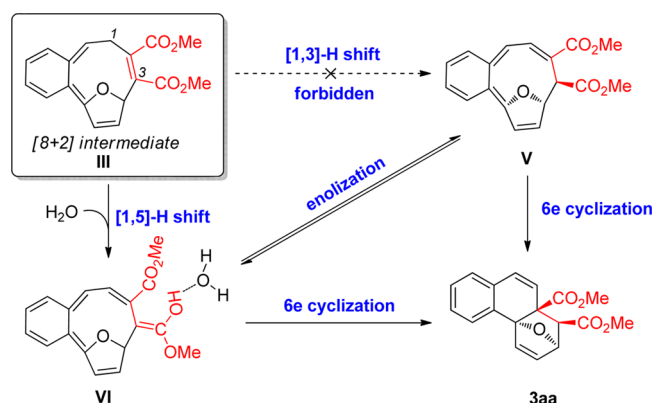
The followed [1,5]-H shift converting *o*-QDM III to IV via TS4 in pathway I is not easy with an activation enthalpy of 31.1 kcal/mol. The distances of the forming and breaking C–H bonds in TS4 are 1.37 and 1.43 Å, respectively. This step is an exothermic process since IV is more stable than III by 2.7 kcal/mol.

We proposed that IV could be converted to V via the [1,7]-H shift process (Figure 3),<sup>17</sup> followed by 6 $\pi$ -electrocyclization to give the experimentally observed product 3aa. [1,7]-H shifts are usually allowed antarafacially. In the present system, such a transition state is not possible in geometry as the rotation of single bonds is restricted due to the ring constraint.<sup>18</sup> A suprafacial [1,7]-H shift is also forbidden here, according to the Woodward–Hoffmann rules.<sup>19</sup> As shown in Figure 3, the orbital coefficients in 1 and 7 positions are out of phase in the SOMO orbital of X.

We can rule out pathway I due to the nonexistence of the [1,7]-H shift. Actually, we can further exclude this pathway by the second reason that the formation of intermediate IV is not favored kinetically than pathway II involving a direct [1,3]-H shift to convert II to 3aa, which will be discussed in the latter part of this article.

Before closing our discussion of pathway I, we want to mention two other possible pathways converting intermediate III to 3aa. One is the possible [1,3]-H shift from III. This is not allowed because in SOMO of X (Figure 3b), the orbitals at 5 and 7 are out of phase. All efforts to locate such a transition state failed. A water-assisted-H transfer pathway was considered as well (Scheme 6).<sup>20</sup> Yu and co-workers have demonstrated experimentally and computationally that water or other proton source such as methanol can act as an efficient proton-transfer catalyst in [1,2]- and [1,3]-H transfers.<sup>21</sup> We speculated that a trace amount of water, which exists in the reagent or solvent, could catalyze the [1,5]-H shift to convert III to VI. The desired product 3aa could then be accessed through 6 $\pi$ -electrocyclization (from VI) or enolization/6 $\pi$ -electrocyclization (from V). However, this water-assisted pathway was not

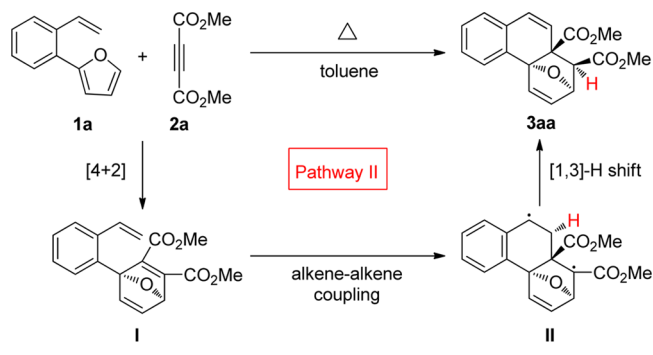
**Scheme 6.** Proposed Water-Assisted Pathway for the Generation of 3aa



supported by DFT calculations and experiments because the conversion from III to VI is very difficult, requiring an activation enthalpy of about 40.2 kcal/mol (see SI for details), and no H/D exchange was observed when the reaction was conducted in toluene with 10 equiv of D<sub>2</sub>O.

**Pathway II.** After the above mechanistic studies, we envisioned that maybe the *o*-QDM intermediate III did not exist. We further hypothesized that intermediate II underwent a [1,3]-H shift directly converting II to product 3aa (pathway II, Scheme 7). The [1,3]-H shift can be regarded as a hydrogen

**Scheme 7.** Pathway II for the Generation of 3aa



radical shift,<sup>22</sup> and this step is very facile with an activation enthalpy of 14.0 kcal/mol (Figure 1). The distances of the forming and breaking C–H bonds in TS5 are 1.66 and 1.29 Å (Figure 2), respectively. This [1,3]-H shift is irreversible because this step is exothermic by 42.1 kcal/mol. This explains why intermediate I could only be observed after a short time and at a low temperature. The final step of the studied reaction is the *retro*-D–A reaction, converting 3aa to the final product with an activation enthalpy of 27.8 kcal/mol (Figure 1). The lengths of two forming carbon–carbon bonds, C1–C10 and C4–C9, in the transition state TS6 are 2.28 and 2.04 Å, respectively (Figure 2).

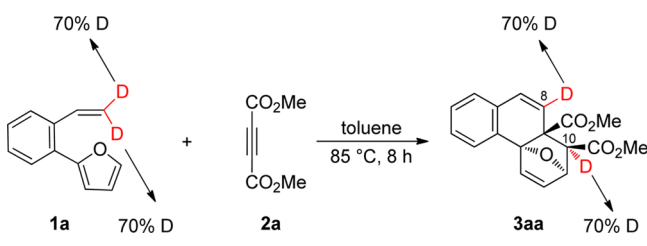
The potential energy surface of pathway II showed that the rate-determining step is the formation of intermediate II. That is why at lower temperature we can obtain the [4 + 2] cycloadduct I. Calculation results here indicate that the overall activation free energy in pathway II is 37.1 kcal/mol in solution. Since there is overestimation of entropy here for the two-molecule to one-molecule (1a + DMAD to II and then to 3aa), the actual activation should be lower than this value by several

kcal/mol. This is consistent with the experimental reaction conditions (refluxing in toluene at 120 °C for 24 h).

Comparison of pathways I and II indicated that the stepwise vinyl shift to give **III** is easy but that the [1,5]-H shift to form **IV** in pathway I is difficult than the [1,3]-H shift from **II** to **3aa**. **TS5** is higher in energy than **TS3** by 4.3 kcal/mol. This could explain why the originally proposed [8 + 2] cycloadduct **IV** was not generated.

To further investigate the direct [1,3]-hydrogen migration mechanism in pathway II, an isotopic labeling experiment was then carried out to track whether the hydrogen at C10 of the product **3aa** comes from the hydrogen at C8 of the starting material **1a** (Scheme 8). Selective isotopic labeled **1a** (70% D)

**Scheme 8. Deuterium Labeling Study of the [1,3]-H-Shift**



at the C8 was reacted with nonlabeled DMAD, affording the product **3aa** with 70% D at C10 (See SI for details). Such results are consistent with the direct intramolecular H shift from C8 to C10. Therefore, based on theoretical and experimental studies, the reaction of vinylphenylfuran and DMAD is suggested to take place through an intramolecular Diels–Alder reaction, followed by a diradical alkene–alkene coupling. Then, a [1,3]-H shift converts diradical intermediate **II** to polycyclic product **3aa**, which then undergoes *retro*-Diels–Alder to furnish final product **4aa**. A key diradical intermediate **II** via the alkene–alkene coupling but not the [8 + 2] cycloaddition compound, *o*-QDM **III**, is supported by our DFT mechanistic studies. Further exploration of this system is also underway in our group.

### 3. CONCLUSIONS

In conclusion, an experimental and theoretical study was carried out to investigate a designed [8 + 2] reaction of vinylphenylfuran **1** and dimethyl acetylenedicarboxylate (DMAD, **2a**) and its derivatives. The reactions occurred efficiently under three different conditions, giving rise to different products. When the reaction was conducted in refluxing toluene, an unexpected epoxypheanthrene derivative **3** ([8 + 2] isomer product) and its *retro*-Diels–Alder product **4** were generated. The scope of this reaction has been investigated in the present study. Experimental and DFT calculations have been conducted to investigate how the reaction between vinylphenylfuran and DMAD took place. The reaction was proposed through an intermolecular Diels–Alder reaction between DMAD **2a** and the furan moiety of vinylphenylfuran **1a**, followed by an unexpected intramolecular alkene–alkene coupling reaction. A diradical species was generated in this process, which then underwent intramolecular [1,3]-H shift to give the experimentally observed epoxypheanthrene **3aa**. Product **3aa** can be transformed to **4aa** via a *retro*-Diels–Alder reaction. The mechanistic study ruled out the originally proposed *o*-QDM intermediate from the [4 + 2]/[1,5]-vinyl shift step (Scheme 3, pathway I). The expected [8 +

2] cycloadduct **IV** (pathway I) was not generated because the [1,5]-H shift from **III** is disfavored compared to the [1,3]-H shift process in pathway II. These theoretical studies, especially the finding of the intramolecular alkene–alkene coupling process via the diradical intermediate, and the [1,3]-H shift mechanisms may provide useful insights and guides for understanding of other [m + n] cycloadditions.

### 4. EXPERIMENTAL SECTION

**General Information.** Unless otherwise noted, all reactions were carried out under nitrogen atmosphere in a Schlenk tube, and solvents were purified by standard methods. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded on 400, 100, and 376 MHz NMR spectrometers, respectively. <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts were determined relative to internal standard TMS at  $\delta$  0.0, and <sup>19</sup>F NMR chemical shifts were determined relative to CFCl<sub>3</sub> as the external standard. Chemical shifts ( $\delta$ ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. The mass analyzer type used for the HRMS is Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). All reagents were purchased from commercial sources, unless specified otherwise, or prepared as described in the literature.

**Synthesis of Vinylphenylfuran.** Under a nitrogen atmosphere at 0 °C, *n*-BuLi (1.2 mL, 2.5 M) was dropped into a solution of CH<sub>3</sub>PPh<sub>3</sub>Br (1.1249 g, 3.140 mmol) in THF (10 mL) in a 50 mL Schlenk tube and was stirred for 30 min before being treated with 2-bromo-benzaldehyde (464.7 mg, 2.512 mmol) dropwise. The resulting solution was stirred at room temperature for 10 h and then filtered through a Celite pad. The filtrate and Pd(PPh<sub>3</sub>)<sub>4</sub> (87.1 mg, 0.0754 mmol) were added into a 50 mL Schlenk tube and stirred for 10 min at room temperature. Then, 2-furanboronic acid (309.2 mg, 2.763 mmol, dissolved in 2 mL of ethanol) and Na<sub>2</sub>CO<sub>3</sub> (532.6 mg, 5.024 mmol, in 2 mL of water) were added into the mixture in sequence. The mixture was heated under reflux for 16 h. After completion of the reaction, the system was filtered, then the solvent was concentrated, and the residue was extracted with 10 mL of ether three times, dried over MgSO<sub>4</sub>, and evaporated under reduced pressure to afford 2-(2-vinylphenyl)furan **1a** (307 mg, 72%), which was purified by column chromatography over silica gel eluting with petroleum ether.

**General Procedure for the Reaction in Toluene.** Under a nitrogen atmosphere, **1a** (25.5 mg, 0.15 mmol) and DMAD **2a** (32.0 mg, 0.225 mmol) were injected into 1 mL of toluene in a 25 mL Schlenk tube. The system was kept at 120 °C for 24 h. After completion of the reaction, the solvent was concentrated and purified by column chromatography over silica gel eluting with petroleum ether/EtOAc (5:1) to afford the desired product **3aa** and **4aa**.

**General Procedure for the Reaction in Water.** Under a nitrogen atmosphere, **1a** (25.5 mg, 0.15 mmol) and DMAD **2a** (32.0 mg, 0.225 mmol) were injected into 1 mL of water in a 25 mL Schlenk tube. The system was kept at 120 °C for 24 h. After completion of the reaction, the reaction mixture was extracted with 3 mL of acetic ether three times, dried over MgSO<sub>4</sub>, and evaporated under reduced pressure. The residue was purified by column chromatography over silica gel eluting with petroleum ether/EtOAc (10:1 to 5:1 to 2:1) to afford the desired product **5aa**, **6aa**, **7aa**, and **8aa**.

**General Procedure for the Reaction in ZnCl<sub>2</sub>/Toluene.** Under a nitrogen atmosphere, **1a** (25.5 mg, 0.15 mmol) and DMAD **2a** (32.0 mg, 0.225 mmol) were injected into 1 mL of toluene (with ZnCl<sub>2</sub> 1.0 mg, 5 mol %) in a 25 mL Schlenk tube. The system was kept at 120 °C for 24 h. After completion of the reaction, the solvent was concentrated and purified by column chromatography over silica gel eluting with petroleum ether/EtOAc (5:1 to 3:1) to afford the desired product **7aa**, **8aa**, and **9aa**.

**2-(2-Vinylphenyl)furan (1a).** Colorless oil, *R*<sub>f</sub> = 0.9 (petroleum ether), yield (307 mg, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.49–7.43 (m, 2H), 7.24 (dd, *J* = 7.3, 1.5 Hz, 2H), 7.01 (dd, *J* = 17.4, 11.0 Hz, 1H), 6.43 (dt, *J* = 3.3, 2.6 Hz, 2H), 5.61 (dd, *J* = 17.4, 1.3 Hz, 1H), 5.24 (dd, *J* = 10.9, 1.3 Hz, 1H). <sup>13</sup>C



NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.8, 142.3, 136.5, 135.7, 129.3, 127.8, 127.8, 127.5, 127.1, 115.7, 111.4, 109.9. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 1767, 1688, 1627, 1402, 1216, 1194, 1091, 1091, 1009, 763. HRMS (EI) mass calcd for  $\text{C}_{12}\text{H}_{10}\text{O}$  ( $[\text{M}]^+$ ): 170.0732; found 170.0728.

**2-(5-Methyl-2-vinylphenyl)furan (1b).** Colorless oil,  $R_f$  = 0.9 (petroleum ether), yield (400 mg, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44–7.40 (m, 1H), 7.36 (d,  $J$  = 7.8 Hz, 2H), 7.02 (d,  $J$  = 8.2 Hz, 1H), 6.97 (dd,  $J$  = 17.5, 11.0 Hz, 1H), 6.40 (td,  $J$  = 3.4, 2.2 Hz, 2H), 5.55 (dd,  $J$  = 17.4, 1.3 Hz, 1H), 5.18 (dd,  $J$  = 10.9, 1.3 Hz, 1H), 2.29 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.9, 142.1, 137.5, 136.2, 132.9, 129.1, 128.7, 128.0, 126.9, 114.8, 111.4, 109.7, 21.2. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2921, 1769, 1687, 1608, 1495, 1401, 1040, 977, 823, 652. HRMS (EI) mass calcd for  $\text{C}_{13}\text{H}_{12}\text{O}$  ( $[\text{M}]^+$ ): 184.0888; found 184.0887.

**2-(4-Methoxy-2-vinylphenyl)furan (1c).** Colorless oil,  $R_f$  = 0.9 (petroleum ether), yield (494 mg, 70%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J$  = 8.6 Hz, 1H), 7.51 (dd,  $J$  = 1.8, 0.7 Hz, 1H), 7.14–7.04 (m, 2H), 6.92 (dd,  $J$  = 8.6, 2.6 Hz, 1H), 6.50 (dd,  $J$  = 3.3, 1.8 Hz, 1H), 6.43 (dd,  $J$  = 3.3, 0.6 Hz, 1H), 5.71 (dd,  $J$  = 17.4, 1.3 Hz, 1H), 5.35 (dd,  $J$  = 10.9, 1.3 Hz, 1H), 3.89 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 152.8, 141.7, 137.1, 136.3, 129.1, 122.6, 115.7, 113.7, 111.7, 111.3, 108.6, 55.4. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2961, 2911, 2836, 1676, 1602, 1563, 1485, 1463, 1419, 1233. HRMS (EI) mass calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_2$  ( $[\text{M}]^+$ ): 200.0837; found 200.0838.

**2-(4-(Trifluoromethyl)-2-vinylphenyl)furan (1d).** Colorless oil,  $R_f$  = 0.9 (petroleum ether), yield (170 mg, 34%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J$  = 10.9 Hz, 2H), 7.59 (d,  $J$  = 5.2 Hz, 2H), 7.12 (dd,  $J$  = 17.4, 11.0 Hz, 1H), 6.67 (d,  $J$  = 3.3 Hz, 1H), 6.56 (dd,  $J$  = 2.9, 1.8 Hz, 1H), 5.78 (d,  $J$  = 17.4 Hz, 1H), 5.46 (d,  $J$  = 11.0 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.3, 143.0, 135.9, 135.6, 132.1, 129.5 (q,  $J_{\text{C-F}}$  = 32.4 Hz), 127.4, 124.3 (dd,  $J_{\text{C-F}}$  = 9.7, 3.8 Hz), 124.2 (d,  $J_{\text{C-F}}$  = 273.1 Hz), 117.3, 111.7, 111.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –62.60. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2960, 2919, 2849, 1401, 1330, 1270, 1167, 1040, 1012, 975. HRMS (EI) mass calcd for  $\text{C}_{13}\text{H}_9\text{F}_3\text{O}$  ( $[\text{M}]^+$ ): 238.0605; found 238.0604.

**2-(4-Fluoro-2-vinylphenyl)furan (1e).** Colorless oil,  $R_f$  = 0.9 (petroleum ether), yield (412 mg, 63%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (dd,  $J$  = 8.7, 5.8 Hz, 1H), 7.54 (d,  $J$  = 0.9 Hz, 1H), 7.27 (dd,  $J$  = 10.2, 2.8 Hz, 1H), 7.10–7.01 (m, 2H), 6.54–6.46 (m, 2H), 5.72 (d,  $J$  = 17.4 Hz, 1H), 5.39 (d,  $J$  = 10.9 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3 (d,  $J_{\text{C-F}}$  = 247.2 Hz), 151.9, 142.2, 137.8 (d,  $J_{\text{C-F}}$  = 7.8 Hz), 135.4, 129.6 (d,  $J_{\text{C-F}}$  = 8.4 Hz), 125.7 (d,  $J_{\text{C-F}}$  = 3.1 Hz), 116.7, 114.8 (d,  $J_{\text{C-F}}$  = 21.9 Hz), 113.3 (d,  $J_{\text{C-F}}$  = 22.2 Hz), 111.4, 109.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –114.18. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2967, 2923, 2852, 1400, 1331, 1278, 1161, 1043, 1021, 964. HRMS (EI) mass calcd for  $\text{C}_{12}\text{H}_9\text{FO}$  ( $[\text{M}]^+$ ): 188.0637; found 188.0638.

**2-(2-(Prop-1-en-2-yl)phenyl)furan (1f).** Colorless oil,  $R_f$  = 0.9 (petroleum ether), yield (734 mg, 80%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J$  = 7.5 Hz, 1H), 7.45 (s, 1H), 7.29 (t,  $J$  = 7.4 Hz, 1H), 7.26–7.16 (m, 2H), 6.66 (s, 1H), 6.42 (d,  $J$  = 1.1 Hz, 1H), 5.16 (s, 1H), 5.00 (s, 1H), 1.92 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.9, 147.4, 141.7, 141.6, 129.5, 128.3, 127.5, 127.2, 126.9, 115.1, 111.5, 108.5, 23.4. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 3060, 3020, 2924, 2860, 1724, 1487, 1441, 1013, 895, 729, 675. HRMS (EI) mass calcd for  $\text{C}_{13}\text{H}_{12}\text{O}$  ( $[\text{M}]^+$ ): 184.0888; found 184.0894.

**Methyl 2-(2-(Furan-2-yl)phenyl)acrylate (1g).** Brown oil,  $R_f$  = 0.6 (petroleum ether/EtOAc = 10:1), yield (620 mg, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J$  = 7.8 Hz, 1H), 7.41 (s, 1H), 7.38 (t,  $J$  = 7.4 Hz, 1H), 7.27 (m, 2H), 6.47 (s, 1H), 6.47 (s, 1H), 6.40 (s, 1H), 5.81 (s, 1H), 3.51 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 153.2, 142.9, 142.1, 134.5, 130.9, 129.9, 128.5, 128.0, 127.6, 126.6, 111.5, 108.3, 52.1. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 3122, 3066, 2926, 2846, 2188, 1638, 1599, 1506, 1290, 1255, 1016, 832, 752, 542. HRMS (ESI) mass calcd for  $\text{C}_{14}\text{H}_{12}\text{O}_3\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ): 251.0679; found 251.0674.

**(E/Z)-2-(2-(Prop-1-en-1-yl)phenyl)furan (1h).** Colorless oil,  $R_f$  = 0.9 (petroleum ether), yield (300 mg, 86%, E/Z = 2:3).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (Z, d,  $J$  = 7.6 Hz, 1H), 7.64–7.59 (E, m, 1H), 7.49 (E, s, 1H), 7.46 (E, s, 1H), 7.44 (Z, m, 1H), 7.33–7.19 (Z, m, 3H), 7.33–7.19 (E, m, 2H), 6.72 (E, d,  $J$  = 15.6 Hz, 1H), 6.63 (Z, d,  $J$

= 3.1 Hz, 1H), 6.56 (Z, d,  $J$  = 11.4 Hz, 1H), 6.48 (E, s, 2H), 6.45–6.43 (Z, m, 1H), 6.12 (E, dq,  $J$  = 13.4, 6.6 Hz, 1H), 5.85 (Z, dq,  $J$  = 13.9, 7.0 Hz, 1H), 1.89 (E, d,  $J$  = 6.6 Hz, 3H), 1.77 (Z, d,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 152.8, 142.0, 141.8, 135.8, 134.0, 130.5, 130.4, 130.3, 129.6, 128.8, 127.7, 127.5, 127.2, 127.0, 126.9, 126.8, 126.8, 126.5, 111.4, 111.3, 109.8, 109.6, 18.7, 14.3. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 3200, 3060, 3020, 2923, 2860, 1487, 1441, 1277, 1014, 968, 756, 730, 594. HRMS (EI) mass calcd for  $\text{C}_{13}\text{H}_{12}\text{O}$  ( $[\text{M}]^+$ ): 184.0888; found 184.0887.

**Dimethyl 1-(2-Vinylphenyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (I).** Yellow oil,  $R_f$  = 0.45 (petroleum ether/EtOAc = 5:1), yield (7 mg, 6%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J$  = 5.3 Hz, 1H), 7.51 (d,  $J$  = 7.6 Hz, 2H), 7.32–7.22 (m, 3H), 7.05 (dd,  $J$  = 17.2, 10.9 Hz, 1H), 5.76 (d,  $J$  = 1.9 Hz, 1H), 5.57 (dd,  $J$  = 17.2, 1.2 Hz, 1H), 5.21 (dd,  $J$  = 10.9, 1.2 Hz, 1H), 3.74 (s, 3H), 3.53 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 162.7, 158.4, 149.5, 144.6, 137.5, 135.3, 130.6, 129.4, 128.1, 127.7, 127.0, 116.4, 98.1, 83.8, 52.4, 52.2. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2951, 2925, 2851, 1721, 1637, 1435, 1269, 1168, 763. HRMS (ESI) mass calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_5\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ): 335.0890; found 335.0895.

**Dimethyl 2,10a-dihydro-1H-2,4a-epoxyphenanthrene-1,10a-dicarboxylate (3aa).** Yellow solid (mp 93–96 °C),  $R_f$  = 0.3 (petroleum ether/EtOAc = 5:1), yield (21 mg, 45%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J$  = 7.2 Hz, 1H), 7.33–7.22 (m, 2H), 7.14 (d,  $J$  = 7.1 Hz, 1H), 6.77 (d,  $J$  = 5.7 Hz, 1H), 6.71 (dd,  $J$  = 5.6, 1.2 Hz, 1H), 6.48 (d,  $J$  = 9.6 Hz, 1H), 6.04 (d,  $J$  = 9.6 Hz, 1H), 4.95 (dd,  $J$  = 4.1, 1.3 Hz, 1H), 3.65 (s, 3H), 3.41 (s, 3H), 3.38 (d,  $J$  = 4.2 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.2, 170.3, 137.4, 137.3, 132.5, 130.1, 129.9, 128.9, 128.6, 128.5, 127.8, 127.0, 89.5, 77.9, 59.9, 56.3, 52.2, 52.0. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 3001, 2952, 2845, 1739, 1644, 1435, 1245, 1169, 1097. HRMS (MALDI) mass calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_5\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ): 335.0890; found 335.0897.

**Dimethyl 2-((Z)-2-(furan-2-yl)styryl)maleate (4aa).** Yellow solid (mp 109 °C),  $R_f$  = 0.5 (petroleum ether/EtOAc = 5:1), yield (19 mg, 41%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J$  = 7.8 Hz, 1H), 7.53 (s, 1H), 7.41–7.36 (m, 1H), 7.28–7.22 (m, 2H), 6.99 (d,  $J$  = 11.8 Hz, 1H), 6.67 (d,  $J$  = 3.2 Hz, 1H), 6.51 (dd,  $J$  = 3.0, 1.7 Hz, 1H), 6.32 (d,  $J$  = 11.8 Hz, 1H), 6.02 (s, 1H), 3.72 (s, 3H), 3.26 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 165.2, 152.1, 145.0, 142.4, 139.0, 131.9, 130.9, 129.5, 128.5, 126.6, 126.0, 125.9, 122.8, 111.7, 110.5, 51.9, 51.9. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2953, 2921, 2850, 1734, 1649, 1437, 1265, 1204, 736. HRMS (MALDI) mass calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_5\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ): 335.0890; found 335.0902.

**Dimethyl-2,3-dihydroxy-1,2,3,10a-tetrahydrophenanthrene-1,10a-(1H)-dicarboxylate (5aa).** Yellow solid (mp 115 °C),  $R_f$  = 0.2 (petroleum ether/EtOAc = 2:1), yield (24 mg, 22%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J$  = 5.3 Hz, 1H), 7.51 (d,  $J$  = 7.6 Hz, 2H), 7.32–7.22 (m, 2H), 7.05 (dd,  $J$  = 17.2, 10.9 Hz, 1H), 5.76 (d,  $J$  = 1.9 Hz, 1H), 5.57 (dd,  $J$  = 17.2, 1.2 Hz, 1H), 5.21 (dd,  $J$  = 10.9, 1.2 Hz, 1H), 3.74 (s, 3H), 3.53 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 171.3, 138.5, 132.6, 131.8, 129.1, 128.5, 128.4, 127.6, 126.5, 125.1, 66.8, 65.2, 52.9, 52.4, 52.1, 49.1. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2953, 2922, 2852, 1734, 1436, 1264, 1229, 1086, 737. HRMS (MALDI) mass calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_6\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ): 353.0996; found 353.1002.

**Dimethyl-2,3-dihydroxy-1,2,3,10a-tetrahydrophenanthrene-1,10a-(1H)-dicarboxylate (6aa).** White solid (mp 225 °C),  $R_f$  = 0.3 (petroleum ether/EtOAc = 2:1), yield (26 mg, 24%).  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  7.43–7.36 (m, 1H), 7.28–7.20 (m, 2H), 7.16–7.07 (m, 1H), 6.56 (d,  $J$  = 9.6 Hz, 1H), 6.01–5.93 (m, 2H), 5.38 (d,  $J$  = 4.7 Hz, 2H), 4.11 (s, 2H), 3.67 (s, 3H), 3.48 (s, 3H), 2.87 (q,  $J$  = 4.3 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  171.4, 170.7, 132.6, 132.3, 132.0, 131.3, 129.0, 128.4, 128.3, 126.8, 126.4, 124.5, 71.3, 70.4, 54.8, 52.4, 51.8, 50.8. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2952, 2844, 1730, 1650, 1433, 1265, 1169, 1121, 740. HRMS (MALDI) mass calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_6\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ): 353.0996; found 353.1002.

**Methyl Phenanthrene-1-carboxylate (7aa).**<sup>23</sup> Yellow solid (mp 95 °C),  $R_f$  = 0.8 (petroleum ether: EtOAc = 5:1), yield (10 mg, 14%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 (d,  $J$  = 8.4 Hz, 1H), 8.70 (d,  $J$  = 9.4 Hz, 1H), 8.62 (d,  $J$  = 8.2 Hz, 1H), 8.14 (dd,  $J$  = 7.4, 1.0 Hz, 1H),

7.87–7.83 (m, 1H), 7.80 (d,  $J = 9.4$  Hz, 1H), 7.63–7.54 (m, 3H), 3.96 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 131.6, 130.9, 130.6, 130.0, 129.8, 128.8, 128.5, 128.2, 127.1, 127.1, 126.9, 125.3, 123.7, 122.8, 52.3.

(*Z*)-Dimethyl-2-(2-(furan-2-yl)styryl)-4,5-dihydroxy-2'-vinyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2,3-dicarboxylate (**8aa**). Brown oil,  $R_f = 0.4$  (petroleum ether/EtOAc = 3:1), yield (34 mg, 45%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49–7.46 (m, 1H), 7.42–7.39 (m, 1H), 7.36 (d,  $J = 7.0$  Hz, 1H), 7.20 (dd,  $J = 7.1$ , 5.6 Hz, 2H), 7.13 (dd,  $J = 14.6$ , 6.7 Hz, 2H), 7.00 (s, 1H), 6.96 (dd,  $J = 13.9$ , 7.3 Hz, 1H), 6.49 (d,  $J = 9.6$  Hz, 1H), 6.37 (d,  $J = 3.2$  Hz, 1H), 6.20 (dd,  $J = 7.9$ , 6.7 Hz, 2H), 6.07 (d,  $J = 5.3$  Hz, 1H), 5.53 (d,  $J = 17.4$  Hz, 1H), 5.15 (d,  $J = 11.0$  Hz, 1H), 4.75 (dd,  $J = 11.4$ , 6.4 Hz, 1H), 4.12 (t,  $J = 5.8$  Hz, 1H), 3.69 (s, 3H), 3.51 (s, 3H), 3.20 (d,  $J = 11.4$  Hz, 1H), 2.39 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 172.0, 153.3, 151.5, 136.5, 135.6, 135.5, 133.4, 131.7, 129.0, 128.9, 128.6, 128.3, 127.7, 127.7, 127.7, 127.3, 127.2, 126.5, 126.1, 124.9, 115.8, 111.8, 110.6, 66.4, 52.9, 52.3, 52.0, 50.9, 41.0. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2952, 2850, 1734, 1634, 1256, 1229, 1204, 763, 737. HRMS (MALDI) mass calcd for  $\text{C}_{30}\text{H}_{26}\text{O}_6\text{Na}$  ( $[\text{M} + \text{Na} - \text{H}_2\text{O}]^+$ ): 505.1622; found 505.1627.

Dimethyl 4-Hydroxy-2'-vinyl-[1,1'-biphenyl]-2,3-dicarboxylate (**9aa**). Yellow oil,  $R_f = 0.6$  (petroleum ether/EtOAc = 5:1), yield (14 mg, 30%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.93 (s, 1H), 7.54 (d,  $J = 7.8$  Hz, 1H), 7.26 (dd,  $J = 11.1$ , 4.1 Hz, 1H), 7.22 (d,  $J = 8.6$  Hz, 1H), 7.16 (dd,  $J = 7.4$ , 1.1 Hz, 1H), 7.07 (dd,  $J = 7.6$ , 1.0 Hz, 1H), 7.01 (d,  $J = 8.6$  Hz, 1H), 6.38 (dd,  $J = 17.5$ , 11.0 Hz, 1H), 5.57 (dd,  $J = 17.5$ , 1.0 Hz, 1H), 5.07 (dd,  $J = 11.0$ , 1.0 Hz, 1H), 3.84 (s, 3H), 3.42 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.4, 168.4, 160.9, 137.6, 137.1, 136.7, 135.1, 135.0, 130.3, 128.2, 127.0, 125.0, 118.6, 114.9, 109.0, 53.0, 51.9. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2952, 2919, 2850, 1738, 1678, 1462, 1442, 1246, 1215. HRMS (MALDI) mass calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_5\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ): 335.0890; found 335.0894.

Diethyl 2,10a-dihydro-1H-2,4a-epoxyphenanthrene-1,10a-dicarboxylate (**3ab**). Yellow oil,  $R_f = 0.3$  (petroleum ether/EtOAc = 5:1), yield (14 mg, 45%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J = 7.2$  Hz, 1H), 7.36 (dt,  $J = 19.6$ , 7.3 Hz, 2H), 7.23 (d,  $J = 7.1$  Hz, 1H), 6.88 (d,  $J = 5.6$  Hz, 1H), 6.79 (d,  $J = 5.6$  Hz, 1H), 6.57 (d,  $J = 9.6$  Hz, 1H), 6.15 (d,  $J = 9.6$  Hz, 1H), 5.04 (d,  $J = 3.4$  Hz, 1H), 4.26–4.12 (m, 2H), 4.05–3.87 (m, 2H), 3.46 (d,  $J = 4.0$  Hz, 1H), 1.33 (t,  $J = 7.1$  Hz, 3H), 1.07 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 169.8, 137.3, 137.2, 132.6, 130.3, 129.8, 129.4, 128.5, 128.4, 127.7, 126.7, 89.5, 78.1, 61.0, 60.9, 60.0, 56.5, 14.2, 13.7. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2982, 2820, 2851, 1730, 1649, 1257, 1197, 1091, 741. HRMS (MALDI) mass calcd for  $\text{C}_{20}\text{H}_{20}\text{O}_5\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ): 363.1203; found 363.1212.

Diethyl 2-((*Z*)-2-(Furan-2-yl)styryl)maleate (**4ab**). Yellow solid (mp 90 °C),  $R_f = 0.5$  (petroleum ether/EtOAc = 5:1), yield (12 mg, 41%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 5.3$  Hz, 1H), 7.51 (d,  $J = 7.6$  Hz, 2H), 7.32–7.22 (m, 3H), 7.05 (dd,  $J = 17.2$ , 10.9 Hz, 1H), 5.76 (d,  $J = 1.9$  Hz, 1H), 5.57 (dd,  $J = 17.2$ , 1.2 Hz, 1H), 5.21 (dd,  $J = 10.9$ , 1.2 Hz, 1H), 3.74 (s, 3H), 3.53 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 164.8, 152.1, 144.8, 142.3, 138.6, 132.0, 131.1, 129.5, 128.5, 126.6, 126.2, 125.7, 123.4, 111.7, 110.6, 61.3, 60.8, 14.1, 13.4. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2982, 2934, 1787, 1730, 1650, 1465, 1394, 1261, 1191. HRMS (MALDI) mass calcd for  $\text{C}_{20}\text{H}_{21}\text{O}_5$  ( $[\text{M} + \text{H}]^+$ ): 341.1384; found 341.1377.

Dimethyl 6-Methyl-2,10a-dihydro-1H-2,4a-epoxyphenanthrene-1,10a-dicarboxylate (**3ba**). Yellow solid (mp 105 °C),  $R_f = 0.3$  (petroleum ether/EtOAc = 5:1), yield (28 mg, 52%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (s, 1H), 7.10 (d,  $J = 7.7$  Hz, 1H), 7.03 (d,  $J = 7.7$  Hz, 1H), 6.77 (d,  $J = 5.7$  Hz, 1H), 6.70 (dd,  $J = 5.7$ , 1.7 Hz, 1H), 6.45 (d,  $J = 9.6$  Hz, 1H), 5.97 (d,  $J = 9.6$  Hz, 1H), 4.94 (dd,  $J = 4.3$ , 1.7 Hz, 1H), 3.65 (s, 3H), 3.41 (s, 3H), 3.37 (d,  $J = 4.3$  Hz, 1H), 2.30 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 170.5, 138.5, 137.4, 137.3, 130.4, 129.9, 129.8, 129.4, 127.8, 126.8, 89.6, 77.9, 59.9, 56.4, 52.2, 52.0, 21.4. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2952, 2921, 2851, 1738, 1436, 1355, 1245, 1169, 735. HRMS (MALDI) mass calcd for  $\text{C}_{19}\text{H}_{18}\text{O}_5\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ): 349.1047; found 349.1051.

Dimethyl 2-((*Z*)-2-(Furan-2-yl)-4-methylstyryl)maleate (**4ba**). Yellow solid (mp 85 °C),  $R_f = 0.5$  (petroleum ether/EtOAc = 5:1), yield

(9 mg, 35%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (s, 1H), 7.42 (d,  $J = 1.2$  Hz, 1H), 7.07 (d,  $J = 7.8$  Hz, 1H), 6.96 (d,  $J = 7.6$  Hz, 1H), 6.85 (d,  $J = 11.7$  Hz, 1H), 6.55 (d,  $J = 3.3$  Hz, 1H), 6.40 (dd,  $J = 3.3$ , 1.8 Hz, 1H), 6.21–6.16 (m, 1H), 5.92 (s, 1H), 3.62 (s, 3H), 3.19 (s, 3H), 2.31 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 165.3, 152.2, 145.2, 142.2, 139.0, 138.4, 130.9, 129.3, 129.3, 127.4, 126.5, 125.6, 122.5, 111.7, 110.4, 51.9, 21.3. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2953, 2921, 2850, 1735, 1647, 1436, 1264, 1202, 1169, 736. HRMS (MALDI) mass calcd for  $\text{C}_{19}\text{H}_{19}\text{O}_5$  ( $[\text{M} + \text{H}]^+$ ): 327.1227; found 327.1237.

Dimethyl 2,3-Dihydroxy-6-methyl-1,2,3,10a-tetrahydrophenanthrene-1,10a-(1H)-dicarboxylate (**5ba**). Yellow solid (mp 165 °C),  $R_f = 0.2$  (petroleum ether/EtOAc = 2:1), yield (25 mg, 46%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.09 (d,  $J = 7.7$  Hz, 1H), 6.96 (d,  $J = 7.6$  Hz, 1H), 6.51 (d,  $J = 9.6$  Hz, 1H), 6.28 (d,  $J = 4.8$  Hz, 1H), 6.18 (d,  $J = 9.6$  Hz, 1H), 4.56–4.42 (m, 2H), 3.84 (s, 3H), 3.59 (s, 3H), 3.16 (dt,  $J = 5.3$ , 2.1 Hz, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 171.4, 138.8, 138.2, 132.5, 129.8, 129.3, 127.4, 127.4, 126.4, 126.1, 125.8, 66.9, 65.2, 52.8, 52.3, 52.1, 49.2, 21.4. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2953, 2918, 2850, 1733, 1639, 1436, 1232, 1086, 736. HRMS (MALDI) mass calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_6\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ): 367.1152; found 367.1153.

Dimethyl 2,3-Dihydroxy-6-methyl-1,2,3,10a-tetrahydrophenanthrene-1,10a-(1H)-dicarboxylate (**6ba**). White solid (mp 175 °C),  $R_f = 0.3$  (petroleum ether/EtOAc = 2:1), yield (16 mg, 28%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (s, 1H), 7.07 (d,  $J = 7.0$  Hz, 1H), 6.96 (d,  $J = 7.6$  Hz, 1H), 6.51 (d,  $J = 9.6$  Hz, 1H), 6.25 (d,  $J = 9.5$  Hz, 1H), 6.09 (s, 1H), 4.40 (d,  $J = 7.5$  Hz, 2H), 3.85 (s, 3H), 3.59 (s, 3H), 3.06 (d,  $J = 11.0$  Hz, 1H), 2.97 (s, 1H), 2.58 (s, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.1, 171.6, 138.3, 135.5, 132.4, 129.5, 129.1, 128.8, 127.7, 127.4, 126.4, 125.8, 72.1, 71.8, 53.9, 53.0, 52.4, 51.7, 21.4. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2953, 2920, 2851, 1734, 1650, 1436, 1262, 1069, 736. HRMS (MALDI) mass calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_6\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ): 367.1152; found 367.1149.

Methyl 6-Methylphenanthrene-1-carboxylate (**7ba**). White solid (mp 90 °C),  $R_f = 0.8$  (petroleum ether/EtOAc = 5:1), yield (7 mg, 31%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (d,  $J = 8.4$  Hz, 1H), 8.61 (d,  $J = 9.3$  Hz, 1H), 8.41 (s, 1H), 8.11 (dd,  $J = 7.4$ , 1.1 Hz, 1H), 7.75 (dd,  $J = 8.6$ , 6.4 Hz, 2H), 7.57 (dd,  $J = 8.2$ , 7.6 Hz, 1H), 7.43–7.36 (m, 1H), 3.95 (s, 3H), 2.56 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 136.7, 130.7, 130.7, 130.1, 129.7, 129.6, 128.8, 128.6, 128.4, 128.2, 127.1, 125.0, 122.7, 122.5, 52.3, 22.2. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2949, 2917, 2849, 1712, 1631, 1254, 1121, 749. HRMS (EI) mass calcd for  $\text{C}_{17}\text{H}_{14}\text{O}_2$  ( $\text{M}^+$ ): 250.0994; found 250.0995.

(*Z*)-Dimethyl 2-(2-(furan-2-yl)-5-methylstyryl)-4,5-dihydroxy-5'-methyl-2'-vinyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2,3-dicarboxylate (**8ba**). Yellow oil,  $R_f = 0.4$  (petroleum ether/EtOAc = 3:1), yield (54 mg, 16%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 8.9$  Hz, 2H), 7.29 (d,  $J = 6.0$  Hz, 2H), 7.19–6.88 (m, 4H), 6.57 (d,  $J = 9.5$  Hz, 1H), 6.46 (d,  $J = 2.9$  Hz, 1H), 6.28 (d,  $J = 3.0$  Hz, 1H), 6.25 (d,  $J = 9.5$  Hz, 1H), 6.18 (d,  $J = 5.3$  Hz, 1H), 5.60 (d,  $J = 17.4$  Hz, 1H), 5.21 (d,  $J = 11.0$  Hz, 1H), 4.89–4.77 (m, 1H), 4.22 (t,  $J = 5.8$  Hz, 1H), 3.80 (s, 3H), 3.62 (s, 3H), 3.29 (d,  $J = 11.4$  Hz, 1H), 2.40 (d,  $J = 6.6$  Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 172.1, 153.4, 151.3, 138.1, 137.4, 136.2, 135.8, 133.3, 132.8, 129.3, 129.1, 128.7, 128.6, 128.0, 127.8, 127.5, 127.1, 126.4, 125.8, 125.6, 115.0, 111.8, 110.4, 66.5, 52.8, 52.3, 52.0, 50.9, 41.0, 21.4, 21.1. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2952, 2921, 2851, 1732, 1633, 1455, 1321, 908, 735. HRMS (MALDI) mass calcd for  $\text{C}_{32}\text{H}_{30}\text{O}_6\text{Na}$  ( $[\text{M} + \text{Na} - \text{H}_2\text{O}]^+$ ): 533.1935; found 533.1944.

Dimethyl 4-Hydroxy-5'-methyl-2'-vinyl-[1,1'-biphenyl]-2,3-dicarboxylate (**9ba**). Yellow oil,  $R_f = 0.6$  (petroleum ether/EtOAc = 5:1), yield (30 mg, 34%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.91 (s, 1H), 7.44 (d,  $J = 8.0$  Hz, 1H), 7.20 (d,  $J = 3.9$  Hz, 1H), 7.07 (d,  $J = 7.9$  Hz, 1H), 7.00 (d,  $J = 8.6$  Hz, 1H), 6.89 (s, 1H), 6.34 (dd,  $J = 17.5$ , 11.0 Hz, 1H), 5.52 (d,  $J = 17.5$  Hz, 1H), 5.00 (d,  $J = 11.0$  Hz, 1H), 3.84 (s, 3H), 3.43 (s, 3H), 2.26 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.4, 168.4, 160.9, 137.6, 137.0, 136.8, 135.0, 134.8, 133.9, 130.9, 130.5, 129.0, 124.8, 118.6, 113.9, 109.0, 52.9, 51.9, 21.0. IR (thin film)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2952, 2918, 2849, 1739, 1677, 1442, 1333, 1245, 1214. HRMS



(MALDI) mass calcd for  $C_{19}H_{18}O_3Na$  ( $[M + Na]^+$ ): 349.1052; found 349.1056.

**Dimethyl 7-Methoxy-1,2-dihydro-10aH-2,4a-epoxyphenanthrene-1,10a-dicarboxylate (3ca).** Yellow solid (mp 147 °C),  $R_f$  = 0.3 (petroleum ether/EtOAc = 5:1), yield (36 mg, 52%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.40 (d,  $J$  = 8.4 Hz, 1H), 6.79–6.75 (m, 1H), 6.74 (d,  $J$  = 5.7 Hz, 1H), 6.69 (dd,  $J$  = 4.0, 2.0 Hz, 2H), 6.43 (d,  $J$  = 9.7 Hz, 1H), 6.05 (d,  $J$  = 9.6 Hz, 1H), 4.93 (dd,  $J$  = 4.3, 1.7 Hz, 1H), 3.75 (s, 3H), 3.65 (s, 3H), 3.42 (s, 3H), 3.37 (d,  $J$  = 4.3 Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  171.2, 170.3, 160.7, 137.5, 137.3, 133.9, 129.9, 129.7, 127.0, 122.4, 113.6, 113.3, 89.4, 77.8, 59.9, 56.3, 55.4, 52.2, 52.0. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 2953, 2918, 2847, 173, 1640, 1603, 1434, 1267, 735. HRMS (MALDI) mass calcd for  $C_{19}H_{18}O_6Na$  ( $[M + Na]^+$ ): 365.1001; found 365.1002.

**Dimethyl 2-((Z)-2-(Furan-2-yl)-5-methoxystyryl)maleate (4ca).** Yellow oil,  $R_f$  = 0.5 (petroleum ether/EtOAc = 5:1), yield (25 mg, 36%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.59 (d,  $J$  = 8.6 Hz, 1H), 7.39 (s, 1H), 6.86 (t,  $J$  = 11.1 Hz, 2H), 6.72 (s, 1H), 6.42 (s, 1H), 6.38 (s, 1H), 6.22 (d,  $J$  = 11.8 Hz, 1H), 5.93 (s, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 3.21 (s, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  167.0, 165.2, 158.0, 152.1, 145.0, 141.8, 138.8, 133.2, 127.5, 126.1, 123.0, 122.5, 115.4, 115.1, 111.6, 108.9, 55.4, 51.9, 51.8. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 2953, 2923, 1850, 1735, 1652, 1435, 1268, 1244, 735. HRMS (MALDI) mass calcd for  $C_{19}H_{18}O_6Na$  ( $[M + Na]^+$ ): 365.1001; found 365.1004.

**Dimethyl 4-Hydroxy-4'-methoxy-2'-vinyl-[1,1'-biphenyl]-2,3-dicarboxylate (9ca).** Yellow oil,  $R_f$  = 0.6 (petroleum ether/EtOAc = 5:1), yield (86 mg, 100%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  11.02 (s, 1H), 7.28 (d,  $J$  = 3.2 Hz, 1H), 7.15 (d,  $J$  = 2.4 Hz, 1H), 7.10 (d,  $J$  = 2.4 Hz, 1H), 7.08 (d,  $J$  = 2.6 Hz, 1H), 6.83 (dd,  $J$  = 8.4, 2.5 Hz, 1H), 6.44 (dd,  $J$  = 17.5, 11.0 Hz, 1H), 5.65 (d,  $J$  = 17.5 Hz, 1H), 5.17 (d,  $J$  = 11.0 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H), 3.54 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  169.4, 168.5, 160.9, 159.4, 138.1, 138.0, 135.4, 135.1, 131.5, 130.0, 129.8, 118.5, 115.0, 112.9, 109.9, 108.9, 55.3, 52.9, 52.0. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 2953, 2840, 1739, 1677, 1600, 1462, 1218, 724. HRMS (MALDI) mass calcd for  $C_{19}H_{18}O_6Na$  ( $[M + Na]^+$ ): 365.1001; found 365.1005.

**Dimethyl 7-(Trifluoromethyl)-1,2-dihydro-10aH-2,4a-epoxyphenanthrene-1,10a-dicarboxylate (3da).** Yellow solid (mp 75 °C),  $R_f$  = 0.3 (petroleum ether/EtOAc = 5:1), yield (19 mg, 33%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.60 (d,  $J$  = 7.9 Hz, 1H), 7.51 (d,  $J$  = 8.0 Hz, 1H), 7.39 (s, 1H), 6.78–6.71 (m, 2H), 6.51 (d,  $J$  = 9.7 Hz, 1H), 6.15 (d,  $J$  = 9.7 Hz, 1H), 4.97 (dd,  $J$  = 4.3, 0.9 Hz, 1H), 3.66 (s, 3H), 3.42 (s, 3H), 3.38 (d,  $J$  = 4.3 Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  171.0, 170.0, 136.6, 133.8, 133.7, 133.4, 130.7, 129.2, 125.9, 125.1 (dd,  $J_{C-F}$  = 7.3, 3.4 Hz), 124.4 (q,  $J_{C-F}$  = 3.7 Hz), 88.7, 78.1, 60.0, 56.0, 52.3, 52.1.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  –62.98. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 2956, 2918, 2848, 1740, 1643, 1434, 1247, 1168, 1126. HRMS (MALDI) mass calcd for  $C_{19}H_{15}O_3F_3Na$  ( $[M + Na]^+$ ): 403.0769; found 403.0775.

**Dimethyl 2-((Z)-2-(Furan-2-yl)-5-(trifluoromethyl)styryl)maleate (4da).** Yellow solid (mp 85 °C),  $R_f$  = 0.5 (petroleum ether/EtOAc = 5:1), yield (17 mg, 30%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.82 (d,  $J$  = 8.2 Hz, 1H), 7.54 (d,  $J$  = 8.3 Hz, 1H), 7.47 (d,  $J$  = 1.3 Hz, 1H), 7.41 (s, 1H), 6.85 (d,  $J$  = 11.8 Hz, 1H), 6.72 (d,  $J$  = 3.4 Hz, 1H), 6.44 (dd,  $J$  = 3.4, 1.8 Hz, 1H), 6.34–6.29 (m, 1H), 5.97 (s, 1H), 3.63 (s, 3H), 3.15 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  166.8, 165.0, 150.7, 144.4, 143.3, 137.4, 132.6 (d,  $J_{C-F}$  = 1.2 Hz), 132.0, 128.3, 127.9 (d,  $J_{C-F}$  = 3.9 Hz), 127.4, 126.0, 125.2 (q,  $J_{C-F}$  = 3.8 Hz), 123.8, 112.4, 112.1, 52.0, 51.9.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  –62.58. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 2956, 2850, 1736, 1650, 1436, 1330, 1169, 1127, 737. HRMS (MALDI) mass calcd for  $C_{19}H_{15}O_3F_3Na$  ( $[M + Na]^+$ ): 403.0769; found 403.0771.

**Dimethyl 2,3-Dihydroxy-7-(trifluoromethyl)-1,2,3,10a-tetrahydro-phenanthrene-1,10a-(1H)-dicarboxylate (5da).** Yellow solid (mp 148 °C),  $R_f$  = 0.2 (petroleum ether/EtOAc = 5:1), yield (17 mg, 29%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.46 (d,  $J$  = 8.1 Hz, 1H), 7.39 (d,  $J$  = 8.0 Hz, 1H), 7.23 (s, 1H), 6.48 (d,  $J$  = 9.6 Hz, 1H), 6.30 (d,  $J$  = 9.7 Hz, 1H), 6.27 (d,  $J$  = 5.0 Hz, 1H), 4.50–4.33 (m, 2H), 3.77 (s, 3H), 3.50 (s, 3H), 3.11 (d,  $J$  = 10.9 Hz, 1H), 3.04 (d,  $J$  = 5.4 Hz,

1H), 2.47 (s, 1H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  172.3, 170.8, 137.2, 136.0, 132.3, 130.9, 130.3, 128.6, 126.6, 125.5, 125.0 (dd,  $J_{C-F}$  = 7.9, 4.7 Hz), 123.2 (d,  $J_{C-F}$  = 5.0 Hz), 123.1, 122.5, 66.8, 65.0, 53.0, 52.5, 52.0, 48.7.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  –62.87. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 2956, 2917, 2850, 1725, 1643, 1433, 1330, 1116, 736. HRMS (MALDI) mass calcd for  $C_{19}H_{17}O_6F_3Na$  ( $[M + Na]^+$ ): 421.0875; found 421.0859.

**Dimethyl 2,3-Dihydroxy-7-(trifluoromethyl)-1,2,3,10a-tetrahydro-phenanthrene-1,10a-(1H)-dicarboxylate (6da).** Yellow solid (mp 175 °C),  $R_f$  = 0.3 (petroleum ether/EtOAc = 2:1), yield (5 mg, 8%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.50 (d,  $J$  = 8.0 Hz, 1H), 7.40 (d,  $J$  = 7.8 Hz, 1H), 7.23 (s, 1H), 6.48 (d,  $J$  = 9.6 Hz, 1H), 6.34 (d,  $J$  = 9.6 Hz, 1H), 6.08 (d,  $J$  = 1.5 Hz, 1H), 4.35–4.28 (m, 2H), 3.77 (s, 3H), 3.50 (s, 3H), 2.97 (d,  $J$  = 10.9 Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  170.4, 170.1, 134.9, 133.1, 131.0, 129.8, 129.2, 126.0, 124.3, 124.1 (d,  $J_{C-F}$  = 3.7 Hz), 122.2 (dd,  $J_{C-F}$  = 7.3, 3.5 Hz), 70.8, 70.7, 52.3, 52.1, 51.6, 50.6, 21.7, 13.1.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  –62.84. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 3445, 2958, 2919, 2850, 1733, 1646, 1329, 1262, 1121, 1082. HRMS (MALDI) mass calcd for  $C_{19}H_{17}O_6F_3$  ( $[M + Na]^+$ ): 421.0875; found 421.0871.

**Methyl 7-(Trifluoromethyl)phenanthrene-1-carboxylate (7da).** White solid (mp 133 °C),  $R_f$  = 0.8 (petroleum ether/EtOAc = 5:1), yield (8 mg, 17%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.82 (t,  $J$  = 9.1 Hz, 2H), 8.70 (d,  $J$  = 8.7 Hz, 1H), 8.24–8.17 (m, 1H), 8.12 (s, 1H), 7.83 (d,  $J$  = 9.4 Hz, 1H), 7.78 (dd,  $J$  = 8.7, 1.5 Hz, 1H), 7.65 (t,  $J$  = 7.9 Hz, 1H), 3.97 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  168.1, 132.0, 131.3, 130.9, 130.8, 130.2, 128.5, 128.4, 127.4, 125.9, 125.8 (d,  $J_{C-F}$  = 4.2 Hz), 125.3, 123.8, 122.7 (dd,  $J_{C-F}$  = 6.7, 3.3 Hz), 52.4.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  –62.14. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 2955, 2923, 2850, 1715, 1644, 1267, 1151, 1117, 748. MS (EI) mass calcd for  $C_{17}H_{11}O_2F_3$  ( $M^+$ ): 304.0711; found 304.0710.

**(Z)-Dimethyl 2-((Z)-2-(Furan-2-yl)-5-(trifluoromethyl)styryl)-4,5-dihydroxy-4'-(trifluoro-methyl)-2'-vinyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2,3-dicarboxylate (8da).** Brown oil,  $R_f$  = 0.4 (petroleum ether/EtOAc = 3:1), yield (20 mg, 21%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.63 (s, 1H), 7.59 (d,  $J$  = 8.3 Hz, 1H), 7.46 (t,  $J$  = 9.3 Hz, 2H), 7.39 (d,  $J$  = 7.9 Hz, 1H), 7.26 (s, 1H), 6.96 (dd,  $J$  = 17.4, 11.0 Hz, 1H), 6.54 (d,  $J$  = 9.6 Hz, 1H), 6.51 (d,  $J$  = 3.3 Hz, 1H), 6.37 (d,  $J$  = 9.6 Hz, 1H), 6.24 (d,  $J$  = 3.3 Hz, 1H), 6.16 (d,  $J$  = 5.3 Hz, 1H), 5.61 (d,  $J$  = 17.4 Hz, 1H), 5.26 (d,  $J$  = 11.0 Hz, 1H), 4.75 (s, 1H), 4.15 (t,  $J$  = 5.8 Hz, 1H), 3.72 (s, 3H), 3.53 (s, 3H), 3.21 (d,  $J$  = 11.4 Hz, 1H), 2.47 (s, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  172.1, 171.3, 152.1, 152.0, 136.6, 135.8, 135.6, 134.6, 132.1, 131.7, 130.7, 130.5, 129.6, 129.3, 128.1, 127.3, 126.8, 125.4, 125.3, 125.0 (d,  $J_{C-F}$  = 3.7 Hz), 124.4 (d,  $J_{C-F}$  = 3.8 Hz), 124.2 (d,  $J_{C-F}$  = 3.8 Hz), 123.2, 122.7, 117.5, 112.1, 66.2, 53.0, 52.4, 51.9, 50.5, 41.0.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  –62.65, –62.81. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 3489, 2955, 2921, 2850, 1735, 1633, 1435, 1330, 1168, 1124. HRMS (MALDI) mass calcd for  $C_{32}H_{24}O_6F_6Na$  ( $[M+Na-H_2O]^+$ ): 641.1369; found 641.1372.

**Dimethyl 7-Fluoro-2,10a-dihydro-1H-2,4a-epoxyphenanthrene-1,10a-dicarboxylate (3ea).** Yellow oil,  $R_f$  = 0.3 (petroleum ether/EtOAc = 5:1), yield (36 mg, 43%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.46 (dd,  $J$  = 8.3, 5.6 Hz, 1H), 6.93 (td,  $J$  = 8.4, 2.6 Hz, 1H), 6.85 (dd,  $J$  = 9.0, 2.5 Hz, 1H), 6.74 (d,  $J$  = 5.7 Hz, 1H), 6.70 (dd,  $J$  = 5.7, 1.5 Hz, 1H), 6.43 (d,  $J$  = 9.7 Hz, 1H), 6.10 (d,  $J$  = 9.7 Hz, 1H), 4.94 (dd,  $J$  = 4.3, 1.5 Hz, 1H), 3.65 (s, 3H), 3.42 (s, 3H), 3.37 (d,  $J$  = 4.3 Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  171.0, 170.0, 163.6 (d,  $J_{C-F}$  = 249.1 Hz), 137.5, 137.1, 134.8 (d,  $J_{C-F}$  = 8.6 Hz), 130.6, 126.13 (d,  $J_{C-F}$  = 2.2 Hz), 126.07 (d,  $J_{C-F}$  = 3.1 Hz), 114.9 (d,  $J_{C-F}$  = 21.8 Hz), 114.6 (d,  $J_{C-F}$  = 21.3 Hz), 113.9, 100.0, 88.9, 77.9, 59.9, 56.1, 52.2.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  –111.80. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 3455, 2953, 2920, 2847, 1739, 1641, 1612, 1434, 1262, 737. HRMS (MALDI) mass calcd for  $C_{18}H_{15}O_3FNa$  ( $[M + Na]^+$ ): 353.0801; found 353.0802.

**Dimethyl 2-((Z)-5-Fluoro-2-(furan-2-yl)styryl)maleate (4ea).** Yellow oil,  $R_f$  = 0.5 (petroleum ether/EtOAc = 5:1), yield (23 mg, 28%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.65 (dd,  $J$  = 8.7, 5.7 Hz, 1H), 7.41 (d,  $J$  = 1.1 Hz, 1H), 7.00 (td,  $J$  = 8.2, 2.3 Hz, 1H), 6.91 (dd,  $J$  = 9.3, 2.5 Hz, 1H), 6.81 (d,  $J$  = 11.8 Hz, 1H), 6.51 (d,  $J$  = 3.2 Hz, 1H), 6.40 (dd,  $J$  = 3.4, 1.8 Hz, 1H), 6.24 (dd,  $J$  = 11.9, 0.9 Hz, 1H), 5.93 (s, 1H), 3.63 (s, 3H), 3.28 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  166.8, 165.1,

161.0 (d,  $^1J_{C-F}$  = 248.1 Hz), 151.2, 144.4, 142.3, 141.9, 137.3, 133.8 (d,  $J_{C-F}$  = 7.9 Hz), 127.9 (d,  $J_{C-F}$  = 8.2 Hz), 126.7, 126.0 (d,  $J_{C-F}$  = 3.3 Hz), 123.4, 117.6 (d,  $J_{C-F}$  = 22.7 Hz), 115.5 (d,  $J_{C-F}$  = 21.5 Hz), 111.7, 110.1, 52.0.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -114.81. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 2953, 2922, 2849, 1738, 1609, 1502, 1436, 1265, 1201, 738. HRMS (MALDI) mass calcd for  $C_{18}H_{15}O_3FNa$  ( $[M + Na]^+$ ): 353.0801; found 353.0795.

**Dimethyl-7-fluoro-2,3-dihydroxy-1,2,3,10a-tetrahydrophenanthrene-1,10a-(1H)-dicarboxylate (5ea).** White solid (mp 280 °C),  $R_f$  = 0.2 (petroleum ether/EtOAc = 2:1), yield (13 mg, 15%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.36–7.29 (m, 1H), 6.83 (t,  $J$  = 8.4 Hz, 1H), 6.69 (d,  $J$  = 8.7 Hz, 1H), 6.39 (d,  $J$  = 9.6 Hz, 1H), 6.21 (d,  $J$  = 9.6 Hz, 1H), 6.12 (d,  $J$  = 4.0 Hz, 1H), 4.39 (s, 2H), 3.75 (s, 3H), 3.50 (s, 3H), 3.08 (d,  $J$  = 11.3 Hz, 2H), 2.61 (s, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  172.3, 171.1, 163.4 (d,  $^1J_{C-F}$  = 248.7 Hz), 137.4, 133.8, 130.1, 128.7, 126.9, 126.4, 115.1, 114.9 (d,  $J_{C-F}$  = 21.4 Hz), 113.1 (d,  $J_{C-F}$  = 22.5 Hz), 66.8, 65.1, 52.9, 52.3, 48.9.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -112.80. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 3508, 3448, 2954, 2917, 2849, 1733, 1400, 1260, 1089, 735. HRMS (MALDI) mass calcd for  $C_{18}H_{17}O_6FNa$  ( $[M + Na]^+$ ): 371.0901; found 371.0909.

**Dimethyl 7-Fluoro-2,3-dihydroxy-1,2,3,10a-tetrahydrophenanthrene-1,10a-(1H)-dicarboxylate (6ea).** White solid (mp 237 °C),  $R_f$  = 0.3 (petroleum ether/EtOAc = 2:1), yield (21 mg, 21%).  $^1H$  NMR (400 MHz, DMSO)  $\delta$  7.51–7.36 (m, 1H), 7.05 (dd,  $J$  = 12.4, 9.2 Hz, 2H), 6.57 (d,  $J$  = 9.5 Hz, 1H), 6.04 (d,  $J$  = 9.5 Hz, 1H), 5.94 (s, 1H), 5.41 (d,  $J$  = 3.9 Hz, 2H), 4.10 (s, 2H), 3.67 (s, 3H), 3.49 (s, 3H), 2.87 (d,  $J$  = 10.6 Hz, 1H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  171.3, 170.7, 162.1 (d,  $^1J_{C-F}$  = 245.5 Hz), 133.4, 131.7, 130.4, 128.6, 126.7, 126.1, 114.9, 112.8, 78.9, 71.2, 70.3, 54.5, 52.2, 50.8.  $^{19}F$  NMR (376 MHz, DMSO)  $\delta$  -113.67. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 3484, 3453, 2849, 1637, 1457, 1400, 1333, 11165, 740, 696. HRMS (MALDI) mass calcd for  $C_{18}H_{17}O_6FNa$  ( $[M + Na]^+$ ): 371.0901; found 371.0908.

**Methyl 7-Fluorophenanthrene-1-carboxylate (7ea).** Yellow solid (mp 115 °C),  $R_f$  = 0.8 (petroleum ether/EtOAc = 5:1), yield (8 mg, 13%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.74 (dd,  $J$  = 8.7, 4.5 Hz, 2H), 8.59 (dd,  $J$  = 9.0, 5.3 Hz, 1H), 8.12 (d,  $J$  = 7.4 Hz, 1H), 7.72 (d,  $J$  = 9.4 Hz, 1H), 7.60 (t,  $J$  = 7.9 Hz, 1H), 7.46 (dd,  $J$  = 9.1, 1.8 Hz, 1H), 7.38–7.29 (m, 1H), 3.96 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  168.3, 161.6 (d,  $^1J_{C-F}$  = 248.2 Hz), 133.1, 130.7, 130.0, 129.6, 128.4, 127.9, 126.9, 126.6, 125.7, 125.2, 115.9, 112.6, 112.4, 52.4.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -114.32. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 3447, 2987, 2918, 2849, 1715, 1649, 1458, 1265, 739, 705. MS (EI) mass calcd for  $C_{16}H_{11}O_2F$  ( $M^+$ ): 254.0743; found 254.0742.

**(Z)-Dimethyl 4'-Fluoro-2-(5-fluoro-2-(furan-2-yl)styryl)-4,5-dihydroxy-2'-vinyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2,3-dicarboxylate (8ea).** Yellow solid (mp 130 °C),  $R_f$  = 0.4 (petroleum ether/EtOAc = 3:1), yield (52 mg, 39%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.43 (dd,  $J$  = 8.7, 5.8 Hz, 1H), 7.33 (dd,  $J$  = 8.5, 5.5 Hz, 1H), 7.12 (d,  $J$  = 10.0, 2.6 Hz, 1H), 6.98–6.87 (m, 2H), 6.82 (td,  $J$  = 8.5, 2.6 Hz, 1H), 6.71 (dd,  $J$  = 8.9, 2.6 Hz, 1H), 6.44 (d,  $J$  = 9.6 Hz, 1H), 6.32 (d,  $J$  = 3.3 Hz, 1H), 6.28 (d,  $J$  = 9.6 Hz, 1H), 6.19 (d,  $J$  = 3.2 Hz, 1H), 6.00 (d,  $J$  = 5.3 Hz, 1H), 5.56 (d,  $J$  = 17.4 Hz, 1H), 5.20 (d,  $J$  = 11.5 Hz, 1H), 4.78–4.68 (m, 1H), 4.10 (t,  $J$  = 5.8 Hz, 1H), 3.71 (s, 3H), 3.52 (s, 3H), 3.18 (d,  $J$  = 11.4 Hz, 1H), 2.36 (d,  $J$  = 6.2 Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  172.2, 171.6, 163.0 (d,  $^1J_{C-F}$  = 248.0 Hz), 162.3 (d,  $J_{C-F}$  = 248.3 Hz), 161.8, 161.1, 152.5, 151.4, 137.7, 137.5, 134.6, 133.5, 130.5, 129.4, 127.0, 126.6, 125.9, 125.4, 118.3, 116.8, 114.9, 113.3, 111.8, 110.2, 66.3, 52.9, 52.3, 52.0, 50.7, 40.9.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -113.62, -114.09. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 3520, 2954, 2849, 1737, 1607, 1575, 1486, 1437, 1262, 737. HRMS (MALDI) mass calcd for  $C_{30}H_{24}O_6F_2Na$  ( $[M+Na-H_2O]^+$ ): 541.1433; found 541.1435.

**Dimethyl 4'-Fluoro-4-hydroxy-2'-vinyl-[1,1'-biphenyl]-2,3-dicarboxylate (9ea).** Yellow oil,  $R_f$  = 0.6 (petroleum ether/EtOAc = 5:1), yield (23 mg, 28%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  10.94 (s, 1H), 7.22 (dd,  $J$  = 10.2, 2.6 Hz, 1H), 7.18 (d,  $J$  = 8.4 Hz, 1H), 7.05 (dd,  $J$  = 8.5, 5.9 Hz, 1H), 7.01 (d,  $J$  = 8.6 Hz, 1H), 6.87 (td,  $J$  = 8.3, 2.6 Hz, 1H), 6.32 (ddd,  $J$  = 17.5, 11.0, 1.6 Hz, 1H), 5.57 (d,  $J$  = 17.4 Hz, 1H), 5.12 (d,  $J$  = 11.0 Hz, 1H), 3.84 (s, 3H), 3.45 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  169.3, 168.3, 162.5 (d,  $^1J_{C-F}$  = 282.1 Hz), 161.1, 139.0, 137.6, 135.4, 134.2, 133.0, 132.1, 129.2, 118.7, 116.1, 114.1,

111.5, 109.0, 53.0, 52.0.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -113.96. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 3088, 2954, 2851, 1739, 1679, 1461, 1443, 1247, 1213, 728. HRMS (MALDI) mass calcd for  $C_{18}H_{15}O_3FNa$  ( $[M + Na]^+$ ): 353.0801; found 353.0803.

**Dimethyl 9-Methyl-1,2-dihydro-10aH-2,4a-epoxyphenanthrene-1,10a-dicarboxylate (3fa).** Yellow oil,  $R_f$  = 0.3 (petroleum ether/EtOAc = 5:1), yield (28 mg, 26%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.60 (d,  $J$  = 7.4 Hz, 1H), 7.43 (s, 1H), 7.39–7.34 (m, 1H), 6.88 (d,  $J$  = 5.6 Hz, 1H), 6.78 (d,  $J$  = 5.7 Hz, 1H), 5.96 (s, 1H), 5.04 (d,  $J$  = 4.1 Hz, 1H), 3.75 (s, 1H), 3.49 (s, 1H), 3.48 (s, 1H), 2.17 (s, 1H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  171.3, 170.6, 137.7, 137.1, 134.1, 131.3, 130.3, 129.7, 128.7, 128.2, 126.2, 124.5, 89.4, 78.2, 59.9, 56.9, 52.1, 52.0, 19.8. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 2952, 2313, 1736, 1603, 1441, 1349, 1239, 1166, 928, 758. HRMS (ESI) mass calcd for  $C_{19}H_{18}O_5Na$  ( $[M + Na]^+$ ): 349.1046; found 349.1055.

**Dimethyl 2-(Z)-2-(2-(Furan-2-yl)phenyl)prop-1-en-1-yl)maleate (4fa).** Yellow oil,  $R_f$  = 0.5 (petroleum ether/EtOAc = 5:1), yield (27 mg, 39%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.68 (d,  $J$  = 7.8 Hz, 1H), 7.39 (s, 1H), 7.27 (t,  $J$  = 7.6 Hz, 1H), 7.18 (d,  $J$  = 8.4 Hz, 1H), 6.99 (s, 1H), 6.59 (d,  $J$  = 2.7 Hz, 1H), 6.37 (d,  $J$  = 1.6 Hz, 1H), 6.11 (s, 1H), 5.71 (s, 1H), 3.57 (s, 1H), 3.07 (s, 1H), 1.97 (s, 1H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  167.0, 165.5, 151.9, 149.8, 146.1, 142.1, 136.0, 129.9, 128.8, 128.1, 127.0, 126.3, 124.0, 120.0, 111.8, 108.8, 100.0, 51.7, 27.3. IR (thin film)  $\nu_{max}$  ( $cm^{-1}$ ) 3121, 2950, 2854, 1728, 1599, 1436, 1382, 1270, 1205, 1160, 812, 666. HRMS (ESI) mass calcd for  $C_{19}H_{18}O_5Na$  ( $[M + Na]^+$ ): 349.1046; found 349.1056.

**Computational Details.** Calculations were performed with the Gaussian 09 program.<sup>24</sup> The hybrid B3LYP functional<sup>25</sup> with the 6-31+G(d) basis set<sup>26</sup> was applied for the optimization of all stationary points in gas phase. Optimizations at different theoretical levels were completed to verify the influence of different methods (see SI), which came to the same conclusion. Singlet diradical points were located with UB3LYP/6-31+G(d).<sup>27</sup> The wave functions of all stationary points have been computationally tested as stable ones. Spin contamination for all singlet diradical stationary points was calculated using the Yamaguchi–Houk spin projection method.<sup>28</sup> Frequency calculations were performed to confirm that each stationary point was either a minimum or a transition structure. IRC calculations<sup>29</sup> were used to confirm the connection between the reactant, product, and transition state. The reported relative energies are Gibbs free energies (G) in gas phase. Solvent effects in toluene were computed by the CPCM model<sup>30</sup> using the gas-phase optimized structures (using keyword: RADII = UAHF). The computed enthalpy changes and relative free energies in solution, referred to as  $\Delta H_{sol}$  and  $\Delta G_{sol}$ , were calculated by adding the solvation energy changes to the computed gas-phase enthalpy changes and relative free energies, respectively. The spin density distribution of all the diradical stationary points is provided in the SI. Computed structures are illustrated using CYLView.<sup>31</sup>

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs-joc.6b00792.

Copies of NMR spectral data for all of the prepared compounds, the crystallographic data of 3aa and 6aa, and computational details (PDF)

X-ray data for compound 3aa (CIF)

X-ray data for compound 6aa (CIF)

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## Notes

The authors declare no competing financial interest.

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