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Regiospecifically Fluorinated Polycyclic Aromatic Hydrocarbons via Julia-Kocienski Olefination and Oxidative Photocyclization. Effect of Fluorine Atom Substitution on Molecular Shape

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Abstract

A modular synthesis of regiospecifically fluorinated polycyclic aromatic hydrocarbons (PAHs) is described. 1,2-Diarylfluoroethenes, synthesized via Julia-Kocienski olefination (70–99% yields), were converted to isomeric 5- and 6-fluorobenzo[*c*]phenanthrene, 5- and 6-fluorochrysene, and 9- and 10-benzo[*g*]chrysene (66–83% yields) by oxidative photocyclization. Photocyclization to 6-fluorochrysene proceeded more slowly than conversion of 1-styrylnaphthalene to chrysene. Higher fluoroalkene dilution led to a more rapid cyclization. Therefore, photocyclizations were performed at higher dilutions. To evaluate the effect of fluorine atom on molecular shapes, X-ray data for 5- and 6-fluorobenzo[*c*]phenanthrene, 6-fluorochrysene, 9- and 10-fluorobenzo[*g*]chrysene, and unfluorinated chrysene as well as benzo[*g*]chrysene were obtained and compared. The fluorine atom caused a small deviation from planarity in the chrysene series, decreased nonplanarity in the benzo[*c*]phenanthrene derivatives, but its influence was most pronounced in the benzo[*g*]chrysene series. A remarkable flattening of the molecule was observed in 9-fluorobenzo[*g*]chrysene, where the short 2.055 Å interatomic distance between bay-region F-9 and H-8, downfield shift of H-8, and a 26.1 Hz coupling between F-9 and C-8 indicate a possible F-9... H-8 hydrogen bond. Also, in 9-fluorobenzo[*g*]chrysene, stacking distance is short at 3.365 Å and there is an additional interaction between the C-11–H and C-10a of a nearby molecule that is almost perpendicular.

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SUPPORTING INFORMATION AVAILABLE

Copies of ¹H and ¹³C NMR spectra, 2D NMR spectra for compounds **4**, **7**, and **8**, UV spectra of 1-styrylnaphthalene and (*E/Z*)-1-(2-fluoro-2-phenylvinyl)naphthalene, details of the X-ray crystallographic analysis, ORTEP figures and CIF files for compounds **3**, **5–8**, chrysene, and benzo[*g*]chrysene.

Graphical Abstract

INTRODUCTION

Fluoroaromatic compounds are of interest in diverse fields, such as materials and supramolecular chemistry, environmental analyses, and biological studies. As examples, applications of fluoroaromatic compounds can be found in liquid crystalline materials, organic light-emitting diodes, and organic field-effect transistors.^{1,2} Recently, polymers containing fluorinated aromatic building blocks have shown improved performance of organic solar cells.^{2d} Use of fluoroaromatics as internal standards in GC-MS analyses has been reported.³ In the area of chemical carcinogenesis by polycyclic aromatic hydrocarbons (PAHs),^{4–10} fluorinated PAHs have frequently been used in carcinogenicity studies.

Polycyclic aromatic hydrocarbons (PAHs) are the products of activities of modern society and are common contaminants in the environment.⁴ PAHs that contain a bay or fjord region are known to undergo metabolic activation via a monooxygenase-epoxide hydrolase pathway, where angular-ring diol epoxides are formed.⁵ The electrophilic diol epoxides covalently bind to DNA ultimately resulting in adverse biological effects.⁶ An alternate metabolic pathway involves formation of reactive, redox active *o*-quinones that can lead to DNA damage.⁷ Fluorine is a powerful modulator of biological activity and introduction of fluorine into a PAH is known to significantly alter its biological activity. For example, 6-fluorobenzo[*c*]phenanthrene (6-F-BcPh) showed increased tumorigenicity as compared to benzo[*c*]phenanthrene (BcPh),⁸ whereas 6-fluorobenzo[*a*]pyrene (6-F-BaP) showed decreased tumorigenicity as compared to benzo[*a*]pyrene (BaP).⁹ In the latter case this is attributed to fluorine-atom-induced conformational change in the metabolite.^{9b} Studies on the effect molecular distortion of PAHs can have on metabolic activation and DNA binding have been conducted using 1,4-difluorobenzo[*c*]phenanthrene as a model compound.¹⁰ In order to better understand the structure-activity relationships on molecular-genetic level, availability of sufficient quantities of regiospecifically fluorinated PAHs is critical.

Our present goal was to explore a convenient, general route to regiospecifically fluorinated PAHs, via the use of fluorinated building blocks, for potential applications in diverse fields. To date, various methods have been used for the introduction of fluorine into polycyclic aromatic systems, such as diazotization-fluorination,¹¹ direct electrophilic substitution,¹² bromine-fluorine exchange,¹³ and cyclizations of smaller fluorinated building blocks.¹⁴

Photocyclizations of stilbene like derivatives with appropriate fluorine atom-substituted and often commercially available aryl moieties are known,^{10,15} and recently photodehydrofluorination approach to polyfluorinated polycyclic aromatic hydrocarbons has been reported.^{15e} Although stilbene can be cyclized readily to phenanthrene, it has been reported that α -fluorostilbene could not be cyclized to the fluoro analogue.^{15a} Introduction of an additional ring increases the feasibility of photocyclization, and β -fluoronaphthyl styrene has been converted to 6-fluorobenzo[*c*]phenanthrene.^{11a} Key to this approach was a substrate-dependent regioselective bromofluorination of β -fluoronaphthyl styrene, followed by elimination, and photochemical closure. On the other hand, synthesis of the isomeric 5-fluorobenzo[*c*]phenanthrene required a completely different approach.^{11a} Transition-metal-catalyzed introduction of fluorine atom into aromatics has been the focus of recent research and in the context of PAHs, synthesis of 4-aza-10-fluorophenanthrene,^{16a} 9-fluorophenanthrene,^{16b} 5- and 6-fluorochrysenes, and fluorinated phenacenes^{16c} has been reported. Several fluorinated PAHs (F-PAHs) were synthesized via indium(III)-catalyzed cyclization of aryl- and cyclopentene-substituted 1,1-difluoroallenes, followed by ring expansion and dehydrogenation.¹⁷ Whereas the latter two methods^{16c,17} are mechanistically interesting, one potential limitation is a substrate-dependent formation of isomeric monofluoro PAHs.

We describe herein a general route to a series of regiospecifically fluorinated aryl hydrocarbons. To our knowledge, the use of a fluoro Julia olefination to regiospecifically place a fluorine atom followed by photocyclization has not been studied to date.

RESULTS AND DISCUSSION

We have been involved with the use of the modified Julia-Kocienski olefination¹⁸ for novel approaches to variously functionalized regiospecifically fluorinated olefins,^{19,20} including 1,2-diarylfluoroethenes.²¹ Since photodehydrocyclizations of a variety of 1,2-diarylethenes to several classes of PAHs and helicenes have been well documented,²² we reasoned that photocyclization of regiospecifically substituted 1,2-diarylfluoroethenes could offer a simple, modular approach to regiospecifically fluorinated PAHs. Importantly, although 1,2-diarylfluoroethenes are formed as *E/Z* mixtures in Julia-Kocienski reactions, the alkene geometry is not critical to the photocyclization, with alkene isomerization occurring under the reaction conditions. Herein, we present a new approach to regiospecifically fluorinated PAHs via a tandem fluoro Julia olefination and oxidative photocyclization. Figure 1 shows a retrosynthetic approach to the modular synthesis of fluorinated PAHs. Also shown in Figure 1 are structures of 5- and 6-fluorobenzo[*c*]phenanthrene (5-F-BcPh and 6-F-BcPh), 5- and 6-fluorochrysene (5-F-Ch and 6-F-Ch), and 9- and 10-fluorobenzo[*g*]chrysene (9-F-BgCh and 10-F-BgCh), the targets of our approach.

Previously we have reported high-yield synthesis of regiospecifically fluorinated stilbene-like derivatives via the Julia-Kocienski olefination.²¹ For this, fluorobenzyl heteroaryl sulfones are required. We have previously developed a general synthesis via heterogeneous metalation fluorination of heteroaryl benzyl sulfones and, more specifically the 1,3-benzothiazol-2-ylsulfonyl (BT-sulfonyl) derivatives.²¹ For the purpose of this study, fluoro(phenyl)methyl (**2a**),²¹ fluoro(1-naphthyl)methyl (**2b**),^{20b} and fluoro(2-

naphthyl)methyl (**2c**)²¹ 1,3-benzothiazol-2-yl sulfones were synthesized (Scheme 1), as described. Fluoro(phenanthren-9-yl)methyl 1,3-benzothiazol-2-yl sulfone (**2d**) was prepared by analogous protocols.^{20b,21} Fluorination of sulfones **1a–d** using our heterogeneous conditions (LDA, toluene, and addition of solid NFSI) afforded fluorinated sulfone derivatives **2a–d** in high 87–93% yields. The yields of the critical fluorination step and ¹⁹F NMR data of fluoro sulfones **2a–d** are displayed in Scheme 1.

With sulfone reagents **2a–d**, synthesis of regiospecifically fluorinated vinyl compounds was performed via a modified Julia olefination. Condensation of fluorinated BT-sulfones **2a–d** with appropriate aldehydes under basic conditions (LHMDS, THF, 0 °C) afforded the *E/Z* monofluoro diarylethylenes (Table 1), the key intermediates for the photocyclization. Initially, photocyclization to 6-F-Ch (**3**) under Katz conditions,²³ was performed on a 1 g scale (4.0 mM concentration) of the fluoroalkene (*E:Z* 74%:26%), and 6-F-Ch was isolated in 74% yield. However, the reaction was extremely slow and it took 112 h to reach completion. Progress of the reaction was monitored by ¹⁹F NMR and is depicted in Figure 2. Upon conducting the photochemical ring closure at a higher dilution (1 mM) of the fluoroalkene, the reaction was complete within 8 h and 6-F-Ch (**3**) was isolated in a comparable 72% yield. Thus, it appears that the overall reaction time is dependent upon substrate concentration, but a longer reaction time does not have a detrimental effect on the yield. In this regard, Katz et al. have shown that in reactions with stoichiometric iodine, a higher substrate concentration led to lower conversion and recovery of starting material, whereas excellent conversion was obtained with increased substrate dilution, in a comparable reaction time.²³

For comparison, the unfluorinated 1-styrylnaphthalene (*E:Z* 97%:3%) was subjected to photocyclization to form chrysene on a 1 g scale (4.38 mM concentration). Progress of the reaction, depicted in Figure 3, was monitored by ¹H NMR, by comparing key resonances of the *cis*- and the *trans*-alkene, to an aromatic resonance of chrysene at 8.80 ppm (d, *J* = 8.3 Hz, 2H). Key resonances of the alkene were the vinylic²⁴ H (=C-H_{*cis*}: 6.85 ppm, d, *J* = 12.4 Hz, 1 H; =C-H_{*trans*}: 7.17 ppm, d, *J* = 16.1 Hz, 1H) and aromatic²⁴ H (Ar-H of *cis*-alkene: 8.09 ppm, br d, *J* = 7.8 Hz, 1 H; Ar-H of *trans*-alkene: 8.24 ppm, d, *J* = 8.2 Hz, 1H). In this case, conversion to chrysene was 97% complete within 1 h.

UV spectra of the alkene mixtures that were subjected to photocyclization (fluoroalkene *E/Z* 3:1 and 1-styrylnaphthalene *E:Z* 97%:3%) were compared, each at 2.3×10^{-5} M concentration. The spectrum of the fluoroalkene mixture shows a hypsochromic shift of both, long- and short-wavelength absorption maxima, as compared to the protio analogue. The long-wavelength absorption of the *E/Z* fluoroalkenes shows hypochromicity, whereas the short-wavelength absorption shows hyperchromicity as compared to the protio olefins (see the Supporting Information).

Photocyclization to 6-F-Ch in benzene, using a catalytic amount of iodine in air was also attempted on a 0.460 g scale (1.85 mM concentration). After 8 hours, analysis of the reaction mixture by ¹⁹F NMR showed resonance corresponding to 6-F-Ch (29%) and *E/Z* fluoroalkene resonances (71%). Further irradiation resulted in consumption of the fluoroalkene after 42 hours, but only a trace of 6-F-Ch was isolated, and other unidentified

products were formed. Photocyclization to 6-F-Ch in acetone as solvent, under a nitrogen atmosphere,²⁵ did not proceed, and the starting material was recovered.

In summary, these results indicated: (a) higher fluoroalkene dilution gave a faster photocyclization, (b) conditions involving catalytic iodine and air were not usable, (c) use of Katz-modified²³ photocyclization proceeded well, and (d) photocyclization in acetone under nitrogen was ineffective. On the basis of these results, photocyclizations were performed in a Hanovia immersion-type photoreactor using a 450 W Hg vapor lamp and a quartz filter. Reactions were conducted in benzene as solvent, with a stoichiometric amount of iodine as the oxidant and propylene oxide as the HI sponge. Under these conditions F-PAHs **4–8** were obtained in 66–83% yields. Table 1 shows the olefination partners, condensation yields, *E/Z* olefin ratios, and ¹⁹F NMR data of intermediate fluoroalkenes, as well as the final photocyclization products along with their yields. Notably, ¹⁹F NMR data of PAHs **3–8** (Table 1) showed that the fluorine resonance appears ca. 10 ppm more downfield when it resides in the hydrocarbon bay region (entries 2 and 6), as opposed to when it is not present in a bay region (compare data of PAHs **4** and **8** to those of **3**, **5**, **6**, and **7**).

The final fluorinated products **3–8** were crystallized for analysis by X-ray crystallography. While this work was in progress, independent syntheses and X-ray data for compounds **3** and **4** were published.¹⁷ In the present work, data analysis of compound **3** originates from the crystallographic information we obtained, whereas the analysis of data for compound **4** comes from its published crystallographic data.¹⁷

In order to gain insight into the influence of the fluorine atom on the shapes of these molecules, angles between the rings of the PAHs were compared to the corresponding unfluorinated PAH (Tables 2–4). Since the X-ray structures of the unfluorinated chrysene (Ch) and benzo[*g*]chrysene (BgCh) were unknown, we also obtained data on these two PAHs (both are commercially available and can also be synthesized via the Julia olefination-photocyclization approach presented here, using unfluorinated alkenes). Crystallographic structures obtained in this work are shown in Figure 4, and details follow.

In the chrysene series (Table 2), Ch is completely planar (0° angle between the four planes), and 6-F-Ch (**3**) shows a small deviation from planarity, with angles between the planes in the range of 0.4–1.8°. Deviation from planarity for 5-F-Ch (**4**)¹⁷ with a bay-region fluorine atom is larger, with angles between the planes in the range of 1.0–5.9°. The overall distortion from planarity (angle between planes A and D) is 1.8° for 6-F-Ch (**3**), and 5.9° for 5-F-Ch (**4**).

Although our structure of 6-F-Ch (**3**) is the same as that published by Fuchibe et al.,¹⁷ our analysis of its crystal structure differed in the treatment of the hydrogen atom fluorine atom positions. All hydrogen atom positions were found and refined from our X-ray data, whereas Fuchibe et al.¹⁷ calculated the idealized hydrogen atom positions. That fluorine exhibits positional disorder is well-established,²⁶ and indeed, for 6-F-Ch (**3**) the fluorine atom occurs 78% of the time at the C-6 (major occupancy position) and 22% of the time at the C-12 position. The remainder of the time, at these positions, fluorine is replaced by a hydrogen atom. The C–F bond length of the major occupancy fluorine is 1.343(3) Å while the C–F bond for the minor occupancy fluorine, as expected, is in between a C–H and C–F bond

length, 1.146(9) Å. From our experimentally determined hydrogen atom positions, we can see two dominant intermolecular interactions, a strong stacking interaction and a C–H...F interaction (Figure 5). The stacking interaction of 3.421(5) Å is between the planes of 6-F-Ch (**3**) molecules. The second interaction is the hydrogen bond between the major occupancy F (at C-6) and the H-8–C-8 of a neighboring molecule at 2.516(9) Å that is perpetuated throughout the crystal structure. This C–H...F distance is shorter than the calculated distance of 2.619 Å from the published crystal structure having calculated hydrogen atom positions of C-6–F...H-8. We also see additional intermolecular interactions between C–H and ring carbon atoms of 2.844 Å, 2.895 Å, and 2.889 Å. These are approximately perpendicular (Figure 5).

In BcPh series, the overall distortion from planarity in 5-F-BcPh (**5**) and in 6-F-BcPh (**6**) is smaller than in the parent hydrocarbon (Table 3 and Figure 4). This is reflected in the angle between rings A and D forming the fjord region and in the angle between rings A and C. The angle between rings A and D is 26.7° in BcPh, and decreases to 24.3° and 23.6° in 6-F-BcPh (**6**) and 5-F-BcPh (**5**), respectively. The angle between rings A and C is 18.1° in BcPh, 16.2° in 6-F-BcPh (**6**), and 14.2° in 5-F-BcPh (**5**).

The most pronounced effect fluorine atom has on the molecular shape is in the benzo[g]chrysene series. Here again, the overall distortion from planarity decreases upon fluorine atom substitution (Table 4 and Figure 4). The angle between rings A and D forming the fjord region is 36.0° in the parent BgCh, and this decreases to 32.6° in 10-F-BgCh (**7**) and to 33.3° in 9-F-BgCh (**8**). However, the angles between rings B and E, which form a bay region, show the most remarkable difference. The angle between rings B and E is 20.1° in the parent hydrocarbon, decreasing to 18.2° in 10-F-BgCh (**7**), and this decreases dramatically to 9.2° in 9-F-BgCh (**8**). In 9-F-BgCh (**8**), the fluorine atom resides in the bay region, and the interatomic distance between F-9 and the bay-region H-8 is 2.055 Å, with a C–H...F angle of 128.73°, which suggests a possible hydrogen bond.^{27,28} In the ¹H NMR spectrum of 9-F-BgCh (**8**), H-8 appears at 9.07 ppm, and is shifted downfield as compared to H-8 in unsubstituted BgCh, where it appears at 8.63 ppm.²⁹ The bay-region H-8 and F-9 resonances in compound **8** show a small ~2 Hz coupling (2.3 and 2.2 Hz, respectively). In the ¹³C NMR spectrum of 9-F-BgCh (**8**), the C-8 resonance appears at 128.0 ppm, as a doublet with a *J* = 26.1 Hz. This is a typical value for a scalar two-bond C–F coupling constant. The downfield shift of the H-8 proton, its coupling to F-9, and the large C-8–F coupling constant further support possible hydrogen bonding between F-9 and H-8.^{27,28} It is plausible, therefore, that the tendency towards F–H bonding is responsible for the planarization in B-, C-, E-ring region, decreasing the angles between these rings in 9-F-BgCh (**8**). The hydrogen atom positions in the 9-F-BgCh structure were calculated. Additional strong intermolecular interactions include the short stacking distance at 3.365 Å and two additional short almost perpendicular interactions: one at 2.875 Å between the C-11–H and C-10a of a nearby molecule and another at 2.872 between C-4–H and C-6 of a neighboring molecule (Figure 6).

In 5-F-Ch (**4**), which also has a fluorine atom residing in the bay region, the interatomic distance between F-5 and the bay-region H-4 is 2.069 Å, with a C–H...F angle of 126.80°, again suggestive of intramolecular hydrogen bonding. The ¹H and ¹³C NMR spectra of 5-F-

Ch (**4**) show similar features to those of 9-F-BgCh (**8**). In the ^1H NMR spectrum of 5-F-Ch (**4**), the bay-region H-4 appears at 9.25 ppm, and is downfield shifted as compared to H-4 in unsubstituted chrysene (Ch), which appears at 8.79 ppm.³⁰ The bay-region H-4 and F-5 resonances in compound **4** show a ~ 3 Hz coupling (2.8 and 3.3 Hz, respectively). In the ^{13}C NMR spectrum of 5-F-Ch (**4**), the bay-region C-4 appears at 128.0 ppm, as a doublet, with a large 26.6 Hz coupling constant with the fluorine atom.

Through-space spin-spin coupling has been a subject of research for several years now.³¹ In previous studies, other investigators have reported comparable NMR spectral features for PAHs containing a bay-region fluorine atom. Mallory et al. suggested through-space H-F coupling interactions in 4-fluorophenanthrene, where a 2.6 Hz H-F coupling was observed between the bay-region fluorine atom and the bay-region H-5.³² In the present case, resonances of bay-region H-8 and F-9 of compound **8** show a similar small ~ 2 Hz coupling, whereas resonances of bay-region H-4 and F-5 of compound **4** show a ~ 3 Hz coupling. Sardella et al. studied ^1H and ^{13}C NMR spectra of PAHs containing a bay-region fluorine atom.³³ Similar to what we have observed for compounds **8** and **4**, a C-F coupling of 24.9 Hz across the bay region was reported, and through-space C-F coupling interactions were suggested.³³

We also obtained ^1H - ^{19}F HOESY spectra of 9-F-BgCh (**8**, left, Figure 7) and 5-F-Ch (**4**, right, Figure 7). The HOESY spectrum of 9-F-BgCh (**8**) shows an intense interaction between the fluorine atom and the H-8 resonance at 9.07 ppm, in support of C-8-H $\cdots$ F hydrogen bonding. The weaker interaction is between the fluorine atom and the H-10 resonance at 7.67 ppm. The HOESY spectrum of 5-F-Ch (**4**) shows an intense interaction between the fluorine atom and the H-4 resonance at 9.25 ppm, in support of C-4-H $\cdots$ F hydrogen bonding. The weaker interaction is between the fluorine atom and the H-6 resonance at 7.68 ppm.

CONCLUSIONS

1,2-Diarylfluoroethenes, which were synthesized via Julia-Kocienski olefination, were subjected to oxidative photocyclization to yield regiospecifically substituted monofluoro PAHs. Photocyclizations of the 1,2-diarylfluoroethenes were much slower as compared to those of their unfluorinated analogues, and higher dilutions produced faster reactions. The method is straightforward, highly modular, and is applicable to the synthesis of fluoro PAHs and potentially to other fluoro PAHs that contain additionally substituted aryl moieties.

It has recently been reported that introduction of fluorine atom into phenacenes does not change their shape.^{16c} However, in the present cases, we have observed that fluorine-atom substitution does elicit influence on the shapes of the molecules when compared to their unfluorinated analogues. A small deviation from planarity was observed for 6-F-Ch in comparison to chrysene, which is planar, and deviation from planarity increased in 5-F-Ch containing a bay-region fluorine atom. On the other hand, in comparison to BcPh, both 5- and 6-F-BcPh are slightly less nonplanar. Also, as reported by other investigators, we have observed positional disorder in the fluorine atom positions. Additionally, the molecular assemblies in the crystal structure are stabilized by π - π stacking interactions as well as

through the formation of C–H...F intermolecular interactions. These features highlight the important role that fluorine substitution plays in organic molecules. Earlier studies by Thalladi et al.³⁴ showed that, in general, C–H...F hydrogen bonds were preferred to F...F contacts. The marked difference in crystal packing behavior between fluorine and the heavier halogens is confirmed with our molecules. In more angularly fused B_gCh series, a more dramatic shape change occurred, with the most pronounced effect in 9-F-B_gCh. In this case, the fluorine atom resides in the bay region and causes substantial planarization of B, C, E rings forming the bay region, possibly via intramolecular F...H bonding.

EXPERIMENTAL SECTION

THF was distilled over LiAlH₄ and then over sodium, toluene and benzene were distilled over sodium, and CH₂Cl₂ was distilled over CaCl₂. DMF was obtained from commercial sources and was used without further purification. For reactions performed in a nitrogen atmosphere, glassware was dried with heat gun under vacuum. LDA (2.0 M solution in heptane/THF/EtPh) and LHMDs (1.0 M in THF) were obtained from commercial sources. All other reagents were obtained from commercial sources and were used as received. We have previously reported syntheses of 2-[fluoro(phenyl)methylsulfonyl]benzo[d]thiazole (**2a**),²¹ 2-[fluoro(naphthalen-1-yl)methylsulfonyl]benzo[d]thiazole (**2b**),^{20b} and of 2-[fluoro(naphthalen-2-yl)methylsulfonyl]benzo[d]thiazole (**2c**),²¹ and their precursor sulfones **1a**,²¹ **1b**,^{20b} and **1c**.²¹ Photocyclizations of alkenes were performed in a Hanovia immersion-type photoreactor using a 450 W Hg vapor lamp and a quartz filter. Thin layer chromatography was performed on glass-backed silica gel plates (250 μm). Column chromatographic purifications were performed on 200–300 mesh silica gel. ¹H NMR spectra were recorded at 500 MHz and were referenced to residual protio solvent. ¹³C NMR spectra were recorded at 125 MHz and were referenced to the carbon resonance of the deuterated solvent. ¹⁹F NMR spectra were recorded at 282 MHz with CFC₃ as the internal standard. Chemical shifts (δ) are reported in parts per million, and coupling constants (*J*) are in hertz (Hz). On the basis of 2D NMR data, some proton and carbon assignments were made for 5-fluorochrysene (**4**), 10-fluorobenzo[*g*]chrysene (**7**), and 9-fluorobenzo[*g*]chrysene (**8**). HRMS data were obtained using a FTICR-MS, the ionization modes are specified under each compound heading.

Synthesis of 2-[[Fluoro(phenanthren-9-yl)methyl]sulfonyl]benzo[d]thiazole **2d**

2-[(Phenanthren-9-ylmethyl)thio]benzo[d]thiazole—To a solution of the sodium salt of 1,3-benzo-2-thiazole (1.324 g, 7.00 mmol, 1.25 molar equiv) in DMF (20 mL) was added a solution of 9-(bromomethyl)phenanthrene (1.518 g, 5.60 mmol) in DMF (30 mL). The mixture was stirred at rt and monitored by TLC (SiO₂, 20% EtOAc in hexanes). After 6.0 h, complete consumption of 9-(bromomethyl)phenanthrene was observed, and the reaction was quenched with aq NH₄Cl solution (30 mL). The mixture was extracted with EtOAc (3x), the combined organic layers were washed aq NaHCO₃ solution (30 mL), brine (30 mL), and dried over anhydrous Na₂SO₄. The organic layer was concentrated under reduced pressure, and crude product was purified by column chromatography (SiO₂, 10% EtOAc in hexanes) to yield pure 2-[(phenanthren-9-ylmethyl)thio]benzo[d]thiazole (1.821 g, 91%) as a colorless solid. ¹H NMR (500 MHz, CDCl₃): δ 8.76 (br dd, *J* = 8.5, 1.4 Hz, 1H), 8.67 (d, *J* =

8.3 Hz, 1H), 8.22 (br dd, $J = 8.3, 1.9$ Hz, 1H), 7.98 (d, $J = 8.3$ Hz, 1H), 7.94 (s, 1H), 7.86 (d, $J = 7.4$ Hz, 1H), 7.77 (d, $J = 8.3$ Hz, 1H), 7.72–7.64 (m, 3H), 7.59 (td, $J = 7.4, 0.9$ Hz, 1H), 7.47 (td, $J = 7.7, 1.2$ Hz, 1H), 7.33 (td, $J = 7.8, 0.9$ Hz, 1H), 5.18 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 166.7, 153.4, 135.6, 131.5, 131.1, 130.8, 130.5, 130.0, 129.4, 128.8, 127.3, 127.2, 127.1, 127.0, 126.3, 124.63, 124.55, 123.6, 122.8, 121.8, 121.3, 36.4. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{22}\text{H}_{16}\text{NS}_2$ 358.0719, found 358.0723.

2-[(Phenanthren-9-ylmethyl)sulfonyl]benzo[d]thiazole 1d—A solution of 2-[(phenanthren-9-ylmethyl)thio]benzo[d]thiazole (0.943 g, 2.64 mmol) in CH_2Cl_2 (40 mL) was added dropwise to a solution of *m*CPBA (1.365 g, 7.91 mmol, 3.00 molar equiv) in CH_2Cl_2 (30 mL), cooled to 0 °C. After complete addition, the mixture was stirred at rt overnight. The reaction was quenched with aq NaHCO_3 (30 mL), the organic layer was separated and washed with aq NaHCO_3 (30 mL), 5% aq NaOH (30 mL, twice), water and then brine (30 mL each), and dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure, and crude product was purified by column chromatography (SiO_2 , 30% EtOAc in hexanes) to yield pure 2-[(phenanthren-9-ylmethyl)sulfonyl]benzo[d]thiazole (**1d**) as a colorless solid (0.728 g, 71%). ^1H NMR (500 MHz, CDCl_3): δ 8.68 (d, $J = 8.3$ Hz, 1H), 8.64 (d, $J = 8.3$ Hz, 1H), 8.29 (d, $J = 8.3$ Hz, 1H), 8.11 (d, $J = 8.3$ Hz, 1H), 7.86 (d, $J = 8.3$ Hz, 1H), 7.75 (s, 1H), 7.72 (d, $J = 7.8$ Hz, 1H), 7.69–7.64 (m, 2H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.57–7.51 (m, 3H), 5.32 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 165.6, 152.8, 137.4, 133.0, 131.05, 130.98, 130.92, 130.5, 129.0, 128.2, 128.0, 127.8, 127.14, 127.12, 127.0, 125.6, 124.6, 123.3, 122.7, 122.4, 121.6, 58.7. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{22}\text{H}_{16}\text{NO}_2\text{S}_2$ 390.0617, found 390.0622.

2-[[Fluoro(phenanthren-9-yl)methyl]sulfonyl]benzo[d]thiazole 2d—A stirring solution of sulfone **1d** (0.488 g, 1.25 mmol) in dry toluene (80 mL) was cooled under nitrogen gas to –78 °C (dry ice/*i*PrOH). LDA (0.800 mL, 1.60 mmol, 1.28 molar equiv) was added, and after 12 min, solid NFSI (0.488 g, 1.55 mmol, 1.24 molar equiv) was added. The reaction mixture was allowed to stir at –78 °C for 50 min, then warmed to rt, and stirring was continued for an additional 50 min. Saturated aq NH_4Cl was added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with EtOAc (3x), and the combined organic layer was washed with saturated aq NaHCO_3 (30 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4 , and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2 , 20% EtOAc in hexanes) to yield pure 2-[[fluoro(phenanthren-9-yl)methyl]sulfonyl]benzo[d]thiazole **2d** as a white solid (0.357 g, 70%). ^1H NMR (500 MHz, CDCl_3): δ 8.76–8.73 (m, 1H), 8.68 (d, $J = 8.3$ Hz, 1H), 8.34–8.32 (m, 2H), 8.21 (s, 1H), 8.02 (d, $J = 8.3$ Hz, 1H), 7.94 (d, $J = 7.8$ Hz, 1H), 7.76–7.60 (m, 6H), 7.54 (d, $J = 45.1$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 163.5, 153.1, 137.7, 131.8, three resonances at 131.0, 130.9, 130.8 (2C, one s and one d), 130.4, 129.9, 129.1 (d, $J = 6.5$ Hz), 128.9, 128.6, 128.0, 127.6, 127.4 (2C), 125.9, 124.3, 123.5, 122.8, 122.5, 121.3 (d, $J = 17.3$ Hz), 99.8 (d, $J = 221.9$ Hz). ^{19}F NMR (282 MHz, CDCl_3): δ –171.5 (d, $J = 42.7$ Hz). HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{22}\text{H}_{14}\text{FNO}_2\text{S}_2\text{Na}$ 430.0342, found 430.0339.

Synthesis of 6-Fluorochrysene 3^{12a,16c,17,35}

Step 1. Condensation of 2a with 1-naphthaldehyde—A solution of 1-naphthaldehyde (0.491 g, 3.14 mmol) and sulfone **2a** (1.161 g, 3.59 mmol, 1.14 molar equiv) in dry THF (60 mL) was cooled to 0 °C under a nitrogen atmosphere. LHMDs (7.60 mL, 7.60 mmol, 2.42 molar equiv) was added dropwise at 0 °C. The mixture was stirred at 0 °C for 10 min, allowed to warm to rt and stirred at rt. After 1 h, TLC (10% EtOAc in hexanes) showed complete disappearance of the aldehyde. Saturated aq NH₄Cl (30 mL) was added and the mixture was extracted with EtOAc (3x). The combined organic layer was washed with NaHCO₃ (30 mL), brine (30 mL), and then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO₂, eluted with hexanes, followed by 2% EtOAc in hexanes) to yield pure (*E/Z*)-1-(2-fluoro-2-phenylvinyl)naphthalene (*E:Z* ratio 2.8:1) as a colorless liquid (0.773 g, 99%). ¹⁹F NMR (282 MHz, CDCl₃): δ -100.0 (d, *J* = 21.4 Hz, 1F), -115.6 (d, *J* = 39.7 Hz, 1F). HRMS (+APPI mode) [M]⁺ calcd. for C₁₈H₁₃F 248.0996, found 248.0997.

Step 2. Photocyclization of (*E/Z*)-1-(2-fluoro-2-phenylvinyl)naphthalene to 3^{12a,16c,17,35}—(*E/Z*)-1-(2-fluoro-2-phenylvinyl)naphthalene (*E:Z* ratio 2.8:1, 63.1 mg, 0.254 mmol) was dissolved in benzene (250 mL), I₂ (71.1 mg, 0.280 mmol, 1.10 molar equiv) was added, and nitrogen was bubbled into the solution for 10 min. Propylene oxide (2.90 mL, 2.41 g, 41.4 mmol, 163 molar equiv) was added, the solution was subjected to irradiation, and the reaction was monitored by ¹⁹F NMR. After 8 h, ¹⁹F NMR showed consumption of the (*E/Z*)-alkene. The solvent was evaporated and the crude product was purified by column chromatography (SiO₂, 2% EtOAc in hexanes) to afford pure 6-fluorochrysene **3** (45.1 mg, 72%) as a white solid. For X-ray analysis, this compound was crystallized from hexanes/2–3 drops of CH₂Cl₂. ¹H NMR (500 MHz, CDCl₃): δ 8.79 (d, *J* = 8.3 Hz, 1H), 8.66 (d, *J* = 9.2 Hz, 1H), 8.63 (d, *J* = 8.3 Hz, 1H), 8.35 (d, *J* = 12.9 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 158.1 (d, *J* = 250.8 Hz), 132.6, 132.2 (d, *J* = 5.8 Hz), 130.4 (d, *J* = 4.4 Hz), 128.9 (one resonance of the doublet partially buried under a singlet), 128.8, 127.9, 127.0, 126.9, 126.7 (d, *J* = 2.2 Hz), 125.5, 123.9 (d, *J* = 17.8 Hz), 123.5 (d, *J* = 3.2 Hz), 123.4, 121.4 (d, *J* = 5.9 Hz), 121.1, 104.1 (d, *J* = 22.0 Hz). ¹⁹F NMR (282 MHz, CDCl₃): δ -123.8 (d, *J* = 15.3 Hz).

Synthesis of 5-Fluorochrysene 4^{16c,17}

Step 1. Condensation of 2b with benzaldehyde—A solution of benzaldehyde (38.8 mg, 0.366 mmol) and sulfone **2b** (147 mg, 0.411 mmol, 1.12 molar equiv) in dry THF (20 mL) was cooled to 0 °C under a nitrogen atmosphere. LHMDs (0.980 mL, 0.980 mmol, 2.68 molar equiv) was added dropwise at 0 °C. The mixture was stirred at 0 °C for 10 min, allowed to warm to rt and stirred at rt. After 1 h, TLC (5% EtOAc in hexanes) showed complete disappearance of the aldehyde. Saturated aq NH₄Cl (30 mL) was added and the mixture was extracted with EtOAc (3x). The combined organic layer was washed with NaHCO₃ (30 mL), brine (30 mL), and then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO₂, eluted with 5% EtOAc in hexanes) to yield pure (*E/Z*)-1-(1-fluoro-2-

phenylvinyl)naphthalene (*E:Z* ratio 2.9:1, 73.5 mg, 81%). ^{19}F NMR (282 MHz, CDCl_3): δ –84.4 (d, J = 18.3 Hz, 1F), –95.2 (d, J = 39.7 Hz, 1F). HRMS (+APPI mode) $[\text{M}]^+$ calcd. for $\text{C}_{18}\text{H}_{13}\text{F}$ 248.0996, found 248.1000.

Step 2. Photocyclization of (*E/Z*)-1-(1-fluoro-2-phenylvinyl)naphthalene to

4.^{16c,17}—(*E/Z*)-1-(1-Fluoro-2-phenylvinyl)naphthalene (*E:Z* ratio 2.9:1, 70.0 mg, 0.282 mmol) was dissolved in benzene (250 mL), I_2 (78.3 mg, 0.308 mmol, 1.10 molar equiv) was added, and nitrogen was bubbled into the solution for 10 min. Propylene oxide (3.20 mL, 2.66 g, 45.8 mmol, 162 molar equiv) was added, the solution was subjected to irradiation, and the reaction was monitored by ^{19}F NMR. After 16 h, ^{19}F NMR showed consumption of the alkene. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2 , 2% CH_2Cl_2 in hexanes) to yield pure 5-fluorochrysene **4** as a white solid (49.2 mg, 71%). For X-ray analysis, this compound was crystallized from hexanes/2–3 drops of CH_2Cl_2 . ^1H NMR (500 MHz, CDCl_3): δ 9.25 (dd, J = 8.3, 2.8 Hz, 1H, H-4), 8.75 (dd, J = 7.8, 0.9 Hz, 1H, H-10), 8.73 (dd, J = 9.2, 2.3 Hz, 1H, H-11), 8.06 (d, J = 8.8 Hz, 1H, H-12), 8.02 (d, J = 7.8 Hz, 1H, H-1), 7.93–7.91 (m, 1H, H-7), 7.73 (br t, J = 8.3 Hz, 1H, H-3), 7.68 (d, J = 15.7 Hz, 1H, H-6), 7.69–7.64 (m, 3H, H-2, H-8, H-9). ^{13}C NMR (125 MHz, CDCl_3): δ 160.0 (d, J = 252.7 Hz, C-5), 132.9, 132.3 (d, J = 11.4 Hz), 131.5 (d, J = 5.5 Hz), 129.2 (d, J = 1.4 Hz, C-12), 129.1 (d, J = 5.5 Hz), 128.7 (C-1), 128.04 (d, J = 1.1 Hz), 128.0 (d, J = 26.6 Hz, C-4), 127.7 (d, J = 5.0 Hz, C-7), 127.5 (d, J = 3.2 Hz), 127.4, 126.9 (d, J = 2.3 Hz), 126.0 (d, J = 2.3 Hz), 123.6 (d, J = 1.4 Hz, C-10), 121.2 (d, J = 3.2 Hz, C-11), 120.1 (d, J = 11.9 Hz), 111.1 (d, J = 24.7 Hz, C-6). ^{19}F NMR (282 MHz, CDCl_3 , resolution enhanced): δ –111.8 (br dt, J = 15.7, 3.3 Hz).

Synthesis of 5-Fluorobenzo[*c*]phenanthrene **5^{11a,15a}**

Step 1. Condensation of 2a with 2-naphthaldehyde—A solution of 2-naphthaldehyde (393 mg, 2.51 mmol) and sulfone **2a** (880 mg, 2.86 mmol, 1.10 molar equiv) in dry THF (25.0 mL) was cooled to 0 °C under a nitrogen atmosphere. LHMDS (6.50 mL, 6.50 mmol, 2.40 molar equiv) was added dropwise at 0 °C. The mixture was stirred at 0 °C for 10 min, allowed to warm to rt and stirred at rt. After 2 h, TLC (10% EtOAc in hexanes) showed complete disappearance of the aldehyde. Saturated aq NH_4Cl (30 mL) was added and the mixture was extracted with EtOAc (3x). The combined organic layer was washed with NaHCO_3 (30 mL), brine (30 mL), and then dried over anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2 , eluted with hexanes, followed by 2% EtOAc in hexanes) to yield pure (*E/Z*)-2-(2-fluoro-2-phenylvinyl)naphthalene²¹ (*E:Z* ratio 2.9:1) as a yellowish solid (581 mg, 99%). ^{19}F NMR (282 MHz, CDCl_3): δ –96.2 (d, J = 18.3 Hz, 1F), –114.4 (d, J = 39.7 Hz, 1F). HRMS (+APPI mode) $[\text{M}]^+$ calcd. for $\text{C}_{18}\text{H}_{13}\text{F}$ 248.0996, found 248.0995.

Step 2. Photocyclization of (*E/Z*)-2-(2-fluoro-2-phenylvinyl)naphthalene to

5.^{11a,15a}—(*E/Z*)-2-(2-Fluoro-2-phenylvinyl)naphthalene (*E:Z* ratio 2.9:1, 60.0 mg, 0.241 mmol) was dissolved in benzene (250 mL), I_2 (64.4 mg, 0.253 mmol, 1.05 molar equiv) was added, and nitrogen was bubbled into the solution for 10 min. Propylene oxide (2.80 mL, 2.32 g, 40.0 mmol, 166 molar equiv) was added, the solution was subjected to irradiation, and the reaction was monitored by ^{19}F NMR. After 12 h, ^{19}F NMR showed consumption of

(*E/Z*)-2-(2-fluoro-2-phenylvinyl)naphthalene. The solvent was evaporated and the crude product was purified by column chromatography (SiO₂, 2% CH₂Cl₂ in hexanes) to yield pure 5-fluorobenzo[*c*]phenanthrene **5** as a white solid (39.1 mg, 66%). For X-ray analysis, this compound was crystallized from hexanes/2–3 drops of CH₂Cl₂. ¹H NMR (500 MHz, CDCl₃): δ 9.16 (d, *J* = 8.3 Hz, 1H), 9.07 (d, *J* = 8.3 Hz, 1H), 8.33 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.77–7.68 (m, 4H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 10.6 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 157.4 (d, *J* = 252.7 Hz), 133.2, 132.0 (d, *J* = 5.0 Hz), 131.2 (d, *J* = 9.2 Hz), 130.4, 128.9, 128.4, 128.1 (d, *J* = 2.8 Hz), 127.7, 127.3, 126.7, 126.5 (d, *J* = 3.7 Hz), 126.4 (d, *J* = 1.4 Hz), 125.9, 124.9 (d, *J* = 17.4 Hz), 124.6 (d, *J* = 2.3 Hz), 121.3 (d, *J* = 6.4 Hz), 108.9 (d, *J* = 20.1 Hz). ¹⁹F NMR (282 MHz, CDCl₃): δ –125.4 (d, *J* = 9.2 Hz).

Synthesis of 6-Fluorobenzo[*c*]phenanthrene **6**^{11a,15a,17}

Step 1. Condensation of 2c with benzaldehyde—A solution of benzaldehyde (228 mg, 2.15 mmol) and sulfone **2c** (920 mg, 2.58 mmol, 1.20 molar equiv) in dry THF (28 mL) was cooled to 0 °C under a nitrogen atmosphere. LHMDS (5.15 mL, 5.15 mmol, 2.40 molar equiv) was added dropwise at 0 °C and the mixture was stirred at 0 °C. After 2 h, TLC (10% EtOAc in hexanes) showed complete disappearance of the aldehyde. Saturated aq NH₄Cl (30 mL) was added and the mixture was extracted with EtOAc (3x). The combined organic layer was washed with NaHCO₃ (30 mL), brine (30 mL), and then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO₂, eluted with 5% EtOAc in hexanes) to yield pure (*E/Z*)-2-(1-fluoro-2-phenylvinyl)naphthalene (*E:Z* ratio 2.75:1) as an off-white solid (460 mg, 76%). ¹⁹F NMR (282 MHz, CDCl₃): δ –96.6 (d, *J* = 21.4 Hz, 1F) and –114.9 (d, *J* = 39.7 Hz, 1F). HRMS (+APPI mode) [M]⁺ calcd. for C₁₈H₁₃F 248.0996, found 248.0999.

Step 2. Photocyclization of (*E/Z*)-2-(1-fluoro-2-phenylvinyl)naphthalene to **6^{11a,15a,17}**—(*E/Z*)-2-(1-fluoro-2-phenylvinyl)naphthalene (*E:Z* ratio 2.75:1, 127 mg, 0.512 mmol) was dissolved in benzene (250 mL), I₂ (144 mg, 0.567 mmol, 1.11 molar equiv) was added, and nitrogen was bubbled into the solution for 10 min. Propylene oxide (7.17 mL, 5.95 g, 102 mmol, 200 molar equiv) was added, the solution was subjected to irradiation, and the reaction was monitored by ¹⁹F NMR. After 26 h, ¹⁹F NMR showed consumption of the alkene. The solvent was evaporated and the crude product was purified by column chromatography (SiO₂, 2.5% EtOAc in hexanes) to yield pure 6-fluorobenzo[*c*]phenanthrene **6** as a white solid (105 mg, 83%). For X-ray analysis, this compound was crystallized from hexanes/2–3 drops of CH₂Cl₂, m.p. 72–73 °C. ¹H NMR (500 MHz, CDCl₃): δ 9.12 (d, *J* = 8.3 Hz, 1H), 9.10 (d, *J* = 9.2 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.99–7.95 (m, 2H), 7.73–7.66 (m, 3H), 7.63 (t, *J* = 3.5 Hz, 1H), 7.56 (d, *J* = 10.6 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 157.2 (d, *J* = 251.3 Hz), 133.9, 133.3 (d, *J* = 10.6 Hz), 130.1 (d, *J* = 2.8 Hz), 129.5 (d, *J* = 4.8 Hz), 129.0, 128.3 (one resonance of the doublet partially buried under a singlet), 128.24, 128.22, 128.19, 128.0, 126.78, 126.77, 126.73, 125.5 (d, *J* = 1.9 Hz), 123.0 (d, *J* = 18.2 Hz), 118.7 (d, *J* = 8.6 Hz), 109.1 (d, *J* = 20.1 Hz). ¹⁹F NMR (282 MHz, CDCl₃): δ –125.8 (d, *J* = 12.2 Hz).

Synthesis of 10-Fluorobenzo[*g*]chrysene 7

Step 1. Condensation of 2a with phenanthrene-9-carboxaldehyde—A solution of phenanthrene-9-carboxaldehyde (79.7 mg, 0.386 mmol) and sulfone **2a** (149 mg, 0.459 mmol, 1.19 molar equiv) in dry THF (10 mL) was cooled to 0 °C under a nitrogen atmosphere. LHMDS (0.90 mL, 0.90 mmol, 2.33 molar equiv) was added dropwise at 0 °C. The mixture was stirred at 0 °C for 10 min, allowed to warm to rt and stirred at rt. After 1 h, TLC (5% EtOAc in hexanes) showed complete disappearance of the aldehyde. Saturated aq NH₄Cl (30 mL) was added and the mixture was extracted with EtOAc (3x). The combined organic layer was washed with NaHCO₃ (30 mL), brine (30 mL), and then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO₂, eluted with 5% EtOAc in hexanes) to yield pure (*E/Z*)-9-(2-fluoro-2-phenylvinyl)phenanthrene (*E:Z* ratio 3.1:1) as a colorless liquid (80.7 mg, 70%). ¹⁹F NMR (282 MHz, CDCl₃): δ -100.3 (d, *J* = 21.4 Hz, 1F), -115.2 (d, *J* = 36.6 Hz, 1F). HRMS (+APPI mode) [M]⁺ calcd. for C₂₂H₁₅F 298.1152, found 298.1159.

Step 2. Photocyclization of (*E/Z*)-9-(2-fluoro-2-phenylvinyl)phenanthrene to 7—(*E/Z*)-9-(2-Fluoro-2-phenylvinyl)phenanthrene (*E:Z* ratio 3.1:1, 80.7 mg, 0.270 mmol) was dissolved in benzene (250 mL), I₂ (84.1 mg, 0.331 mmol, 1.23 molar equiv) was added, and nitrogen was bubbled into the solution for 10 min. Propylene oxide (3.12 mL, 2.59 g, 44.6 mmol, 165 molar equiv) was added, the solution was subjected to irradiation, and the reaction was monitored by ¹⁹F NMR. After 8.5 h, ¹⁹F NMR showed consumption of (*E/Z*)-9-(2-fluoro-2-phenylvinyl)phenanthrene. The solvent was evaporated and the crude product was purified by column chromatography (SiO₂, 4% EtOAc in hexanes) to yield pure 10-fluorobenzo[*g*]chrysene **7** as a white solid (61.3 mg, 77%). For X-ray analysis, this compound was crystallized from hexanes/2–3 drops of CH₂Cl₂, m.p. 141 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.95 (d, *J* = 7.4 Hz, 1H), 8.81 (d, *J* = 7.8 Hz, 1H), 8.72 (d, *J* = 8.3 Hz, 1H), 8.71–8.68 (m, 1H), 8.50–8.48 (m, 1H), 8.31–8.29 (m, 1H), 8.24 (d, *J* = 12.4 Hz, 1H, H-9), 7.72–7.62 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 158.3 (d, *J* = 251.7 Hz, C-10), 131.9 (d, *J* = 5.0 Hz), 130.7, 130.4, 129.5 (d, *J* = 3.5 Hz), 129.4, 129.2, 128.7 (d, *J* = 2.7 Hz), 127.8, 127.6, 127.2, 126.7, 126.5, 126.4, 124.6 (d, *J* = 17.4 Hz), 124.3 (d, *J* = 2.6 Hz), 124.0, 123.7, 123.4, 121.0 (d, *J* = 5.5 Hz), 104.1 (d, *J* = 21.5 Hz, C-9). ¹⁹F NMR (282 MHz, CDCl₃): δ -124.3 (d, *J* = 12.2 Hz). HRMS (+APPI mode) [M]⁺ calcd. for C₂₂H₁₃F 296.0996, found 296.0998.

Synthesis of 9-Fluorobenzo[*g*]chrysene 8

Step 1. Condensation of 2d with benzaldehyde—A solution of benzaldehyde (59.7 mg, 0.563 mmol) and sulfone **2d** (270 mg, 0.664 mmol, 1.18 molar equiv) in dry THF (10 mL) was cooled to 0 °C under a nitrogen atmosphere. LHMDS (1.40 mL, 1.40 mmol, 2.49 molar equiv) was added dropwise at 0 °C. The mixture was stirred at 0 °C for 10 min, allowed to warm to rt and stirred at rt. After 1 h, TLC (10% EtOAc in hexanes) showed complete disappearance of the aldehyde. Saturated aq NH₄Cl (30 mL) was added and the mixture was extracted with EtOAc (3x). The combined organic layer was washed with NaHCO₃ (30 mL), brine (30 mL), and then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the crude product was purified by column

chromatography (SiO₂, eluted with 5% EtOAc in hexanes) to yield pure (*E/Z*)-9-(1-fluoro-2-phenylvinyl)phenanthrene (*E:Z* ratio 2.88:1) as a colorless liquid (149 mg, 89%). ¹⁹F NMR (282 MHz, CDCl₃): δ -85.0 (d, *J* = 21.4 Hz, 1F), -95.3 (d, *J* = 36.6 Hz, 1F). HRMS (+APPI mode) [M]⁺ calcd. for C₂₂H₁₅F 298.1152, found 298.1151.

Step 2. Photocyclization of (*E/Z*)-9-(1-fluoro-2-phenylvinyl)phenanthrene to 8—(*E/Z*)-9-(1-Fluoro-2-phenylvinyl)phenanthrene (*E:Z* ratio 2.88:1, 76.1 mg, 0.255 mmol) was dissolved in benzene (250 mL), I₂ (71.3 mg, 0.281 mmol, 1.10 molar equiv) was added, and nitrogen was bubbled into the solution for 10 min. Propylene oxide (2.80 mL, 2.32 g, 40.0 mmol, 157 molar equiv) was added, the solution was subjected to irradiation, and the reaction was monitored by ¹⁹F NMR. After 8 h, ¹⁹F NMR showed consumption of the alkene. The solvent was evaporated and the crude product was purified by column chromatography (SiO₂, 2% EtOAc in hexanes) to yield pure 9-fluorobenzo[*g*]chrysene **8** as a white solid (55.1 mg, 73%). For X-ray analysis, this compound was crystallized from EtOH/2–3 drops of benzene/1 drop of CH₂Cl₂. ¹H NMR (500 MHz, CDCl₃): δ 9.07 (dt, *J* = 8.1, 2.2 Hz, 1H, H-8), 8.82 (d, *J* = 8.3 Hz, 1H), 8.79 (d, *J* = 8.3 Hz, 1H), 8.71 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 7.4 Hz, 1H, H-11), 7.75–7.70 (m, 3H), 7.67 (d, *J* = 15.2 Hz, 1H, H-10), 7.65–7.55 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 159.3 (d, *J* = 251.7 Hz, C-9), 133.2 (d, *J* = 11.0 Hz), 131.5, 131.3 (d, *J* = 4.1 Hz), 130.4, 130.1, 129.2 (d, *J* = 2.4 Hz), 129.0, 128.0 (d, *J* = 26.1 Hz, C-8), 127.8, 127.7, 127.6, 127.4, 127.2 (d, *J* = 5.0 Hz, C-11), 126.9, 126.4, 125.2, 123.8, 123.1, 119.9 (d, *J* = 11.5 Hz, C-10a), 111.3 (d, *J* = 24.7 Hz, C-10). ¹⁹F NMR (282 MHz, CDCl₃, resolution enhanced): δ -114.6 ppm (dd, *J* = 15.1; 2.3 Hz). HRMS (+APPI mode) [M]⁺ calcd. for C₂₂H₁₃F 296.0996, found 296.1002.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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FIGURE 1. Retrosynthetic route to regiospecifically fluorinated PAHs via Julia olefination and oxidative photocyclization, and structures of the targets selected for this work.

FIGURE 2. Formation of 6-F-Ch (% conversion in green bars and the *E/Z* fluoroalkene ratio in orange bars). Reaction was monitored by ^{19}F NMR.

FIGURE 3.
Formation of chrysene (% conversion in green bars and the *E/Z* alkene ratio in orange bars).

FIGURE 4.
Crystal structures of PAHs and F-PAHs obtained in this work (C, gray; H, white; F, green).

FIGURE 5.
Intermolecular interactions in the X-ray crystal structure of 6-F-Ch (**3**) (our data).

FIGURE 6.
Intermolecular interactions in the X-ray crystal structure of 9-F-BgCh (**8**).

FIGURE 7.

^1H - ^{19}F HOESY spectra of 9-F-BgCh (8, left) and of 5-F-Ch (4, right).

SCHEME 1.
Synthesis of (Aryl)fluoromethyl BT Sulfones 2a–d

TABLE 1

Synthesis of Fluoroalkenes and the Regiospecifically Fluorinated PAHs

entry	sulfone; Ar_1 CHO; $\text{Ar}_1 =$	fluoroalkene intermediate: yield; ^a $E:Z$ ratio; ^b ^{19}F NMR data ^c	F-PAHs 3-8: yield; ^a ^{19}F NMR data ^c
1	2a; 	 99%, 2.8:1; δ -100.0 ppm (d, $^3J_{\text{FH}} = 21.4$ Hz, E -isomer); -115.6 ppm (d, $^3J_{\text{FH}} = 39.7$ Hz, Z -isomer)	 3: 72%; δ -123.8 ppm (d, $J = 15.3$ Hz)
2	2b; 	 81%, 2.9:1; δ -84.4 ppm (d, $^3J_{\text{FH}} = 18.3$ Hz, E -isomer); -95.2 ppm (d, $^3J_{\text{FH}} = 39.7$ Hz, Z -isomer)	 4: 71%; δ -111.8 ppm (br dt, $^dJ = 15.7, 3.3$ Hz)
3	2a; 	 99%, 2.9:1; δ -96.2 ppm (d, $^3J_{\text{FH}} = 18.3$ Hz, E -isomer); -114.4 ppm (d, $^3J_{\text{FH}} = 39.7$ Hz, Z -isomer)	 5: 66%; δ -125.4 ppm (d, $J = 9.2$ Hz)
4	2c; 	 76%, 2.75:1; δ -96.6 ppm (d, $^3J_{\text{FH}} = 21.4$ Hz, E -isomer); -114.9 ppm (d, $^3J_{\text{FH}} = 39.7$ Hz, Z -isomer)	 6: 83%; δ -125.8 ppm (d, $J = 12.2$ Hz)
5	2a; 	 70%, 3.1:1; δ -100.3 ppm (d, $^3J_{\text{FH}} = 21.4$ Hz, E -isomer); -115.2 ppm (d, $^3J_{\text{FH}} = 36.6$ Hz, Z -isomer)	 7: 77%; δ -124.3 ppm (d, $J = 12.2$ Hz)

entry	sulfone; Ar ₁ CHO: Ar ₁ =	fluoroalkene intermediate: yield, ^a <i>E</i> : <i>Z</i> ratio; ^b ¹⁹ F NMR data ^c	F-PAHs 3-8: yield; ^a ¹⁹ F NMR data ^c
6	2d ;	89%, 2.88:1; δ –85.0 ppm (d, ³ J _{FH} = 21.4 Hz, <i>E</i> -isomer); – 95.3 ppm (d, ³ J _{FH} = 36.6 Hz, <i>Z</i> -isomer)	8 : 73%; δ –114.6 ppm (dd, ^d J = 15.1, 2.3 Hz)

^aYields are of isolated and purified products.

^b*E*/*Z* olefin ratios in the crude reaction mixtures were determined by ¹⁹F NMR prior to isolation.

^cObtained at 282 MHz in CDCl₃, with CFCl₃ as an internal reference.

^dObtained with resolution enhancement.

TABLE 2

Angles between the Four Planes of Ch, 6-F-Ch, and 5-F-Ch^a

angle between

A, B	0°	0.9°	1.4°
A, C	0°	1.6°	1.1°
B, C	0°	0.8°	3.7°
B, D	0°	0.9°	1.0°
C, D	0°	0.4°	2.2°
A, D	0°	1.8°	5.9°
estimated error e.s.d	0°	0.4°	0.1°

^a Angles between the planes of 5-F-Ch were calculated from the published X-ray information.¹⁷

TABLE 3

Angles between the Four Planes of Unfluorinated and Fluorinated BcPh

angle between
A, B	10.3°	9.4°	8.2°
A, C	18.1°	16.2°	14.2°
B, C	7.9°	6.8°	7.1°
B, D	16.6°	15.2°	17.0°
C, D	8.8°	8.8°	9.9°
A, D	26.7°	24.3°	23.6°
estimated error e.s.d	0.1°	0.2°	0.2°

TABLE 4

Angles between the Five Planes of Unfluorinated and Fluorinated BgCh

angle between
A, B	11.5°	12.0°	9.7°	
A, C	25.7°	21.5°	22.5°	
B, C	14.2°	9.6°	12.°8	
B, D	24.6°	20.9°	23.7°	
C, D	10.7°	11.4°	11.1°	
B,E	20.1°	9.2°	18.2°	
C,E	8.6°	4.5°	8.5°	
D,E	11.9°	12.8°	12.7°	
A,E	31.1°	20.1°	27.2°	
A, D	36.0°	32.6°	33.3°	
estimated error e.s.d	0.1°	0.1°	0.1°	