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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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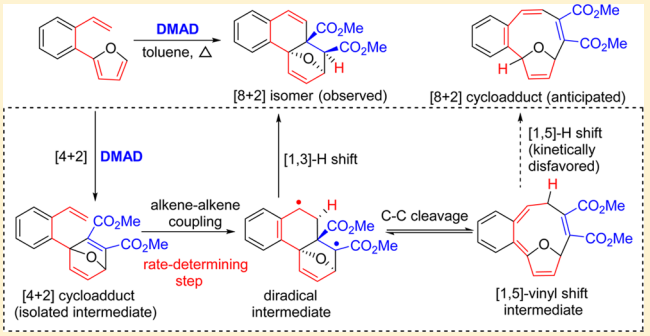
Supporting Information

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, expoxyphenanthrene, 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 expoxyphenanthrene. 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.

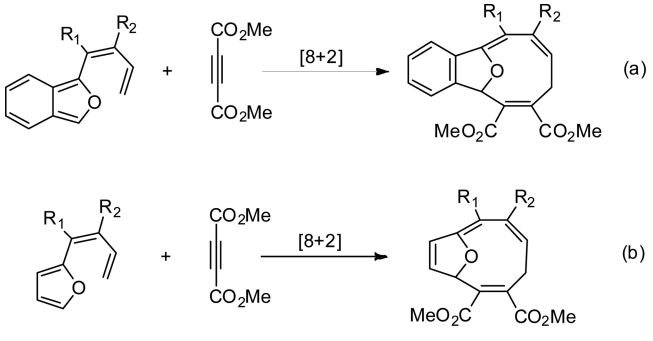


1. INTRODUCTION

The [8 + 2]-cycloaddition reaction can provide a straightforward approach for the synthesis of 10-membered ring compounds.[1] However, before 2003, all reported [8 + 2] reactions were limited to using geometrically constrained tetraenes as the 8π components (such as heptafulvenes,[1b] tropones,[2] and indolizines[3]), 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 (dienyliso-benzofurans) and tetraenophile [dimethyl acetylenedicarboxylate (DMAD)], as shown in Scheme 1a, which provided an incredibly simple entry into furan-bridged 10-membered rings.[4] 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).[5] These [8 + 2] cycloadditions provide a potentially powerful method to synthesize the skeleton of a variety of biologically active coral-derived natural products.[6]

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[4,5]



reactions.[7] 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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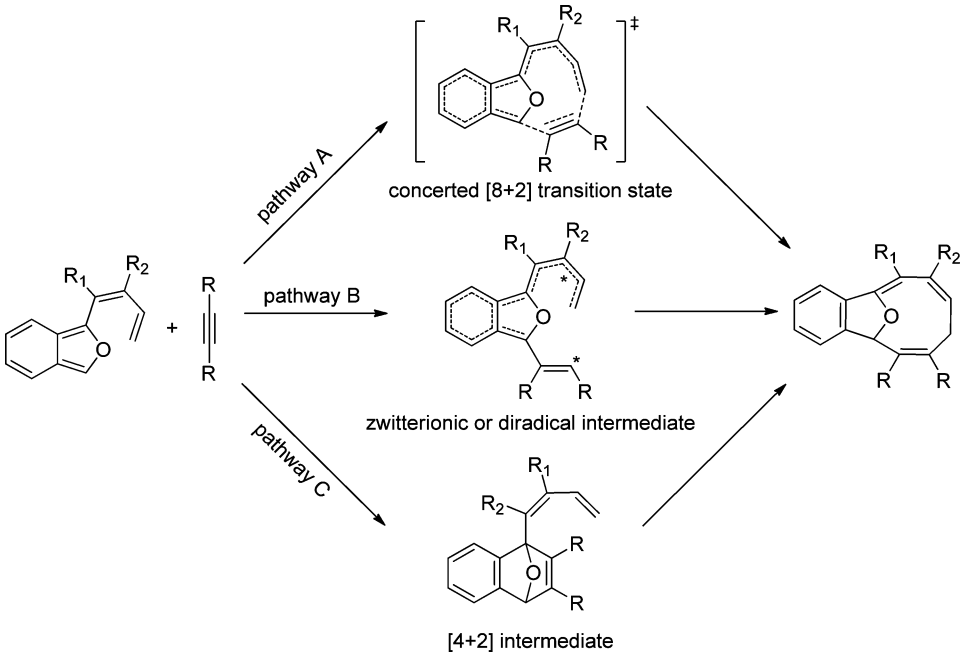
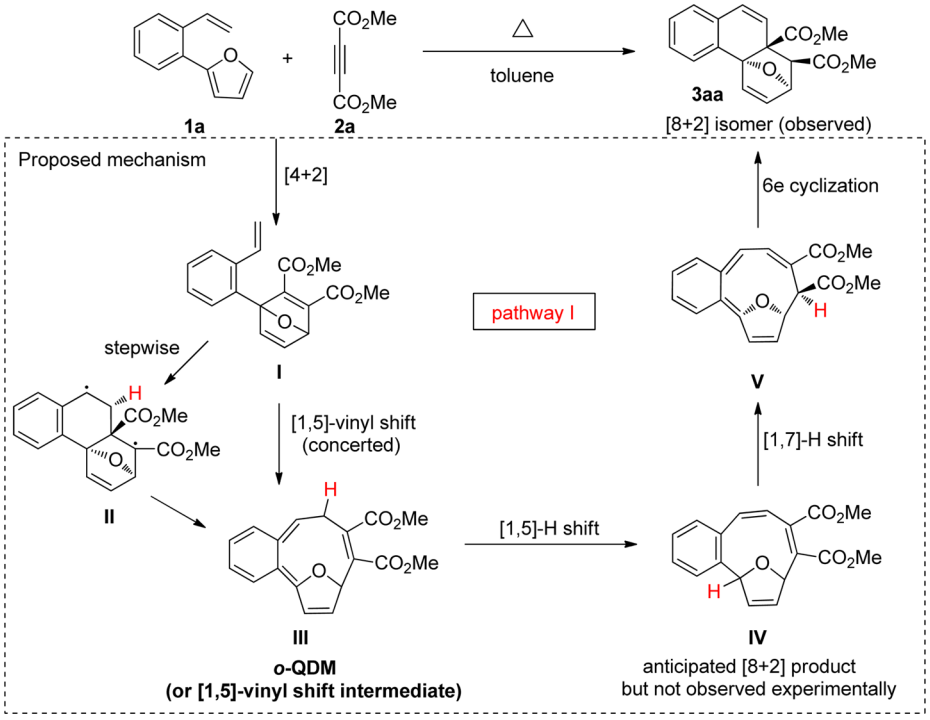
Scheme 2. Three Pathways for Dienylisobenzofuran-alkyne [8 + 2] Cycloaddition Proposed by Yu and Co-workers[8]



Scheme 3. Design and Experimental Finding of the [8 + 2] Reaction between Enylfuran and DMAD



1a.[8] 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.[9]

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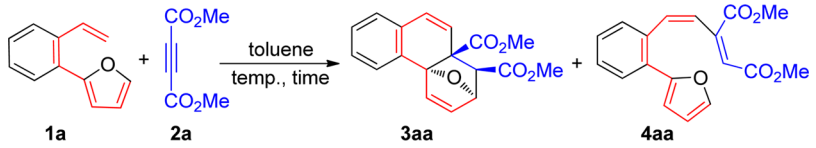
Table 1. Optimization of Reaction Conditions[a]

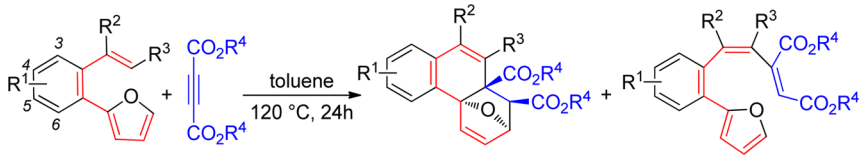


1a 2a 3aa 4aa

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

[a]Unless otherwise noted, the reaction was carried out using sealed tubes in toluene under N_2. [b]The oil bath temperature. [c]Isolated yield. [d]Yield determined by ^{1}H NMR spectroscopy.

Table 2. Substrate Scope of the Reaction of Vinylphenylfuran and Alkyne in Toluene[a]



1 2 3 4

entry	1	2	yield (%)[b] total	3	4
1	**1a** (R^1, R^2, R^3 = H)	**2a** (R^4 = Me)	86	45 (**3aa**)	41 (**4aa**)
2	**1a** (R^1, R^2, R^3 = H)	**2b** (R^4 = Et)	86	45 (**3ab**)	41 (**4ab**)
3	**1b** (R^1 = 5-Me; R^2, R^3 = H)	**2a** (R^4 = Me)	87	52 (**3ba**)	35 (**4ba**)
4	**1c** (R^1 = 4-OMe; R^2, R^3 = H)	**2a** (R^4 = Me)	88	52 (**3ca**)	36 (**4ca**)
5	**1d** (R^1 = 4-CF_3; R^2, R^3 = H)	**2a** (R^4 = Me)	63	33 (**3da**)	30 (**4da**)
6	**1e** (R^1 = 4-F; R^2, R^3 = H)	**2a** (R^4 = Me)	71	43 (**3ea**)	28 (**4ea**)
7	**1f** (R^1, R^3 = H; R^2 = Me)	**2a** (R^4 = Me)	65	26 (**3fa**)	39 (**4fa**)
8	**1g** (R^1, R^3 = H; R^2 = CO_2Me)	**2a** (R^4 = Me)			
9	**1h** (R^1, R^2 = H; R^3 = Me)	**2a** (R^4 = Me)			

[a]The reaction was carried out using sealed tubes in toluene under N_2 for 24 h. The molar ratio of **1**/**2** = 1:1.5. The oil bath temperature was set at 120 °C. [b]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.[10] As part of our continuing efforts to develop *o*-QDM chemistry,[11] 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**.[12] Following the conditions reported in previous work,[4,8] 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 ^{1}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

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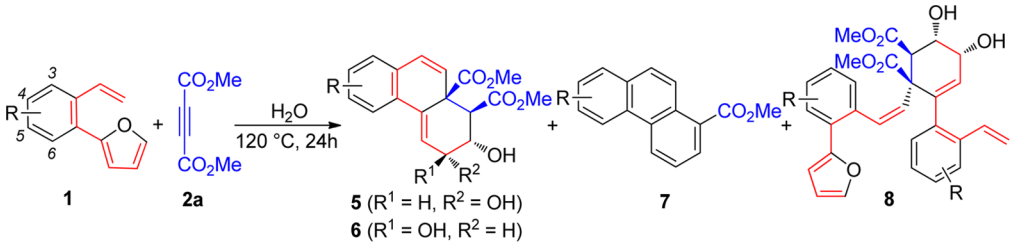
Table 3. Reaction of Vinylphenylfuran and Alkyne in Water[a]



entry	1	5	6	7	8	yield[b]
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_3)	**5da** (29%)	**6da** (8%)	**7da** (8%)	**8da** (−)	45%
4	**1e** (R = 4-F)	**5ea** (15%)	**6ea** (21%)	**7ea** (13%)	**8ea** (13%)	62%

[a]The reaction was carried out using sealed tubes in water for 24 h under N_2. The molar ratio of **1**/**2** = 1:1. The oil bath temperature was set at 120 °C. [b]Yield of isolated product.

Scheme 4. Control Reaction

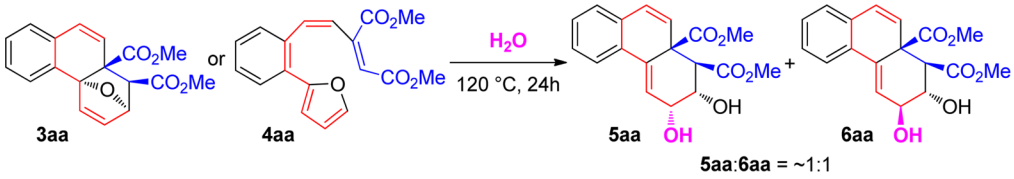
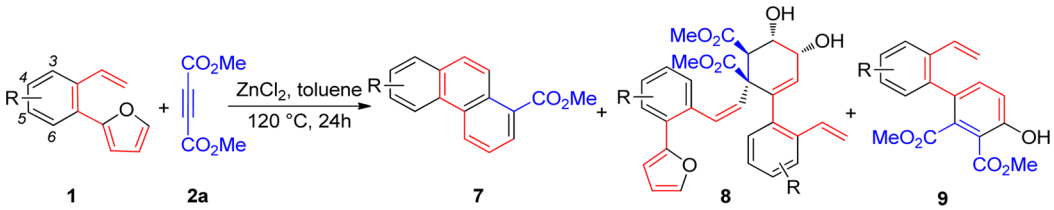


Table 4. Reaction of Vinylphenylfuran and Alkyne in Toluene with the Zinc Catalyst[a]



entry	1	7	8	9	yield[b]
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_3)	**7da** (17%)	**8da** (21%)	**9da** (--)	38%
5	**1e** (R = 4-F)	**7ea** (6%)	**8ea** (39%)	**9ea** (28%)	73%

[a]The reaction was carried out using sealed tubes in toluene for 24 h using 5 mol % $ZnCl_2$ under N_2. The molar ratio of **1**/**2** = 1:1. The oil bath temperature was set at 120 °C. [b]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 $CHCO_2Me$ 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.[13]

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 $-CF_3$) (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 dienylisobenzofurans with dienophiles reported previously by Yu and Herndon.[4,5,8] Substituents in the alkene moiety of **1** was explored as well, and a methyl group at R^2 could be tolerated, affording the desired products **3fa** and **4fa** in yields of 26% and 39%, respectively. However, an electron-withdrawing group ($-CO_2Me$) at R^2 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).[14] Product **7** was generated possibly from a decarboxylative

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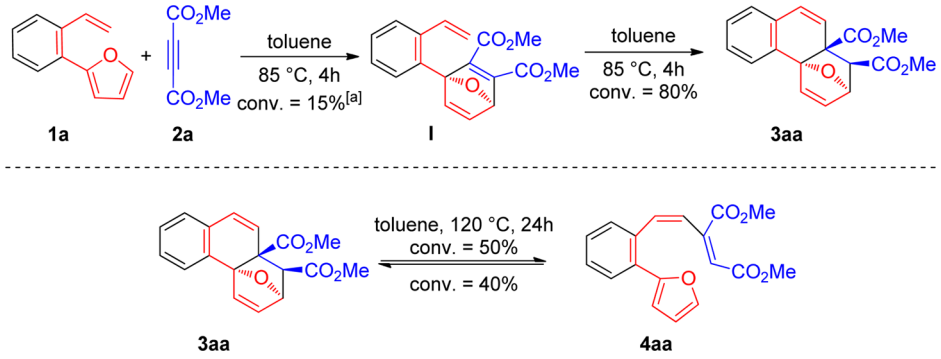
Scheme 5. Interconversion of Products in Toluene[a]



[a]The yield of **I**/**3aa**/**4aa** = 6%:8%:2%. The molar ratio was determined by ^{1}H NMR spectroscopy.

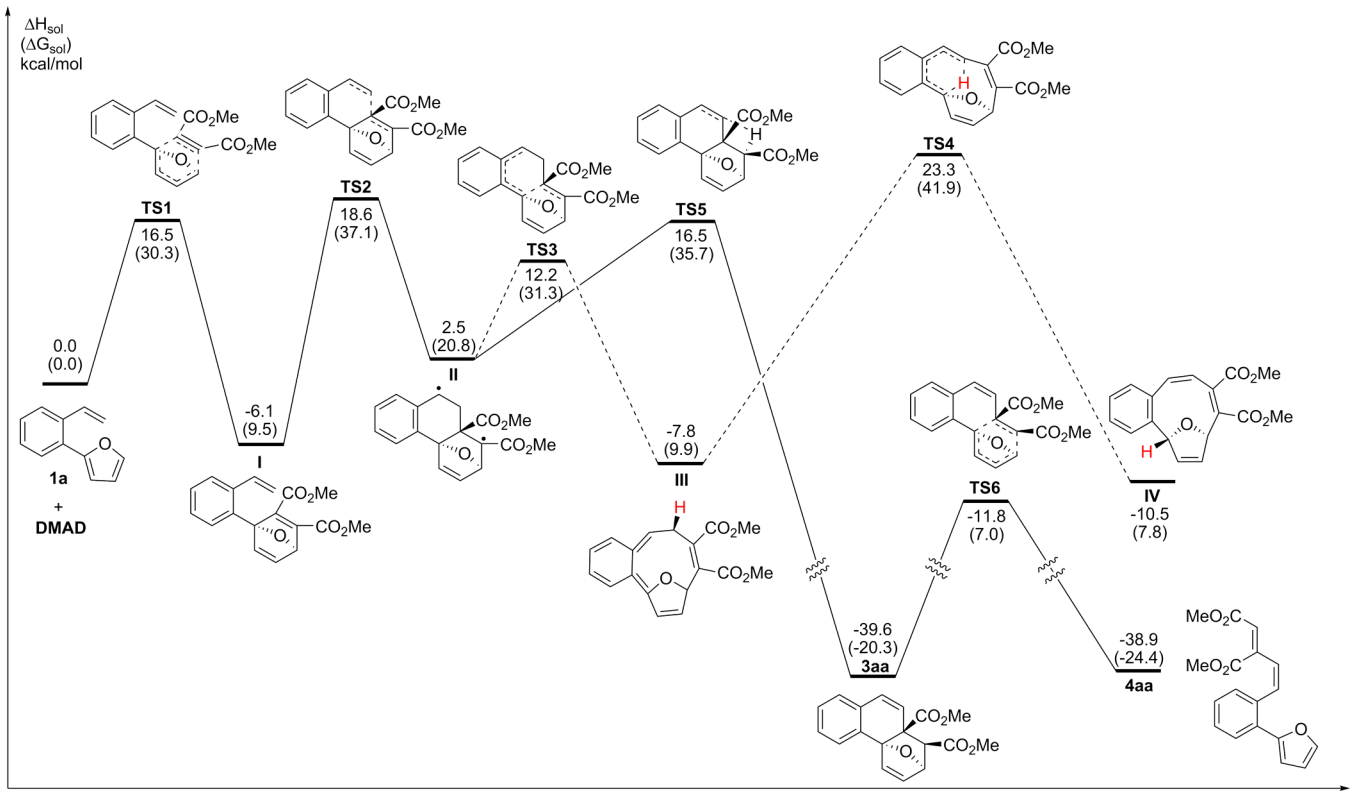


Figure 1. Computed potential energy surfaces for pathways I and II at the (U)B3LYP/6-31+G(d) level in toluene.

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 $ZnCl_2$ or $FeCl_3$, was used as catalyst for this transformation in toluene, a different distribution of products was observed. Taking the $ZnCl_2$-catalyzed system as an example, in additional 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.[8,15] It was

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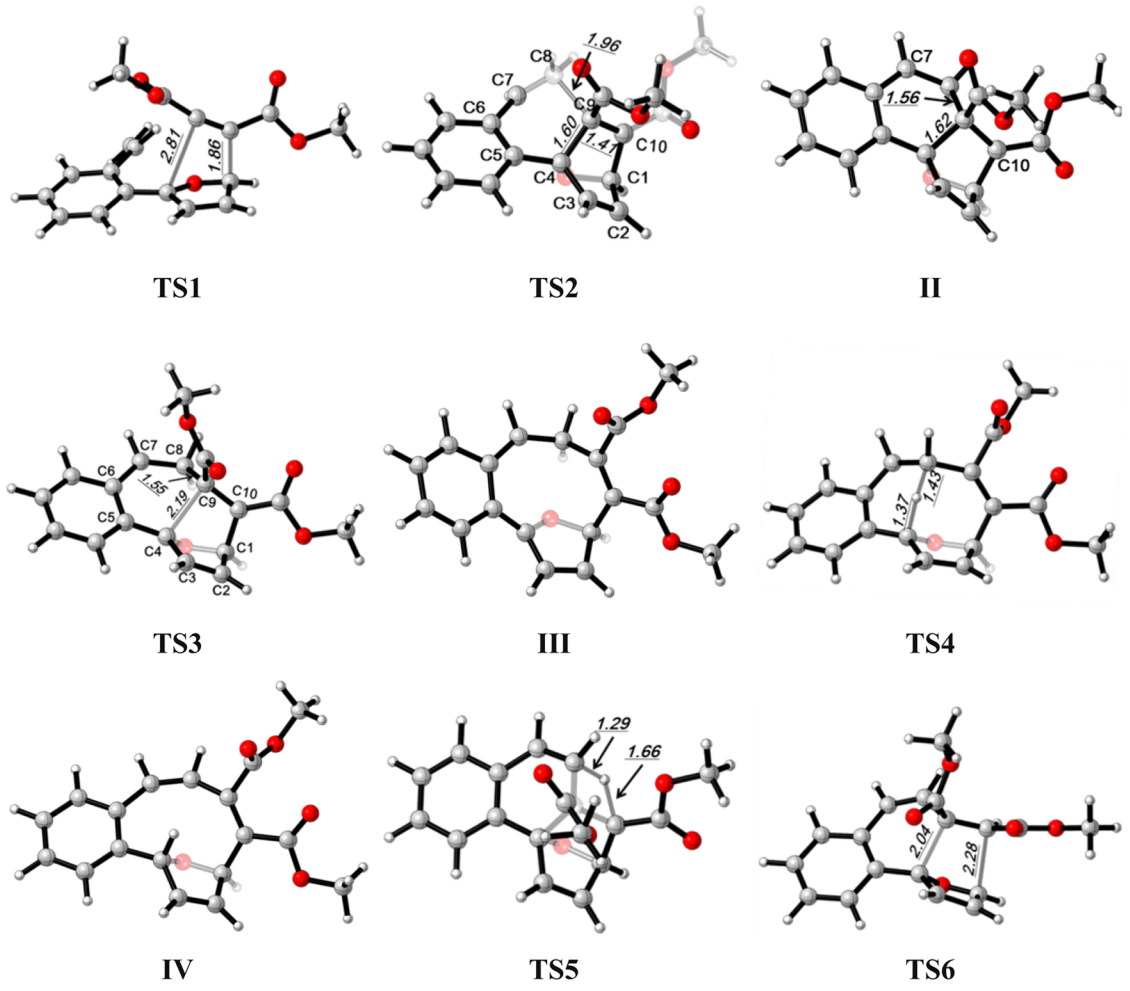

Figure 2. Optimized geometries of key transition states and intermediates. Bond distances are in Å.

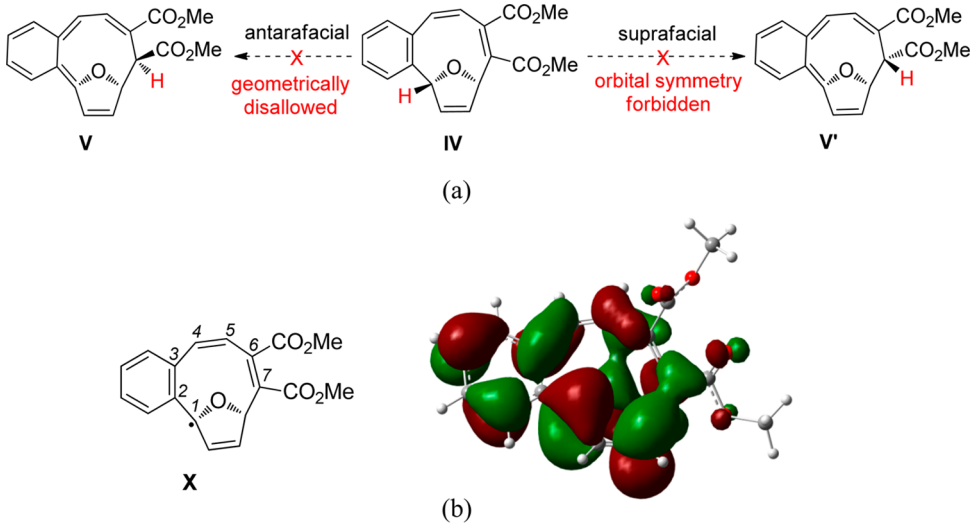

Figure 3. (a) Antarafacial or suprafacial [1,7]-H shift from **IV** to **V** (or **V**′). (b) The SOMO of **X**.

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).[16]

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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.

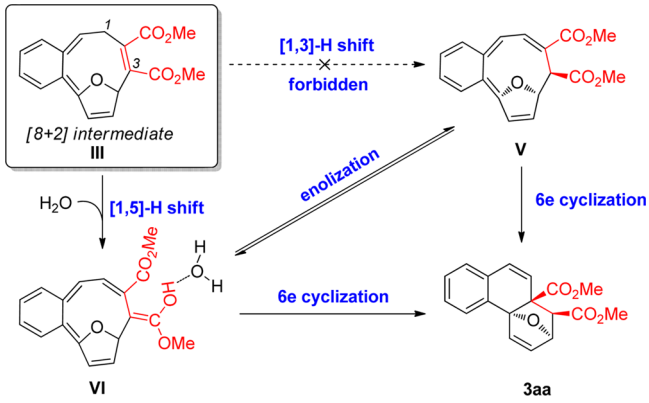
The followed [1,5]-H shift converting *o*-QDM **III** to **IV** via **TS4** in pathway I is not easy with an activation enthalpy of 31.1 kcal/mol. The distances of the forming and breaking C−H bonds in **TS4** are 1.37 and 1.43 Å, respectively. This step is an exothermic process since **IV** is more 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),[17] followed by 6e-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.[18] A suprafacial [1,7]-H shift is also forbidden here, according to the Woodward−Hoffmann rules.[19] 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).[20] 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.[21] 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 6π-electrocyclization (from **VI**) or enolization/6π-electrocyclization (from **V**). However, this water-assisted pathway was not

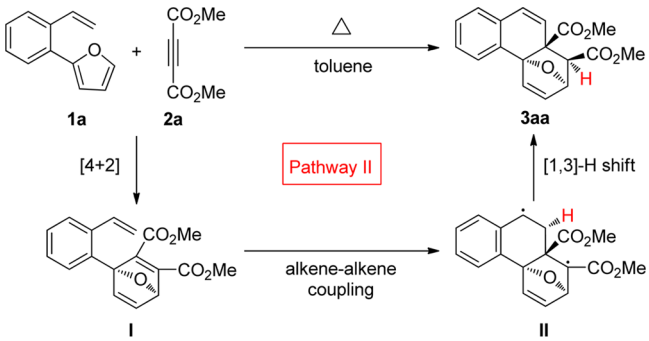
Scheme 6. Proposed Water-Assisted Pathway for the Generation of 3aa



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_2O.

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,[22] 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

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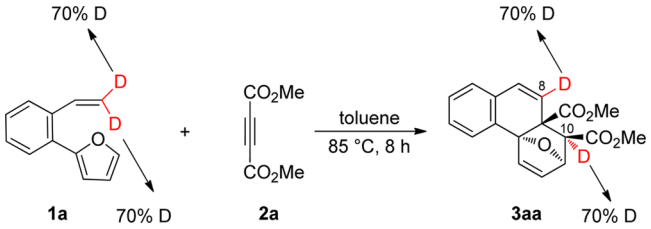
kcal/mol. This is consistent with the experimental reaction conditions (refluxing in toluene at 120 °C for 24 h).

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) 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.

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



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 expoxyphenanthrene 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 expoxyphenanthrene **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. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on 400, 100, and 376 MHz NMR spectrometers, respectively. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0, and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard. Chemical shifts (δ) 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_3PPh_3Br (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 $Pd(PPh_3)_4$ (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_2CO_3 (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 $MgSO_4$, 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 $MgSO_4$, 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 $ZnCl_2$/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 $ZnCl_2$ 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_f = 0.9 (petroleum ether), yield (307 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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). ^{13}C

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NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 1767, 1688, 1627, 1402, 1216, 1194, 1091, 1091, 1009, 763. HRMS (EI) mass calcd for $C_{12}H_{10}O$ ($[M]^+$): 170.0732; found 170.0728.

*2-(5-Methyl-2-vinylphenyl)furan (**1b**).* Colorless oil, R_f = 0.9 (petroleum ether), yield (400 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2921, 1769, 1687, 1608, 1495, 1401, 1040, 977, 823, 652. HRMS (EI) mass calcd for $C_{13}H_{12}O$ ($[M]^+$): 184.0888; found 184.0887.

*2-(4-Methoxy-2-vinylphenyl)furan (**1c**).* Colorless oil, R_f = 0.9 (petroleum ether), yield (494 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2961, 2911, 2836, 1676, 1602, 1563, 1485, 1463, 1419, 1233. HRMS (EI) mass calcd for $C_{13}H_{12}O_2$ ($[M]^+$): 200.0837; found 200.0838.

*2-(4-(Trifluoromethyl)-2-vinylphenyl)furan (**1d**).* Colorless oil, R_f = 0.9 (petroleum ether), yield (170 mg, 34%). ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 151.3, 143.0, 135.9, 135.6, 132.1, 129.5 (q, J_{C-F} = 32.4 Hz), 127.4, 124.3 (dd, J_{C-F} = 9.7, 3.8 Hz), 124.2(d, J_{C-F} = 273.1 Hz), 117.3, 111.7, 111.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.60. IR (thin film) ν_{max} (cm^{-1}) 2960, 2919, 2849, 1401, 1330, 1270, 1167, 1040, 1012, 975. HRMS (EI) mass calcd for $C_{13}H_9F_3O$ ($[M]^+$): 238.0605; found 238.0604.

*2-(4-Fluoro-2-vinylphenyl)furan (**1e**).* Colorless oil, R_f = 0.9 (petroleum ether), yield (412 mg, 63%). ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 162.3(d, J_{C-F} = 247.2 Hz), 151.9, 142.2, 137.8(d, J_{C-F} = 7.8 Hz), 135.4, 129.6(d, J_{C-F} = 8.4 Hz), 125.7(d, J_{C-F} = 3.1 Hz), 116.7, 114.8(d, J_{C-F} = 21.9 Hz), 113.3(d, J_{C-F} = 22.2 Hz), 111.4, 109.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.18. IR (thin film) ν_{max} (cm^{-1}) 2967, 2923, 2852, 1400, 1331, 1278, 1161, 1043, 1021, 964. HRMS (EI) mass calcd for $C_{12}H_9FO$ ($[M]^+$): 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%). ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (101 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 3060, 3020, 2924, 2860, 1724, 1487, 1441, 1013, 895, 729, 675. HRMS (EI) mass calcd for $C_{13}H_{12}O$ ($[M]^+$): 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%). ^1H NMR(400 MHz, $CDCl_3$) δ 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}C NMR (101 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 3122, 3066, 2926, 2846, 2188, 1638, 1599, 1506, 1290, 1255, 1016, 832, 752, 542. HRMS (ESI) mass calcd for $C_{14}H_{12}O_3Na$ ($[M + Na]^+$): 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). ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (101 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 3200, 3060, 3020, 2923, 2860, 1487, 1441, 1277, 1014, 968, 756, 730, 594. HRMS (EI) mass calcd for $C_{13}H_{12}O$ ($[M]^+$): 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%). ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2951, 2925, 2851, 1721, 1637, 1435, 1269, 1168, 763. HRMS (ESI) mass calcd for $C_{18}H_{16}O_5Na$ ($[M + Na]^+$): 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%). ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 3001, 2952, 2845, 1739, 1644, 1435, 1245, 1169, 1097. HRMS (MALDI) mass calcd for $C_{18}H_{16}O_5Na$ ($[M + Na]^+$): 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%). ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2953, 2921, 2850, 1734, 1649, 1437, 1265, 1204, 736. HRMS (MALDI) mass calcd for $C_{18}H_{16}O_5Na$ ($[M + Na]^+$): 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%). ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2953, 2922, 2852, 1734, 1436, 1264, 1229, 1086, 737. HRMS (MALDI) mass calcd for $C_{18}H_{18}O_6Na$ ($[M + Na]^+$): 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%). ^1H NMR (400 MHz, DMSO) δ 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}C NMR (100 MHz, DMSO) δ 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) ν_{max} (cm^{-1}) 2952, 2844, 1730, 1650, 1433, 1265, 1169, 1121, 740. HRMS (MALDI) mass calcd for $C_{18}H_{18}O_6Na$ ($[M + Na]^+$): 353.0996; found 353.1002.

*Methyl Phenanthrene-1-carboxylate (**7aa**).*[23] Yellow solid (mp 95 °C), R_f = 0.8 (petroleum ether: EtOAc = 5:1), yield (10 mg, 14%). ^1H NMR (400 MHz, $CDCl_3$) δ 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),

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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}C NMR (100 MHz, $CDCl_3$) δ 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}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2952, 2850, 1734, 1436, 1256, 1229, 1204, 763, 737. HRMS (MALDI) mass calcd for $C_{30}H_{26}O_6Na$ ([M+Na−H_2O]$^+$): 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}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2952, 2919, 2850, 1738, 1678, 1462, 1442, 1246, 1215. HRMS (MALDI) mass calcd for $C_{18}H_{16}O_5Na$ ([M + 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}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2982, 2820, 2851, 1730, 1649, 1257, 1197, 1091, 741. HRMS (MALDI) mass calcd for $C_{20}H_{20}O_5Na$ ([M + 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}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2982, 2934, 1787, 1730, 1650, 1465, 1394, 1261, 1191. HRMS (MALDI) mass calcd for $C_{20}H_{21}O_5$ ([M + 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}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 171.3, 170.5, 138.5, 137.4, 137.3, 130.4, 129.9, 129.8, 129.4, 127.8, 127.7, 126.8, 89.6, 77.9, 59.9, 56.4, 52.2, 52.0, 21.4. IR (thin film) ν_{max} (cm^{-1}) 2952, 2921, 2851, 1738, 1436, 1355, 1245, 1169, 735. HRMS (MALDI) mass calcd for $C_{19}H_{18}O_5Na$ ([M + 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}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2953, 2921, 2850, 1735, 1647, 1436, 1264, 1202, 1169, 736. HRMS (MALDI) mass calcd for $C_{19}H_{19}O_5$ ([M + 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}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2953, 2918, 2850, 1733, 1639, 1436, 1232, 1086, 736. HRMS (MALDI) mass calcd for $C_{19}H_{20}O_6Na$ ([M + 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}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2953, 2920, 2851, 1734, 1650, 1436, 1262, 1069, 736. HRMS (MALDI) mass calcd for $C_{19}H_{20}O_6Na$ ([M + 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}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2949, 2917, 2849, 1712, 1631, 1254, 1121, 749. HRMS (EI) mass calcd for $C_{17}H_{14}O_2$ (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}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (101 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2952, 2921, 2851, 1732, 1633, 1455, 1321, 908, 735. HRMS (MALDI) mass calcd for $C_{32}H_{30}O_6Na$ ([M+Na−H_2O]$^+$): 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}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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) ν_{max} (cm^{-1}) 2952, 2918, 2849, 1739, 1677, 1442, 1333, 1245, 1214. HRMS

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(MALDI) mass calcd for $C_{19}H_{18}O_5Na$ ([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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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) ν_{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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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) ν_{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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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) ν_{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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ −62.98. IR (thin film) ν_{max} (cm^{-1}) 2956, 2918, 2848, 1740, 1643, 1434, 1247, 1168, 1126. HRMS (MALDI) mass calcd for $C_{19}H_{15}O_5F_3Na$ ([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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ −62.58. IR (thin film) ν_{max} (cm^{-1}) 2956, 2850, 1736, 1650, 1436, 1330, 1169, 1127, 737. HRMS (MALDI) mass calcd for $C_{19}H_{15}O_5F_3Na$ ([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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ −62.87. IR (thin film) ν_{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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ −62.84. IR (thin film) ν_{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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ −62.14. IR (thin film) ν_{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-(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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ −62.65, −62.81. IR (thin film) ν_{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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 171.0, 170.0, 163.6 (d, $^1J_{C-F}$ = 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, $CDCl_3$) δ −111.80. IR (thin film) ν_{max} (cm^{-1}) 3455, 2953, 2920, 2847, 1739, 1641, 1612, 1434, 1262, 737. HRMS (MALDI) mass calcd for $C_{18}H_{15}O_5FNa$ ([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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 166.8, 165.1,

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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, $CDCl_3$) δ −114.81. IR (thin film) ν_{max} (cm^{-1}) 2953, 2922, 2849, 1738, 1609, 1502, 1436, 1265, 1201, 738. HRMS (MALDI) mass calcd for $C_{18}H_{15}O_5FNa$ ([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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ −112.80. IR (thin film) ν_{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%). ^{1}H NMR (400 MHz, DMSO) δ 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) δ 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) δ −113.67. IR (thin film) ν_{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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ −114.32. IR (thin film) ν_{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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.7, 5.8 Hz, 1H), 7.33 (dd, J = 8.5, 5.5 Hz, 1H), 7.12 (dd, 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, $CDCl_3$) δ 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, $CDCl_3$) δ −113.62, −114.09. IR (thin film) ν_{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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ −113.96. IR (thin film) ν_{max} (cm^{-1}) 3088, 2954, 2851, 1739, 1679, 1461, 1443, 1247, 1213, 728. HRMS (MALDI) mass calcd for $C_{18}H_{15}O_5FNa$ ([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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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) ν_{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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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) ν_{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.[24] The hybrid B3LYP functional[25] with the 6-31+G(d) basis set[26] 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).[27] 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.[28] Frequency calculations were performed to confirm that each stationary point was either a minimum or a transition structure. IRC calculations[29] 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[30] using the gas-phase optimized structures (using keyword: RADII = UAHF). The computed enthalpy changes and relative free energies in solution, referred to as ΔH_{sol} and ΔG_{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.[31]

■ ASSOCIATED CONTENT

Supporting Information

The . 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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