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Exploring the Acid-Catalyzed Reactions of 10,11-Epoxy-Dibenzo[*a*,*d*]cycloheptan-5-ol as the Synthetic Modules toward Polycyclic Aromatic Scaffolds

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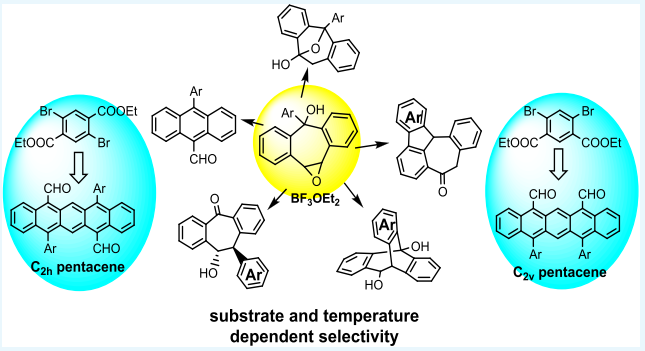
ABSTRACT: The structural diversity of polycyclic aromatic hydrocarbons (PAHs) offers exciting opportunities for their applications. Yet, selective synthesis of such conjugated networks poses a formidable challenge. Compared to the prominence of transition-metal-catalyzed cross-coupling and oxidative Scholl reactions, cationic rearrangement in the synthesis of polycyclic aromatic hydrocarbon is an underexplored subject. In this study, we reveal that cationic intermediate generated from epoxy dibenzocycloheptanol can be transformed into acenes, azulene-embedded PAHs, and dibenzocycloheptanone derivatives. Reactive patterns, including Meinwald rearrangement, Nazarov cyclization, transannular aryl migration, and transannular Friedel−Crafts cyclization were identified. Both substrate structures and reaction temperature affect the reaction pathways in predictable and manageable manners. A mechanistic scheme was postulated as the working model to guide the reactivity for further application. Substrates containing heterocyclic and ferrocenyl groups exhibit similar reactivity profiles. The inquiry culminates in the selective synthesis of 5, 7, 12, 14-tetrasubstituted C_{2h} and C_{2v} pentacene derivatives. Our results demonstrate that polycyclic aromatic hydrocarbons can be selectively prepared with this cation-initiated strategy by methodically tuning the reactivity.



INTRODUCTION

In the last three decades, the discoveries of fullerenes, carbon nanotubes, and graphene ignited a rapid growth in the research of polycyclic aromatic hydrocarbons (PAH).[1] The vast structural and property diversity of the PAH derivatives is a boundless reservoir of functions to solve real-life problems. It is long recognized that selective construction of designated PAH structures is only feasible through bottom-up stepwise synthesis. To form the C−C bonds within PAH skeletons, Diels−Alder reaction,[2] metal-catalyzed coupling,[3] and benzannulation[4] all play indispensable roles. Since Mullen's synthesis of hexabenzocoronene,[5] intramolecular Scholl cyclization via radical cation intermediates has become the most prominent protocol to connect multiple C−C bonds in the PAH structures.[6] Recently, several reports demonstrated that Scholl cyclization can also lead to PAH products with skeletal rearrangements.[7] Inspired by these discoveries, we perceive cationic rearrangement reactions present an alternative approach toward various PAH skeletons. Yet, due to the capricious reactivity of cationic intermediates, synthetic selectivity and efficiency with rearrangement strategy must be managed via deeper mechanistic insights. This requires a systematic analysis of substrate structures, reaction products, and reaction conditions. In this manuscript, we reveal that the titled rearrangement reaction can be guided through substrate and temperature control to furnish several different classes of products, including acene derivatives, azulene-embedded PAHs, and substituted dibenzocycloheptanone.

We recently discovered an oxidative ring contraction reaction of mesityl dibenzocycloheptenol to produce 9,10-disubstituted anthracene.[8] As shown in Scheme 1, the [6,7,6]-fused skeleton was converted into anthracene in acidic medium. Mechanistically, this reaction is peculiar because the presumed cation intermediate should be aromatic and fairly stable. However, as indicated by its facile rearrangement, this structure is readily oxidized by oxygen. Although a definitive mechanism cannot yet be verified, an epoxy dibenzocycloheptenol (EDCH-mesityl) intermediate is likely to undergo Meinwald rearrangement[9] to give the [6,6,6]-fused anthracene skeleton. Dehydration then furnishes the anthracene product. Recognizing the potential of this rearrangement,

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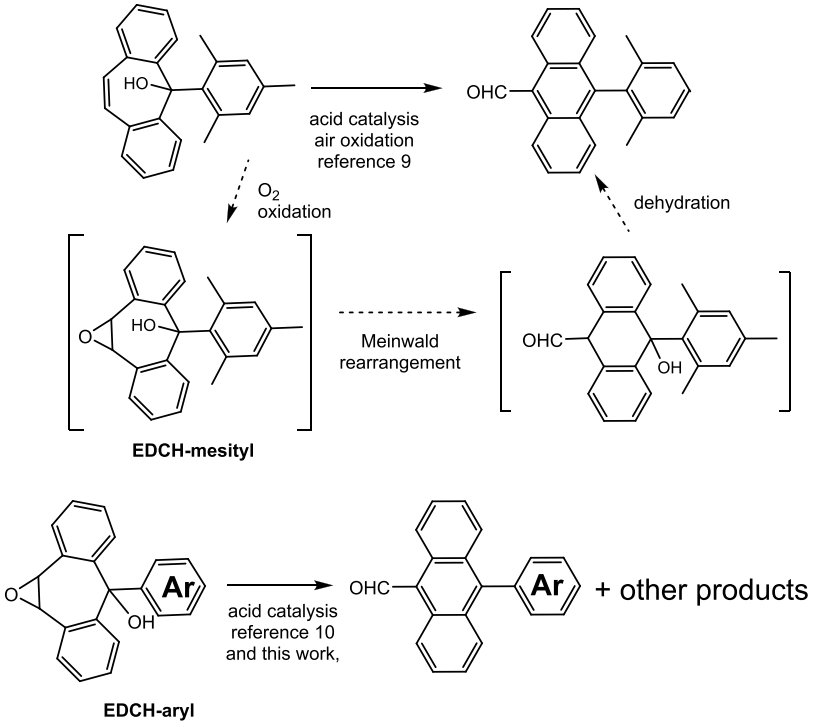
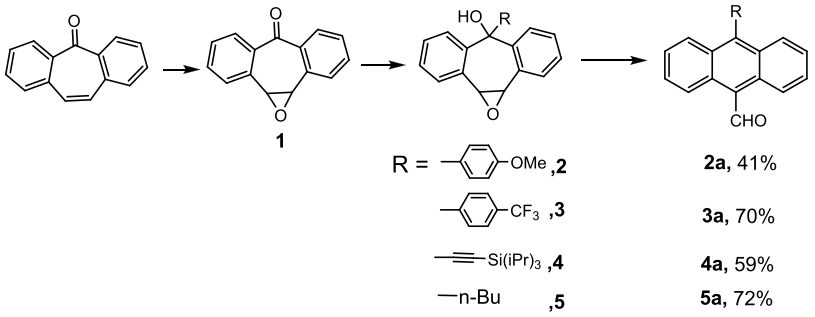
Scheme 1. Synthesis of 10-Aryl 9-anthracene Carboxaldehyde via Ring Contraction of [6,7,6]-Fused EDCH Scaffold



Scheme 2. Synthesis of 10-Substituted 9-Anthracene Carboxaldehyde from EDCH Derivatives via Meinwald Rearrangement



[a](a) *m*-CPBA. $NaHCO_3$, CH_2Cl_2; (b) R-Li, tetrahydrofuran (THF); (c) $BF_3{\cdot}OEt_2$, CH_2Cl_2.

we launched an innovated synthesis of a range PAH of derivatives employing this rearrangement. Since the epoxy dibenzocycloheptenol (EDCH) is the proposed intermediate, this key structural motif is directly utilized as the precursors in the current investigation. As we were preparing this manuscript, Dr. Ploypradith reported the synthesis of 9-anthracene carboxaldehyde derivatives employing a very similar protocol (semipinacol under Dr. Ploypradith's nomenclature).[10] In the present contribution, the substrate scope of this strategy was greatly expanded to include PAH and heterocyclic substituents. Novel reaction pathways, such as aryl migration and transannular cyclization, were also revealed in more elaborated substrates. We found the selectivity among different pathways is modulated by substrate structures as well as reaction temperature. Furthermore, it was demonstrated that this rearrangement can be applied to the selective synthesis of various PAH motifs, including pentacene derivatives of C_{2h} and C_{2v} symmetries. Our study provides a more comprehensive assessment of this versatile reaction and therefore is complementary to the prior contribution from Dr. Ploypradith's group.

RESULTS AND DISCUSSION

The simpler EDCH derivatives with aryl (**2** and **3**), alkynyl (**4**), and alkyl (**5**) substituents were first tested. (Dr. Ploypradith's team has extensively explored such examples. The present four reactions offer moderately improved yields with convenient reagents and conditions.) The required starting compounds (**2**–**5**) were synthesized by the addition of lithium reagents to EDCH-one (**1**), which is prepared from dibenzocycloheptenone via epoxidation (mCPBA). Judged from the simplicity of their ^1H and ^{13}C NMR spectrum, all epoxy alcohols were produced as single diastereomers, presumably the cis isomer from the lithium reagent attacking the ketone from the opposite side of the epoxide. The *cis*-selectivity was assumed for all subsequent epoxy alcohols intermediates, one of which (**14**) was confirmed by X-ray crystallography. When these epoxy alcohols were treated with boron trifluoride etherate ($BF_3{\cdot}OEt_2$) at room temperature, anthracene aldehyde products (**2a**–**5a**) were obtained in good to moderate yields. A small amount (<5%) of deformylated anthracene products was also observed in these reactions.

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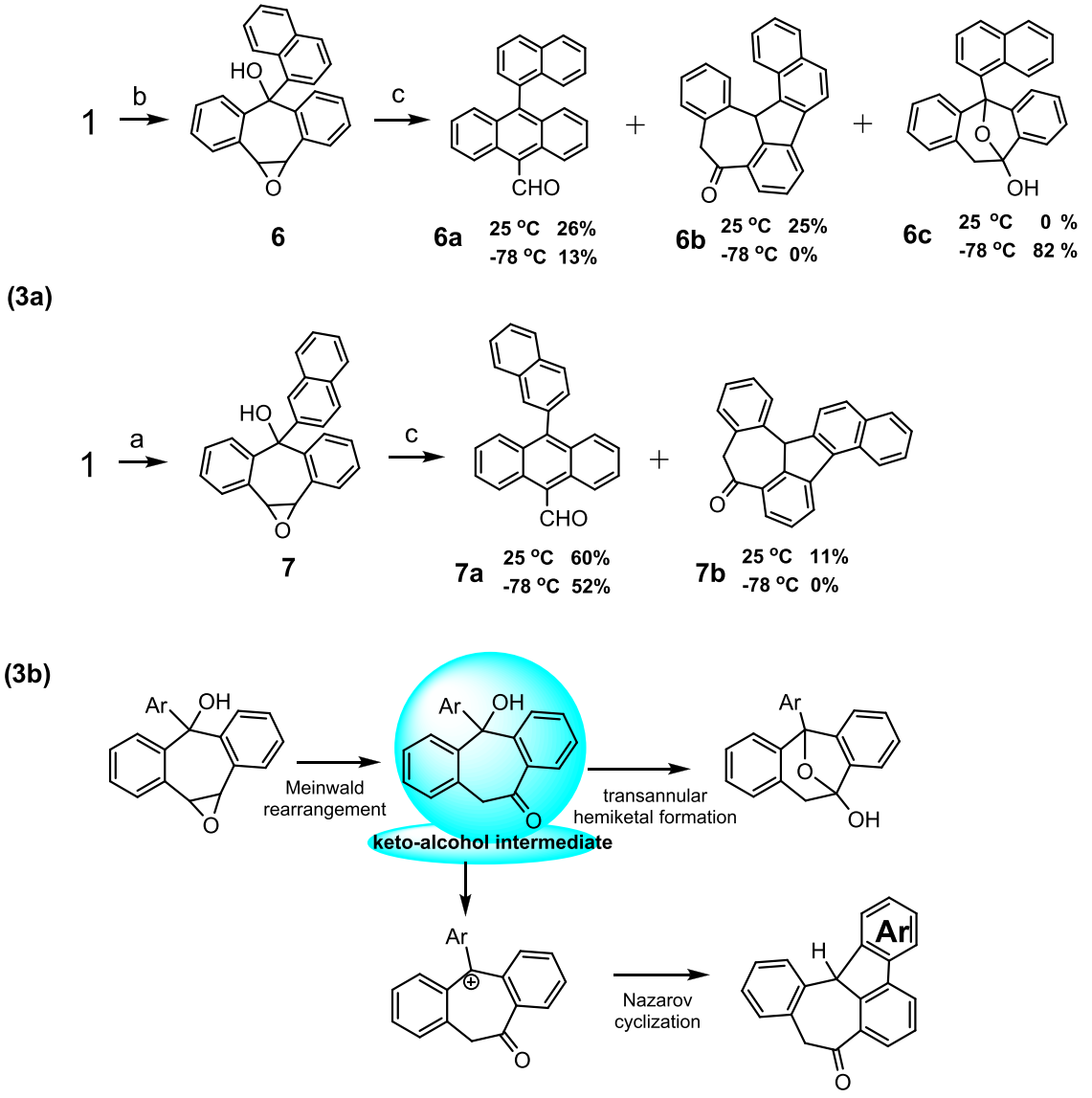
Scheme 3. (a) BF_3·OEt_2-Catalyzed Rearrangement of Naphthyl-EDCH (6 and 7) to Produce Anthracene Carboxaldehyde (6a and 7a), Azulene-Embedded PAHs (6b and 7b), and Oxo-Bridged Hemiketal (6c). (b) Meinwald Rearrangement toward Keto-Alcohol Intermediate and Subsequent Transformation to Various Products



[a](a) 1-Bromonaphthalene, *n*-BuLi, THF −78 °C, then **1**. (b) 2-Bromonaphthalene, *n*-BuLi, THF −78 °C, then **1**. (c) BF_3·OEt_2, CH_2Cl_2, 25 and −78 °C.

These anthracene carboxaldehydes are convenient building blocks of more elaborated conjugated systems for curiosity and function-driven research (Scheme 2).

After establishing the scope of BF_3·OEt_2-catalyzed rearrangement to construct anthracene derivatives with aldehyde and simple substituents (**2a**−**5a**), we attempted to extend this protocol to systems where PAH groups (naphthyl, anthryl, and pyrenyl) located at 10 position of 9-anthracene carboxaldehyde. As shown in Scheme 3a, the required naphthalene-substituted **6** and **7** were prepared by nucleophilic addition to **1** with the corresponding 1- and 2-lithiated naphthalene. The rearrangement of **6** gave the expected anthracene-naphthalene dyad product (**6a**) in moderate yield. Yet, a peculiar ketone product **6b** (^{13}C signal at 193.75 ppm) with an AB-type methylene (4.88 ppm and 4.13 ppm, J = 14.3 Hz) and a triaryl methine (5.96 ppm) was also isolated in comparable yield. Heteronuclear multiple bond correlation (HMBC) and heteronuclear single quantum coherence (HSQC) two-dimensional (2D) NMR spectroscopy (Figure S25) establish **6b**'s hexacyclic framework where a [5,7]-fused azulene core is surrounded by four annulated six-membered rings. This structure is confirmed by X-ray crystallography. **6b** is a secondary product derived from the dibenzocycloheptanone intermediate after the Meinwald rearrangement. The mechanism (Scheme 3b) is formally the Nazarov cyclization of a triaryl cation[11] generated from the keto-alcohol intermediate under the acidic condition. The ketone group in **6b** is attached to the phenyl ring where the cyclization occurs. This unanticipated regioselectivity implies that **6b** is derived from a destabilized cation intermediate. Hence, the selective formation of **6b** is likely the result of kinetic control. To manage the selectivity between **6a** and **6b**, the reaction was also conducted at −78 °C. We found the Nazarov cyclization is shut down at a low temperature, while the oxo-bridged

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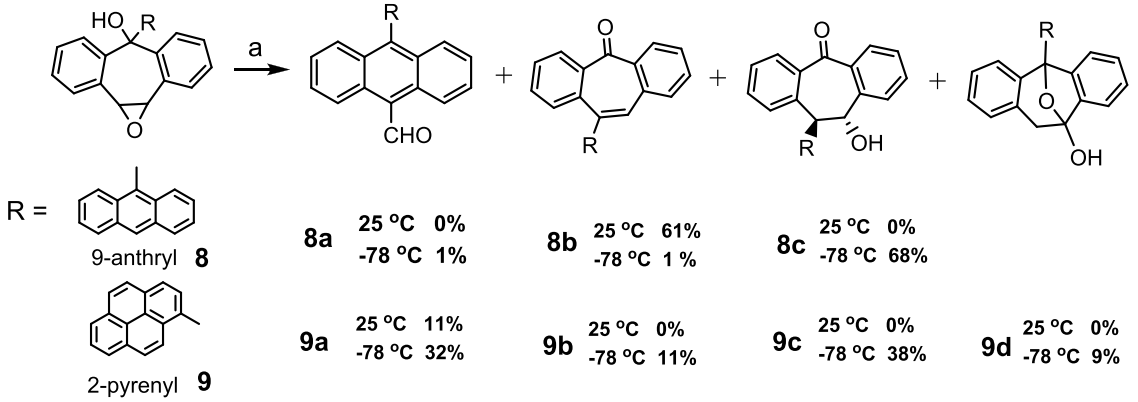
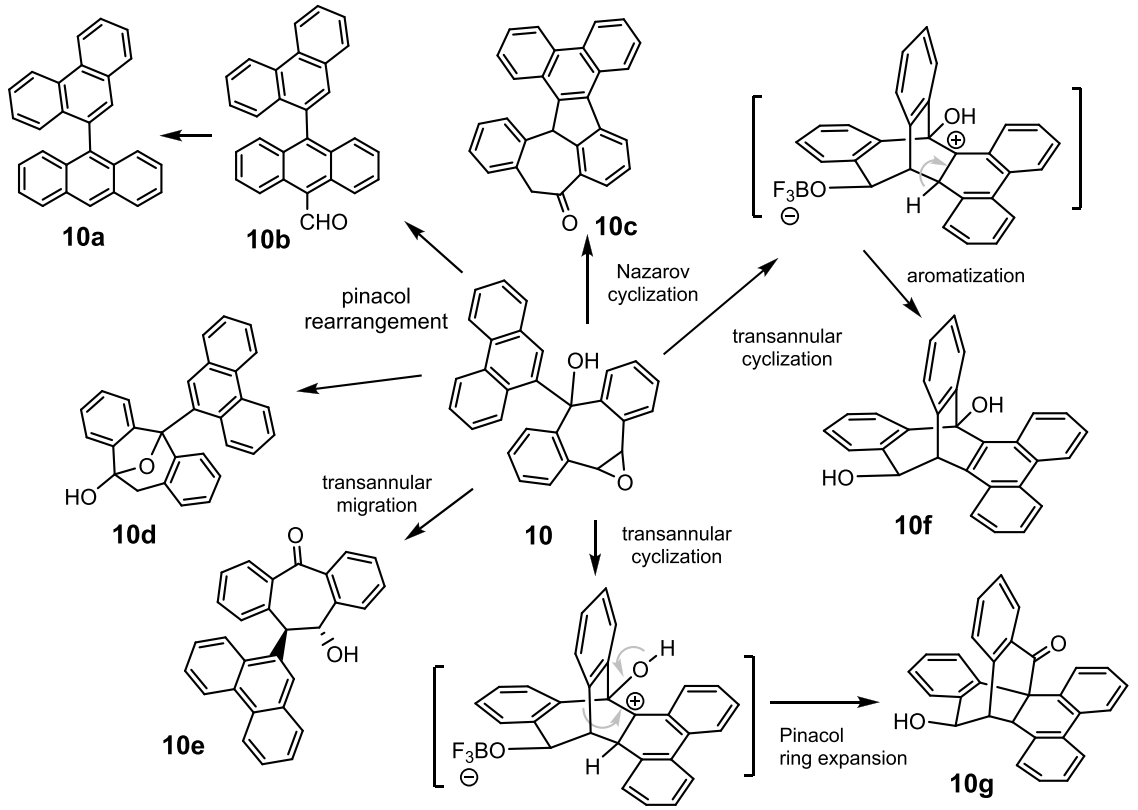
Scheme 4. BF_3·OEt_2-Catalyzed Rearrangement of Anthryl-EDCH (8) and Pyrenyl-EDCH (9)



[a] BF_3·OEt_2, CH_2Cl_2, 25 and −78 °C.

Scheme 5. BF_3·OEt_2-Catalyzed Rearrangement of Phenanthrene-EDCH (10)



hemiketal **6c** (hemiketal ^{13}C chemical shift = 104.5 ppm) derived from the keto-alcohol intermediate becomes the major product (Scheme 3b). A similar product was previously observed in a much lower yield during the **3** → **3a** transformation. Ploypradith et al. has also documented these products. When **6c** is treated with BF_3·OEt_2 at a higher temperature (refluxed dichloroethane), **6b** is produced in 75% yield. These results demonstrate that **6c** can be reversibly converted into keto-alcohol intermediates. This intermediate then undergoes irreversible dehydration at higher temperatures to furnish the Nazarov cyclization product **6b**. When 1-naphthyl-substituted **7** was put under identical condition, the anthracene derivative **7a** and Nazarov cyclization product **7b** were likewise obtained. However, when the rearrangement was performed at −78 °C, **7a** becomes the sole product in slightly lower yields.

To gather more information on the potential reaction pathways EDCH can undertake, EDCH containing anthryl and pyrenyl units (**8** and **9**) were synthesized and reacted with BF_3·OEt_2 at room temperature and −78 °C (Scheme 4). Surprisingly, the yield for the expected bis-anthryl aldehyde **8a** is only 1%. The overwhelming major products are those with the anthryl group shift to the other side of the seven-membered ring. In the low-temperature product **8c** (carbonyl signal in ^{13}C spectrum = 198.4 ppm. An alcohol type signal at 73.1 ppm is also present.) the epoxide ring opens via a concerted backside attack from the migrating anthryl moiety. This reaction pathway is consistent with the assumption that **8** is a cis-epoxy alcohol. The resulting trans stereoselectivity is

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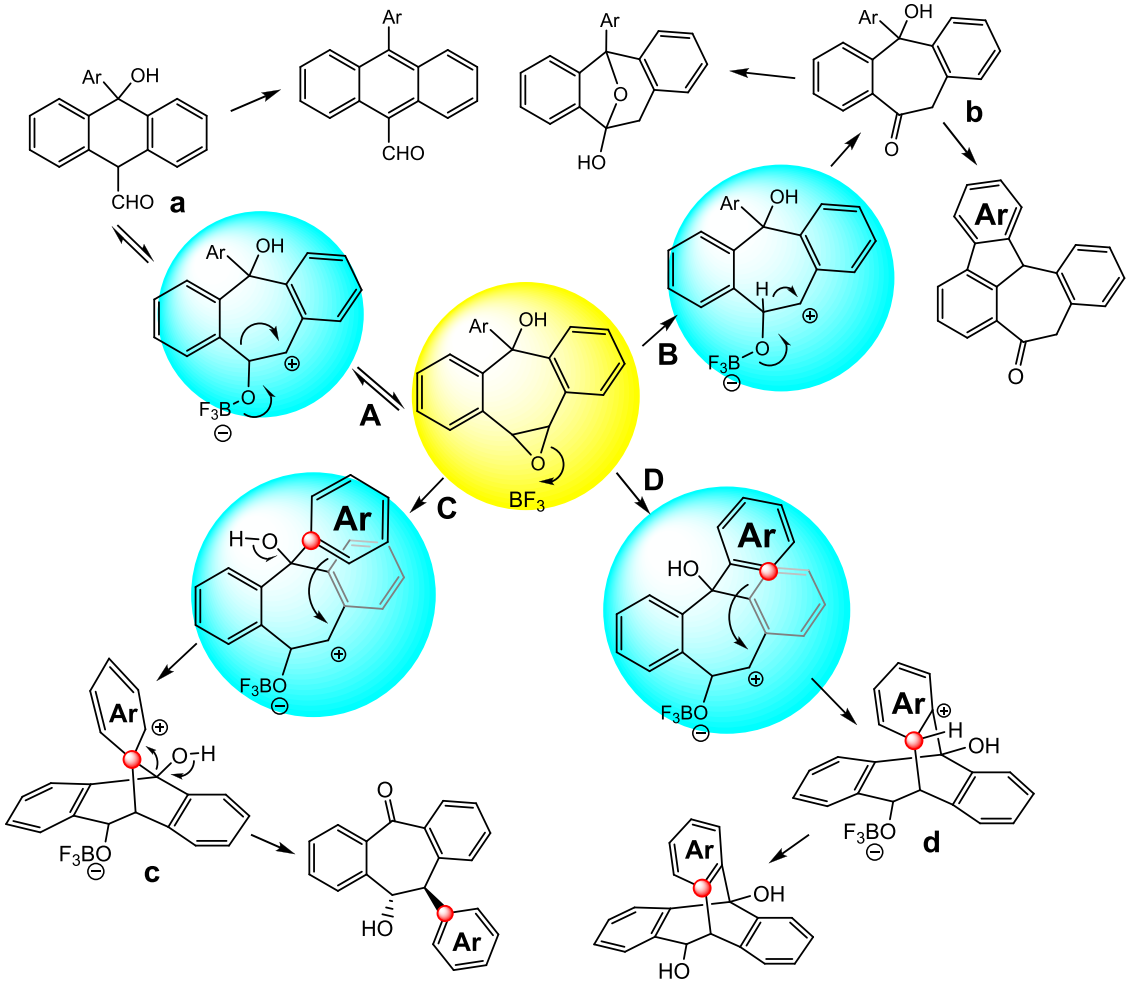
Scheme 6. Diverse Reactivity of BF_3·OEt_2-Induced Skeletal Rearrangement of aryl-EDCH



[a]A: Meiwald rearrangement + dehydration. B: Meiwald rearrangement + transannular hemiketal formation. C: Transannular aryl migration. D: Transannular Friedel–Crafts cyclization.

confirmed by X-ray crystallography and 2D NMR (Figure S43). The room-temperature product **8b** is the dehydrated form of **8c** with an anthracene-dibenzocycloheptenone dyad architecture. Similar migratory reactivity was also observed for pyrene-substituted **9** (**9b** and **9c**). Because the structural motif of **8b** and **9b** are also found in the skeleton of stilbenoid hemsleyanol and parviflorol, the transannular migration might be a convenient entry toward similar natural products.[12] The Meinwald rearrangement products, anthracene **9a** and bridged hemiketal **9d** (structure confirmed by X-ray crystallography), were also isolated in moderate yields. Notably, the yield of **9a** at room temperature is uncharacteristically low despite being the sole identifiable product.

The BF_3·OEt_2-catalyzed rearrangement of phenanthrene-EDCH (**10**) reveals the most complicated reactivity pattern in this study. Fortunately, the combined yield of the seven identifiable products (**10a**–**10g**) is high enough (>85%) that a more comprehensive understanding of various reaction pathways can be extracted (Scheme 5). Anthracene-phenanthrene dyad **10a** and **10b** are produced, yet the deformylated **10a** is more prominent than in previous cases. Nazarov cyclization product (**10c**), bridged hemiketal (**10d**), and transannular aryl migration product (**10e**) were likewise observed. Two bridged cyclic products (**10f** and **10g**) were identified by HMBC and HSQC 2D NMR spectroscopy (Figures S67 and S70). The bicyclic scaffolds in both compounds result from transannular Friedel–Crafts cyclization. **10f** is the straightforward Friedel–Crafts product (no carbonyl signal is observed in ^{13}C spectrum and two alcohol type signals, 77.5 and 69.7 ppm, are present), while a late-stage semipinacol ring expansion leads to the [3.3.1] bicyclic ring system in **10g** (carbonyl signal in ^{13}C spectrum = 196.5 ppm. The presence of four sp^3 ^{13}C signals indicates the B-ring of phenanthrene no longer contains the original olefin unit).

According to the results accumulated thus far, four reaction pathways are summarized in Scheme 6. Pathways A and B are the two modes of Meinwald rearrangement that produce the ring contraction aldehyde intermediate **a** and the dibenzocycloheptanone intermediate **b**. Pathways C and D are the two transannular reactions where intermediate **c** and **d** lead to the migratory and cyclization products, respectively. Several trends can be deduced from these results. (1) For substrates with nonaryl groups (**4** and **5**) or para-substituted phenyl groups (**2** and **3**) attached to EDCH, 9,10-disubstituted anthracene derivatives are the major products (pathway A). (2) Room-temperature condition usually increases the yields of the anthracene and the Nazarov cyclization products, while low temperatures enhance the production of bridged hemiketal.

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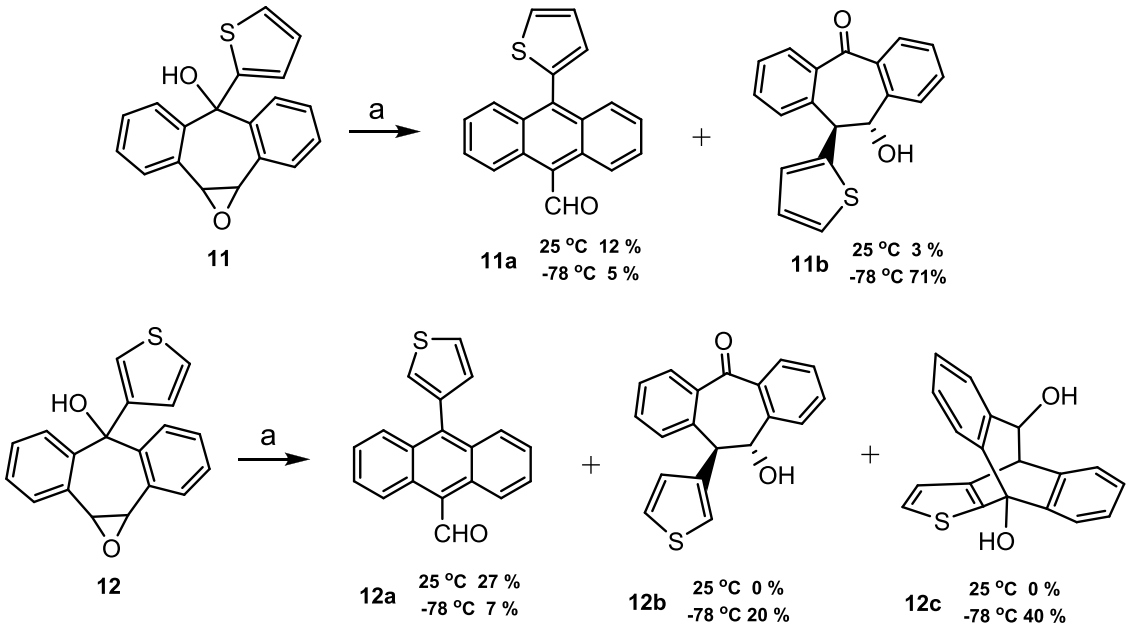
Scheme 7. BF_3·OEt_2-Catalyzed Rearrangement of Thienyl-EDCH (11 and 12)



[a]BF_3·OEt_2, CH_2Cl_2 25 and −78 °C.

(3) With PAH groups attached to EDCH (**8**, **9**, and **10**), transannular reactions, including aryl migration (pathway C) and Friedel−Crafts cyclization (pathway D), can also take place. Crucial structure−activity relationships can be drawn from these trends. (1) All transformations are initiated by epoxide opening. (2) The formations of anthracene and Nazarov cyclization products are generally facilitated by higher temperatures. This observation can be attributed to the entropic factor because both reactions involve dehydration. Yet, this generic interpretation cannot explain the different product distributions between **6** and **7** (Scheme 3a). A more nuanced model should consider most cationic intermediates that lead to dehydration products are destabilized due to the orthogonal conformation of the aryl substituents. Consequently, these products are suppressed at lower temperatures. Yet the precursor cation toward **7a** can adopt a more planar conformation, therefore the yield of **7a** shows little temperature dependency. (3) On the other hand, the oxo-bridged hemiketal is favored at low temperatures because intermediate **a** and intermediate **b** are interconvertible when the former cannot dehydrate to form anthracene. (4) The pronounced temperature dependence of product distribution indicates that many intermediates are formed reversibly at low temperatures before collapsing to respective products. (5) When the ipso positions of the substituted PAH groups are nucleophilic (**8** and **9**), the aryl groups undergo transannular migration to furnish the aryl-substituted EDCH-one. (6) In **10** where the ortho sites of the aryl group at 6 position is also nucleophilic, transannular Friedel−Crafts cyclization can take place to produce the [3.2.2] bicyclic **10f**. (7) The rearrangement of **9** to **9a** proceeds in low yield (11%) accompanied by substantial decomposition. The side products are attributed to the reactions between the excess nucleophilic sites (3, 6, 8 positions) and the endogenous cations.

After establishing the basic guidelines to steer the selectivity of these cationic rearrangements, the principles were tested on substrates containing heterocycles and ferrocene (**11**−**18**). 2-Thienyl (**11**)- and 3-thienyl (**12**)-substituted EDCHs were synthesized[13] and underwent BF_3·OEt_2-catalyzed rearrangement at room temperature and −78 °C (Scheme 7). The results strongly suggest that the selectivity principles for PAH systems (**6**−**10**) are equally applicable to thienyl-EDCH substrates. Since the thienyl unit in **11** was attached through the highly nucleophilic 2-position, the transannular thienyl migration product **11b** dominates at low temperatures. At room temperature, the formyl anthracene derivative **11a** was generated in low yield concomitantly with unidentified polymeric side products. This temperature-reactivity profile is similar to that of **9** where the pyrenyl moiety is connected through the nucleophilic 1-position. When 3-thienyl-EDCH **12** was treated with BF_3·OEt_2, at room temperature, the anthracene aldehyde **12a** is produced in moderate yield. However, when the reaction temperature was lowered to −78 °C, three products were isolated. Anthracene aldehyde **12a** is now the minor component. The nucleophilic 2-position of thiophene undergoes transannular cyclization to furnish **12c** (40%, structure confirmed by X-ray crystallography) while transannular thienyl migration product **12b** was also isolated (20%). These results reinforce the aforementioned principles including (1) the temperature dependence of selectivity, (2) the correspondence of transannular reactivity to the nucleophilic sites, and (3) the commutability of intermediates at low temperatures.

Two more electron-rich heterocyclic systems (dithiophene and carbazole) were appended to the ECHD system (**13**−**15**), and their rearrangement reactivity was investigated (Scheme 8). The mono- and disubstituted dithiophene (**13** and **14**) can be synthesized via selective lithiation.[14] The reactivity of **13** is identical to those of **9** and **11**. The low-temperature condition leads to the migratory product (**13b**) in moderate yield, while the anthracene derivative (**13a**) is produced in low yield at room temperature. For the rearrangement of dithiophene-$EDCH_2$ substrate (**14**), only a double-migratory product **14a** was observed at low temperatures. The crystal structure of **14**

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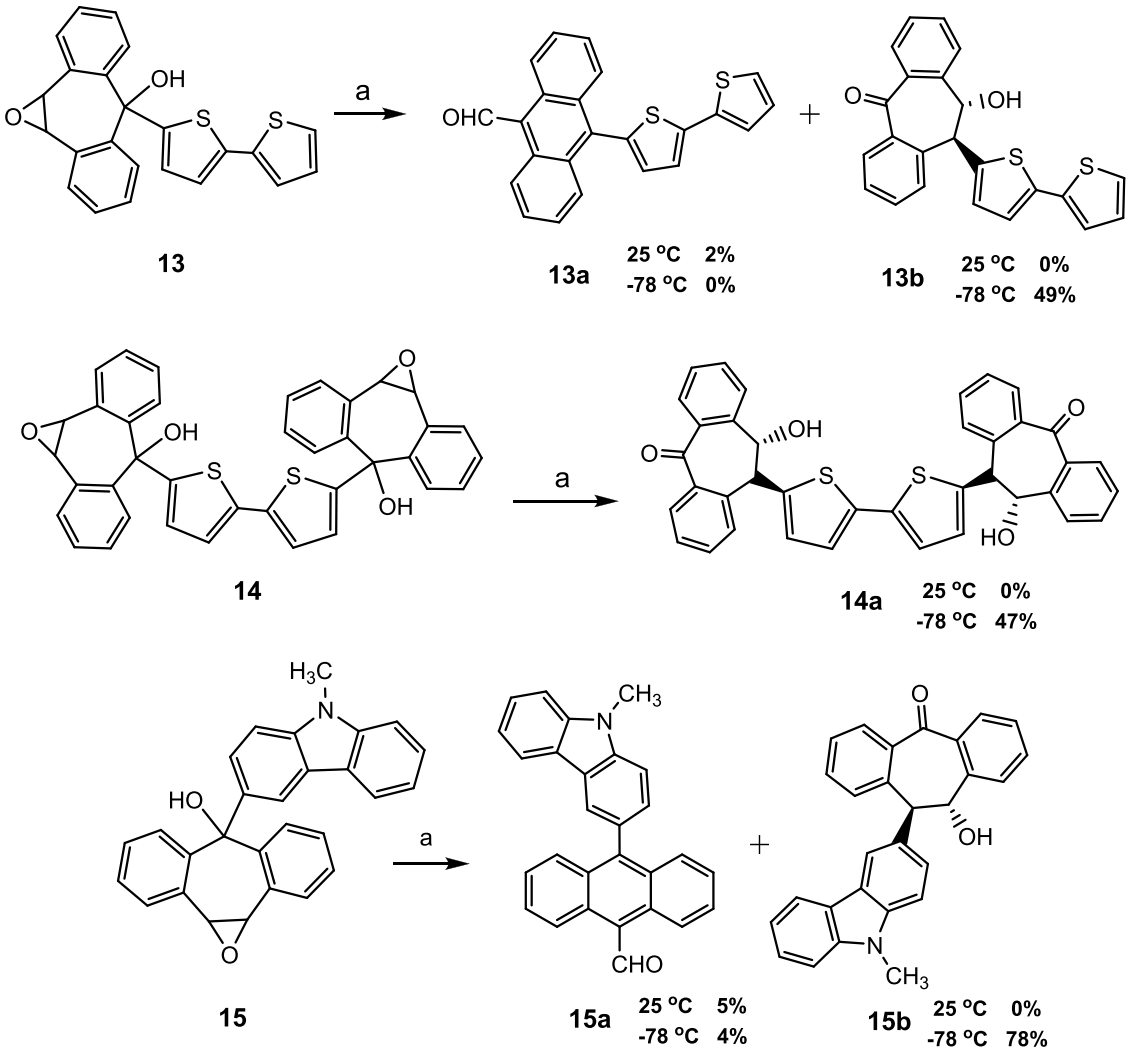
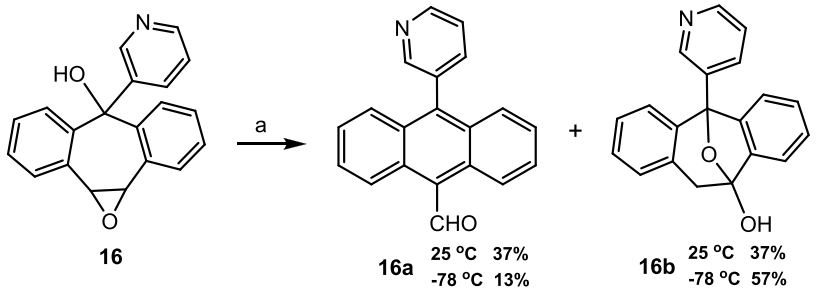
Scheme 8. BF_3·OEt_2-Catalyzed Rearrangement of Bisthiophene-EDCH$_{1,2}$ (13 and 14) and Carbazole-EDCH (15)



[a]BF_3·OEt_2, CH_2Cl_2 25 and −78 °C.

Scheme 9. BF_3·OEt_2-Catalyzed Rearrangement of Pyridyl-EDCH (16)



[a]BF_3·OEt_2, CH_2Cl_2 25 and −78 °C.

(Supporting Information, SI) confirms the *cis*-epoxy alcohol configuration and close contact between the ipso and epoxide carbon (~3 Å). Both further validate the migratory reactivity. Likewise, because the 3-position of carbazole is highly nucleophilic, the ipso migration pathway dominates the rearrangement of **15** to furnish **15a** at low temperatures.

To reverse the effect of electron-rich aryl groups, compound **16** (3-pyridyl-EDCH) was synthesized and put under the identical reaction condition (Scheme 9). The product distribution is in stark contrast to previous examples. The transannular migration that dominates the electron-rich substrates (**11**−**15**) is completely absent. Instead, Meinwald rearrangements are the only detectable pathways with the electron-deficient pyridyl substituent. The anthracene aldehyde (**16a**) and bridged hemiketal (**16b**) were generated in about 70% combined yield, while the higher reaction temperature favors the anthracene product as already inferred from previous examples.

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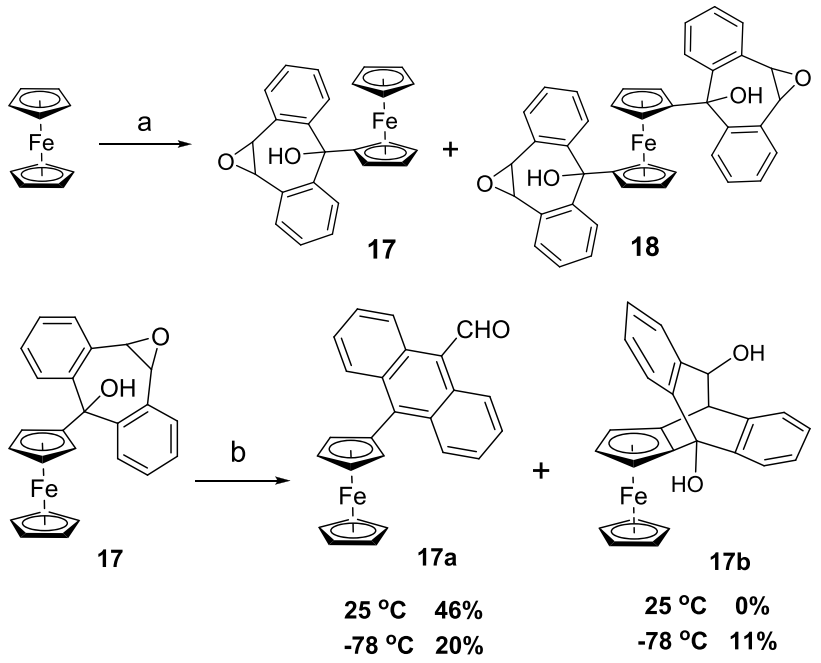
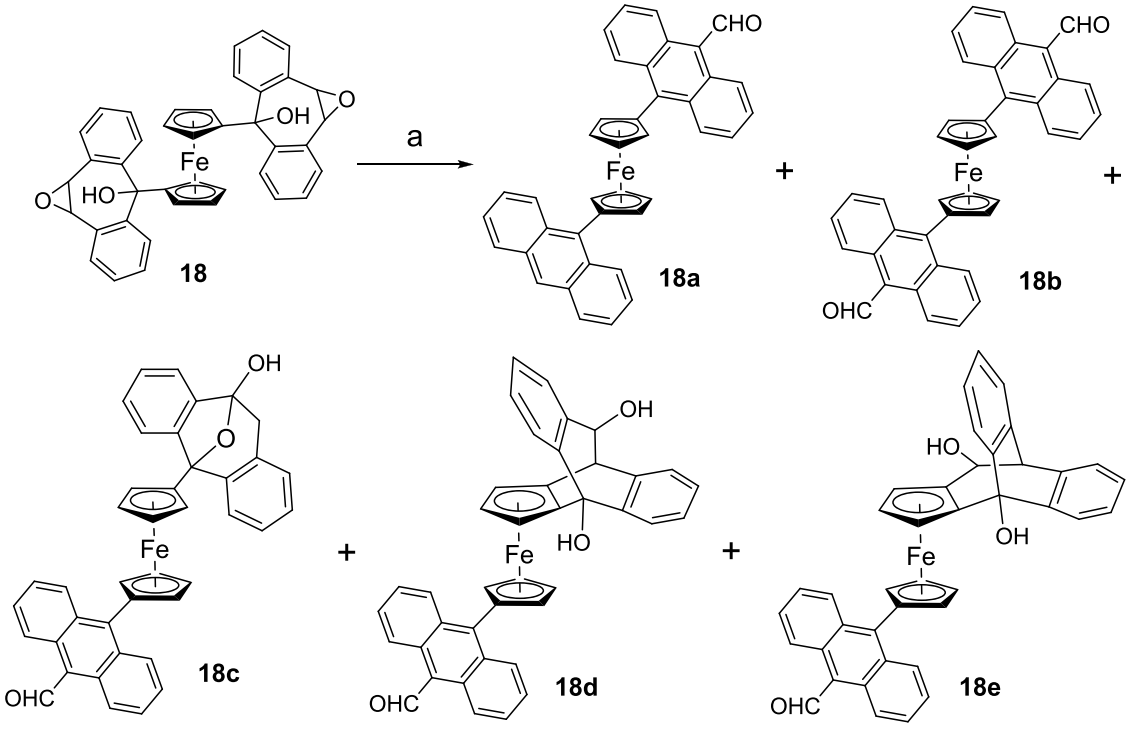
Scheme 10. BF_3·OEt_2-Catalyzed Rearrangement of Ferrocenyl-EDCH (17)



[a](a) Tetramethylethylenediamine (TMEDA), *n*-BuLi, THF; then **1**. (b) BF_3·OEt_2, CH_2Cl_2 25 and −78 °C.

Scheme 11. BF_3·OEt_2-Catalyzed Rearrangement of Ferrocenyl-$EDCH_2$ (18)



[a]BF_3·OEt_2, CH_2Cl_2 25 and −78 °C.

Ferrocene is an important building block for redox-active materials because of its robust electrochemical property. Yet, there are only a few reported ferrocene-PAH conjugated systems in the literature, which mostly employed the Suzuki–Miyuara coupling.[15] With this Meinwald rearrangement protocol, we perceive the opportunity to construct anthracene-ferrocene dyad or triad molecules. The mono- and di-EDCH-substituted ferrocene (**17** and **18**) was synthesized via lithiated ferrocene[16] in moderate yields (Scheme 10). The rearrangement of **17** furnishes the ferrocenyl-anthracene aldehyde **17a** as the major product (Scheme 10). The transannular cyclization product **17b** was also formed at low temperatures due to the nucleophilic nature of cyclopentadiene rings. However, transannular migration product was not observed. This exception to the prior trend is likely due to the large size of the ferrocenyl group, which renders the

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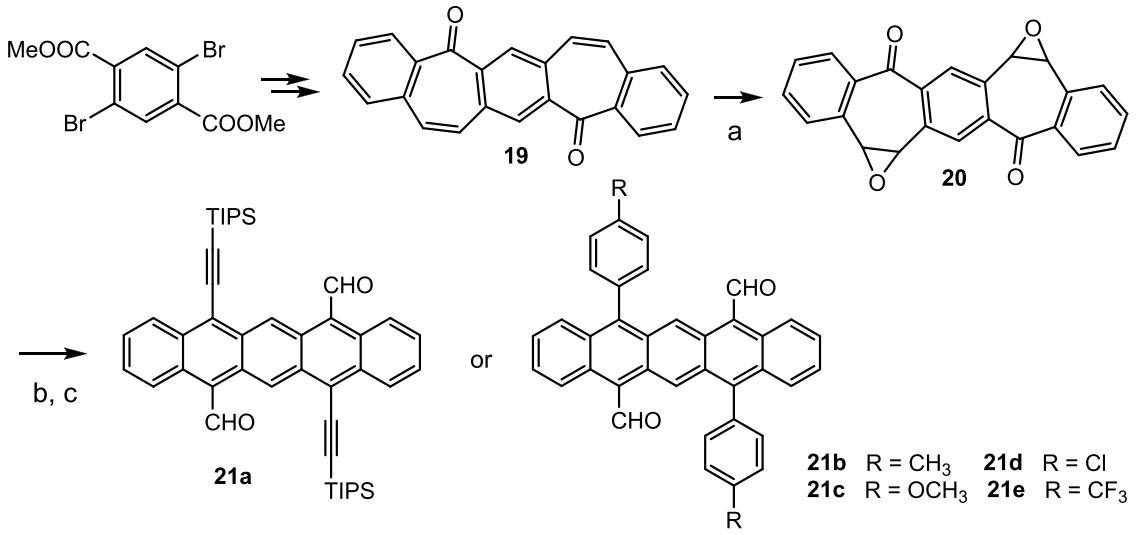
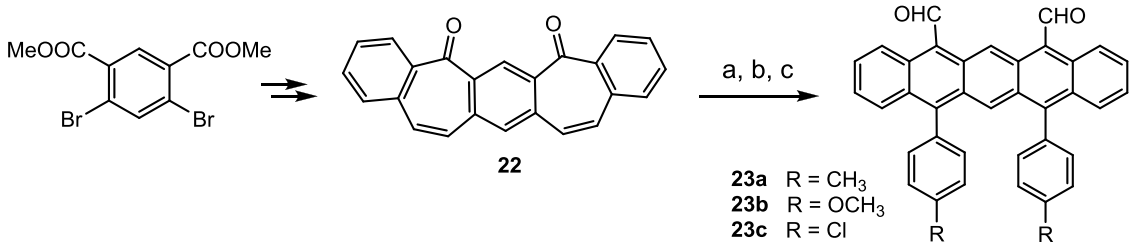
Scheme 12. Selective Synthesis of C_{2h} Pentacene Derivatives via Meinwald Rearrangement



combined yields (b,c): **21a** = 12 %, **21b** =45% , **21c** = 34%, **21d**= 39%, **21e**=22%

[a](a) *m*-CPBA, $NaHCO_3$, CH_2Cl_2. (b) Aryl lithium or alkynyl lithium, THF, −78 °C. (c) CF_3COOH, CH_2Cl_2.

Scheme 13. Selective Synthesis of C_{2v} Pentacene Derivatives via Meinwald Rearrangement



combined yields (b,c): **23a**=29%, **23b**=48%, **23c**=58%

[a](a) *m*-CPBA, $NaHCO_3$, CH_2Cl_2. (b) Aryl lithium, THF, −78 °C. (c) CF_3COOH, CH_2Cl_2.

corresponding transition-state unattainable due to steric hindrance.

The rearrangement of bis-EDCH ferrocene **18** exhibits more complex reactivity than its mono-substituted counterpart **17**. As depicted in Scheme 11, the bis-anthryl **18b** and its deformylated secondary product **18a** were formed in about 20% combined yield. The lower yields are anticipated because the rearrangement of mono-EDCH **17** only gave 46% yield. Three hybrid rearrangement products (**18c**, **18d**, and **18e**), where the substituents on the two cyclopentadiene units differ, were also isolated in low yields. The formation of bridged hemiketal containing **18c** was expected. The structures of both **18d** (isolated as a mixture with **18c**) and **18e** were determined by comparison with **17b** and 2D NMR spectroscopy (HMBS and HSQC) to contain bicyclic moieties. A transannular Friedel−Crafts cyclization installs the [3.2.2] bicyclic scaffold in **18d** as in **17b**. In compound **18e**, a different [3.2.2] bicyclic scaffold is formed from the Meinwald rearrangement intermediate (**a** in Scheme 6).

After screening a variety of EDCH derivatives, it can be concluded that Meinwald rearrangement grants the anthracene products more cleanly with the simple phenyl substituents at room temperature. Endowed with a deeper understanding of the protocol, we set out to synthesize novel PAH derivatives that are hitherto inaccessible by other synthetic strategies.

Pentacene is the benchmark compound among organic electronic materials. Pentacene derivatives possess excellent charge-transporting capacity which enables their widespread applications in various devices.[17] However, the syntheses of pentacene derivatives in the literature are limited in their scopes.[18] Especially, access to pentacene derivatives with C_{2v} and C_{2h} symmetry remains a challenge.[19] A selective synthetic strategy requires that the regiochemical feature of desired product encodes in its starting materials. Since [6,7,6]-fused EDCH has been established as a precursor to anthracene skeletons, a [6,7,6,7,6]-fused pentacyclic system could lead to pentacene derivatives under proper acid catalysis. The execution of this retrosynthetic vision is depicted in Scheme 12. The [6,7,6,7,6]-fused **19** was synthesized from dimethyl 2,5-dibromoterephthalate via a known procedure.[20] The C_{2h} symmetry of **19** is inherited from that of starting material. The subsequent epoxidation (**19** → **20**) and aryl lithium (or alkynyl lithium) addition were carried out as in Scheme 2. After optimizing the double Meinwald rearrangement, C_{2h} pentacene derivatives (**21a**-**21e**) with aryl, alkynyl, and aldehyde substituents at 5, 7, 12, 14 positions were produced. $BF_3{\cdot}OEt_2$ is replaced by CF_3COOH to provide cleaner products after the double-ring contraction. This strategy achieves the selective synthesis of several C_{2h} pentacene derivatives in useful yields from a readily accessible common intermediate (**20**).

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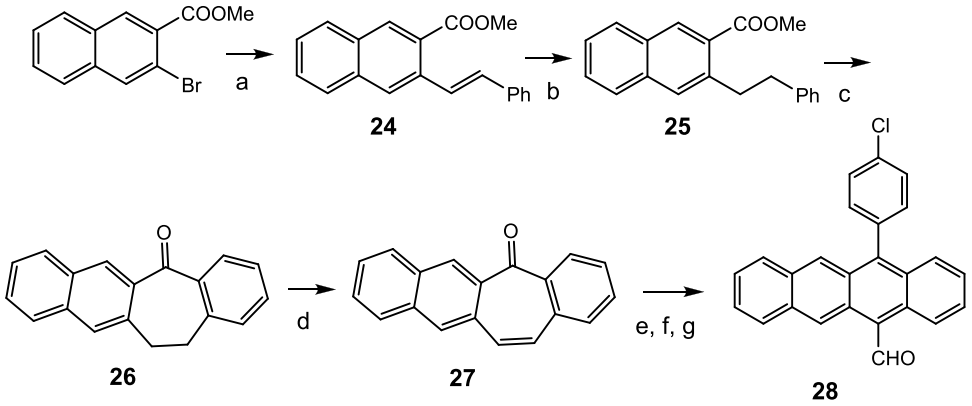
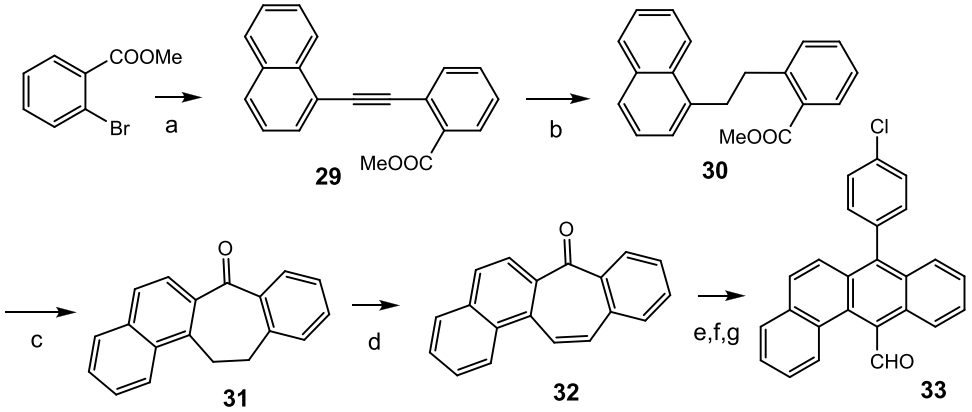
Scheme 14. Selective Synthesis of Tetracene Carboxaldehyde via Meinwald Rearrangement



[a](a) Styrene, $Pd(OAc)_2$, P(*o*-tolyl)$_3$, Et_3N, *N*,*N*-dimethylformamide (DMF). (b) 10% palladium on charcoal, H_2. MeOH/THF. (c) NaOH, H_2O/EtOH, then $SOCl_2$, then $AlCl_3$, CH_2Cl_2. (d) *N*-Bromosuccinimide, benzoyl peroxide, then Et_3N, (e) *m*-CPBA, $NaHCO_3$, (f) p-Li-C_4H_4-Cl, (g) CF_3COOH, CH_2Cl_2.

Scheme 15. Selective Synthesis of Benz[*a*]anthracene Carboxaldehyde via Meinwald Rearrangement



[a]1-Ethynylnaphthalene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N. (b) 10% palladium on charcoal, H_2, MeOH/THF, then DDQ, reflux toluene. (c) NaOH, H_2O/EtOH, then $SOCl_2$, then $AlCl_3$, CH_2Cl_2. (d) *N*-bromosuccinimide, benzoyl peroxide, then Et_3N. (e) *m*-CPBA, $NaHCO_3$, (f) p-Li-C_4H_4-Cl, THF, (g) CF_3COOH, CH_2Cl_2.

When the identical reaction sequence (epoxidation, aryl lithium addition, and CF_3COOH) was applied to a [6,7,6,7,6]-fused precursor with C_{2v} symmetry, pentacene derivatives of C_{2v} symmetry should emerge. The realization of this plan is presented in Scheme 13. Compound **22** was synthesized from dimethyl 4,6-dibromoisophthalate with the same protocol as that employed for **19**. After **22** was treated sequentially with mCPBA, aryl lithium, and CF_3COOH, three pentacene derivatives (**23a**, **23b**, and **23c**) were generated without isolating the intermediates. For these C_{2v} pentacene derivatives, the protons at 6 and 13 positions show weak but measurable spin−spin coupling ($J \sim 1$ Hz). The observation of such peculiar long-range *J*-5 couplings can be attributed to the pronounced aromatic character of the central ring.[21]

Two more PAH derivatives were synthesized to test the scope of this new strategy. As shown in Scheme 14, the synthesis of tetracene derivative **28** started from the Heck coupling of methyl 3-bromo-2-naphthoate (prepared via palladium-catalyzed ortho bromination)[22] with styrene. The olefin unit in **24** was then hydrogenated (**25**) to facilitate the subsequent Friedel−Crafts cyclization. After the methyl ester was hydrolyzed, Friedel−Crafts cyclization ($SOCl_2/AlCl_3$) furnished the [6,6,7,6]-fused **26**. The double bond was then reinstated (*N*-bromosuccinimide, benzoyl peroxide/Et_3N) to give **27**. The standard reaction sequence (epoxidation, aryl lithium addition, CF_3COOH) was then conducted to furnish tetracene **28** in moderate yield.

Compound **33** was chosen as the next target to test whether it is feasible to construct angular fused PAH through ring contraction. As shown in Scheme 15, methyl 2-bromobenzoic acid and 1-naphthyl acetylene first undergo Sonogashira coupling to produce **29**. The hydrogenation of triple bond inevitably leads to the partial reduction of naphthalene units, which was rearomatized (DDQ) to give **30**. The subsequent steps (hydrolysis, Friedel−Crafts cyclization, bromination, elimination, epoxidation, aryl lithium addition, and CF_3COOH-induced rearrangement) are identical to those in Scheme 14 to generate benz[*a*]anthracene derivative **33** in good yield. These examples demonstrate that a range of PAH aldehydes can be conveniently constructed with the rearrangement tactic.

In summary, we have broadly explored the acid-catalyzed rearrangement of EDCH as a module to synthesize various aromatic scaffolds. The accessible rearrangement pathways include Meinwald ring contraction, Nazarov cyclization, transannular aryl migration, and transannular Friedel−Crafts

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cyclization. Structures of representative products (**7b**, **8c**, **9d**, **12c**, **18b**) from each pathway were confirmed by X-ray crystallography. The reactivity is chiefly modulated by substrate structures. Furthermore, reaction temperature also has a pronounced influence on product distribution. By screening these factors, useful mechanistic insights were acquired. The information thus obtained can be utilized to further the scope of this protocol. By employing this approach on more elaborated substrates, tetracene, benz[*a*]anthracene, and pentacene derivatives were prepared in a selective manner. Most notably, pentacene derivatives of C_{2h} and C_{2v} symmetry can be selectively prepared. The aldehyde group resulting from the rearrangement can serve as the handle for further functionalization. With the versatility and adaptability of the acid-catalyzed rearrangement, the EDCH can serve as the launching board toward many valuable yet hard-to-access PAH systems.

EXPERIMENTAL SECTION

1a,10b-Dihydro-6*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*b*]oxiren-6-one (1). A solution of 5*H*-dibenzo[*a*,*d*][7]-annulen-5-one (0.10 g, 0.48 mmol, 1 equiv) and mCPBA (0.6 g, 2.42 mmol, 5 equiv) in dry CH_2Cl_2 (5 mL) was stirred at room temperature for 16 h. The mixture was then extracted with 1 N NaOH solution. The organic portion was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude compound was purified by flash column chromatography (hex/CH_2Cl_2 = 1:1) to give **1** (90 mg, 87%).

IR (KBr, cast) ν (cm^{-1}) 3070, 1671, 1601, 1299, 1158, 933, 753, 635; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.63 (dd, J = 7.5, 1.0 Hz, 2H), 7.56−7.50 (m, 4 H,), 7.44 (dt, J = 7.5, 1.5 Hz, 2H), 4.46 (s, 2H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 197.9, 138.4, 134.8, 131.4, 129.8, 129.3, 128.4, 61.7; HRMS (FAB) m/z [M + H]$^+$ calcd for $C_{15}H_{11}O_2$: 223.0759; found: 223.0755.

6-(4-Methoxyphenyl)-1a,10b-dihydro-6*H*-dibenzo-[3,4:6,7]cyclohepta[1,2-*b*]oxiren-6-ol (2). To a solution of p-bromoanisole (0.22 mL, 1.45 mmol, 3 equiv) in THF (10 mL) was added 2.5 M *n*-BuLi (0.58 mL, 1.45 mmol, 3 equiv) at −78 °C and the reaction was stirred for 1 h. To the mixture was added **1** (0.11 g, 0.48 mmol, 1 equiv) and the reaction was slowly warmed back to room temperature and stirred for 3 h. The mixture was quenched by water and concentrated. The mixture was partitioned between saturated aqueous NH_4Cl solution and CH_2Cl_2. The organic portion was then washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude mixture was purified by flash chromatography (hex/CH_2Cl_2 = 2:1) to furnish **2** (0.32 g, 70%).

IR (KBr, cast) ν (cm^{-1}) 2838, 1609, 1509, 1418, 1252, 1025, 725, 608; ^1H NMR (500 MHz; $CDCl_3$) δ (ppm) 7.95−7.94 (m, 2 H), 7.52−7.50 (m, 2 H), 7.35−7.29 (m, 4 H), 7.04−7.01 (d, J = 7.5 Hz, 2 H), 6.82−6.79 (d, J = 7.5 Hz, 2 H), 3.97(s, 3H), 3.69 (s, 2H), 2.17 (s, 1H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 159.1, 145.8, 142.2, 131.7, 131.3, 128.1, 127.9, 124.2, 114.1, 78.4, 57.2, 55.2; HRMS (FAB) m/z [M$^+$] calcd for $C_{22}H_{18}O_3$: 330.1256; found: 330.1258.

10-(4-Methoxyphenyl)anthracene-9-carbaldehyde (2a). To a solution of **2** (0.14 g, 0.42 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added boron trifluoride ethyl etherate (0.21 mL, 0.85 mmol, 2 equiv) at −78 °C and the reaction was stirred for 0.5 h. The mixture was then diluted and extracted with saturated aqueous $NaHCO_3$ solution. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude compound was purified by flash chromatography (hex/CH_2Cl_2 = 4:1) to give **2a** (54 mg, 41%).

IR (KBr, cast) ν (cm^{-1}) 2839, 1672, 1604, 1511, 1247, 1034, 831, 764; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.6 (s, 1H), 9.01 (d, J = 9.0 Hz, 2H), 7.77 (d, J = 9.0 Hz, 2H), 7.68−7.64 (m, 2H), 7.43−7.40 (m, 2H), 7.33−7.30 (d, J = 8.5 Hz, 2H), 7.15−7.12 (d, J = 8.5 Hz, 2H), 3.96 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$, 125 MHz) δ 193.4, 159.4, 145.5, 131.8, 131.8, 130.3, 130.2, 128.6, 128.1, 125.4, 124.9, 123.5, 113.9, 55.4; HRMS (EI) m/z for [M$^+$] calcd for $C_{22}H_{16}O$: 312.1150; found: 312.1146.

6-(4-(Trifluoromethyl)phenyl)-1a,10b-dihydro-6*H*-dibenzo[3,4:6,7]cyclohepta [1,2-b]oxiren-6-ol (3). To a solution of 4-bromobenzotrifluoride (0.34 mL, 2.4 mmol, 2 equiv) in THF (25 mL) was added 2.5M *n*-BuLi (1.0 mL, 2.5 mmol, 2 equiv) at −78 °C and the mixture was stirred for 1 h. **1** was then added to the reaction (0.27 g, 1.2 mmol, 1 equiv, in 2.0 mL THF). The reaction was warmed to room temperature and stirred for 3 h. The reaction was quenched by saturated NH_4Cl solution and concentrated. The residue was redissolved in CH_2Cl_2, and the solution was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 2:1) to give **3** (0.16 g, 44%).

IR (KBr, cast) ν (cm^{-1}) 3072, 1620, 1418, 1329, 1170, 907, 849, 755; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.94−7.93 (m, 2H), 7.57 (d, J = 8.3 Hz, 2H), 7.52 (m, 2H), 7.38−7.33 (m, 4H), 7.25 (d, J = 8.2 Hz, 2H), 3.66 (s, 2H), 2.28 (s, 1H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 153.1, 144.6, 131.9, 131.0, 130.2 (q, J = 32.7 Hz), 128.5, 128.4, 127.2, 127.1, 126.0 (q, J = 24.8 Hz), 124.1, 123.8 (q, J = 273.3 Hz), 78.5, 57.1; HRMS (FAB) m/z [M + H$^+$] calcd for $C_{22}H_{16}F_3O_2$: 369.1102; found: 3369.1100.

10-(4-(Trifluoromethyl)phenyl)anthracene-9-carbaldehyde (3a). To a CH_2Cl_2 solution of **3** (0.10 g, 0.27 mmol, 1 equiv, in 5 mL) was added boron trifluoride etherate (0.14 mL, 0.54 mmol, 2 equiv) at room temperature, and the reaction was stirred for 0.5 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution and diluted with CH_2Cl_2. The organic portion was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by flash chromatography (hex/CH_2Cl_2 = 4:1) to give **3a** (67 mg, 70%).

IR (KBr, cast) ν (cm^{-1}) 1678, 1616, 1327, 1169, 1121, 1068, 837, 621; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.58 (s, 1H), 9.00 (d, J = 9.0 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.69−7.66 (m, 2 H), 7.60 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.46−7.43 (m, 2H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 193.4, 143.1, 142.2, 131.4, 131.1, 130.4 (q, J = 32.6 Hz), 129.6, 128.7, 127.4, 126.0, 125.8, 125.3 (q, J = 3.6 Hz), 124.2 (q, J = 317.8 Hz), 123.6; HRMS (EI) m/z [M + H$^+$] calcd for $C_{22}H_{14}F_3O$: 351.0997; found: 351.0989.

6-((Triisopropylsilyl)ethynyl)-1a,10b-dihydro-6*H*-dibenzo[3,4:6,7]cyclohepta [1,2-b]oxiren-6-ol (4). To a solution of TIPS acetylene (0.33 mL, 3.636 mmol, 3 equiv) in THF (25 mL) was added 2.5 M *n*-BuLi (1.45 mL, 3.6 mmol, 3 equiv) at 0 °C and the mixture was stirred for 1 h. To the reaction mixture was added **1** (0.27 g, 1.2 mmol, 1 equiv, in 2 mL solution). The reaction was warmed back to room temperature and stirred for 3 h. The reaction was quenched

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with water and concentrated. The residue was diluted with CH_2Cl_2, and the solution was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by flash chromatography (hex/CH_2Cl_2 = 2:1) to give **4** (0.37 g, 77%).

IR (KBr, cast) ν (cm^{-1}) 2944, 2863, 1650, 1466, 1169, 880, 748, 677; ^1H NMR (500 MHz, acetone-d_6) δ (ppm) 7.85 (m, 2H), 7.58−7.56 (m, 2H), 7.32−7.26 (m, 4H), 6.16 (s, 1H), 4.54 (s, 2H), 1.07−1.06 (m, 21H); ^{13}C {^1H} NMR (125 MHz, acetone-d_6) δ 145.8, 132.9, 129.1, 128.9, 123.8, 112.8, 86.0, 70.6, 58.9, 19.1, 12.2; HRMS (FAB) m/z [M + H^+] calcd for $C_{26}H_{33}O_2Si$: 405.2250; found: 405.2250.

10-((Triisopropylsilyl)ethynyl)anthracene-9-carbaldehyde (4a). To a CH_2Cl_2 solution of **4** (0.15 g, 0.37 mmol in 5 mL, 1 equiv) was added boron trifluoride etherate (0.19 mL, 0.75 mmol, 2 equiv) at room temperature, and the reaction was stirred for 0.5 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution and diluted with CH_2Cl_2. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The crude compound was purified by flash column chromatography (hex/CH_2Cl_2 = 2:1) to give **4a** (84 mg, 59%).

IR (KBr, cast) ν (cm^{-1}) 2946, 2863, 2137, 1681, 1463, 1263, 1078, 882; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.48 (s, 1H), 8.93−8.91 (m, 2H), 8.75−8.73 (m, 2H), 7.70−7.67 (m, 2H), 7.65−7.62 (m, 2H), 1.29−1.27 (m, 21H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 193.04, 132.27, 131.16, 128.89, 127.73, 126.72, 125.68, 125.194, 123.84, 108.05, 102.83, 18.84, 11.46; HRMS (FAB) m/z [M + H^+] calcd for $C_{26}H_{31}OSi$: 387.2144; found: 387.2141.

6-Butyl-1a,10b-dihydro-6*H*-dibenzo[3,4:6,7]-cyclohepta[1,2-*b*]oxiren-6-ol (5). To a THF solution of **1** (0.27 g, 1.2 mmol in 25 mL, 1 equiv) was added 2.5 M *n*-BuLi (0.48 mL, 1.2 mmol, 1 equiv) at −78 °C. The reaction was warmed to room temperature and stirred for 2 h. The mixture was quenched by water, and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and the solution was washed with saturated aqueous NH_4Cl and brine. The solution was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 2:1) to give **5** (0.10 g, 30%).

IR (KBr, cast) ν (cm^{-1}) 2963, 2858, 1464, 1375, 1174, 976, 909, 758; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.76−7.73 (m, 2H), 7.60−7.57 (m, 2H), 7.29−7.26 (m, 4H), 4.50 (s, 2H), 2.44−2.41 (m, 2H), 2.29 (s, 1H), 1.31−1.25 (m, 2 H), 1.23−1.17 (m, 2 H), 0.85 (t, 3 H, J = 7.3 Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 145.8, 132.4, 130.5, 128.4, 127.5, 123.9, 57.7, 46.1, 26.3, 22.8, 13.9; HRMS (EI) m/z [M^+] calcd for $C_{19}H_{20}O_2$: 280.1463; found: 280.1458.

10-Butylanthracene-9-carbaldehyde (5a). To a CH_2Cl_2 solution of **5** (0.04 g, 0.14 mmol in 5 mL, 1 equiv) was added boron trifluoride etherate (0.072 mL, 0.28 mmol, 2 equiv) at room temperature, and the reaction was stirred for 0.5 h. The mixture was diluted before being extracted with saturated aqueous $NaHCO_3$ solution. The organic portions were further washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 4:1) to give **5a** (27 mg, 72%).

IR (KBr, cast) ν (cm^{-1}) 2960, 2874, 1737, 1673, 1595, 1292, 932, 762. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 11.50 (s, 1H), 8.99 (d, J = 8.2 Hz, 2H), 8.37 (d, J = 8.2 Hz, 2H), 7.66 (t, J = 8.2 Hz, 2H), 7.58 (t, J = 8.2 Hz, 2H), 3.68 (t, J = 8.1 Hz, 2H), 1.86−1.81 (m, 2H), 1.67−1.61 (m, 2H), 1.05 (t, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.5, 145.0, 131,8, 129.1, 128.3,125.7, 125.2, 124.2, 124.1, 33.6, 28.8, 23.5, 14.0; HRMS (EI) m/z [M^+] calcd for $C_{19}H_{18}O$: 262.1358; found: 262.1357.

General Procedure for the Reaction of Polycyclic Aryl Lithium and Dibenzocycloheptanone Epoxides (1). Aryl bromide was dissolved in THF (∼1.0 g/20 mL), and to this solution was added 1 equiv of *n*-BuLi dropwise at −78 °C. A THF solution of **1** (0.5 equiv, 1.0 g/40 mL) was added after 1 h. The reaction was then warmed to room temperature and stirred overnight. The reaction was quenched with ammonia chloride solution and extracted with EtOAc. The combined organic portions were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude product was purified by column chromatography to give the desired product.

General Procedure for the BF_3·OEt_2-Catalyzed Rearrangement of Aryl Dibenzocycloheptanol Epoxides (6−17). To a CH_2Cl_2 solution of aryl dibenzocycloheptanol epoxides (**6**−**17**, 0.1 g/5 mL) was added BF_3·OEt_2 (2 equiv) at room temperature or −78 °C. The reaction was diluted and quenched with saturated $NaHCO_3$ solution after 30 min. The organics layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product(s) was purified by flash column chromatography to give various products.

*6-(Naphthalen-1-yl)-1a,10b-dihydro-6H-dibenzo[3,4:6,7]-cyclohepta[1,2-b]oxiren-6-ol (**6**).* 65%, ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.13(brs, 1H), 7.97 (brs, 1H), 7.81 (dd, J = 8.0, 3.4 Hz, 2 H), 7.78 (d, J = 8.8 Hz, 1H), 7.51 (brs, 2H), 7.40−7.32 (m, 5H), 7.29 (brs, 2H), 7.14 (t, J =7.4 Hz, 1H), 3.68 (brs, 1H), 3.21 (brs, 1H), 2.64 (s, 1H); ^{13}C {^1H} NMR (150 MHz, $CDCl_3$) δ 147.5, 146.9, 143.2, 135.2, 131.6, 130.4, 130.1, 129.1, 128.7, 128.0, 126.9, 126.0, 125.7, 125.7, 124.8, 123.5, 79.8, 58.3, 55.5 (The extra signal is due to rotamers.); HRMS (FAB): m/z [M^+] calcd for $C_{25}H_{18}O_2$: 350.1307; found: 350.1306.

*10-(Naphthalen-1-yl)anthracene-9-carbaldehyde (**6a**).* ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.63 (s, 1H), 9.03 (d, J = 9.0 Hz, 2H), 8.07 (d, J = 8.3 Hz, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.68 (m, 1H), 7.64 (dd, J = 6.5, 1.3 Hz, 1H), 7.63 (dd, J = 6.5, 1.3 Hz, 1H), 7.50−7.44 (m, 4H), 7.30 (dd, J = 6.5, 1.0 Hz, 1H), 7.28 (dd, J = 6.5, 1.0 Hz, 1H), 7.22−7.17 (m, 1H), 6.97 (d, J = 8.5 Hz, 1H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 193.7, 143.9, 135.9, 133.7, 133.1, 131.8, 130.8, 128.9, 128.8, 128.5, 128.2, 126.8, 126.4, 125.9, 125.6, 123.7 (3 signals missing); HRMS (FAB): m/z [M^+] calcd for $C_{25}H_{17}O$ = 333.1279, found: 333.1274.

*10,15b-Dihydro-11H-benzo[a]benzo[4,5]cyclohepta-[1,2,3-jk]fluoren-11-one (**6b**).* ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.05−7.95 (m, 5H), 7.77 (d, J = 8.1 Hz, 1H), 7.54−7.45 (m, 3H), 7.39 (d, J = 7.5 Hz, 1H), 7.16 (t, J = 7.4 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 7.7 Hz, 1H), 5.96 (s, 1H), 4.88 (d, J = 14.3 Hz, 1H), 4.13 (d, J = 14.3 Hz, 1H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 193.7, 149.0, 141.1, 139.0, 138.7, 138.4, 134.0, 133.7, 131.5, 130.9, 130.0, 129.6, 129.3, 128.3, 127.4, 127.3, 126.9, 126.9, 126.2, 125.9, 125.7, 124.6, 119.0, 51.6, 51.5; HRMS (ESI) m/z [M+Na^+] calcd for $C_{25}H_{16}ONa$: 355.1093; found: 355.1091.

*5-(Naphthalen-1-yl)-5,11-dihydro-10H-5,10-epoxydibenzo[a,d][7]annulen-10-ol (**6c**).* ^1H NMR (600 MHz, $CDCl_3$): δ 8.28 (dd, J = 7.2, 1.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.53−7.46 (m, 3H), 7.38 (td, J = 7.5, 1.2 Hz, 1H), 7.34 (td, J =

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7.5, 1.2 Hz, 1H), 7.29 (td, J = 7.5, 1.2 Hz, 1H), 7.21 (td, J = 7.5, 1.2 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 7.04 (td, J = 7.5, 1.2 Hz, 1H), 6.82 (t, J = 7.5 Hz, 1H), 6.57 (d, J = 7.5 Hz, 1H), 3.69 (1H, d, J = 16.3 Hz), 3.51 (1H, s), 3.04 (1H, d, J = 16.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.6, 142.9, 141.1, 135.3, 132.9, 132.8, 131.9, 130.4, 130.0, 129.1, 128.6, 128.5, 127.8, 126.9, 126.8, 126.5, 125.7, 125.7, 124.6, 124.0, 122.8, 121.6, 104.5, 89.3, 39.2; HRMS (FAB): m/z [M^+] calcd for $C_{25}H_{19}O_2$: 351.1385, found: 351.1382.

*6-(Naphthalen-2-yl)-1a,10b-dihydro-6H-dibenzo[3,4:6,7]-cyclohepta[1,2-b]oxiren-6-ol (**7**).* 82%, ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.99 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.6 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.55 (s, 1H), 7.52 (dd, J = 7.3, 1.2 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.37 (td, J = 7.5, 1.5 Hz, 2H), 7.34 (td, J = 7.5, 1.5 Hz, 2H), 7.20 (dd, J = 8.6, 1.5 Hz, 1H), 3.61 (2H, s), 2.23 (1H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 145.6, 133.4, 132.9, 131.9, 131.4, 129.2, 128.5, 128.5, 128.2, 127.8, 126.8, 126.6, 125.7, 125.0, 124.4, 79.2, 57.3; HRMS (FAB): m/z [M^+] calcd for $C_{25}H_{18}O_2$: 350.1307; found: 350.1297.

*10-(Naphthalen-2-yl)anthracene-9-carbaldehyde (**7a**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 11.60 (s, 1H), 9.02 (d, J = 8.9 Hz, 2H), 8.06 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 7.4 Hz, 1H), 7.91−7.86 (m, 2H), 7.71 (d, J = 8.9 Hz, 2H), 7.65 (td, J = 7.5, 1.2 Hz, 2H), 7.60 (td, J = 7.2, 1.5 Hz, 2H), 7.49 (dd, J = 8.2, 1.6 Hz, 1H), 7.38 (dd, J = 6.7, 0.8 Hz, 1H), 7.36 (dd, J = 6.4, 0.9 Hz, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$) δ 193.5, 145.5, 135.8, 133.3, 133.0, 131.8, 130.2, 129.8, 128.8, 128.7, 128.2, 128.1, 126.9, 126.7, 125.7, 125.3, 123.6 (missing two signals); HRMS (FAB): m/z [M + H^+] calcd for $C_{25}H_{17}O$: 333.1279; found: 333.1278.

*8,13b-Dihydro-9H-benzo[c]benzo[4,5]cyclohepta[1,2,3-jk]fluoren-9-one (**7b**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.71 (d, J = 8.4 Hz, 1H), 8.48 (d, J = 7.7 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 8.0 (d, J = 7.7 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.68 (t, J = 7.1 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.53 (t, J =7.8 Hz, 1H), 7.38 (d, J = 7.4 Hz, 1H), 7.21−7.16 (m, 1H), 7.05 (m, 2H), 5.66 (s, 1H), 4.71 (d, J = 14.2 Hz, 1H), 4.07 (d, J = 14.3 Hz, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 193.8, 149.2, 141.6, 141.6, 138.5, 136.0, 134.0, 132.9, 130.1, 129.8, 129.6, 128.8, 128.4, 127.6, 127.5, 127.4, 127.3, 126.4, 126.0, 124.9, 124.1, 123.7, 52.2, 51.5 (one signal missing); HRMS (FAB): m/z [M^+] calcd for $C_{25}H_{16}O$: 332.1201; found: 332.1207.

*6-(Anthracen-9-yl)-1a,10b-dihydro-6H-dibenzo[3,4:6,7]-cyclohepta[1,2-b]oxiren-6-ol (**8**).* (71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.45 (s, 1H), 8.15 (d, J = 8.1 Hz, 2H), 7.91 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H), 7.35 (t, J = 8.1 Hz, 2H), 7.27 (t, J = 8.1 Hz, 2H), 7.15 (t, J = 8.1 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 6.92 (t, J = 8.1 Hz, 2H), 3.43 (s, 1H), 2.26 (s, 2H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 150.9, 138.0, 132.1, 131.3, 130.2, 130.0, 129.7, 128.7, 128.6, 127.5, 125.6, 124.7, 124.2, 122.1, 79.9, 55.8; HRMS (FAB): m/z [M^+] calcd for $C_{29}H_{20}O_2$: 400.1463; found: 400.1468.

*[9,9′-Bianthracene]-10-carbaldehyde (**8a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 11.70 (s, 1H), 9.07 (d, J = 9.0 Hz, 2H), 8.70 (s, 1H), 8.15 (d, J = 8.6 Hz, 2H), 7.64 (dd, J = 6.0, 1.7 Hz, 1H), 7.62 (dd, J = 6.0, 1.7 Hz, 1H), 7.47−7.42 (m, 2H), 7.21−7.12 (m, 6H), 6.99 (d, J = 9.0 Hz, 2H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 193.8, 142.5, 132.2, 131.8, 131.5, 131.4, 131.4, 129.0, 128.1, 128.1, 128.0, 126.5, 126.4, 126.2, 125.9, 125.6, 123.9; HRMS (FAB): m/z [M + H^+] calcd for $C_{29}H_{19}O$: 383.1436; found: 383.1437.

*10-(Anthracen-9-yl)-5H-dibenzo[a,d][7]annulen-5-one (**8b**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.55 (s, 1H), 8.17 (t, J = 8.4 Hz, 2H), 8.06 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.47−7.42 (m, 3H), 7.35 (t, J = 8.4 Hz, 2H), 7.23 (s, 1H), 7.19 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 7.5 Hz, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$) δ 195.4, 140.0, 139.3, 138.8, 137.3, 136.5, 135.0, 134.5, 132.1, 131.9, 131.7, 130.8, 130.4, 129.8, 129.8, 129.2, 129.1, 128.7, 127.4, 126.5, 126.4, 125.5 (1 signal missing); HRMS (FAB): m/z [M + H^+] calcd for $C_{29}H_{19}O$: 383.1436; found: 383.1437.

*10-(Anthracen-9-yl)-11-hydroxy-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (**8c**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.50 (s, 1H), 8.41 (brs, 1H), 8.16 (dd, J = 8.1, 1.5 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 7.0 Hz, 1H), 7.63 (dd, J = 7.0, 1.1 Hz, 1H), 7.59 (brs, 1H), 7.54 (d, J = 6.6 Hz, 1H), 7.49−7.42 (m, 1H), 7.42−7.36 (m, 3H), 7.30 (brs, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.09 (td, J = 8.1, 1.5 Hz, 1H), 7.02 (brs, 1H), 6.66 (d, J = 7.9 Hz, 1H), 6.21 (d, J = 8.6 Hz, 1H), 5.93 (dd, J = 8.6, 2.2 Hz, 1H), 1.82 (d, J = 2.2 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.4, 142.9, 140.7, 139.3, 136.6, 133.0, 131.8, 131.7, 131.1, 130.3, 129.7, 129.5, 128.8, 128.1, 127.4, 127.3, 127.3, 126.6, 125.6, 125.4, 125.2, 124.8, 123.7, 123.6, 123.5, 73.1, 52.1 (Some extra signals are due to the presence of rotamers.); HRMS (FAB): m/z [M^+] calcd for $C_{29}H_{20}O_2$: 400.1463; found: 400.1457.

*6-(Pyren-1-yl)-1a,10b-dihydro-6H-dibenzo[3,4:6,7]-cyclohepta[1,2-b]oxiren-6-ol (**9**).* (55%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.23 (brs, 1H), 8.16 (d, J = 7.5 Hz, 1H), 8.07 (d, J = 8.8 Hz, 2H), 8.05−7.99 (m, 3H), 7.97 (m, 2H), 7.88 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 9.5 Hz, 1H), 7.53 (brs, 1H), 7.46−7.38 (m, 2H), 7.29 (brs, 3H), 3.57 (brs, 1H), 3.0 (brs, 1H), 2.83 (s, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 140.8, 131.7, 131.3, 130.3, 128.7, 128.4, 128.3, 128.0, 127.2, 126.4, 126.3, 126.1, 125.6, 125.4, 124.7, 124.5, 124.4, 123.5, 80.1, 58.0, 55.7 (lack 3 signals, due to the signal overlapping); HRMS (FAB): m/z [M^+] calcd for $C_{31}H_{20}O_2$: 424.1463; found: 424.1458.

*10-(Pyren-1-yl)anthracene-9-carbaldehyde (**9a**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 11.68 (1H, s), 9.08 (d, J = 9.1 Hz, 2H), 8.38 (d, J = 7.7 Hz, 1H), 8.26 (d, J = 7.6 Hz, 1H), 8.22 (m, 2H), 8.12 (d, J = 7.6 Hz, 1H), 8.02 (t, J = 7.6 Hz, 1H), 7.97 (d, J = 7.7 Hz, 1H), 7.80 (d, J = 9.2 Hz, 1H), 7.67−7.62 (m, 2H), 7.41 (d, J = 8.9 Hz, 2H), 7.28−7.20 (m, 3H, overlapping with $CHCl_3$ signal); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 193.7, 144.3, 133.1, 131.8, 131.6, 131.5, 131.1, 131.1, 130.5, 129.0, 128.8, 128.4, 128.3, 128.25, 128.18, 127.5, 126.5, 126.0, 125.9, 125.7, 125.4, 124.9, 124.8, 123.8, 123.7; HRMS (FAB): m/z [M + H^+] calcd for $C_{31}H_{19}O$: 407.1436; found: 407.1437.

*10-(Pyren-1-yl)-5H-dibenzo[a,d][7]annulen-5-one (**9b**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.26 (d, J = 7.6 Hz, 1H), 8.21 (d, J = 7.6 Hz, 1H), 8.15−8.11 (m, 4H), 8.05 (d, J = 7.6 Hz, 1H), 8.0 (t, J = 7.6 Hz, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.87 (d, J = 9.3 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.60−7.55 (m, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.36 (s, 1H), 7.23 (m, 2H), 6.92 (d, J = 8.1 Hz, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 195.6, 141.5, 140.2, 139.3, 138.8, 136.8, 134.5, 134.1, 132.0, 131.5, 131.5, 131.2, 131.0, 130.8, 130.4, 129.5, 129.1, 129.1, 129.0, 128.1, 128.1, 127.9, 127.5, 126.4, 125.6, 125.4, 125.3,

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125.1, 125.0, 124.9 (one signal missing); HRMS (FAB): m/z [M + H$^+$] calcd for $C_{31}H_{19}O$: 407.1436; found: 407.1445.

*10-Hydroxy-11-(pyren-1-yl)-10,11-dihydro-5H-dibenzo-[a,d][7]annulen-5-one (**9c**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.61 (d, J = 9.3 Hz, 1H), 8.28−8.22 (m, 3H), 8.19 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.87 (d, J = 8.6 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.41−7.36 (m, 2H), 7.25 (t, J = 7.5 Hz, 1H), 7.11−7.08 (m, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.24 (d, J = 7.4 Hz, 1H), 6.18 (d, J = 5.7 Hz, 1H), 5.48 (d, J = 5.7 Hz, 1H), 2.76 (brs, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 197.2, 140.6, 140.2, 139.2, 138.1, 134.6, 133.4, 133.3, 131.5, 130.9, 130.8, 130.2, 130.0, 129.0, 128.7, 128.6, 128.6, 128.2, 127.6, 127.5, 127.1, 126.2, 125.7, 125.3, 125.1, 124.9, 124.80, 122.2, 76.8, 52.9; HRMS (FAB): m/z [M$^+$] calcd for $C_{31}H_{20}O_2$: 424.1463; found: 424.1458.

*5-(Pyren-1-yl)-5,11-dihydro-10H-5,10-epoxydibenzo[a,d]-[7]annulen-10-ol (**9d**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.77 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 7.5 Hz, 1H), 8.16 (d, J = 9.4 Hz, 1H), 8.12−8.09 (m, 3H), 7.98 (t, J = 7.6 Hz, 1H), 7.83 (d, J = 9.4 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.37 (td, J = 7.6, 1.0 Hz, 1H), 7.26 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.77 (t, J = 7.6 Hz, 1H), 6.50 (d, J = 7.6 Hz, 1H), 3.87 (brs, 1H), 3.75 (d, J = 16.4 Hz, 1H), 3.06 (d, J = 16.4 Hz, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 147.6, 143.6, 141.1, 132.9, 132.3, 131.3, 130.6, 130.4, 130.1, 129.1, 128.3, 127.9, 127.4, 127.4, 127.0, 126.9, 126.5, 126.3, 126.2, 125.7, 125.4, 124.7, 124.2, 124.1, 122.9, 121.6, 104.8, 89.7, 39.3; HRMS (FAB): m/z [M + H$^+$] calcd for $C_{31}H_{20}O_2$: 424.1463; found: 424.1462.

*6-(Phenanthren-9-yl)-1a,10b-dihydro-6H-dibenzo-[3,4:6,7]cyclohepta[1,2-b]oxiren-6-ol (**10**).* (74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.68 (d, J = 8.2 Hz, 1H), 8.63 (d, J = 8.6 Hz, 1H), 8.16 (brs, 1H), 8.0 (d, J = 8.4 Hz, 2H), 7.69−7.60 (m, 3H), 7.53 (m, 3H), 7.38 (m, 3 Hz), 7.30−7.19 (3H, m), 3.68 (1H, brs), 3.23 (1H, brs), 2.89 (1H, s); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.2, 146.7, 141.3, 131.9, 131.6, 130.7, 130.4, 129.3, 129.2, 128.7, 128.3, 128.1, 127.7, 127.0, 126.9, 126.4, 126.1, 123.6, 123.2, 122.4, 79.8, 58.1, 55.2 (The two broad signals at 58.12 and 55.20 are due to rotamers); HRMS (FAB): m/z [M$^+$] calcd for $C_{29}H_{20}O_2$: 400.1463; found: 400.1468.

*9-(Anthracen-9-yl)phenanthrene (**10a**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.85 (d, J = 8.5 Hz, 2H), 8.59 (s, 1H), 8.09 (2d, J = 8.6 Hz, 2H), 7.89 (d, J = 7.7 Hz, 1H), 7.80 (s, 1H), 7.75 (t, J = 7.7 Hz, 1H), 7.66 (t, J = 7.4 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 8.9 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.27 (t, J = 7.5 Hz, 1H), 7.22 (t, J = 7.5 Hz, 2H), 7.12(d, J = 8.2 Hz, 1H) The spectrum is identical with the reported values; HRMS (FAB): m/z [M$^+$] calcd for $C_{28}H_{18}$: 354.1409; found: 354.1404.

*10-(Phenanthren-9-yl)anthracene-9-carbaldehyde (**10b**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 11.65 (s, 1H), 9.04 (d, J = 9.0 Hz, 2H), 8.86 (d, J = 8.3, 3.6 Hz, 2H), 7.90 (d, J = 7.7 Hz, 1H), 7.78 (t, J = 7.8 Hz, 1H), 7.77 (1H, s), 7.69 (d, J = 7.8 Hz, 1H), 7.67−7.62 (m, 3H), 7.61 (d, J = 8.9 Hz, 2H), 7.31−7.26 (m, 3H), 7.04 (d, J = 8.2 Hz, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 193.7, 143.8, 134.6, 132.2, 131.8, 131.5, 130.8, 130.6, 130.6, 129.7, 129.0, 128.9, 128.2, 127.42, 127.4, 127.3, 127.2, 127.1, 126.0, 125.7, 123.8, 123.1, 122.9; HRMS (FAB) m/z [M + H$^+$] calcd for $C_{29}H_{19}O$: 383.1436; found: 383.1442.

*12,17b-Dihydro-13H-dibenzo[3,4:7,8]azuleno[1,2-l]-phenanthren-13-one (**10c**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.90−8.85 (m, 1H), 8.83−8.80 (m, 1H), 8.79 (d, J = 8.3 Hz, 1H), 8.50 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.80−7.75 (m, 2H), 7.74 (d, J = 8.3 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.53 (m, 2H), 7.38 (d, J = 7.4 Hz, 1H), 7.14 (t, J = 7.4 Hz, 1H), 6.89 (t, J = 7.8 Hz, 1H), 6.58 (d, J =7.8 Hz, 1H), 5.86 (s, 1H), 4.84 (d, J = 14.5 Hz, 1H), 4.14 (d, J = 14.5 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 193.8, 149.9, 141.7, 139.4, 138.8, 135.1, 134.0, 131.6, 131.2, 130.7, 129.9, 129.1, 128.9, 128.4, 127.6, 127.4, 127.4, 127.1, 127.0, 126.8, 126.7, 126.4, 126.4, 124.5, 124.0, 123.6, 51.6, 51.5; HRMS (FAB) m/z [M + H]$^+$ calcd for $C_{29}H_{18}O$: 383.1436; found: 383.1434.

*5-(Phenanthren-9-yl)-5,11-dihydro-10H-5,10-epoxydibenzo[a,d][7]annulen-10-ol (**10d**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.76−8.66 (m, 2H), 8.56 (s, 1H), 8.0 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.55 (m, 2H), 7.44 (d, J = 7.3 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.7 Hz, 1H), 7.27 (d, J = 7.4 Hz, 1H), 7.10−6.99 (m, 2H), 6.80 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 7.8 Hz, 1H), 3.70 (d, J = 16.3 Hz, 1H), 3.65 (s, 1H), 3.04 (d, J = 16.4 Hz, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 147.4, 142.6, 141.0, 132.8, 132.0, 131.3, 131.2, 130.9, 130.2, 130.1, 129.6, 129.4, 129.1, 128.7, 127.9, 127.7, 127.0, 126.9, 126.5, 126.4, 126.1, 123.9, 122.9, 122.8, 122.6, 121.6, 104.7, 89.2, 39.2; HRMS (FAB) m/z [M$^+$] calcd for $C_{29}H_{20}O_2$: 400.1463; found: 400.1464.

*10-Hydroxy-11-(phenanthren-9-yl)-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (**10e**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.76 (d, J = 9.4 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.43 (d, J = 8.0 Hz, 1H), 8.25−8.21 (m, 1H), 7.77−7.70 (m, 2H), 7.68 (d, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.40−7.33 (m, 3H), 7.27 (d, J = 8.2 Hz, 1H), 7.20 (td, J = 7.5, 1.1 Hz, 1H), 7.13−7.10 (m, 1H), 6.93 (td, J = 7.5, 1.0 Hz, 1H), 6.61 (s, 1H), 6.40 (d, J = 7.4 Hz, 1H), 5.89 (d, J = 5.6 Hz, 1H), 5.48 (d, J = 5.6 Hz, 1H), 2.74 (brs, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 197.1, 140.5, 139.8, 139.4, 138.0, 135.3, 133.3, 131.3, 131.1, 130.8, 130.5, 130.1, 129.9, 129.6, 129.0, 128.6, 128.6, 127.5, 127.5, 127.1, 126.8, 126.7, 126.7, 126.6, 123.8, 123.4, 123.3, 75.9, 52.9; HRMS (FAB) m/z [M$^+$] calcd for $C_{29}H_{20}O_2$: 400.1463; found: 400.1461.

*14,15-Dihydro-9H-9,15-[1,2]benzenobenzo[4,5]-cyclohepta[1,2-l]phenanthrene-9,14-diol (**10f**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.44 (d, J = 7.5 Hz, 1H), 8.73−8.65 (m, 2H), 8.51 (d, J = 8.3 Hz, 1H), 8.19 (d, J = 7.7 Hz, 1H), 7.83 (d, J = 6.8 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.61−7.51 (m, 3H), 7.35−7.28 (m, 3H), 7.22 (m, 1H), 7.13 (t, J = 7.5 Hz, 1H), 5.43 (d, J = 3.4 Hz, 1H), 4.88 (dd, J = 11.0, 3.4 Hz, 1H), 3.06 (1H, s), 1.92 (d, J = 11.0 Hz, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 148.8, 141.6, 141.1, 136.6, 133.3, 132.4, 131.2, 130.7, 130.6, 129.1, 128.6, 128.5, 127.9, 127.7, 127.6, 127.5, 127.3, 126.9, 126.6, 126.2, 126.2, 123.5, 123.4, 123.4, 121.8, 121.2, 77.5, 69.7, 47.5; HRMS (FAB) m/z [M$^+$] calcd for $C_{29}H_{20}O_2$: 400.1463; found: 400.1457

*15-Hydroxy-14,14a-dihydro-9H-8b,14-([1,2]-benzenomethano)benzo[f]tetraphen-9-one (**10g**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.20 (d, J = 7.7 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.76 (m, 2H), 7.71 (d, J = 7.7 Hz, 1H), 7.62−7.54 (m, 2H), 7.52−7.37 (m, 3H), 7.37−7.25 (m, 3H), 7.16 (d, J = 7.6 Hz, 1H), 7.08−6.96 (m, 2H), 5.35−5.25 (m, 1H), 4.57−4.49 (brs, 1H), 4.17 (s, 1H), 1.40 (d, J = 11.7, 1H);

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^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 196.5, 139.8, 137.3, 136.1, 134.8, 134.7, 134.0, 133.8, 133.4, 131.9, 131.0, 130.2, 129.4, 128.8, 128.7, 128.5, 128.2, 128.1 (×2), 127.7, 127.6, 127.5, 125.6, 125.2, 124.3, 65.9, 51.6, 43.8, 41.1; HRMS (FAB) m/z [M^+] calcd for $C_{29}H_{20}O_2$: 400.1463; found: 400.1463.

*6-(Thiophen-2-yl)-1a,10b-dihydro-6H-dibenzo[3,4:6,7]-cyclohepta[1,2-b]oxiren-6-ol (**11**).* Thiophene (340 mg, 4.05 mmol) was dissolved in THF (10 mL) at −78 °C. *n*-BuLi (1.6 M, 2.53 mL, 4.05 mmol) was slowly added under N_2 at −78 °C. The reaction mixture was stirred for 1 h at −78 °C before a THF solution of **1** (450 mg, 2.03 mmol in 10 mL) was added. The mixture was then stirred for 3 h at room temperature before being quenched with NH_4Cl solution and extracted with EtOAc. The combined organic portions were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography to give the desired product **11** (455 mg, 74%).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.94−7.90 (m, 2H), 7.55−7.50 (m, 2H), 7.32−7.30 (m, 4H), 7.26 (dd, J = 5.1, 1.2 Hz, 1H), 6.91 (dd, J = 5.1, 3.6 Hz, 1H), 6.72 (dd, J = 3.6, 1.2 Hz, 1H), 3.89 (s, 2H), 2.35 (s, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 155.7, 145.7, 132.0, 131.9, 128.5, 128.3, 127.1, 126.6, 125.9, 123.9, 75.1, 57.5; HRMS (EI) m/z [M^+] calcd for $C_{19}H_{14}O_2S$: 306.0715; found: 306.0708.

*10-(Thiophen-2-yl)anthracene-9-carbaldehyde (**11a**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 11.55 (s, 1H), 8.93 (d, J = 8.9 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H), 7.68−7.61 (m, 3H), 7.46 (t, J = 8.2 Hz, 2H), 7.31 (dd, J = 5.0, 2.7 Hz, 1H), 7.19 (d, J = 2.7 Hz, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 193.7, 138.1, 137.4, 131.7, 131.4, 129.9, 128.8, 127.8, 127.4, 126.4, 126.1, 123.6 (one signal missing); HRMS (FAB) m/z [$M + H^+$] calcd for $C_{19}H_{13}OS$: 289.0687; found: 289.0692.

*10-Hydroxy-11-(thiophen-2-yl)-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (**11b**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.07 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.35−7.30 (m, 2H), 7.28 (d, J = 7.6 Hz, 1H), 7.06−7.01 (m, 2H), 6.71 (dd, J = 5.1, 3.6 Hz, 1H), 6.40 (d, J = 3.5 Hz, 1H), 5.29−5.26 (m, 1H), 5.16 (d, J = 5.8 Hz, 1H), 2.47 (brs, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 195.6, 143.9, 139.1, 138.9, 138.2, 137.6, 132.9, 132.7, 131.7, 130.3, 129.7, 129.4, 128.8, 127.6, 126.5, 126.1, 124.9, 77.8, 52.2; HRMS (EI) m/z [M^+] calcd for $C_{19}H_{14}O_2S$: 306.0715; found: 306.0713.

*6-(Thiophen-3-yl)-1a,10b-dihydro-6H-dibenzo[3,4:6,7]-cyclohepta[1,2-b]oxiren-6-ol (**12**).* 3-Bromothiophene (403 mg, 2.48 mmol) was dissolved in diethyl ether (5 mL) at −78 °C. *n*-BuLi (2.5 M, 1 mL, 2.61 mmol) were slowly added. The reaction mixture was stirred for 1 h at −78 °C. A THF solution of **1** (500 mg, 2.25 mmol in 5 mL) was transferred into the reaction. The mixture was stirred overnight at room temperature. It was then quenched with ammonia chloride solution and extracted with EtOAc. The combined organic portions were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude product was purified by column chromatography to give **12** (490 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98−7.94 (m, 2H), 7.56−7.53 (m, 2H), 7.37−7.31 (m, 4H), 7.30−7.27 (m, 1H), 6.98−6.95 (m, 1H), 6.78−6.75 (m, 1H), 3.83 (s, 2H), 2.37 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.0, 145.9, 131.9, 131.5, 128.3, 128.1, 127.0, 126.9, 123.7, 123.1, 75.2, 57.3; HRMS (EI) m/z [$M]^+$ calcd for $C_{19}H_{14}O_2S$: 306.0715, found: 306.0708.

12 (100 mg, 0.33 mmol) was dissolved in CH_2Cl_2 (5 mL), then $BF_3{\cdot}OEt_2$ (93 mg, 0.65 mmol) was added at different temperatures (room temperature or −78 °C). The reaction mixture was stirred for 30 min before being quenched with saturated $NaHCO_3$ solution. The mixture was then extracted with CH_2Cl_2. The combined organic portions were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude mixture was purified by column chromatography to give **12a**, **12b**, and **12c**.

*10-(Thiophen-3-yl)anthracene-9-carbaldehyde (**12a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.54 (s, 1H), 8.97 (d, J = 9.0 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.67−7.61 (m, 2H), 7.60 (dd, J = 4.9, 3.0 Hz, 1H), 7.45−7.40 (m, 2H), 7.38 (dd, J = 3.0, 1.3 Hz, 1H), 7.19 (dd, J = 4.9, 1.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.6, 140.8, 138.0, 131.7, 130.6, 130.6, 128.8, 128.0, 126.1, 125.8, 125.6, 125.4,123.6; HRMS (EI) m/z [$M]^+$ calcd for $C_{19}H_{12}OS$: 288.0609, found: 288.0606.

*10,11-Dihydro-5H-5,10-[2,3]thiophenodibenzo[a,d][7]-annulene-5,11-diol (**12b**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85−7.80 (m, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.33 (dd, J = 7.2, 1.0 Hz, 1H), 7.31−7.27 (m, 1H), 7.27−7.23 (m, 1H), 7.20 (td, J = 7.3, 1.2 Hz, 1H), 7.18−7.12 (m, 2H), 7.11 (d, J = 5.0 Hz, 1H), 7.01 (d, J = 5.0 Hz, 1H), 4.82 (dd, J = 11.0, 4.2 Hz, 1H), 4.39 (d, J = 4.2 Hz, 1H), 3.19 (s, 1H), 1.85 (d, J = 11.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 151.3, 148.7, 142.4, 136.4, 134.7, 134.1, 132.7, 128.7, 127.8, 127.6, 127.5, 127., 123.5, 122.3, 121.2, 120.7, 75.3, 70.6, 48.0; HRMS (EI) m/z [$M]^+$ calcd for $C_{19}H_{14}O_2S$: 306.0715, found: 306.0711.

*10-Hydroxy-11-(thiophen-3-yl)-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (**12c**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 7.4 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.33−7.25 (m, 2H), 7.20 (d, J = 7.7 Hz, 1H), 7.06−7.02 (m, 1H), 6.97−6.92 (m, 1H), 6.59 (s, 1H), 6.49−6.45 (m, 1H), 5.22 (s, 1H), 5.0−4.96 (m, 1H), 2.52 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.2, 141.5, 139.4, 139.3, 138.7, 137.9, 133.0, 132.7, 131.7, 130.2, 129.5, 128.9, 128.7, 127.4, 127.4, 125.8, 122.9, 77.2 (merged with $CDCl_3$ signal), 52.71; HRMS (EI) m/z [$M]^+$ calcd for $C_{19}H_{14}O_2S$: 306.0715, found: 306.0712

*6-([2,2′-Bithiophen]-5-yl)-1a,10b-dihydro-6H-dibenzo-[3,4:6,7]cyclohepta[1,2-b]oxiren-6-ol (**13**).* To a THF of bisthiophene (200 mg, 1.20 mmol in 1.5 mL) were added TMEDA (0.2 mL) and *n*-BuLi (2.5 M, 0.48 mL, 1.20 mmol) at −78 °C. The reaction mixture was then stirred for 30 min at room temperature before a THF solution of **1** (220 mg, 0.99 mmol in 1.5 mL) was added. The reaction was stirred at room temperature for 16 h before being quenched with NH_4Cl solution. The mixture was extracted with EtOAc. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography to give **12** (195 mg, 51%).

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.96−7.88 (2H, m), 7.57−7.51 (2H, m), 7.35−7.28 (4H, m), 7.18 (1H, d, J = 5.0 Hz), 7.07 (1H, d, J = 3.2 Hz), 6.97−6.93 (2H, m), 6.60 (1H, d, J = 3.7 Hz), 4.0 (2H, s), 2.48 (1H, s); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 154.1, 145.2, 138.6, 137.0, 132.1, 131.8, 128.7, 128.4, 128.0, 126.5, 124.9, 124.1, 123.9, 123.4, 123.3, 75.3, 57.6; HRMS (FAB) m/z [M^+] calcd for $C_{23}H_{16}O_2S_2$: 388.0592; found: 388.0590.

10-([2,2′-Bithiophen]-5-yl)anthracene-9-carbaldehyde (**13a**; Due to its low yield, **13a** cannot be fully purified. Therefore, its ^{13}C NMR spectrum is not obtained.)

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^{1}H NMR (500 MHz, $CDCl_3$): δ 11.56 (s, 1H), 8.93 (d, J = 9.0 Hz, 2H), 8.04 (dt, J = 8.9, 1.0 Hz, 2H), 7.67 (td, J = 6.5, 1.3 Hz, 2H), 7.50 (td, J = 6.5, 1.1 Hz, 2H), 7.37 (d, J = 3.6 Hz, 1H), 7.30−7.25 (m, 2H), 7.09 (d, J = 3.6 Hz, 1H), 7.07−7.02 (m, 2H).

*10-([2,2′-Bithiophen]-5-yl)-11-hydroxy-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (**13b**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.07 (dd, J = 8.0, 1.2 Hz, 1H), 7.78−7.73 (m, 1H), 7.47 (td, J = 8.0, 1.4 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.34−7.30 (m, 2H), 7.29 (d, J = 7.4 Hz, 1H), 7.11 (dd, J = 5.1, 1.0 Hz, 1H), 7.08−7.04 (m, 1H), 6.96−6.93 (m, 1H), 6.90 (dd, J = 5.0, 3.7 Hz, 1H), 6.76 (d, J = 3.7 Hz, 1H), 6.28 (d, J =3.2 Hz, 1H), 5.23 (d, J = 5.9 Hz, 1H), 5.08 (d, J = 5.9 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 195.8, 143.1, 139.2, 138.9, 138.0, 137.7, 137.3, 137.0, 133.1, 132.9, 131.9, 130.4, 129.8, 129.5, 128.9, 127.8, 127.8, 127.0, 124.4, 123.6, 123.2, 77.6, 52.5; HRMS (EI) m/z [M$^+$] calcd for $C_{23}H_{16}O_2S_2$: 388.0592; found: 388.0589.

*6,6′-([2,2′-Bithiophene]-5,5′-diyl)bis(1a,10b-dihydro-6H-dibenzo[3,4:6,7]cyclohepta [1,2-b]oxiren-6-ol) (**14**).* To a hexane solution of bisthiophene (200 mg, 1.20 mmol in 6 mL) were added TMEDA (0.45 mL, 3.01 mmol) and n-BuLi (2.5 M, 1.15 mL, 1.20 mmol). The mixture was heated was refluxed for 1 h before a THF solution of **1** (670 mg, 3.01 mmol in 6 mL) was added dropwise at room temperature. The reaction was stirred for 16 h at room temperature and quenched with NH_4Cl solution. The mixture was extracted with EtOAc, and the combined organic portions were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography to give **14** (442 mg, 60%).

^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) 7.86−7.82 (m, 4H), 7.49−7.45 (m, 4H), 7.34−7.30 (m, 8H), 7.03 (d, J = 3.8 Hz 2H), 6.68 (s, 2H), 6.42 (d, J = 3.8 Hz, 2H), 3.95 (s, 4H); ^{13}C {^{1}H} NMR (150 MHz, DMSO-d_6): δ 154.2, 146.0, 136.3, 131.9, 131.7, 128.0, 127.8, 127.7, 126.4, 123.1, 73.9, 54.9 (A few extra signals in the ^{13}C spectrum indicates the presence of impurities.); HRMS (FAB) m/z [M + H$^+$] calcd for $C_{38}H_{27}O_4S_2$: 611.1351; found: 611.1353.

*11,11′-([2,2′-Bithiophene]-5,5′-diyl)bis(10-hydroxy-10,11-dihydro-5H-dibenzo [a,d] [7] annulen-5-one) (**14a**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.04 (d, J = 7.7 Hz, 2H), 7.77−7.73 (m, 2H), 7.46 (t, J = 7.4 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.33−7.29 (m, 4H), 7.26−7.23 (m, 2H), 7.09−7.04 (m, 2H), 6.55(d, J = 3.8 Hz, 2H), 6.19 (d, J = 3.8 Hz, 2H), 5.23 (d, J = 5.7 Hz, 2H), 5.03 (d, J = 5.7 Hz, 2H), 2.42 (s, 2H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 195.5, 142.9, 139.0, 138.8, 137.9, 137.7, 136.7, 133.0, 132.7, 132.0, 130.4, 129.9, 129.6, 129.0, 127.9, 126.9, 122.9, 77.6, 52.5; HRMS (FAB) m/z [M + H$^+$] calcd for $C_{38}H_{27}O_4S_2$: 611.1351; found: 611.1355.

*6-(9-Methyl-9H-carbazol-3-yl)-1a,10b-dihydro-6H-dibenzo[3,4:6,7]cyclohepta[1,2-b] oxiren-6-ol (**15**).* (54%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.03 (dd, J = 7.8, 1.3 Hz, 2H), 7.92 (dt, J = 7.8 Hz, 1H), 7.78 (d, J = 1.8 Hz, 1H), 7.51 (dd, J = 7.2, 1.3 Hz, 2H), 7.48−7.44 (t, J =7.8 Hz, 1H), 7.33−7.39 (m, 5H), 7.27 (d, J = 8.4 Hz, 1H), 7.20 (dd, J = 8.4, 1.3 Hz, 1H), 7.19−7.15 (t, J = 7.8 Hz, 1H), 3.82 (s, 3H), 3.61 (s, 2H), 2.22 (s, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 146.5, 141.6, 141.1, 140.5, 131.9, 131.7, 128.3, 128.0, 126.3, 125.0, 124.5, 123.1, 122.7, 120.6, 119.3, 118.7, 108.9, 108.8, 79.4, 57.4, 29.3: HRMS (FAB) m/z [M$^+$] calcd for $C_{28}H_{21}NO_2$: 403.1572; found: 403.1562.

*10-(9-Methyl-9H-carbazol-3-yl)anthracene-9-carbaldehyde (**15a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 11.61 (s, 1H), 9.04 (d, J = 8.7 Hz, 2H), 8.11 (d, J = 1.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.8 Hz, 2H), 7.65 (dd, J = 8.6, 8.7 Hz, 2H), 7.61 (d, J = 8.2 Hz, 1H), 7.46−7.54 (m, 1H), 7.37 (dd, J = 8.8, 8.7 Hz, 2H), 7.24 (td, J = 8.2, 1.3 Hz, 1H), 3.99 (s, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 193.6, 147.0, 141.7, 140.8, 132.0, 130.9, 128.8, 128.7, 128.6, 128.5, 126.5, 125.5, 123.7, 123.6, 123.0, 122.7, 122.6, 120.7, 119.5, 108.9, 108.6, 29.1; HRMS (FAB) m/z [M + H$^+$] calcd for $C_{28}H_{20}NO$: 386.1545; found: 386.1543

*10-Hydroxy-11-(9-methyl-9H-carbazol-3-yl)-10,11-dihydro-5H-dibenzo[a,d][7] annulen-5-one (**15b**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.15 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.59 (s, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 7.7 Hz, 1H), 7.32 (d, J = 8.3 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 7.19−7.16 (m, 2H), 7.10 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H), 6.72 (d, J = 7.8 Hz, 1H), 5.26 (d, J = 5.8 Hz, 1H), 5.14 (d, J = 5.8 Hz, 1H), 3.73 (s, 3H), 2.58 (brs, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 197.2, 141.3, 140.3, 140.3, 140.0, 139.2, 137.7, 133.4, 133.0, 131.5, 131.2, 129.8, 128.9, 128.5, 128.1, 126.9, 126.9, 125.9, 122.8, 122.5, 121.0, 120.3, 119.0, 108.6, 108.4, 78.3, 57.4, 29.2; HRMS (FAB) m/z [M$^+$] calcd for $C_{28}H_{21}NO_2$: 403.1572; found: 403.1571.

*6-(Pyridin-3-yl)-1a,10b-dihydro-6H-dibenzo[3,4:6,7]-cyclohepta[1,2-b]oxiren-6-ol (**16**).* (22%), ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.29 (dd, J = 4.8, 1.5 Hz, 1H), 7.97−7.90 (m, 3H), 7.51−7.47 (m, 2H), 7.39−7.35 (m, 1H), 7.34−7.28 (m, 4H), 7.11 (dd, J = 8.0, 4.8 Hz, 1H), 4.42 (brs, 1H), 3.60 (s, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 148.6, 148.2, 145.4, 144.8, 135.1, 132.1, 131.0, 128.6, 128.5, 124.4, 123.8, 77.3, 57.2; HRMS (FAB) m/z [M + H$^+$] calcd for $C_{20}H_{16}NO_2$: 302.1181; found: 302.1182.

*10-(Pyridin-3-yl)anthracene-9-carbaldehyde (**16a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 11.57 (1H, s), 8.98 (d, J = 8.5 Hz, 2H), 8.84 (brs, 1H), 8.66 (brs, 1H), 7.75 (td, J = 8.5, 1.8 Hz, 2H), 7.67 (td, J = 8.5, 1.3 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.59−7.54 (m, 1H), 7.45 (dd, J = 6.5, 1.1 Hz, 1H), 7.43 (dd, J = 6.5, 1.1 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 193.6, 151.1, 149.6, 140.8, 138.4, 134.3, 131.5, 130.3, 128.8, 127.4, 126.3, 123.9, 123.6 (1 signal missing); HRMS (FAB) m/z [M + H$^+$] calcd for $C_{20}H_{14}NO_2$: 284.1075; found: 284.1073.

*5-(Pyridin-3-yl)-5,11-dihydro-10H-5,10-epoxydibenzo-[a,d][7]annulen-10-ol (**16b**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.53 (d, J = 4.8 Hz, 1H), 8.32 (brs, 1H), 7.95 (dt, J = 7.9, 1.7 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.29 (dd, J = 7.9, 4.8 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.08 (t, J = 8.1 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 7.4 Hz, 1H), 6.80 (d, J = 7.4 Hz, 1H), 3.58 (d, J = 16.4 Hz, 1H), 3.01 (d, J = 16.4 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.6, 148.9, 146.4, 142.2, 140.7, 138.4, 135.1, 134.0, 130.4, 129.3, 127.6, 127.4, 125.9, 124.2, 123.5, 121.9, 120.5, 104.7, 86.7, 39.3; HRMS (FAB) m/z [M + H$^+$] calcd for $C_{20}H_{16}NO_2$: 302.1181; found: 302.1179 **17** and **18:** Ferrocene (500 mg, 2.69 mmol) was dissolved in ether (6 mL), and TMEDA (1.1 mL, 7.38 mmol) and n-BuLi (2.5 M, 2.95 mL, 7.38 mmol) were slowly added at 0 °C. The reaction mixture was stirred for 16 h at room temperature before a THF solution of **1** (1.64 g, 7.38 mmol in 6 mL) was added. After another 16 h, the reaction was quenched with NH_4Cl solution

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and extracted with EtOAc. The combined organic portions were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography to give the desired products (**17**: 154 mg, 14%; **18**: 195 mg, 12%).

*$FeCp_2$-EDCH (**17**).* (14%) ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.06 (dd, J = 7.6, 1.5 Hz, 2H), 7.47 (dd, J = 7.6, 1.5 Hz, 2H), 7.26−7.30 (m, 4H), 4.27 (5H, s), 4.19 (t, J = 1.9 Hz, 2H), 4.07(t, J = 1.9 Hz, 2H), 3.89 (2H, s), 3.67 (1H, s); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 146.6, 131.7, 131.5, 128.0, 127.7, 124.0, 108.1, 72.4, 69.1, 68.6, 67.7, 57.6; HRMS (FAB) m/z [M^+] calcd for $C_{25}H_{20}O_2Fe$: 408.0813; found: 408.0818.

*$FeCp_2$-$EDCH_2$ (**18**).* (12%) ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.92 (4H, d, J = 7.9 Hz), 7.45 (4H, d, J = 7.2 Hz), 7.32−7.24 (8H, m), 4.17−4.19 (m, 8H), 3.81 (4H, s), 3.54 (2H, s); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 146.2, 131.9, 131.5, 128.3, 128.0, 123.8, 108.3, 72.6, 69.6, 67.9, 57.6; HRMS (FAB) m/z [M^+] calcd for $C_{40}H_{30}O_4Fe$: 630.1493; found: 630.1502.

*Ferrocene Anthryl-CHO (**17a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 11.48 (s, 1H), 9.19 (d, J = 8.3 Hz, 2H), 8.93 (d, J = 8.3 Hz, 2H), 7.61 (t, J = 8.3 Hz, 2H), 7.49 (t, J = 8.3 Hz, 2H), 4.77 (s, 2H), 4.62 (s, 2H), 4.19 (s, 5H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 193.6, 142.5, 131.9, 130.6, 128.7, 128.4, 124.6, 124.3, 123.6, 83.9, 74.3, 70.3, 68.7; HRMS (EI) m/z [M^+] calcd for $C_{25}H_{18}OFe$: 390.0707; found: 390.0700.

*(**17b**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.76−7.73 (m, 2H), 7.40 (dd, J = 7.2, 1.1 Hz, 1H), 7.33−7.28 (m, 2H), 7.27−7.24 (m, 1H), 7.14−7.08 (m, 2H), 4.68 (dd, J = 11.3, 4.0 Hz, 1H), 4.33−4.31 (m, 1H), 4.22−4.19 (m, 1H), 4.0−3.97 (m, 2H), 3.67 (s, 5H), 2.50 (brs, 1H), 1.77 (d, J = 11.3 Hz, 1H); ^{13}C {^{1}H} 1NMR (150 MHz, $CDCl_3$): δ 149.3, 142.7, 136.9, 135.6, 132.8, 128.0, 127.5, 127.3, 127.2, 126.6, 120.6, 120.5, 97.7, 84.7, 73.3, 72.0, 68.8, 66.3, 65.3, 60.9, 47.2; HRMS (EI) m/z [M^+] calcd for $C_{25}H_{20}O_2Fe$: 408.0813; found: 408.0811.

*(**18a**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 11.41 (s, 1H, s), 9.0 (brs, 4H), 8.81 (d, J = 8.8 Hz, 2H), 8.35 (s, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.27 (t, J = 7.4 Hz, 2H), 6.95 (brs, 2H), 6.81 (t, J = 7.3 Hz, 2H), 4.77 (s, 4H), 4.72 (s, 2H), 4.66 (s, 2H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 193.6, 149.9, 144.6, 142.9, 141.5, 140.9, 134.4, 131.7, 131.7, 128.6, 128.6, 128.4, 127.3, 125.0, 124.4, 124.2, 123.3, 86.5, 85.4, 76.2, 75.8, 70.0, 69.4; HRMS (EI) m/z [M^+] calcd for $C_{39}H_{26}OFe$: 566.1333; found: 566.1328.

*(**18b**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 11.39 (2H, s), 8.90 (brd, J = 8.0 Hz, 4H), 8.76 (4H, d, J = 8.0 Hz), 7.35−7.39 (m, 4 H), 6.84 (*t*, J = 8.0 Hz, 4H), 4.80−4.78 (m, 4H), 4.77−4.75 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.6, 140.4, 131.5, 130.0, 128.2, 128.0, 124.8, 124.2, 123.2, 86.0, 76.5, 69.9; HRMS (EI) m/z [M^+] calcd for $C_{40}H_{26}O_2Fe$: 594.1282; found: 594.1280

*(**18c**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 11.50 (s, 1H), 9.11 (brs, 2H), 8.93 (d, J = 8.2 Hz, 2H), 7.60 (t, J = 8.2 Hz, 2H), 7.46 (t, J = 8.2 Hz, 2H), 7.26−7.24 (m, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.98−6.93 (m, 2H), 6.89 (d, J = 7.4 Hz, 1H), 6.81−6.76 (m, 2H), 6.62 (t, J = 7.5 Hz, 1H), 4.79 (s, 1H), 4.61 (s, 1H), 4.51 (s, 1H), 4.49 (s, 1H), 4.46 (s, 1H), 4.43 (s, 1H), 4.37 (s, 1H), 4.34 (s, 1H), 3.39 (d, J = 16.5 Hz, 1H), 3.20 (s, 1H), 2.93 (d, J = 16.5 Hz, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 193.5, 141.6, 133.1, 131.8, 130.4, 129.4, 128.6, 128.5, 128.4, 128.3, 128.2, 127.3, 127.2, 125.8, 124.4, 124.2, 123.5, 123.4, 123.1, 120.4, 119.4, 104.0, 89.0, 85.4, 84.0, 75.9, 75.3, 71.1, 70.9, 70.3 (×2), 69.4, 68.9, 38.8; HRMS (EI) m/z [M^+] calcd for $C_{40}H_{28}O_3Fe$: 612.1388; found: 612.1389.

*(**18d**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 11.51 (s, 1H), 8.99 (d, J = 8.8 Hz, 2H), 8.94 (d, J = 8.8 Hz, 2H), 7.65−7.60 (m, 3H), 7.51−7.46 (m, 2H), 7.41 (d, J = 7.7 Hz, 1H), 7.06 (m, 2H), 6.98−6.93 (m, 2H), 6.84−6.80 (m, 2H), 4.59 (dd, J = 11.1, 3.9 Hz, 1H), 4.42 (s, 1H), 4.35 (s, 1H), 4.27 (s, 1H), 4.20 (dd, J = 7.5, 1.0 Hz, 2H), 4.10 (dd, J = 8.8, 1.0 Hz, 2H), 3.77 (d, J = 4.0 Hz, 1H), 2.28 (s, 1H), 1.61 (d, J = 11.1 Hz, 1H); ^{13}C NMR spectrum is unavailable because **18d** is obtained as a mixture with **18c**. Yet, a comparison with **17b** confirms the presence of the [2,2,3] bicyclic system. HRMS (EI) m/z [H^+] calcd for $C_{40}H_{28}O_3Fe$: 612.1388; found: 612.1381.

*(**18e**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 11.52(s, 1H), 9.06 (d, J = 8.9 Hz, 2H), 8.97 (d, J = 8.9 Hz, 2H), 7.65 (td, J = 8.8, 1.2 Hz, 2H), 7.57 (td, J = 8.9, 1.2 Hz, 2H), 7.48 (dd, J = 7.6, 1.1 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.27 (dd, J = 7.6, 1.2 Hz, 1H), 7.14−7.18 (m, 2H), 7.13−7.07 (m, 2H), 6.83 (td, J = 7.6, 1.2 Hz, 1H), 4.93 (dd, J = 11.2, 4.1 Hz, 1H), 4.47−4.43 (m, 2H), 4.33−4.30 (m, 2H), 4.19−4.15 (m, 1H), 4.02 (t, J = 2.5 Hz), 3.93−3.90 (m, 1H), 3.69−3.66 (m, 1H), 2.52 (s, 1H), 1.50 (d, J = 11.2 Hz, 1H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 193.6, 148.6, 148.5, 141.9, 136.0, 133.8, 131.9, 130.5, 129.1, 128.7, 128.6, 127.3, 127.2, 127.1, 126.8, 126.5, 124.7, 124.6, 123.7, 120.6, 120.0, 95.4, 84.6, 81.7, 74.3, 74.0, 72.1, 70.4, 70.2, 70.1, 68.3, 66.7, 54.0, 29.9; HRMS (EI) m/z [M^+] calcd for $C_{40}H_{28}O_3Fe$: 612.1388; found: 612.1381.

*(**20**).* To a CH_2Cl_2 solution of **19** (0.20 g, 0.60 mmol, 1 equiv in 60 mL) were added mCPBA (1.47 g, 6.0 mmol, 10 equiv) and $NaHCO_3$ (0.50 g, 6.0 mmol, 10 equiv), and the reaction was stirred at room temperature for 16 h. The mixture was then extracted with 1 N NaOH. The organic layer was washed with brine, combined, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 1:1 to 1: 5) to give **20** (0.10 g, 46%).

IR (KBr, cast) ν (cm^{-1}) 1684, 1345, 1232, 1185, 959, 868, 755, 718; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.79 (s, 2H), 7.67 (d, J = 7.8 Hz, 2H), 7.60 (d, J = 7.3 Hz, 2H), 7.57 (t, J = 7.5 Hz, 2H), 7.49 (t, J = 7.2 Hz, 2H), 4.49 (s, 4 H).; ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$) δ 196.3, 140.5, 137.7, 136.0, 134.8, 132.0, 130.2, 130.1, 129.6, 128.6, 61.9, 61.1; HRMS (MALDI) m/z [M + H^+] calcd for $C_{24}H_{15}O_4$: 367.0970; found: 367.0961.

*7,14-Bis((triisopropylsilyl)ethynyl)pentacene-5,12-dicarbaldehyde (**21a**).* To a THF solution of TIPSA (0.40 mL, 1.80 mmol, 6 equiv in 10 mL) was added 2.5M *n*-BuLi (0.72 mL, 1.80 mmol, 6 equiv) at 0 °C, and the reaction was stirred for 1 h. To the mixture was added diepoxide **20** (0.11 g, 0.30 mmol, 1 equiv in 2 mL THF). The reaction was warmed back to room temperature and stirred for 2.5 h. The mixture was quenched by water, and the solvent was evaporated. The residue was partitioned between water and CH_2Cl_2. The organic portion was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to furnish the crude product. The intermediate diol was dissolved in CH_2Cl_2 (5 mL), and to the solution was added TFA (0.046 mL, 0.60 mmol, 2 equiv). The reaction was stirred at room temperature for 10 min. After the solvent was removed under reduced pressure, the crude product was purified by flash chromatography (hex/CH_2Cl_2 = 2:1) to give **21a** (25 mg, 12%).

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IR (KBr, cast) ν (cm^{-1}) 2941, 2866, 2151, 1683, 1464, 1075, 884, 676; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.71 (s, 2H), 10.62 (s, 2H), 8.98 (d, J = 8.5 Hz, 2H), 8.75 (d, J = 9.0 Hz, 2H), 7.67−7.63 (m, 2H), 7.59−7.56 (m, 2H), 1.36−1.35 (m, 42H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 192.14, 133.6, 132.6, 131.1, 129.8, 128.2, 128.1, 127.1, 126.6, 124.9, 124.5, 124.2, 110.9, 103.1, 18.9, 11.5; UV (λ_{max}, nm) = 687; HRMS (MALDI) m/z [M + H^+] calcd for $C_{46}H_{55}O_2Si_2$: 695.3741; found: 695.3732.

*7,14-Di-p-tolylpentacene-5,12-dicarbaldehyde (**21b**).* To a THF solution of 4-bromotoluene (0.22 mL, 1.80 mmol, 6 equiv in 10 mL) was added 2.5 M *n*-BuLi (0.72 mL, 1.80 mmol, 6 equiv) at −78 °C and the reaction was stirred for 1 h. The mixture was added **20** (0.10 g, 0.30 mmol, 1 equiv) and stirred for 2.5 h. The mixture was then quenched with water, and the solvent was removed *in vacuo*. The residue was partitioned between water and CH_2Cl_2. The organic portion was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to get the crude intermediate. The diol intermediate was dissolved in CH_2Cl_2 (10 mL) and to the solution was added TFA (0.046 mL, 0.60 mmol, 2 equiv). The reaction was stirred at room temperature for 10 min, and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 2:1) to give **21b** (41 mg, 45%).

IR (KBr, cast) ν (cm^{-1}) 2970, 1652, 1425, 1280, 1156, 1024, 817, 752; ^1H NMR (500 Mhz, $CDCl_3$) δ (ppm) 11.41 (s, 2H), 9.80 (s, 2H), 9.01 (d, J = 9.0 Hz, 2H), 7.75 (d, J = 9.0 Hz, 2H), 7.58 (m, 2H), 7.53 (d, J = 7.7 Hz, 4H), 7.42 (d, J = 7.8 Hz, 4H), 7.31 (m, 2H), 2.63 (s, 6 H); ^{13}C {^1H} NMR ($CDCl_3$, 125 MHz) δ 192.3, 147.4, 138.4, 134.8, 133.6, 130.7, 130.3, 130.1, 129.6, 129.5, 128.6, 128.1, 125.4, 124.6, 123.9, 123.5, 21.6; UV (λ_{max}, nm) = 667; HRMS (MALDI) m/z [M^+] calcd for $C_{38}H_{26}O_2$: 514.1933; found: 514.1941.

*7,14-Bis(4-methoxyphenyl)pentacene-5,12-dicarbaldehyde (**21c**).* (34%); IR (KBr, cast), ν (cm^{-1}) 2923, 1657, 1606, 1512, 1249, 1176, 1027, 827. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.43 (s, 2H), 9.82 (s, 2H), 9.00 (d, J = 9.5 Hz, 2H), 7.78 (d, J = 9.0 Hz, 2H), 7.58 (m, 2 H), 7.46 (d, J = 8.7 Hz, 4H), 7.32 (m, 2 H), 7.25 (d, 4 H, J = 8.7 Hz, 4H), 4.04 (s, 6 H); ^{13}C {1H} NMR (125 MHz, $CDCl_3$) δ 192.3, 159.8, 147.1, 133.7, 132.0, 130.5, 130.3, 129.9, 129.6, 128.5, 128.1, 125.4, 124.6, 123.9, 123.5, 114.2, 55.4; UV (λ_{max}, nm) = 667; HRMS (EI) m/z [M^+] calcd for $C_{38}H_{26}O_4$: 546.1831; found: 546.1823.

*7,14-Bis(4-chlorophenyl)pentacene-5,12-dicarbaldehyde (**21d**).* (39%); IR (KBr, cast) ν (cm^{-1}) 2919, 1651, 1534, 1261, 1057, 830, 749, 534; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.44 (s, 2H), 9.81 (s, 2H), 8.94 (d, J = 9.5 Hz, 2H), 7.72 (d, J = 8.0 Hz, 4H), 7.69 (d, J = 9.0 Hz, 2H), 7.62−7.58 (m, 2H), 7.49 (d, J = 8.0 Hz, 4H), 7.36−7.33 (m, 2H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 192.1, 145.3, 136.3, 134.8, 133.9, 132.2, 130.3, 130.0, 129.6, 129.2, 128.1, 127.6, 125.9, 124.7, 124.5, 123.2; UV (λ_{max}, nm) = 668; HRMS (EI) m/z [M^+] calcd for $C_{36}H_{20}Cl_2O_2$: 554.0840; found: 554.0844.

*7,14-Bis(4-(trifluoromethyl)phenyl)pentacene-5,12-dicarbaldehyde (**21e**).* (22%); IR (KBr, cast) ν (cm^{-1}) 1660, 1537, 1323, 1172, 1105, 1068, 1018, 840; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.43 (s, 2H), 9.78 (s, 2H), 9.00 (d, J = 9.5 Hz, 2H), 8.02 (d, J = 7.5 Hz, 4H), 7.69 (d, J = 8.0 Hz, 4H), 7.62−7.59 (m, 4H), 7.37−7.34 (m, 2H).; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 192.0, 144.8, 141.8, 134.0, 131.3, 130.9 (q, J = 55.7 Hz,), δ 130.1, 129.8, 129.6 (×2), 127.9, 127.3, 126.1, 125.9 (q, J = 4.2 Hz), 124.7, 123.1; UV (λ_{max}, nm) = 659; HRMS (MALDI) m/z [M^+] calcd for $C_{38}H_{20}F_6O_2$: 622.1367; found: 622.1234.

Dimethyl 4,6-Di((E)-styryl)isophthalate. To a DMF solution of dimethyl 4,6-dibromoisophthalate (3.60 g, 10.3 mmol, 1 equiv in 30 mL) were added tri-*n*-octylphosphine (0.38 g, 1.03 mmol, 0.1 equiv) and $Pd(OAc)_2$ (0.23 g, 1.0 mmol, 0.1 equiv). Styrene (4.72 mL, 41.2 mmol, 4 equiv) and Et_3N (14.4 mL, 103 mmol, 10 equiv) were then added, and the mixture was heated for 2 h at 110 °C. The mixture was cooled and filtered through celite. The solvent was removed *in vacuo*, and the residue was partitioned between water and CH_2Cl_2. The organic portion was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 2:1) to give **22** (2.7 g, 65%).

IR (KBr, cast) ν (cm^{-1}) 2949, 1716, 1634, 1435, 1290, 1231, 1105, 962; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.57 (s, 1H), 8.08 (d, J = 16.5 Hz, 2H), 8.03 (s, 1H), 7.61 (d, J = 7.2 Hz, 4H), 7.39 (t, J = 7.2 Hz, 4H), 7.31 (t, J = 7.2 Hz, 2H), 7.17 (d, J = 16.0 Hz, 2H), 3.96 (s, 6H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 166.8, 142.9, 137.0, 133.9, 133.3, 128.8, 128.4, 127.1, 126.7, 126.6, 125.5, 52.3; HRMS (APCI) m/z [M + H^+] calcd for $C_{26}H_{22}O_4$: 398.1518; found: 399.1592.

Dimethyl 4,6-Diphenethylisophthalate. Dimethyl 4,6-di-((*E*)-styryl)isophthalate (6.02 g, 15.1 mmol, 1 equiv) was dissolved in THF (80 mL) and MeOH (50 mL), and to the solution was added 10% Pd/C (3.24 g). A hydrogen balloon was connected to the flask, and the reaction was stirred at room temperature for 16 h. The solution was filtered through a pad of celite, and the solvent was removed *in vacuo*. The crude product was purified with flash chromatography (hex/EtOAc = 40:1) to give the reduced product as a colorless oil (4.41 g, 70%).

^1H NMR ($CDCl_3$, 500 MHz) δ (ppm) 8.50 (s, 1H), 7.28 (m, 4H), 7.19 (m, 6H), 6.90 (s, 1H), 3.96 (s, 6H), 3.24 (m, 4H), 2.83 (m, 4H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.1, 147.8, 141.7, 134.8, 134.0, 128.8, 128.5, 127.2, 126.1, 52.2, 37.8, 36.8. HRMS (FAB) m/z [M + $H]^+$ calcd for $C_{26}H_{27}O_4$: 403.1909, found: 403.1914.

4,6-Diphenethylisophthalic Acid. To a THF solution of diester (4.41 g, 10.9 mmol in 50 mL) was added 5% aqueous sodium hydroxide (20 mL). The solution was stirred and refluxed at 80 °C overnight. Tetrahydrofuran was removed *in vacuo*, and the residue was extracted with EtOAc. The aqueous layer was acidified (pH1) with hydrochloric acid. The white solid suspension was collected and dissolved in EtOAc. The solution was dried over $MgSO_4$, and the solvent was removed to give the diacid as a white solid (3.46 g, 75%). The crude compound was used in the next step with further purification.

^1H NMR (CD_3OD, 500 MHz) δ (ppm) 8.56 (s, 1H), 7.12 (t, J = 7.5 Hz, 4H), 7.19 (m, 6H), 6.82 (s, 1H), 4.50 (br, 2H), 3.20 (m, 4H), 2.78 (m, 4H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 147.3, 141.5, 134.3, 134.3, 128.3, 127.9, 127.2, 125.6, 37.3, 36.4.

Dibenzo-2,3,9,10-tetrahydrobenzo[1,2:4,5]di[7]annulene-1,11-dione. To a CH_2Cl_2 solution of diacid (3.46 g, 9.25 mmol, in 50 mL) were added a few drops of DMF and thionyl chloride (5 mL) at 0 °C. The solution was stirred at a reflux temperature for 2 h. The volatiles were removed under reduced pressure to give the intermediate acyl chloride. To a CH_2Cl_2 suspension of $AlCl_3$ (2.0 g in 10 mL) was added a CH_2Cl_2 solution of acyl chloride intermediate (15 mL over 40

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min) at 0 °C. The reaction was stirred at 0 °C for another 30 min before being warmed back to room temperature. The reaction was quenched with hydrochloric acid after 16 h. The solution was extracted with CH_2Cl_2, and the combined organic portions were dried over $MgSO_4$ before being concentrated *in vacuo*. The crude product was purified by flash chromatography to give the pentacyclic product as a yellow solid (0.50 g, 13.6%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.699 (s, 1H), 8.01 (dd, J = 7.8, 2.5 Hz, 2H), 7.43 (m, 2H), 7.33 (m, 2H), 7.22 (d, J = 7.5, 2H), 7.10 (s, 1H), 3.20 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.3, 146.0, 141.6, 138.5, 137.2, 134.2, 132.6, 130.8, 130.5, 129.3, 126.9, 35.0, 34.7; HRMS (FAB) m/z [M + H]$^+$ calcd for $C_{24}H_{19}O_2$: 339.1385, found: 339.1392.

22. To a solution of the product from the last step (0.50 g, 1.5 mmol, 1 equiv) in 1,2-dichloroethane was added *N*-bromosuccinimide (0.62 g, 3.5 mmol, 2.3 equiv) and benzoyl peroxide (30 mg). The solution was stirred at 95 °C for 18 h. The solvent was removed *in vacuo* to give the brominated intermediate. The crude mixture was dissolved in benzene (10 mL), and to the solution was added trimethylamine (2 mL). The reaction was refluxed for 16 h. The volatiles were removed *in vacuo*, and the residue was extracted with dichloromethane. After the organic portion was concentrated, the crude mixture was purified by flash chromatography to give **23** as a pale yellow solid (120 mg, 25%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.98 (s, 1H, Ph), 8.26 (dd, J = 8, 1.5 Hz, 2H), 7.66 (m, 3H), 7.57 (m, 4H), 7.07 (d, J = 10 Hz, 2H), 7.02 (d, J= 10 Hz, 2H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.1, 138.7, 138.4, 137.3, 134.6, 134.1, 133.9, 133.1, 132.4, 131.3, 130.5, 130.4, 129.6; HRMS (FAB) m/z [M + H]$^+$ calcd for $C_{24}H_{15}O_2$: 335.1072, found: 335.1065.

*12,14-Di-p-tolylpentacene-5,7-dicarbaldehyde (**23a**).* (29%): IR (KBr, cm^{-1}) 2922, 1781, 1668, 1506, 1284, 1052, 821, 753; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 11.76 (s, 2H), 11.21 (d, J = 1 Hz, 1H), 9.00 (d, J = 9.0 Hz, 2H), 8.31 (d, J = 1Hz, 1H), 7.77 (d, J = 9.0 Hz, 2H), 7.58 (m, 2 H), 7.28 (m, 2 H), 7.25 (d, J = 7.5 Hz, 4H), 7.15 (d, J = 8.0 Hz, 4H), 2.52 (s, 6H).; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 192.7, 147.4, 137.5, 134.5, 134.4, 130.6, 129.9, 129.7, 129.6, 129.3, 128.7, 128.5, 125.1, 123.9, 123.4, 119.4, 119.4, 21.3; UV (λ_{max}, nm) = 698.; HRMS (MALDI) calcd for $C_{38}H_{26}O_2$(M+): 514.1933; found: 514.1930.

*12,14-Bis(4-methoxyphenyl)pentacene-5,7-dicarbaldehyde (**23b**).* (48%); IR (KBr, cast) ν (cm^{-1}) 2917, 1665, 1606, 1293, 1252, 1176, 1027, 756; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.77 (s, 2H), 11.23 (d, $J \sim$ 1 Hz. 1H), 9.02 (d, J = 9.0 Hz, 2H), 8.32 (d, $J \sim$ 1 Hz, 1H), 7.82 (d, J = 8.5 Hz, 2H), 7.60 (m, 2 H), 7.30 (m, 2 H), 7.20 (d, J = 8.5 Hz, 4H), 6.99 (d, J = 8.5 Hz, 4H), 3.97 (s, 6 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 125 MHz) δ 192.7, 159.4, 147.1, 134.6, 131.9, 130.0, 129.7, 129.7, 129.5, 129.5, 128.7, 128.5, 125.1, 123.9, 123.4, 119.4, 113.7, 55.3; UV (λ_{max}, nm) = 683; HRMS (MALDI) m/z [M$^+$] calcd for $C_{38}H_{26}O_4$: 546.1831; found: 546.1833

*12,14-Bis(4-chlorophenyl)pentacene-5,7-dicarbaldehyde (**23c**).* (58%); IR (KBr, cast) ν (cm^{-1}) 2970, 1630, 1488, 1391, 1282, 1090, 1016, 750; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.78 (s, 2H), 11.24 (d, J = 1 Hz, 1H), 9.00 (d, J = 8.0 Hz, 2H), 8.12 (d, J = 1 Hz. 1H), 7.72 (d, J = 8.1 Hz, 2H), 7.62 (t, J = 8.0 Hz, 2H), 7.50−7.47 (d, J = 8.0 Hz, 4 H), 7.34 (m, 2H), 7.23−7.21 (d, J = 8.0 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 145.1, 135.8, 134.6, 134.3, 132.2, 131.9, 129.7, 129.3, 128.5, 128.3, 127.9, 125.7, 124.6, 123.5, 120.1; UV (λ_{max}, nm) = 678; HRMS (EI) m/z [M$^+$] calcd for $C_{36}H_{20}Cl_2O_2$: 554.0840; found: 554.0841

Methyl 3-Bromo-2-naphthoate. To a MeOH solution of 3-bromo-2-naphthoic acid (0.34 g, 1.37 mmol, 1 equiv) were added $SOCl_2$ (2.0 mL, 27.3 mmol, 20 equiv) and a few drops of DMF. The reaction was stirred at a reflux temperature for 3 h. The solvent was removed under reduced pressure. The residue was partitioned between water and CH_2Cl_2. The organic portion was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 2:1) to give the methyl ester (0.26 g, 73%).

IR (KBr, cast) ν (cm^{-1}) 2950, 1732, 1454, 1280, 1200, 1111, 996, 747; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.33 (s, 1H), 8.13 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.59−7.51 (m, 2H), 3.99 (s, 3 H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 166.6, 135.2, 133.0, 132.2, 131.0, 129.1, 128.8, 128.6, 127.1, 126.7, 117.0, 52.5; HRMS (FAB) m/z [M$^+$] calcd for $C_{12}H_9BrO_2$: 264.9864; found: 264.9863.

*Methyl (E)-3-Styryl-2-naphthoate (**24**).* To a DMF solution of methyl 3-bromo-2-naphthoate (0.23 g, 0.86 mmol, 1 equiv in 10 mL) were added tri-o-tolylphosphine (26 mg, 0.086 mmol, 0.1 equiv) and $Pd(OAc)_2$ (19 mg, 0.086 mmol, 0.1 equiv). After styrene (0.15 mL, 1.3 mmol, 1.5 equiv) and Et_3N (1.2 mL, 8.6 mmol, 10 equiv) were added, the reaction was refluxed at 110 °C for 2 h. The mixture was filtered through a pad of celite, and the solvent was removed *in vacuo*. The residue was partitioned between water and CH_2Cl_2. The organic portion was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (hex/CH_2Cl_2= 5:1 to 2:1) to give **24** (1.70 g, 68%).

IR (KBr, cast) ν (cm^{-1}) 2949, 1716, 1447, 1270, 1120, 1131, 1062, 743; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.52 (s, 1H), 8.12 (s, 1H), 8.07 (d, J = 16.0 Hz, 1H), 7.88 (t, J = 7.8 Hz, 2H), 7.63−7.61 (m, 2H), 7.60−7.57 (m, 1H), 7.52−7.49 (m, 1H), 7.40 (t, J = 7.8 Hz, 2H), 7.32−7.29 (m, 1H), 7.10 (d, J = 16.0 Hz, 1H), 4.00 (s, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.8, 137.6, 135.5, 134.9, 132.0, 131.6, 130.9, 128.7, 128.6, 128.4, 127.9, 127.7, 126.9, 126.8, 126.5, 126.0, 52.2; HRMS (FAB) m/z [M$^+$] calcd for $C_{20}H_{16}O_2$: 288.1150; found: 288.1153.

*Methyl 3-Phenethyl-2-naphthoate (**25**).* To a MeOH/THF solution of **24** (1.31 g, 4.54 mmol in 10 mL/30 mL) was added 10% Pd/C (0.54 g). The reaction was stirred at room temperature for 4 h with a H_2 balloon attached. The mixture was filtered through a pad of celite, and the solvent was evaporated. The crude product was purified by flash column chromatography (hex/CH_2Cl_2= 5:1 to 2:1) to give **25** (1.05 g, 80%).

IR (KBr, cast) ν (cm^{-1}) 2949, 1721, 1454, 1282, 1203, 1131, 1059, 699; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.51 (s, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.66 (s, 1H), 7.57−7.54 (m, 1H), 7.51−7.47 (m, 1H), 7.33−7.27 (m, 4H), 7.24−7.20 (m, 1H), 3.99 (s, 3H), 3.45−3.42 (m, 2H), 3.01−2.98 (m, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 168.0, 142.0, 139.0, 135.0, 132.2, 131.1, 129.4, 128.7, 128.6, 128.3, 128.1, 127.9, 127.1, 126.0, 125.8, 52.1, 38.3, 36.9; HRMS (EI) m/z [M$^+$] calcd for $C_{20}H_{18}O_2$: 290.1307; found: 290.1306.

3-Phenethyl-2-naphthoic Acid. To an EtOH solution of **25** (0.84 g, 2.88 mmol in 40 mL) in EtOH (40 mL) was added 40 mL of 10% NaOH solution (40 mL). The reaction was stirred

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at a reflux temperature for 16 h. The solvent was evaporated *in vacuo*, and the residue was acidified to pH∼1. The acidic aqueous suspension was extracted with EtOAc, and the combined organic portions were washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* to give crude acid (0.74 g, 93%). The material is used in the subsequent cyclization reaction without further purification.

IR (KBr, cast) ν (cm^{-1}) 2927, 1683, 1464, 1289, 1210, 1137, 745, 698; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.71 (s, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 8.3 Hz, 1H), 7.68 (s, 1H), 7.60−7.57 (m, 1H), 7.53−7.50 (m, 1H), 7.31−7.27 (m, 4H), 7.22−7.19 (m, 1H), 3.51−3.47 (m, 2H), 3.04−3.01 (m, 2H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 172.0, 142.1, 139.6, 135.5, 133.7, 131.1, 129.7, 129.0, 128.7, 128.6, 128.4, 127.1, 126.3, 126.2, 125.9, 38.3, 37.1.; HRMS (EI) m/z [M^+] calcd for $C_{19}H_{16}O_2$: 276.1150; found: 276.1154.

*12,13-Dihydro-5H-benzo[4,5]cyclohepta[1,2-b]-naphthalen-5-one (**26**).* To a CH_2Cl_2 solution of the acid (0.41 g, 1.47 mmol in 15 mL) were added $SOCl_2$ (4.26 mL, 58.7 mmol) and a few drops of DMF. The reaction was stirred at a reflux temperature for 3 h. The solvent was evaporated to furnish the chloride intermediate. To a suspension of $AlCl_3$ (0.29 g, 2.20 mmol, 1.5 equiv) in CH_2Cl_2 (150 mL) was added the acyl chloride intermediate (dissolved in 10 mL of CH_2Cl_2) at 0 °C, and the reaction was stirred at room temperature for 16 h. The mixture was then washed with 1 N HCl. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 5:1 to 2:1) to give **26** (0.26 g, 69%).

IR (KBr, cast) ν (cm^{-1}) 2916, 1652, 1445, 1288, 1255, 943, 747, 478; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.49 (s, 1H), 8.16 (dd, J = 8.0, 1.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.66 (s, 1H), 7.56−7.52 (m, 1H), 7.49−7.44 (m, 2H), 7.37−7.34 (m, 1H), 7.25 (d, J = 8.0 Hz, 1H), 3.37−3.29 (m, 4H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 195.6, 142.6, 138.0, 137.9, 137.7, 135.2, 132.5, 131.7, 131.5, 131.0, 129.8, 129.3, 128.1, 126.9, 126.7, 126.6, 126.0, 35.8, 35.0; HRMS (EI) m/z [M^+] calcd for $C_{19}H_{14}O$: 258.1045; found: 258.1041.

*5H-Benzo[4,5]cyclohepta[1,2-b]naphthalen-5-one (**27**).* To a dichloroethane solution of **26** (0.22 g, 0.86 mmol, 1 equiv in 10 mL) were added N-bromosuccinimide (0.15 g, 0.86 mmol, 1 equiv) and benzoyl peroxide (28 mg, 0.086 mmol, 0.1 equiv), and the reaction was stirred at a reflux temperature for 16 h. The mixture was diluted with CH_2Cl_2 and washed with saturated $Na_2S_2O_3$ solution, 1 N NaOH. The organic layer was further washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was redissolved in benzene (10 mL), and to this solution was added Et_3N (1.44 mL, 10.3 mmol, 12 equiv). The reaction was stirred at reflux temperature for another 16 h. The solvent then was removed *in vacuo*, and the residue was partitioned between water and CH_2Cl_2. The organic portion was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 2:1 to 1:1) to give **27** (150 mg, 67%).

IR (KBr, cast) ν (cm^{-1}) 3053, 1620, 1418, 1324, 1279, 888, 749, 475; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.73 (s, 1H), 8.22 (dd, J = 7.5, 1.0 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.95 (s, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.62−7.47 (m, 6H), 7.14 (d, J = 12.2 Hz, 1H), 6.94 (d, J = 12.5 Hz, 1H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 193.8, 138.1, 137.1, 134.9, 134.5, 132.5, 132.1, 132.0, 131.8, 131.2, 130.6, 130.5, 130.2, 130.0, 129.2, 128.4, 128.3, 127.6, 126.9; HRMS (EI) m/z [M^+] calcd for $C_{19}H_{12}O$: 256.0888; found: 256.0893.

*12-(4-Chlorophenyl)tetracene-5-carbaldehyde (**28**).* To a CH_2Cl_2 solution of **27** (0.13 g, 0.50 mmol, 1 equiv in 10 mL) were added mCPBA (0.61 g, 2.48 mmol, 5 equiv) and $NaHCO_3$ (0.21 g, 2.48 mmol, 5 equiv). The reaction was stirred at room temperature for 16 h. The mixture was then diluted with CH_2Cl_2 and extracted with 1 N NaOH. The organic portion was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* to give the intermediate epoxide. To a THF solution of 1-bromo-4-chlorobenzene (0.28 g, 1.48 mmol, 3 equiv in 10 mL) was added 2.5 M *n*-BuLi (0.60 mL, 1.50 mmol, 3 equiv) at −78 °C, and the reaction was stirred for 1 h. The mixture was transferred to the crude epoxide intermediate, and the reaction was stirred for 2.5 h at room temperature. The mixture was quenched with water, and the solvent was removed *in vacuo*. The residue was partitioned between water and CH_2Cl_2. The organic portion was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give the crude epoxide alcohol. This intermediate was dissolved in CH_2Cl_2 (10 mL), and to this solution was added TFA (0.038 mL, 0.5 mmol, 1 equiv). The reaction was stirred at room temperature for 10 min. The solvent was evaporated, and the crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 2:1) to give **28** (0.16 g, 88%).

IR (KBr, cast) ν (cm^{-1}) 3052, 1669, 1489, 1090, 1016, 821, 740, 570; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.72 (s, 1H), 9.83 (s, 1H), 8.97 (d, J = 9.0 Hz, 1H), 8.27 (s, 1H), 8.09 (d, J = 8.7 Hz, 1H), 7.83 (d, J = 9.3 Hz, 1H), 7.68−7.61 (m, 4H), 7.51−7.48 (m, 1H), 7.43−7.40 (m, 3H), 7.38−7.35 (m, 1H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 193.0, 144.6, 136.9, 134.4, 133.4, 133.1, 132.2, 131.2, 129.2, 129.0, 128.8, 128.8, 128.5, 128.4, 127.9, 126.8, 126.7, 126.1, 125.3, 124.6, 123.4, 123.0; HRMS (EI) m/z [M^+] calcd for $C_{25}H_{15}ClO$: 366.0811, found: 366.0804.

*Methyl 2-(Naphthalen-1-ylethynyl)benzoate (**29**).* Methyl 2-bromobenzoate (0.85 g, 3.94 mmol, 1 equiv), ethynylnaphthalene (0.9 mL, 5.8 mmol, 1.5 equiv), CuI (75 mg, 0.39 mmol, 0.1 equiv), and $Pd(PPh_3)_2Cl_2$ (0.28 g, 0.39 mmol, 0.1 equiv) were dissolved in Et_3N (40 mL) in a sealed tube under nitrogen. The reaction was refluxed for 16 h. The mixture was filtered through a pad of celite, and the solvent was evaporated. The residue was dissolved in CH_2Cl_2, and the solution was extracted with water. The organic portion was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 3:1 to 2:1) to give **29** (1.09 g, 96%).

IR (KBr, cast) ν (cm^{-1}) 2949, 2210, 1728, 1486, 1294, 1086, 756, 567; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.61 (dd, J = 8.3, 1.0 Hz, 1H), 8.04 (dd, J = 8.3, 1.0 Hz, 1H), 7.88−7.86 (m, 2H), 7.82 (dd, J = 7.4, 1.1 Hz, 1H), 7.78 (dd, J = 7.4, 1.1 Hz, 1H), 7.65−7.62 (m, 1H), 7.56−7.53 (m, 2H), 7.50−7.46 (m, 1H), 7.44−7.40 (m, 1H), 4.00 (s, 3H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 166.8, 134.2, 133.5, 133.2, 131.7, 130.7, 130.6, 129.0, 128.2, 128.0, 126.8, 126.5, 126.4, 125.3, 123.8, 121.0, 93.0, 92.6, 52.3; HRMS (FAB) m/z [M + H^+] calcd for $C_{20}H_{15}O_2$: 287.1072; found: 287.1064.

*Methyl 2-(2-(Naphthalen-1-yl)ethyl)benzoate (**30**).* To a THF solution of **29** (0.54 g, 1.09 mmol, 1 equiv in 10 mL) was added 10% Pd/C (0.26 g). The mixture was placed in a sealed

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autoclave that was pressurized to 150 psi of H_2. The mixture was stirred at room temperature for 40 h. The solution was filtered through a pad of celite, and the solvent was removed *in vacuo* to give the reduced product. To rearomatize the product, the raw material and DDQ (2.40 g, 10.5 mmol, 3 equiv) were dissolved in toluene (40 mL) and the solution was refluxed for 3 h. The reaction was filtered, and the solvent was evaporated *in vacuo*. The crude product was then purified by flash column chromatography (hex/CH_2Cl_2 = 2:1) to give **30** (0.52 g, 51%).

IR (KBr, cast) ν (cm^{-1}) 2950, 1715, 1599, 1434, 1258, 1127, 966, 753; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.24 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.53−7.50 (m, 1 H), 7.45−7.40 (m, 2H), 7.34−7.29 (m, 2H), 7.26 (d, J = 7.7 Hz, 1H), 3.89 (s, 3H), 3.42 (s, 4H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 168.0, 143.6, 138.0, 133.8, 132.0, 131.9, 131.2, 130.7, 129.6, 128.7, 126.7, 126.3, 126.1, 125.8, 125.6, 125.4, 123.9, 51.9, 35.8, 35.1; HRMS (FAB) m/z [M^+] calcd for $C_{20}H_{18}O_2$: 290.1307; found: 290.1302.

*2-(2-(Naphthalen-1-yl)ethyl)benzoic Acid (**30′**).* To an EtOH solution of **30** (0.42 g, 1.45 mmol, 1 equiv 15 mL) was added 20% NaOH solution (15 mL), and the reaction was stirred at a reflux temperature for 16 h. The solvent was removed *in vacuo*. The residue was acidified with 12N HCl to pH ∼ 1 before being extracted with EtOAc. The organic portion was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* to give **30′** (0.41 g, 99%).

IR (KBr, cast) ν (cm^{-1}) 3064, 1688, 1599, 1398, 1266, 1085, 777, 749; ^1H NMR (500 MHz, acetone-d_6) δ (ppm) 8.38 (d, J = 8.5 Hz, 1H), 8.02 (dd, J = 8.0, 1.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.78−7.76 (m, 1H), 7.56−7.53 (m, 1H), 7.51−7.48 (m, 2H), 7.43−7.39 (m, 3H), 7.37−7.34 (m, 1H), 3.41 (s, 4H); ^{13}C {^1H} NMR (125 MHz, acetone-d_6) δ 169.1, 144.8, 139.4, 135.0, 133.1, 133.0, 132.3, 131.8, 130.7, 129.5, 127.6, 127.2, 127.1, 126.8, 126.6, 126.4, 125.1, 37.1, 36.1; HRMS (FAB) m/z [M^+] calcd for $C_{19}H_{16}O_2$: 276.1150; found: 276.1151.

*12,13-Dihydro-7H-benzo[4,5]cyclohepta[1,2-a]-naphthalen-7-one (**31**).* **30′** (0.40 g, 1.45 mmol, 1 equiv) and $SOCl_2$ (2.1 mL, 29.1 mmol, 20 equiv) were dissolved in CH_2Cl_2 (15 mL). A few drops of DMF were added, and the mixture was stirred at a reflux temperature for 3 h. The solvent was removed *in vacuo* to give the acyl chloride intermediate. To a suspension of $AlCl_3$ (0.29 g, 2.18 mmol, 1.5 equiv) in CH_2Cl_2 (140 mL) was added a CH_2Cl_2 solution of aforementioned acyl chloride (in 5 mL) at 0 °C. The reaction was stirred at room temperature for 16 h. The mixture was diluted with CH_2Cl_2 and washed with 1 N HCl. The organic portion was further washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 3:1) to give **31** (0.22 g, 57%).

IR (KBr, cast) ν (cm^{-1}) 3061, 1652, 1425, 1316, 1141, 905, 752, 524; ^1H NMR (500 MHz, $CDCl_3$) δ (pm) 8.21−8.19 (m, 1H), 8.00 (d, J = 8.7 Hz, 1H), 7.88−7.84 (m, 2H), 7.78 (d, J = 8.7 Hz, 1H), 7.58−7.55 (m, 2H), 7.44 (td, J = 7.4, 1.4 Hz, 1H), 7.33 (td, J = 7.6, 1.0 Hz, 1H), 7.28−7.26 (m, 1H), 3.70−3.68 (m, 2H), 3.33−3.30 (m, 2H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 197.8, 140.8, 139.9, 139.2, 136.3, 135.2, 132.0, 131.3, 129.2, 128.7, 128.6, 127.6, 127.0, 126.71, 126.66, 126.0, 124.2, 33.6, 29.9; HRMS (FAB) m/z [$M + H^+$] calcd for $C_{19}H_{15}O$: 259.1123, found: 259.1127.

*7H-Benzo[4,5]cyclohepta[1,2-a]naphthalen-7-one (**32**).* To a dichloroethane solution of **31** (0.19 g, 0.76 mmol, 1 equiv in 20 mL) were added *N*-bromosuccinimide (0.15 g, 0.83 mmol, 1.1 equiv) and benzoyl peroxide (24 mg, 0.076 mmol, 0.1 equiv). The solution was stirred at a reflux temperature for 16 h. The mixture was diluted with CH_2Cl_2 and extracted with saturated $Na_2S_2O_3$ solution, 1 N NaOH. The organic portion was further washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was redissolved in benzene (10 mL). To this solution was added Et_3N (1.27 mL, 9.10 mmol, 12 equiv), and the reaction was stirred at a reflux temperature for 16 h. The solvent was evaporated *in vacuo*, and the residue was extracted with water and CH_2Cl_2. The organic portion was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude compound was purified by flash column chromatography (hex/CH_2Cl_2 = 3:1 to 2:1) to give **32** (0.19 g, 97%).

IR (KBr, cast) ν (cm^{-1}) 1640, 1593, 1457, 1330, 957, 805, 774, 716; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.50 (d, J = 8.3 Hz, 1H), 8.13−8.10 (m, 2H), 7.99−7.91 (m, 3H), 7.69−7.55 (m, 5H), 7.34 (d, J = 12.5 Hz, 1H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 194.7, 140.1, 138.1, 134.8, 134.6, 132.0, 131.5, 130.7, 129.8, 129.6, 129.2, 129.1, 128.7, 127.8, 127.3, 125.8, 125.7, 125.1; HRMS (FAB) m/z [$M + H^+$] calcd for $C_{19}H_{13}O$: 257.0966, found: 257.0971.

*11b,12a-Dihydro-7H-benzo[3,4]naphtho[2′,1′:6,7]-cyclohepta[1,2-b]oxiren-7-one (**32′**).* To a CH_2Cl_2 solution of **32** (60 mg, 0.24 mmol, 1 equiv in 5 mL) were added mCPBA (0.25 g, 1.19 mmol, 5 equiv) and $NaHCO_3$ (1.0 g, 1.19 mmol, 5 equiv), and the reaction was stirred at a reflux temperature for 3 h. The mixture was diluted and extracted with 1 N NaOH. The organic portion was then washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (hex/CH_2Cl_2 = 1:1 to 1:4) to give **32′** (15 mg, 26%).

^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.33 (d, J = 8.5 Hz, 1H), 7.90−7.88 (m, 2H), 7.69−7.62 (m, 2H), 7.61−7.58 (m, 3H), 7.52−7.48 (m, 1H), 7.47−7.42 (m, 1H), 5.42 (d, J = 4.0 Hz, 1H), 4.73 (d, J = 4.0 Hz, 1H) (Some extra signals are due to decomposition); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 198.6, 139.1, 136.5, 134.8, 134.7, 131.8, 131.2, 130.6, 129.4, 129.3, 129.2, 129.1, 127.6, 127.5, 127.4, 124.4, 122.7, 62.1, 57.8; HRMS (EI) m/z [M^+] calcd for $C_{19}H_{12}O_2$: 272.0837; found: 272.0836.

*7-(4-Chlorophenyl)tetraphene-12-carbaldehyde (**33**).* To a THF solution of 1-bromo-4-chlorobenzene (14 mg, 0.073 mmol, 2 equiv in 5 mL) was added 2.5 M *n*-BuLi (0.046 mL, 0.073 mmol, 2 equiv) at −78 °C, and the reaction was stirred for 1 h at that temperature. To the mixture was added **32′** (10 mg, 0.037 mmol, 1 equiv in 2 mL THF), and the reaction was stirred for 2.5 h at room temperature. The reaction was quenched with water and the solvent was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2, and the solution was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The intermediate epoxy alcohol was dissolved in CH_2Cl_2 (5 mL), and TFA (0.003 mL, 0.04 mmol, 1.1 equiv) was added. The reaction was stirred at room temperature for 10 min before the solvent was removed *in vacuo*. The crude mixture was purified by flash column chromatography (hex/CH_2Cl_2 = 5:1) to give **33** (9 mg, 68%).

IR (KBr, cast) ν (cm^{-1}) 2922, 1674, 1489, 1263, 1090, 1016, 805, 750; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 10.62 (s, 1H), 9.35 (d, J = 9.2 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H),

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7.92 (d, J = 7.5 Hz, 1H), 7.77−7.69 (m, 4H), 7.57−7.62 (m 3H), 7.55 (t, J = 7.5 Hz, 1H), 7.45 (d, J = 9.2 Hz, 1H), 7.38 (d, J = 8.2 Hz, 2H); ^{13}C {^{1}H} NMR ($CDCl_3$, 125 MHz) δ 194.3, 141.1, 136.8, 134.2, 133.5, 132.5, 132.3, 131.8, 130.6, 129.4, 129.2, 128.9, 128.8, 128.7, 128.6, 128.2, 128.1, 127.6, 127.0, 126.6, 126.4, 125.2, 124.8; HRMS (FAB) m/z [M + H$^+$] calcd for $C_{25}H_{16}ClO$: 367.0890; found: 367.0888.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01024.

Azulene-embedded PAH **6b** (CIF)
Transannular anthryl migration **8c** (CIF)
Pyrene oxo-bridge hemiketal **9d** (CIF)
Transannular cyclization product **12b** (CIF)
Epoxy alcohol **14** (CIF)
Ferrocene-dianthracene-dialdehyde **18a** (CIF)
^{1}H and ^{13}C NMR spectra of new compounds **1**−**33**; 2D HMBC and HSQC spectrum for selective compounds (PDF)

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Notes

The authors declare no competing financial interest.

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