An Intramolecular Arene–Triflate Coupling Reaction for the Regiospecific Synthesis of Substituted Benzofluoranthenes[1]

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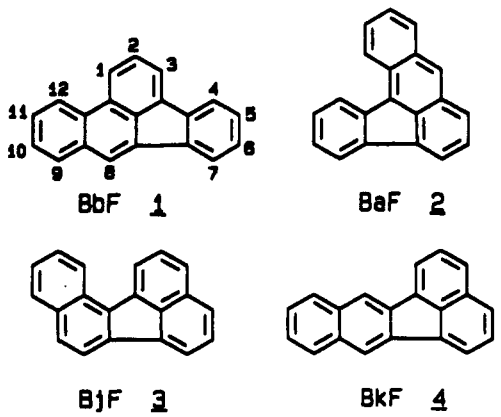
An intramolecular triflate–arene coupling reaction mediated by bis(triphenylphosphine)palladium-(II) chloride has been developed for the synthesis of each of the isomeric benzofluoranthenes. This reaction, which results in formation of a new five-membered ring, proceeds in highest yield when performed using 0.1 equiv of the palladium catalyst, 3 equiv of lithium chloride, and 1.2 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene in *N,N*-dimethylformamide at 140 °C. The biaryl precursors needed for the coupling reaction can be prepared by [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride catalyzed coupling of an aryl bromide with an [*o*-(methoxymethoxy)aryl]magnesium bromide (prepared by ortho-lithiation of an aryl methoxymethyl ether followed by transmetalation with magnesium bromide). Using this procedure benzo[*a*]fluoranthene, benzo[*b*]fluoranthene, benzo-[*j*]fluoranthene, and benzo[*k*]fluoranthene were prepared in yields of 84%, 85%, 93%, and 64%, respectively. The reaction to prepare benzo[*j*]fluoranthene was regiospecific and afforded none of the six-membered ring product, perylene. The method was extended to the preparation of benzo-[*b*]fluoranthene (BbF) derivatives with fluoro or methoxy groups on the benzo ring. The cyclization of compounds possessing a methoxy group on the same ring as the triflate required the addition of 0.4 equiv of triphenylphosphine to the reaction mixture. Strategies are reported for the regiospecific preparation of 4-, 5-, 6-, and 7-substituted benzo[*b*]fluoranthenes. Evidence is presented which suggests the intermediacy of radicals in the oxidative-addition of aryl triflates to the palladium catalyst.

Introduction

The isomeric benzofluoranthenes (benzo[*b*]fluoranthene, BbF, 1; benzo[*a*]fluoranthene, BaF, 2; benzo[*j*]-fluoranthene, BjF, 3; and benzo[*k*]fluoranthene, BkF, 4) are among the more prevalent polycyclic aromatic hydrocarbons (PAH) found in the human respiratory environment. Several of these compounds are powerful animal carcinogens and may pose a human health hazard.[2]



Studies on the metabolism and bioactivation of the benzofluoranthenes have shown that the benzo ring (e.g., positions 4–7 on 1) is a major site of metabolic attack.[3] To properly investigate the biological activation of these compounds reliable methods are needed for the synthesis of derivatives substituted in the benzo ring. A recent report of a fluoranthene derivative which is undergoing evaluation as a potential antineoplastic agent further highlights the need for new synthetic methodology applicable to these compounds.[4] Although methods have been reported for the synthesis of the parent hydrocarbons[5] it is unfortunate that most of these are unsuitable for the efficient preparation of substituted derivatives, especially those in the benzo ring. Methods which have been used successfully for the preparation of such derivatives often proceed under harsh conditions, give mixtures of products, or give unacceptably poor yields.[6] We have recently reported a preliminary account of a new method for the preparation

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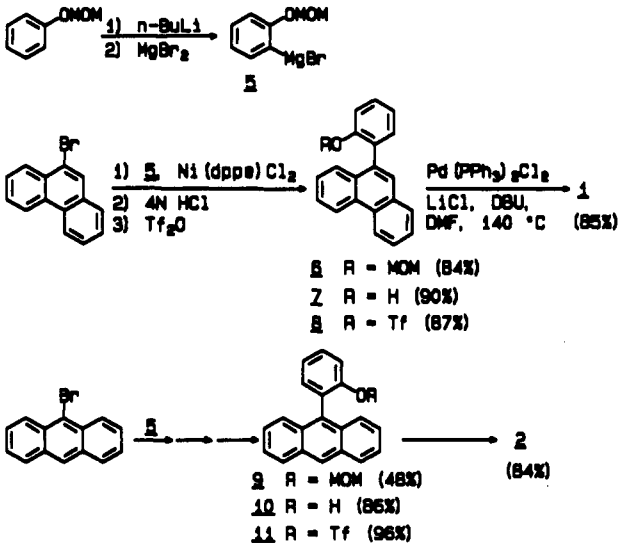
Scheme I

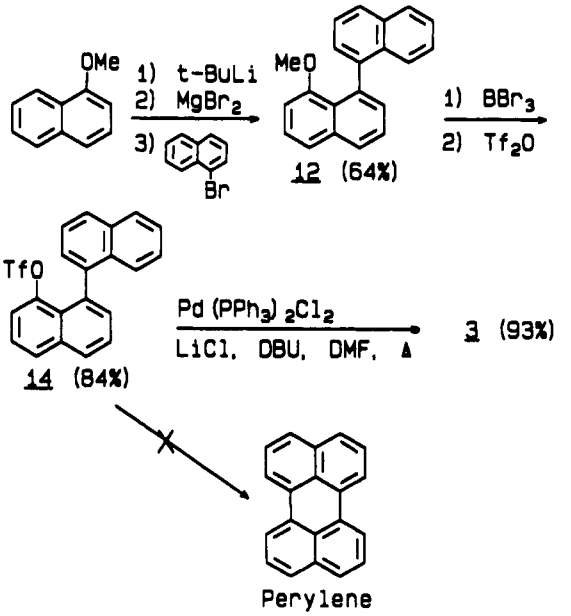


of these compounds which employs successive coupling reactions to effect the attachment of an aryl ring across the peri-positions of a naphthalene (or a higher polycyclic analog).[1] This reaction proceeds in good to excellent yield and is amenable to the preparation of substituted derivatives. We now report the full details of this reaction, its extension to the preparation of 3 and 4, and its utility for the regiospecific preparation of fluoro- and methoxy-substituted benzo[*b*]fluoranthenes.

Results and Discussion

The synthesis of 1 and 2 can be viewed as the attachment of a benzene ring across the peri-positions of phenanthrene and anthracene (Scheme I). This ring fusion is actually the result of two separate coupling reactions. The first C–C bond is formed by the well-precedented Ni(II)-catalyzed coupling of a Grignard reagent with a sp^2 halide.[7] For the synthesis of 1 and 2, [2-(methoxymethoxy)phenyl]-magnesium bromide 5 was coupled with commercially-available 9-bromophenanthrene (84%) and 9-bromoanthracene (48%) in the presence of [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride (Ni(dppe)Cl_2, THF, −78 °C and then reflux). The Grignard reagent was prepared by ortho-lithiation of methoxymethyl phenyl ether using *n*-BuLi in ether at room temperature[8] followed by transmetalation with $MgBr_2$. The low yield associated with the Ni(II)-catalyzed coupling to 9-bromoanthracene is likely the result of steric hinderance from the two peri-hydrogens on the anthracene ring. MOM ethers 6 and 9 were converted to trifluoromethanesulfonates (triflates) by hydrolysis with 4 N HCl in THF at reflux followed by treatment with triflic anhydride in the presence of 2,6-lutidine (CH_2Cl_2, −30 °C, 1 h). Formation of the second C–C bond was accomplished by coupling the triflate-bearing carbon to the unsubstituted 1-position on the phenanthrene or anthracene nucleus. Treatment of triflates 8 and 11 with bis(triphenylphosphine)palladium-(II) chloride (0.1 equiv), LiCl (3 equiv), and DBU (1.2 equiv) in DMF at 135–140 °C for 6 h afforded 1 and 2 in yields of 85% and 84%, respectively.

Scheme II



The palladium-catalyzed intramolecular coupling of an aryl triflate with an unsubstituted aromatic carbon represents a new high-yielding method for the synthesis of fluoranthenoid hydrocarbons. One advantage of this method is that no leaving group (other than hydrogen) is required on one of the aromatic rings undergoing coupling, a fact which simplifies the preparation of precursors. Examples of intramolecular palladium-catalyzed coupling reactions involving aryl halides and arenes have been reported.[9] These reactions have found use in the synthesis of five-membered ring heterocycles and in the preparation of six-membered ring or larger lactams and lactones. The present method also results in formation of a new five-membered ring but differs in several respects from the methods cited above. First, triflates which are derived from readily available phenols are employed in place of halides. Second, the products of the reaction are hydrocarbons as opposed to heterocycles, and each carbon in the newly formed five-membered ring is aromatic. Other methods for preparing five-membered rings by cyclizing aryl halides have, as part of the newly formed ring, a saturated atom or carbonyl group.

Reports detailing the ready formation of six-membered ring lactams and lactones by Pd-catalyzed reactions led us to consider whether any selectivity would be observed in the triflate–arene coupling reaction in cases where six-membered ring formation could compete with the creation of a new five-membered ring. To evaluate this possibility, binaphthyl triflate 14 was prepared (Scheme II) and subjected to the reaction conditions described above. 1-Methoxynaphthalene was lithiated selectively at the

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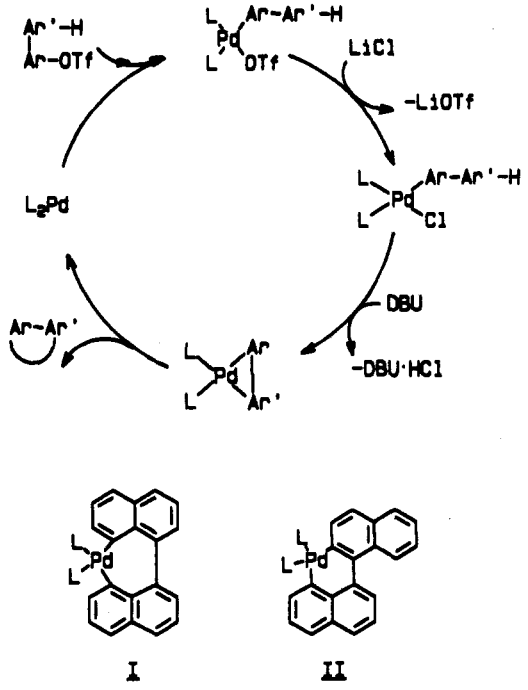


I II

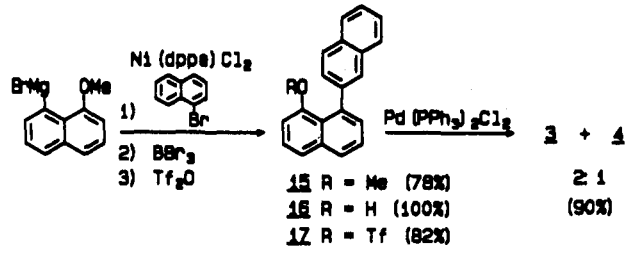
Figure 1. Proposed mechanism for the intramolecular palladium-catalyzed triflate–arene coupling reaction. The ligand, L, is PPh_3.

8-position by treatment with *tert*-butyllithium in cyclohexane at room temperature.[10] Transmetalation with $MgBr_2$ and treatment with 1-bromonaphthalene in the presence of Ni(dppe)Cl_2 afforded the coupled product **12** in 64% yield. Demethylation (BBr_3, CH_2Cl_2, −78 °C) followed by treatment with Tf_2O afforded triflate **14** in 84% yield for the two steps. Treatment of **14** with Pd(PPh_3)$_2Cl_2$ as described above could give rise to either the six-membered ring product, perylene, or BjF, **3**. A single product **3** was isolated from this reaction in 93% yield. We did not observe the formation of perylene.

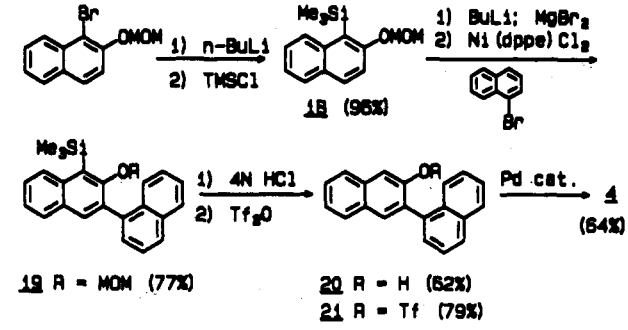
A detailed investigation into the mechanism of this reaction has not been attempted, although a plausible mechanism can be proposed (Figure 1). The reaction of aryl triflates with Pd(PPh_3)$_2Cl_2$ in the presence of LiCl to give a reactive intermediate [Pd(PPh_3)$_2$Ar(Cl)] has been proposed as the initial sequence of events in certain Pd-catalyzed coupling reactions.[11] When a biaryl triflate such as **14** reacts with the palladium catalyst to form a similar intermediate, the metal is positioned for cyclopalladation of a proximal C–H bond. Inclusion of a base (DBU) in the reaction mixture assists the palladation by removal of HCl. Triflate **14** can give rise to two isomeric cyclopalladated intermediates, **I** and **II**. Intermediate **I**, which would lead to perylene formation after reductive elimination of the two aryl moieties, has Pd incorporated within a seven-membered ring whereas the intermediate for BjF formation (**II**) has the metal within a six-membered ring. The selectivity observed in the cyclization of **14** suggests that the formation of intermediate **II** is favored.

The formation of a single product from triflate **14** led us to consider whether similar levels of selectivity could be observed for the cyclization of a compound which could form isomeric six-membered cyclopalladated intermediates (Scheme III). The triflate derived from 1-(2′-naphthyl)-8-naphthol (**16**) could cyclize under our reaction conditions to form either BjF **3** or BkF **4**. Triflate **17** was prepared in 64% overall yield from 1-methoxynaphthalene by an analogous route to that used above (employing 2-bromonaphthalene). Cyclization afforded a 90% yield of a 2:1 mixture (from the ^{1}H-NMR spectrum) of BjF:BkF. These results may reflect differences in the rates of metalation at the 1′- vs the 3′-naphthyl position. Alternatively, there may be some subtle differences in the steric environment of the two possible intermediates leading to **3** and **4**. This result also demonstrates that each isomer of benzofluoranthene is accessible via the intramolecular triflate–arene coupling sequence.

Scheme III



Scheme IV



Although **4** was prepared by the sequence outlined above, its separation from **3** is difficult on a preparative scale. A method was desired for the selective preparation of **4**. It was recognized that 3-(1′-naphthyl)-2-hydroxynaphthalene triflate **21** might undergo Pd-catalyzed cyclization to give **4** as the exclusive product. This compound is accessible by coupling 1-bromonaphthalene with [3-(2-methoxymethoxy)naphthyl]magnesium bromide. Unfortunately, the best conditions for ortho-lithiation of 2-(methoxymethoxy)naphthalene at the 3-position gave the desired lithio derivative as a 3:4 mixture with the 1-lithio species.[12] It was found however, that 1-bromo-2-(methoxymethoxy)-naphthalene when treated with *n*-butyllithium followed by quenching with TMSCl affords a 96% yield of 2-(methoxymethoxy)-1-(trimethylsilyl)naphthalene (**18**) (Scheme IV). Ortho-lithiation of **18** using *n*-butyllithium followed by transmetalation ($MgBr_2$) and Ni(dppe)Cl_2-catalyzed coupling with 1-bromonaphthalene afforded **19** in 77% yield. This was heated at reflux with 4 N HCl which effected MOM ether hydrolysis and protiodesilylation to give 3-(1′-naphthyl)-2-naphthol (**20**) in 62% yield. Conversion to triflate **21** (79% yield) followed by Pd-catalyzed cyclization afforded BkF **4** in 64% yield.

The utility of this coupling reaction for the regiospecific synthesis of BbF derivatives with methoxy and fluoro substituents in the benzo ring was also investigated

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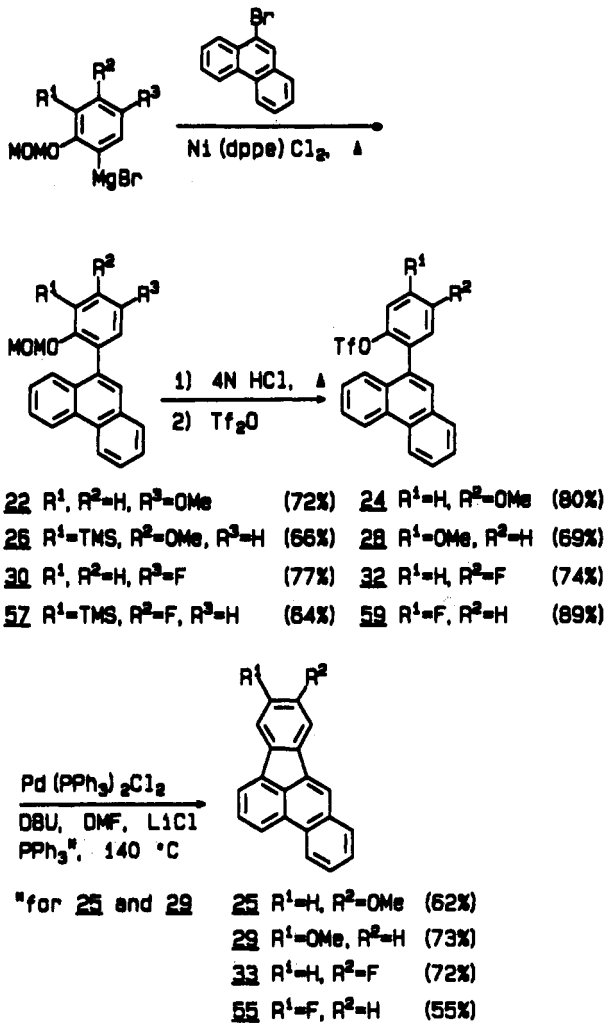
Scheme V



(Scheme V). We reported previously[1b] that while 6-fluoro-BbF was prepared in 72% yield using the standard reaction conditions described above, initial attempts to prepare 5- and 6-methoxy-BbF afforded very low yields (<5%) of products. Appreciable quantities of unreacted starting materials were recovered in these cases suggesting that oxidative-addition of the triflate to the Pd catalyst was occurring slowly at best. Oxidative-addition of aryl halides to transition metals is known to be accelerated by electron-withdrawing groups on the ring.[13] Electron-donating substituents such as methoxy groups may retard the rate of oxidative-addition to such an extent that preferential catalyst degradation may occur. It was found that addition of 0.4 equiv of triphenylphosphine to the reaction mixture had a profound effect on the yields of 6-MeOBfF (**25**) and 5-MeOBbF (**29**), allowing for their isolation in 62% and 73% yield, respectively. Palladium-catalyzed coupling reactions of electron-rich aryl triflates with organostannanes were also recently reported to require the addition of 0.4 equiv of triphenylphosphine to effect the reaction.[14] The yields of coupling reactions of aryl triflates which do not possess an electron-donating substituent were indifferent to added triphenylphosphine, e.g. 6-fluoro-BbF **33** (68% + PPh_3; 72% - PPh_3) and fluoranthene (90% + PPh_3; 89% - PPh_3).[1b] It has been reported that excess triphenylphosphine may stabilize $Pd(PPh_3)_2Cl_2$ against degradation and thereby allow catalytic reactions to proceed.[15]

Table I. Reaction Conditions for the Preparation of 6-Methoxybenzo[*b*]fluoranthene[a]

expt	temp (°C)	time (h)	$Pd(PPh_3)_2Cl_2$ (equiv)	phosphine	yield[b] (%)
1	100	40	0.10	PPh_3	13
2	120	40	0.10	PPh_3	25
3	120	20	0.10	P(*o*-tolyl)$_3$	23
4	120	20	0.10	PPh_3	21
5	140	10	0.10	PPh_3	62
6	140	10	0.05	PPh_3	22

[a] These reactions were performed using 0.3 mmol of triflate **24** in DMF (1.5 mL) in the presence of 1.2 equiv of DBU, 0.4 equiv of a phoshine, and 0.3 equiv of LiCl. [b] Yields were determined after filtering the reaction mixture through a plug of silica gel eluting with 5% EtOAc/hexanes. The yield was determined by ^{1}H-NMR spectroscopy from the ratio of integrals for absorptions corresponding to the methoxy groups of **24** (3.86 ppm) and **25** (3.97 ppm) in the product mixture.

Reaction conditions were investigated for the preparation of **25**. The results of this investigation are shown in Table I. The reaction temperature was found to be one of the most important variables affecting the yield of **25**. When the reaction was conducted at 100 and 120 °C the yields of **25** were 13% and 25%, respectively, while at 140 °C the yield was 62%. The amount of catalyst is also important as 0.05 equiv gave a 22% yield of **25** while 0.1 equiv afforded a 62% yield. This is consistent with the results obtained by coupling electron-rich aryl triflates with organostannanes which required 0.10–0.15 equiv of $Pd(PPh_3)Cl_2$.[14] The effect of the added phosphine was also investigated briefly. Tri(*o*-tolyl)phosphine was found to offer little advantage over triphenylphosphine affording a 23% yield of **25** as compared to 21% for the latter case under similar reaction conditions. From Table I it can be seen that the best yield for 6-methoxy-BbF is realized when the reaction is conducted using 0.1 equiv of $Pd(PPh_3)Cl_2$, 0.4 equiv of PPh_3, 3 equiv of LiCl, and 1.2 equiv of DBU in DMF at 140 °C for 10 h. These reaction conditions were adopted for the preparation of other substituted BbFs with the only modification being that PPh_3 was not needed to effect the cyclization of fluoro-BbF derivatives.

The synthesis of 7-fluoro-BbF (**39**) by cyclization of triflate **38** proceeded in 60% yield using the reaction conditions developed above. While it may be envisioned that a precursor to triflate **38** could be prepared by Ni(II)-catalyzed coupling of [2-fluoro-6-methoxyphenyl]-magnesium bromide with 9-bromophenanthrene, this would prove troublesome as under the reaction conditions elimination of fluoride could occur to give 3-methoxybenzyne.[16] Fortunately, Suzuki coupling[17] of 9-phenanthrylboronic acid with 2-bromo-3-fluoroanisole provided a method for the preparation of this key intermediate (Scheme VI). 9-Phenanthrylboronic acid (**34**) was prepared in 92% yield from 9-bromophenanthrene [(a) *n*-BuLi, THF, -78 °C; (b) B(*i*-OPr)$_3$; (c) HCl].[18] 3-Fluoroanisole was lithiated selectively at the 2-position (*n*-BuLi,

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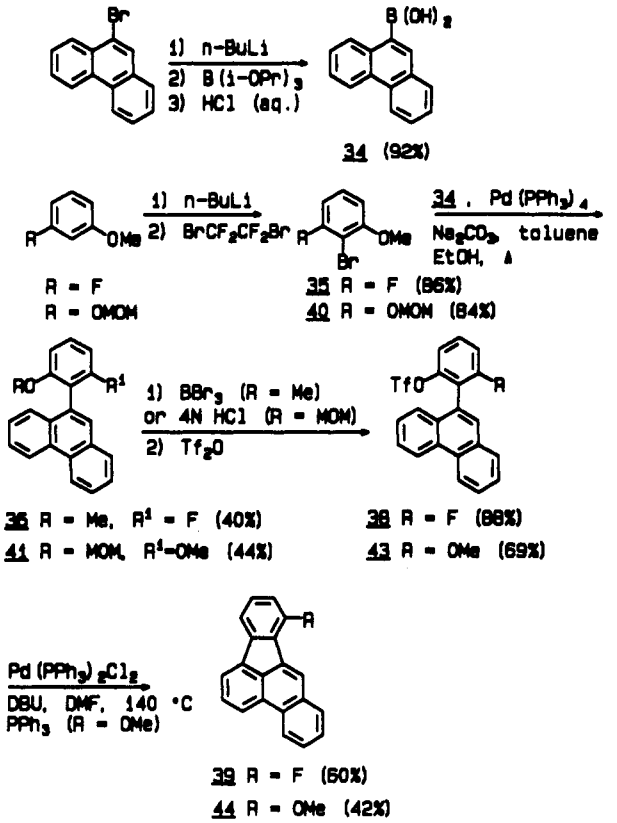
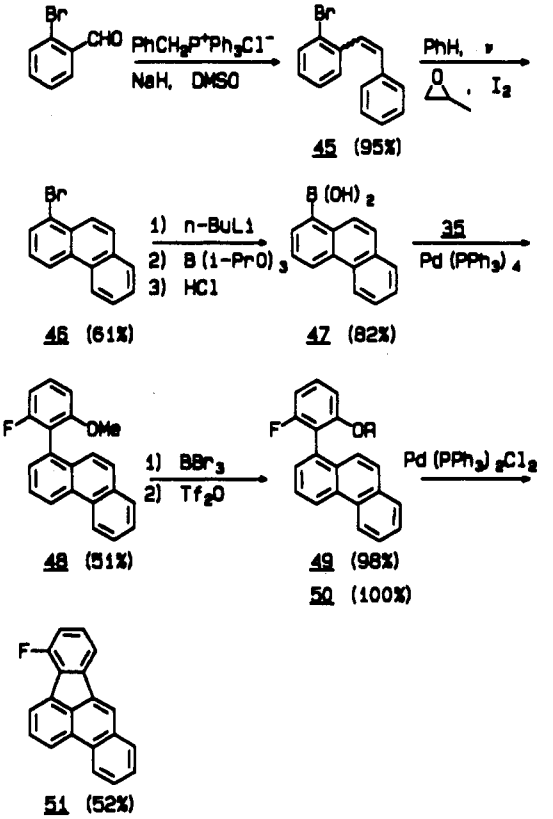
Scheme VI



Scheme VII



THF, −78 °C)[19] and treated with 1,2-dibromotetrafluoroethane to give 2-bromo-3-fluoroanisole (**35**) in 86% yield. This was coupled with **34** in 40% yield using $Pd(PPh_3)_4$ and 2 M Na_2CO_3 in toluene at 80 °C. The low yield for this coupling is again likely due to steric crowding from the two ortho substituents on the aryl bromide since coupling 2-fluorobromobenzene with **34** proceeded in >80% yield under identical reaction conditions.[20] Demethylation of **36** was effected by treatment with boron tribromide (CH_2Cl_2, −78 °C, 93% yield), and the phenol was then converted to triflate **38** in 95% yield.

A similar strategy was employed for the preparation of 7-methoxy-BbF (**44**) (Scheme VI). 3-(Methoxymethoxy)anisole was ortho-lithiated selectively between the two directing groups using *tert*-butyllithium in hexane,[21] transmetalated with $MgBr_2$, and coupled to 9-bromophenanthrene in the presence of $Ni(dppe)Cl_2$ to give biaryl **41** in only 7% yield. It was found, however, that Suzuki coupling of 2-bromo-3-(methoxymethoxy)anisole (**40**) (prepared in 84% yield by ortho-lithiation followed by treatment with 1,2-dibromotetrafluoroethane) with 9-phenanthrylboronic acid proceeded more smoothly to give the coupled product **41** in 44% yield. The MOM group was hydrolyzed (81% yield) and the resulting phenol converted to triflate **43** in 85% yield. Cyclization to **44** proceeded in 42% yield in the presence of PPh_3.

The reactions which have been investigated up to this point rely on coupling to the 1-position of phenanthrene. The ease of coupling to the 10-position was investigated for the synthesis of 4-fluoro-BbF (**51**) (Scheme VII). Wittig reaction of 2-bromobenzaldehyde with benzyltriphenylphosphonium chloride gave 2-bromostilbene (**45**) in 95% yield as a mixture of *E*- and *Z*-isomers. Irradiation of a benzene solution of this compound (400-W medium-pressure Hg vapor lamp, Pyrex filter) in the presence of 1.0 equiv of I_2 and 63 equiv of propylene oxide afforded 1-bromophenanthrene (**46**) in 61% yield.[22] This was converted to 1-phenanthrylboronic acid (**47**) in 82% yield as described above and subjected to Suzuki coupling with 2-bromo-3-fluoroanisole. Biaryl **48** was formed in 51% yield. This was demethylated and converted to triflate **50** in 98% overall yield. Application of the standard coupling procedure afforded 4-fluoro-BbF (**51**) in 52% yield. Since 7-fluoro-BbF was prepared from a similar intermediate in 60% yield by coupling to the 1-position of phenanthrene, this demonstrates that coupling to either the 1- or 10-position of phenanthrene is equally facile.

A route to 5-fluoro-BbF (**55**) which makes use of coupling to the 10-position of phenanthrene was developed (Scheme VIII). As envisioned, this route would have an advantage over that employed in the preparation of 5-methoxy-BbF (**29**) in that a TMS positional protecting group would not be required to achieve selectivity in the lithiation step. $Ni(dppe)Cl_2$-catalyzed coupling of 1-bromophenanthrene (**46**) with [5-fluoro-2-(methoxymethoxy)phenyl]magnesium bromide gave **52** in 65% yield. This was converted uneventually to triflate **54** in 84% yield for the two steps. To our suprise application of the Pd-catalyzed coupling procedure gave a 58% yield of a 1:1 mixture of 5-fluoro-BbF (**55**) together with 7-fluoro-BbF (**39**). The formation of mixtures was not observed in any of the other coupling reactions described above. Fortunately, the regiospecific preparation of **55** was successfully realized in 55% yield by employing a reaction sequence analogous to that used for the synthesis of **29** (Scheme V).

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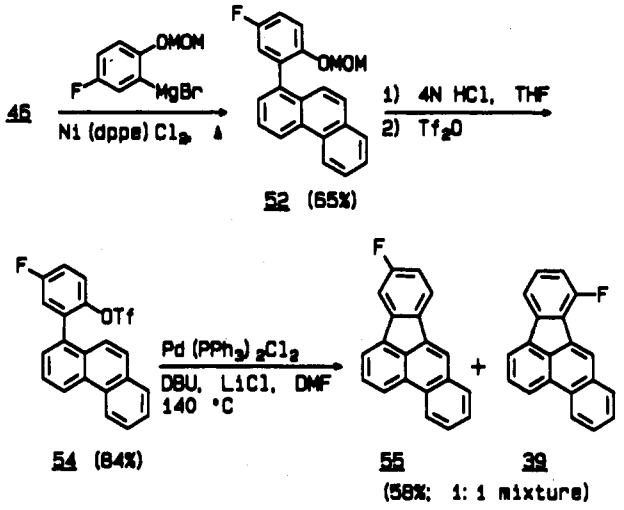
(22) Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769.

Scheme VIII



The formation of isomeric products from the cyclization of **54** draws attention once again to the mechanism of the intramolecular triflate–arene coupling reaction. As discussed above, it is reasonable to propose that the initial event is oxidative–addition of an aryl triflate to a coordinatively-unsaturated palladium species. While the exact mechanism of oxidative-addition to transition metals is a question which is still under investigation, at least two distinct modes of addition have been proposed, a three-center mechanism and a radical mechanism.[23] There is some evidence that oxidative-addition of aryl bromides to transition metals proceeds via the radical pathway.[24] If a radical mechanism is in operation in the present situation, reaction of the metal with an aryl triflate would give rise initially to a transition metal complex and an aryl radical (Figure 2). In the absence of alternative pathways, capture of this radical by the transition metal complex would lead to the expected oxidative-addition product and ultimately to 5-fluoro-BbF. If, however, abstraction of a proton from the 10-position of phenanthrene were to occur more rapidly than reaction with the metal, then a new 10-phenanthryl radical would be formed. Reaction of this with the palladium complex would complete the oxidative-addition process and give an intermediate which could palladate the aryl ring at sites ortho and para to the fluorine. The products from such a reaction sequence would be 7-fluoro-BbF and 5-fluoro-BbF. Our results are consistent with such a mechanism. It is of interest to note that an identically substituted aryl ring, when attached to the 10-position of phenanthrene, cyclized regiospecifically to the 1-position giving 6-fluoro-BbF. The different results observed for these two reactions may reflect differences in the ease (or rate) of proton abstraction from the 10-position (K-region) of phenanthrene as compared to the 1-position.[25] The synthesis of 4- and 7-fluoro-BbF were also regiospecific despite the fact that the first case involved cyclization to the 10-position of phenanthrene whereas the second cyclized to the 1-position. In each instance,

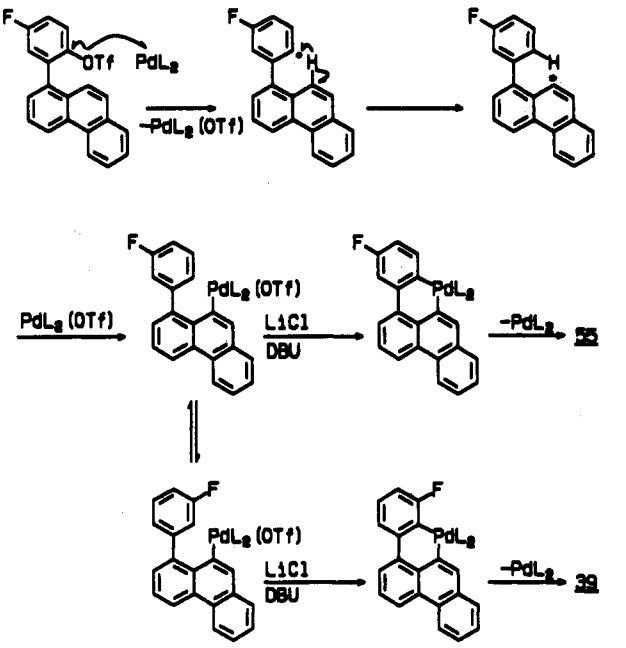


Figure 2. Possible involvement of radicals in the oxidative-addition of aryl triflates to palladium resulting in isomeric products. The ligand, L, is PPh_3.

however, only one unsubstituted ortho-position is available for palladation. Products of defluorination were never observed.

The use of the intramolecular palladium-catalyzed triflate–arene coupling reaction for the synthesis of proximate and ultimate carcinogenic metabolites of BbF and other benzofluoranthenes is in progress. These results, as well as those from studies employing the isomeric fluorinated benzo[*b*]fluoranthenes for elucidating the mechanism of activation of BbF, will be reported in due course.

Experimental Section

Ether and THF were freshly distilled from sodium and benzophenone prior to use. Methylene chloride, hexane, cyclohexane, 2,6-lutidine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and DMF were freshly distilled from CaH_2. Triflic anhydride was distilled from P_2O_5. [1,2-Bis(diphenylphosphino)ethane]-nickel(II) chloride (Alfa) was dried under reduced pressure at 60 °C before use. Bis(triphenylphosphine)palladium(II) chloride and tetrakis(triphenylphosphine)palladium(0) were purchased from Aldrich and used as received. Flash chromatography was performed using 230–400-mesh silica gel as described previously.[26] NMR spectra (200-MHz ^1H and 50-MHz ^{13}C) were recorded in $CDCl_3$ with chemical shifts reported as ppm downfield from tetramethylsilane. Coupling constants are reported in Hz. The designations (u) and (d) in the ^{13}C-NMR data are from attached proton test (APT) experiments in which quaternary carbons and CH_2 are (u) and CH and CH_3 carbons are (d). Combustion analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. Methoxymethyl phenyl ether, 1-bromo-2-(methoxymethoxy)naphthalene, 3-(methoxymethoxy)anisole, 4-(methoxymethoxy)-anisole, 3-[(fluoromethoxy)methoxy]benzene, and 4-[(fluoromethoxy)methoxy]benzene were all prepared from the corresponding phenols by treatment with chloromethyl methyl ether (1.5 equiv) and diisopropylethylamine (1 equiv) in CH_2Cl_2 at 0 °C. Additional (0.5 equiv) portions of the amine were added after 30 min and 1 h.[27]

(23) (a) Osborn, J. A. *Organotransition-Metal Chemistry*; Ishii, Y., Tsutsui, M. Eds.; Plenum Press: New York, 1975; pp 65–80. (b) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; pp 168–177.

(24) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319.

(25) The formation of isomeric products during intramolecular Pschorr cyclization of a 1-(2′-amino-4′,5′-difluorophenyl) group to the K-region of pyrene may also be the result of abstraction of an accessible proton by a radical. See ref 6c.

(26) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

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General Procedure for Preparing Biaryl MOM Ethers. 9-[2-(Methoxymethoxy)phenyl]phenanthrene (6). A solution of methoxymethyl phenyl ether (483 mg, 3.5 mmol) in dry ether (20 mL) was treated at room temperature, under N_2, with *n*-BuLi (1.4 M in hexanes, 4.2 mmol) and stirred for 3 h to give a yellowish suspension. At this time a solution of freshly prepared $MgBr_2$ (0.2 M in ether, 3.9 mmol) (prepared by reacting 102 mg (4.2 mmol) of Mg and 173 mg (3.85 mmol) of 1,2-dibromoethane in 20 mL of ether for 3 h) was added to give a clear solution. A solution of 9-bromophenanthrene (563 mg, 2.19 mmol) and [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride (Ni(dppe)Cl_2), 37 mg, 0.07 mmol, 0.03 equiv based on the aryl bromide) in THF (10 mL) was cooled to −78 °C under N_2 and treated via syringe with the Grignard reagent prepared above. After the addition, the solution was allowed to warm slowly to room temperature and then heated at reflux overnight. The reaction mixture was cooled and passed through a short silica gel column eluting with 50% CH_2Cl_2 in hexanes. The eluate was concentrated and further purified by flash chromatography on silica gel eluting with 0–7% EtOAc/hexanes to give 579 mg (84% yield) of **6** as an oil which solidified on standing in the freezer: mp 111–112 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.80–8.72 (m, 2), 7.94–7.88 (m, 1), 7.73–7.61 (m, 5), 7.60–7.14 (m, 5), 5.05, 4.96 (AB quartet, 2, J = 6.7 $\Delta\nu$ = 14), 3.22 (s, 3); ^{13}C-NMR δ 155.7, 136.4, 132.5, 132.3, 132.0, 131.2, 130.8, 130.7, 129.7, 129.2, 128.3, 127.8, 127.2, 127.0, 126.8 (2C), 123.2, 123.1, 122.6, 115.5, 95.00, 56.4. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.08; H, 5.73. Found: C, 83.93; H, 5.74.

9-[2-(Methoxymethoxy)phenyl]anthracene (9). Prepared in 48% yield from methoxymethyl phenyl ether and 9-bromoanthracene as described above for **6**: solid; mp 166–167 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.51 (s, 1), 8.06 (d, 2, J = 8.4), 7.66 (d, 2, J = 8.6), 7.54–7.20 (m, 8), 4.92 (s, 2), 3.05 (s, 3); ^{13}C-NMR δ 156.0 (u), 134.2 (u), 133.4 (d), 131.9 (u), 130.9 (u), 129.8 (d), 128.9 (u), 128.9 (d), 127.3 (d), 127.0 (d), 125.7 (d), 125.5 (d), 122.5 (d), 115.7 (d), 94.7 (u), 56.3 (d). Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.08; H, 5.73. Found: C, 83.97; H, 5.78.

8-Methoxy-1-(1-naphthyl)naphthalene (12). To a solution of 1-methoxynaphthalene (2.75 g, 15 mmol) in 12 mL of freshly distilled cyclohexane under N_2 was added 10.6 mL of a 1.7 M solution of *tert*-butyllithium in pentane. The solution was stirred at room temperature for 2 days. The solution of 8-lithio-1-methoxynaphthalene was then treated with $MgBr_2$ followed by coupling with 1-bromonaphthalene in the presence of Ni(dppe)Cl_2 as described above for **6** to give **12** as a white solid: 1.82 g (64% yield); mp 148–149.5 °C (EtOAc/hexanes); ^{1}H-NMR δ 7.89 (m, 3), 7.60–7.20 (m, 9), 6.70 (d, 1, J = 7.5), 3.03 (s, 3); ^{13}C-NMR δ 157.2 (u), 144.2 (u), 137.3 (u), 136.0 (u), 133.8 (u), 133.2 (u), 129.7 (d), 128.4 (d), 128.3 (d), 126.9 (d), 126.8 (d), 126.6 (d), 126.2 (d), 125.7 (d), 125.6 (d), 125.5 (d), 125.5 (u), 125.4 (d), 125.4 (d), 121.7 (d), 107.0 (d), 55.9 (d). Anal. Calcd for $C_{21}H_{16}O$: C, 88.73; H, 5.63. Found: C, 88.79; H, 5.61.

8-Methoxy-1-(2-naphthyl)naphthalene (15). Prepared from 1-methoxynaphthalene and 2-bromonaphthalene as a white solid in 78% yield as described above for **12**: mp 102–104 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.02–7.87 (m, 5), 7.66–7.45 (m, 7), 6.87 (d, 1, J = 7.5), 3.49 (s, 3); ^{13}C-NMR δ 157.3 (u), 144.0 (u), 139.4 (u), 136.4 (u), 133.6 (u), 130.0 (d), 129.5 (d), 128.6 (d), 128.4 (d), 128.2 (d), 126.7 (d), 126.5 (d), 126.3 (d), 126.1 (d), 125.9 (d), 125.8 (d), 124.1 (u), 121.9 (d), 106.7 (d), 55.7 (d).

2-(Methoxymethoxy)-1-(trimethylsilyl)naphthalene (18). A solution of 1-bromo-2-(methoxymethoxy)naphthalene (2.3 g, 8.5 mmol) in THF (20 mL) was cooled to −78 °C under N_2 and was treated with *n*-butyllithium (5.8 mL of a 1.6 M solution in hexane). The solution was stirred at −78 °C for 30 min and was then treated with chlorotrimethylsilane (1.2 mL, 9.3 mmol). After being warmed to room temperature the reaction mixture was poured into 50 mL of a 15% aqueous solution of NH_4Cl and extracted with ether. The ether layer was dried over Na_2SO_4 and evaporated. Flash chromatography on silica gel eluting with 4% EtOAc/hexanes gave **18** as a oil: 2.13 g (96%); ^{1}H-NMR δ 8.17 (d, 1, J = 8.4), 7.84 (d, 1, J = 9.2), 7.80 (dd, 1, J = 8.4, 1.5), 7.49–7.31 (m, 3), 5.26 (s, 2), 3.54 (s, 3), 0.53 (s, 9); ^{13}C-NMR δ 161.4 (u), 138.7 (u), 132.4 (d), 130.5 (u), 129.3 (d), 127.9 (d), 126.3 (d), 123.8 (d), 121.8 (u), 115.9 (d), 95.3 (u), 56.6 (d), 3.3 (d).

2-(Methoxymethoxy)-3-(1-naphthyl)-1-(trimethylsilyl)naphthalene (19). Prepared from **18** and 1-bromonaphthalene as an oil in 77% yield as described above for **6**: ^{1}H-NMR δ 8.29 (d, 1, J = 8.8), 7.96–7.81 (m, 5), 7.63 (s, 1), 7.62–7.46 (m, 5), 4.53 (AB quartet, 2, J = 4.9, $\Delta\nu$ = 19.8), 2.52 (s, 3), 0.64 (s, 9); ^{13}C-NMR δ 159.0 (u), 138.5 (u), 138.0 (u), 134.5 (d), 134.4 (u), 134.1 (u), 132.7 (u), 131.7 (u), 129.4 (d), 129.0 (u), 128.6 (d, 2 C), 128.4 (d), 128.4 (d), 127.1 (d), 126.6 (d), 126.3 (d), 126.2 (d), 125.8 (d), 125.2 (d), 100.3 (u), 57.3 (d), 3.4 (d).

9-[5-Methoxy-2-(methoxymethoxy)phenyl]phenanthrene (22). Prepared from 4-(methoxymethoxy)anisole and 9-bromophenanthrene as an oil in 72% yield as described above for **6**: ^{1}H-NMR δ 8.75 (m, 2), 7.91 (d, 1, J = 7.1), 7.71–7.53 (m, 6), 7.24 (d, 1, J = 8.5), 6.98 (dd, 1, J = 8.4, 1.1), 6.96 (d, 1, J = 1.1), 4.89 (s, 2), 3.83 (s, 3), 3.16 (s, 3); ^{13}C-NMR δ 155.4, 149.8, 136.2, 132.6, 130.8, 130.7, 129.2, 128.7, 128.3, 127.8, 127.2, 127.1, 126.9 (2 C), 123.2, 123.1, 117.8, 117.7, 114.6, 96.1, 56.2, 56.1.

9-[4-Methoxy-2-(methoxymethoxy)-3-(trimethylsilyl)phenyl]phenanthrene (26). Prepared from 3-(methoxymethoxy)-2-(trimethylsilyl)anisole[28] and 9-bromophenanthrene as a white solid in 66% yield as described above for **6**: mp 156–157 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.75 (m, 2), 7.93–7.83 (m, 2), 7.76 (s, 1), 7.71–7.52 (m, 4), 7.37 (d, 1, J = 8.4), 6.80 (d, 1, J = 8.4), 4.57, 4.41 (AB quartet, 2, J = 3.8, $\Delta\nu$ = 17), 3.89 (s, 3), 2.49 (s, 3), 0.42 (s, 9); ^{13}C-NMR δ 166.0 (u), 161.0 (u), 136.9 (u), 134.9 (d), 132.2 (u), 132.2 (u), 130.9 (u), 130.4 (u), 129.1 (d), 129.1 (d), 127.9 (d), 127.3 (d), 127.0 (d, 2C), 126.9 (d), 132.1 (d), 123.1 (d), 121.4 (u), 106.7 (d), 99.7 (u), 57.0 (d), 55.7 (d), 1.7 (d). Anal. Calcd for $C_{26}H_{28}SiO_3$: C, 75.00; H, 6.73. Found: C, 75.02; H, 6.78.

9-[5-Fluoro-2-(methoxymethoxy)phenyl]phenanthrene (30). Prepared from 4-(methoxymethoxy)fluorobenzene and 9-bromophenanthrene as an oil in 77% yield as described above for **6**: ^{1}H-NMR δ 8.77 (m, 2), 7.92 (dd, 1, J = 7.2, 1.9), 7.71–7.63 (m, 5), 7.56 (m, 1), 7.27 (m, 1), 7.19–7.11 (m, 2), 4.96 (d, 1, J = 6.8), 4.91 (d, 1, J = 6.8), 3.20 (s, 3); ^{13}C-NMR δ 158.4 (u) (d, J_{CF} = 239.9), 151.8 (u) (d, J_{CF} = 2.4), 135.2 (u), 132.9 (u) (d, J_{CF} = 7.5), 132.0 (u), 131.6 (u), 130.8 (u), 129.2 (d), 128.4 (d), 127.5 (d), 127.3 (d, 2 C), 127.0 (d, 2 C), 123.3 (d), 123.1 (d), 119.0 (d) (d, J_{CF} = 22.9), 117.2 (d) (d, J_{CF} = 8.3), 115.8 (d) (d, J_{CF} = 22.4), 95.8 (u), 56.5 (d).

1-[5-Fluoro-2-(methoxymethoxy)phenyl]phenanthrene (52). Prepared from 4-(methoxymethoxy)fluorobenzene and **46** as an oil in 65% yield as described above for **6**: ^{1}H-NMR δ 8.80 (d, 1, J = 7.4), 8.79 (d, 1, J = 5.3), 7.93 (dd, 1, J = 7.2, 2.1), 7.70 (m, 6), 7.30 (m, 1), 7.18 (m, 2), 4.95 (AB quartet, 2, J = 6.8, $\Delta\nu$ = 8.6), 3.23 (s, 3); ^{13}C-NMR δ 158.3 (u) (d, J_{CF} = 239.6), 151.6 (u) (d, J_{CF} = 2.5), 137.0 (u), 133.3 (u) (d, J_{CF} = 7.7), 132.3 (u), 130.1 (u), 129.0 (d), 128.6 (d), 127.4 (d), 127.3 (d), 127.2 (d), 126.5 (d), 125.4 (d), 123.5 (d), 123.1 (d), 119.1 (d) (d, J_{CF} = 22.8), 117.4 (d) (d, J_{CF} = 8.3), 115.8 (d) (d, J_{CF} = 22.4), 95.9 (u), 56.5 (d).

3-(Methoxymethoxy)-2-(trimethylsilyl)fluorobenzene (56). A solution of 3-(methoxymethoxy)fluorobenzene (3.12 g, 20 mmol) in THF (50 mL) was cooled to −78 °C under N_2 and treated slowly (so that the internal temperature did not exceed −65 °C) with *n*-butyllithium (22 mmol, 1.6 M in hexane). After the addition the solution was stirred at −78 °C for 40 min, and then chlorotrimethylsilane (2.7 g, 25 mmol) was added. The solution was stirred at −78 °C for 2 h and was then allowed to warm to room temperature overnight. The reaction was quenched with 70 mL of a 15% aqueous solution of NH_4Cl and extracted with ether. The ether layer was dried over Na_2SO_4 and purified by column chromatography on silica gel eluting with hexanes to give **56** as a colorless liquid: 4.43 g (97% yield); ^{1}H-NMR δ 7.27 (m, 1), 6.87 (d, 1, J = 8.1), 6.67 (m, 1), 5.19 (s, 2), 3.49 (s, 3), 0.38, 0.37 (2 singlets, 9); ^{13}C-NMR δ 168.0 (u) (d, J_{CF} = 240.1), 163.4 (u) (d, J_{CF} = 15.0), 132.1 (d) (d, J_{CF} = 10.6), 114.8 (u) (d, J_{CF} = 31.9), 109.3 (d) (d, J_{CF} = 27.0), 109.1 (d) (d, J_{CF} = 3.2), 94.6 (u), 56.7 (d), 1.3 (d), 1.2 (d).

9-[4-Fluoro-2-(methoxymethoxy)-3-(trimethylsilyl)phenyl]phenanthrene (57). Prepared from **56** and 9-bromophenanthrene in 64% yield as described above for **6**: white flakes; mp 116–117 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.78 (d, 1, J = 6.7), 8.74 (d, 1, J = 7.0), 7.92 (dd, 1, J = 7.2, 2.1), 7.70 (m, 6), 7.38 (dd, 1, J = 8.4, 8.3), 6.95 (dd, 1, J = 8.4, 8.4), 4.48 (AB quartet, 2, J = 5.0, $\Delta\nu$ = 23.9), 2.59 (s, 3), 0.48, 0.47 (2 singlets, 9); ^{13}C-NMR δ

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167.9 (u) (d, J_{CF} = 241.8), 160.8 (u) (d, J_{CF} = 14.0), 136.0 (u), 135.3 (d) (d, J_{CF} = 10.5), 132.0 (u), 131.6 (u), 130.9 (u), 130.5 (u), 129.5 (u) (d, J_{CF} = 3.6), 129.1 (d), 129.1 (d), 127.6 (d), 127.4 (d), 127.3 (d), 127.1 (d), 127.1 (d), 123.2 (d), 123.1 (d), 120.5 (u) (d, J_{CF} = 29.4), 111.6 (d) (d, J_{CF} = 27.2), 99.5 (u), 57.3 (d), 1.5 (d), 1.5 (d). Anal. Calcd for $C_{25}H_{25}FO_2Si$: C, 74.26; H, 6.19. Found: C, 74.05; H, 6.22.

9-Phenanthrylboronic Acid (34). A solution of 9-bromophenanthrene (5.14 g, 20 mmol) in THF (50 mL) was cooled to −78 °C under N_2 and treated dropwise with *n*-butyllithium (44 mmol, 1.6 M in hexane). After the addition the solution was stirred at −78 °C for 45 min, and then triisopropylborate (7.52 g, 40 mmol) was added in one portion. The resulting mixture was stirred at −78 °C for 30 min and then at room temperature for 1 h. The solution was partitioned between 400 mL of ether and 200 mL of 10% HCl. The ether extract was washed with H_2O (200 mL) and dried over Na_2SO_4. The crude product was dried over P_2O_5 in a vacuum desiccator and then washed with cold ether and dried to give a white solid: 4.1 g (92%); mp 230–233 °C (MeOH/H_2O); ^{1}H-NMR (DMSO-d_6) δ 8.85 (m, 2), 8.49 (s, 2, OH), 8.40 (m, 1), 8.05 (s, 1), 7.99 (dd, 1, *J* = 7.8, 1.8), 7.67 (m, 4).

2-Bromostilbene (45). Sodium hydride (528 mg, 20 mmol of a 80% dispersion in mineral oil) was placed in a 100-mL flask under N_2 and rinsed with hexane via cannula. The flask was evacuated and filled with N_2, and then DMSO (10 mL) was introduced. The mixture was heated at 75–80 °C for 45 min until the evolution of H_2 ceased. The solution of sodium dimsylate was then cooled in an ice bath, and benzyltriphenylphosphonium chloride (7.78 g, 20 mmol) in DMSO (20 mL) was added dropwise. To this orange-red solution was added 2-bromobenzaldehyde (3.33 g, 18 mmol) at 0 °C, and the solution was stirred at room temperature for 10 h. DMSO was removed in vacuo, and the residue was applied to a column of silica gel and eluted with 6% EtOAc/hexanes to afford 4.46 g (96% yield) of **45** as an oil (a mixture of *E*- and *Z*-isomers). *E*-isomer: ^{1}H-NMR δ 7.62 (dd, 1, *J* = 5.5, 3.6), 7.26–7.08 (m, 8), 6.72 (d, 1, *J* = 12.2), 6.63 (d, 1, *J* = 12.1); ^{13}C-NMR δ 138.5 (u), 136.8 (u), 133.2 (d), 131.9 (d), 131.3 (d), 130.0 (d), 129.5 (d, 2 C), 129.2 (d), 128.7 (d, 2 C), 127.8 (d), 127.5 (d), 124.4 (u). *Z*-isomer (obtained pure after UV irradiation as described below): ^{1}H-NMR δ 7.72–7.56 (m, 4), 7.47–7.27 (m, 5), 7.16 (dd, 1, *J* = 7.9, 1.7), 7.07 (d, 1, *J* = 16); ^{13}C-NMR δ 137.7 (u), 137.6 (u), 133.6 (d), 132.0 (d), 129.3 (d), 129.3 (d, 2 C), 128.6 (d), 128.1 (d), 128.0 (d), 127.4 (d, 2 C), 127.2 (d), 124.7 (u).

1-Bromophenanthrene (46). A solution of (*E*)- and (*Z*)-**45** (2.07 g, 8 mmol) in 1 L of benzene was irradiated using a 400-W medium-pressure Hg vapor lamp with a Pyrex filter in the presence of I_2 (2.03 g, 8 mmol) and propylene oxide (25 mL, 358 mmol). After 24 h an additional 10-mL portion (143 mmol) of propylene oxide was added and the irradiation continued for another 50 h whereupon the iodine color had disappeared. The solution was washed with H_2O and filtered through a short column of silica gel. The solvent was evaporated, and the solid was triturated with MeOH giving 1.26 g (61% yield) of **46** as an off-white solid: mp 109–110 °C (lit.[29] mp 109.5–110 °C); ^{1}H-NMR δ 8.63–8.57 (m, 2), 8.24 (d, 1, *J* = 9.5), 7.93–7.89 (m, 2), 7.83 (d, 1, *J* = 9.2), 7.70–7.65 (m, 2), 7.44 (dd, 1, *J* = 8.2, 7.7).

1-Phenanthrylboronic Acid (47). Prepared in 82% yield from 1-bromophenanthrene as described above for **34**: mp 206–209 °C (MeOH/H_2O); ^{1}H-NMR (DMSO-d_6) δ 8.86 (m, 2), 8.47 (s, 2, OH), 8.27 (d, 1, *J* = 8.8), 7.98 (dd, 1, *J* = 6.4, 2.4), 7.83 (m, 2), 7.70 (m, 3).

2-Bromo-3-fluoroanisole (35). Prepared in 86% yield as described previously[19] by ortho-lithiation of 3-fluoroanisole followed by treatment with 2.2 equiv of 1,2-dibromotetrafluoroethane: ^{1}H-NMR δ 7.30–7.18 (m, 1), 6.81–6.68 (m, 2), 3.92 (s, 3).

2-Bromo-3-(methoxymethoxy)anisole (40). Prepared as described above for **35** with the exception that hexane solution of 3-(methoxymethoxy)anisole was lithiated selectively at the 2-position using *tert*-butyllithium at 0 °C for 2.5 h. The yield of **40** as a liquid was 84%: ^{1}H-NMR δ 7.19 (dd, 1, *J* = 8.3, 8.4), 6.79 (dd, 1, *J* = 8.4, 1.1), 6.60 (dd, 1, *J* = 8.3, 1.0), 5.24 (s, 2), 3.88 (s, 3), 3.51 (s, 3); ^{13}C-NMR δ 157.7, 155.5, 128.7, 109.0, 106.1, 102.9, 95.6, 56.9, 56.9.

9-(2-Fluoro-6-methoxyphenyl)phenanthrene (36). A stirred mixture of aryl bromide **35** (820 mg, 4 mmol) and tetrakis(triphenylphosphine)palladium(0) (138 mg, 0.12 mmol) in toluene (60 mL) was treated successively with boronic acid **34** (1.11 g, 5 mmol) dissolved in 6 mL of EtOH and 5 mL of a 2 M aqueous solution of Na_2CO_3. Nitrogen was bubbled through the solution for 5 min to remove dissolved air, and the solution was heated at 85 °C for 6 h. The layers were separated, and the organic layer was dried over Na_2SO_4. Flash chromatography on silica gel eluting with 4% EtOAc/hexanes gave **36** as a white solid: 480 mg (40%); mp 120–121 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.83 (d, 1, *J* = 8.0), 8.79 (d, 1, *J* = 7.4), 7.96 (dd, 1, *J* = 7.4, 1.8), 7.81 (s, 1), 7.69 (m, 5), 7.45 (m, 1), 6.94 (m, 2), 3.71 (s, 3); ^{13}C-NMR δ 161.7 (u) (d, J_{CF} = 243.0), 159.6 (u) (d, J_{CF} = 7.0), 132.2 (u), 131.9 (u), 131.0 (u), 131.0 (u), 130.1 (d) (d, J_{CF} = 10.3), 129.7 (d), 129.3 (d), 129.1 (u), 127.3 (d), 127.2 (d), 127.1 (d), 126.9 (d), 126.9 (d), 123.4 (d), 123.2 (d), 117.7 (u) (d, J_{CF} = 19.5), 108.8 (d) (d, J_{CF} = 23.0), 107.2 (d) (d, J_{CF} = 2.8), 56.6 (d). Anal. Calcd for $C_{21}H_{15}FO$: C, 83.44; H, 4.97. Found: C, 83.23; H, 5.01.

9-[2-Methoxy-6-(methoxymethoxy)phenyl]phenanthrene (41). Prepared from **34** and **40** as an oil in 44% yield as described above for **36**: ^{1}H-NMR δ 8.88 (d, 1, *J* = 7.3), 8.84 (d, 1, *J* = 6.6), 8.05 (dd, 1, *J* = 6.6, 2.7), 7.89 (s, 1), 7.75 (m, 5), 7.53 (dd, 1, *J* = 8.3, 7.2), 7.13 (d, 1, *J* = 8.3), 6.87 (d, 1, *J* = 8.3), 5.06 (AB quartet, 2, *J* = 7.4, Δν = 12.6), 3.70 (s, 3), 3.25 (s, 3); ^{13}C-NMR δ 159.5 (u), 156.9 (u), 132.7 (u, 2 C), 132.2 (u), 131.1 (u), 130.9 (u), 130.0 (d), 129.3 (d, 2 C), 127.3 (d), 127.2 (d), 127.0 (d, 2 C), 126.8 (d), 123.5 (d), 123.3 (d), 119.8 (u), 108.6 (d), 105.8 (d), 95.1 (u), 56.5 (d), 56.4 (d).

1-(2-Fluoro-6-methoxyphenyl)phenanthrene (48). Prepared from **35** and **47** in 51% yield as described above for **36**: white solid; mp 156–157 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.87 (d, 1, *J* = 8.3), 8.83 (d, 1, *J* = 7.4), 7.96 (dd, 1, *J* = 7.4, 1.9), 7.50 (m, 6), 7.45 (m, 1), 6.95 (m, 2), 3.72 (s, 3); ^{13}C-NMR δ 161.5 (u) (d, J_{CF} = 243), 159.3 (u) (d, J_{CF} = 7.0), 132.4 (u), 131.5 (u), 131.1 (u, 2 C), 131.0 (u), 130.1 (d) (d, J_{CF} = 10.5), 129.7 (d), 129.0 (d), 127.6 (d), 127.2 (d), 127.2 (d), 126.6 (d), 125.1 (d), 123.5 (d), 123.4 (d), 118.0 (u) (d, J_{CF} = 20), 108.8 (d) (d, J_{CF} = 23.0), 107.3 (d) (d, J_{CF} = 3.0), 56.6 (d). Anal. Calcd for $C_{21}H_{15}FO$: C, 83.44; H, 4.97. Found: C, 83.45; H, 5.03.

General Procedure for Hydrolysis of the MOM Ethers. 9-(2-Hydroxyphenyl)phenanthrene (7). A solution of MOM ether **6** (440 mg, 1.4 mmol) in THF (20 mL) was treated with 4 N HCl (10 mL) and heated at reflux for 3 h. The solution was cooled, extracted with ether, dried over Na_2SO_4, and concentrated. Flash chromatography on silica gel eluting with 5–8% EtOAc in hexanes afforded phenol **7** as an oil: 340 mg (90%); ^{1}H-NMR δ 8.79 (m, 2), 7.95 (m, 9), 7.14–7.07 (m, 2), 4.95 (s, 1); ^{13}C-NMR δ 154.0, 133.2, 132.0, 131.8, 131.4, 131.3, 131.0, 130.2, 129.74, 129.3, 127.8, 127.7, 127.7, 127.6, 127.1, 126.8, 123.6, 123.2, 121.2, 116.2.

9-(2-Hydroxyphenyl)anthracene (10). Prepared from **9** in 86% yield as described above for **7**: solid; mp 178–180 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.55 (s, 1), 8.07 (d, 2, *J* = 8.1), 7.70 (d, 2, *J* = 8.0), 7.54–7.39 (m, 5), 7.31–7.13 (m, 3), 4.57 (s, 1).

8-Hydroxy-1-(1-naphthyl)naphthalene (13). A solution of methyl ether **12** (427 mg, 1.5 mmol) in CH_2Cl_2 (50 mL) was cooled to −78 °C under N_2 and treated via syringe with BBr_3 (7.5 mL, 1 M in CH_2Cl_2). The solution was stirred at −78 °C for 1 h and then at room temperature for 2 h. Water (50 mL) was added, and the organic layer was separated and dried over Na_2SO_4. Flash chromatography on silica gel eluting with 5% EtOAc/hexanes afforded **13** as an oil: 390 mg (96% yield); ^{1}H-NMR δ 8.09–7.98 (m, 3), 7.66–7.31 (m, 9), 6.91 (dd, 1, *J* = 7.5, 1.3), 5.49 (s, 1).

8-Hydroxy-1-(2-naphthyl)naphthalene (16). Prepared from **15** in quantitative yield as described above for **13**: white solid; mp 105–107 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.07–7.89 (m, 4), 8.03 (s, 1), 7.67–7.41 (m, 6), 7.30 (m, 1), 6.96 (dd, 1, *J* = 7.4, 1.2), 5.52 (s, 1). Anal. Calcd for $C_{20}H_{14}O$: C, 88.89; H, 5.19. Found: C, 88.72; H, 5.20.

2-Hydroxy-3-(1-naphthyl)naphthalene (20). Prepared from **19** as a white solid in 77% yield as described above for **7**: mp 135–136 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.02–7.96 (m, 2), 7.85–

(29) Pan, H.-L.; Fletcher, T. L. *Synthesis* **1973**, 610.

7.81 (m, 3), 7.71–7.39 (m, 8), 4.94 (s, 1). Anal. Calcd for $C_{20}H_{14}O$: C, 88.89; H, 5.19. Found: C, 88.87; H, 5.21.

9-(2-Hydroxy-5-methoxyphenyl)phenanthrene (23). Prepared from **22** as an oil in 87% yield as described above for **7**: ^{1}H-NMR δ 8.79 (d, 1, J = 8.1), 8.75 (d, 1, J = 8.1), 7.92 (dd, 1, J = 7.1, 1.8), 7.81–7.55 (m, 6), 7.08–6.92 (m, 3), 4.77 (s, 1), 3.81 (s, 3).

9-(2-Hydroxy-4-methoxyphenyl)phenanthrene (27). Prepared from **26** as a white solid in 78% yield as described above for **7**: mp 155–156 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.78 (m, 2), 7.92 (dd, 1), 7.77–7.54 (m, 6), 7.24 (d, 1, J = 9.2), 6.69 (d, 1, J = 2.2), 6.67 (dd, 1), 4.94 (s, 1), 3.90 (s, 3). Anal. Calcd for $C_{21}H_{16}O_2$: C, 84.00; H, 5.33. Found: C, 83.69; H, 5.46.

9-(5-Fluoro-2-hydroxyphenyl)phenanthrene (31). Prepared from **30** as an oil in 90% yield as described above for **7**: ^{1}H-NMR δ 8.75 (m, 2), 7.91 (dd, 1, J = 7.0, 1.9), 7.79–7.56 (m, 6), 7.16–7.02 (m, 3), 5.03 (s, 1).

9-(2-Fluoro-6-hydroxyphenyl)phenanthrene (37). Prepared from **36** as a white solid in 93% yield as described above for **13**: mp 153–155 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.80 (d, 1, J = 8.1), 8.76 (d, 1, J = 8.1), 7.93 (dd, 1, J = 7.6, 1.5), 7.84 (s, 1), 7.70 (m, 5), 7.40 (m, 1), 6.93 (m, 2), 5.10 (s, 1). Anal. Calcd for $C_{20}H_{13}FO$: C, 83.33; H, 4.51. Found: C, 83.17; H, 4.58.

9-(2-Hydroxy-6-methoxyphenyl)phenanthrene (42). Prepared from **41** as a white solid in 81% yield as described above for **7**: mp 126–128 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.78 (d, 1, J = 8.1), 8.76 (d, 1, J = 8.0), 7.93 (dd, 1, J = 7.5, 1.6), 7.79 (s, 1), 7.65 (m, 5), 7.37 (dd, 1, J = 8.3, 8.2), 7.36 (d, 1, J = 8.3), 6.67 (d, 1, J = 8.3), 4.96 (s, 1), 3.66 (s, 3).

1-(2-Fluoro-6-hydroxyphenyl)phenanthrene (49). Prepared from **48** as a white solid in 98% yield as described above for **13**: mp 128–130 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.82 (d, 1, J = 8.4), 8.75 (dd, 1, J = 7.2, 1.8), 7.93 (dd, 1, J = 5.5, 2.2), 7.70 (m, 6), 7.40 (m, 1), 6.95 (m, 2), 5.02 (s, 1).

1-(5-Fluoro-2-hydroxyphenyl)phenanthrene (53). Prepared from **52** as an oil in 91% yield as described above for **7**: ^{1}H-NMR δ 8.76 (d, 1, J = 7.7), 8.73 (d, 1, J = 7.0), 7.93 (dd, 1, J = 7.0, 2.2), 7.66 (m, 6), 7.30 (m, 3), 4.88 (s, 1).

9-(4-Fluoro-2-hydroxyphenyl)phenanthrene (58). Prepared from **57** as an oil as described above for **7**: ^{1}H-NMR δ 8.78 (d, 1, J = 8.8), 8.74 (d, 1, J = 7.7), 7.90 (dd, 1, J = 7.3, 1.5), 7.70 (m, 6), 7.28 (dd, 1, J = 8.0, 7.2), 6.83 (m, 2), 5.48 (s, 1).

General Procedure for the Preparation of Triflates. 9-(2-Hydroxyphenyl)phenanthrene Triflate (8). A solution of phenol **7** (270 mg, 1.0 mmol) and freshly distilled 2,6-lutidine (150 mg, 1.4 mmol) in dry CH_2Cl_2 (10 mL) was cooled to −30 °C under N_2 and treated dropwise with a solution of freshly distilled triflic anhydride (338 mg, 1.2 mmol) in CH_2Cl_2 (5 mL). The solution was allowed to warm to 0 °C over 1 h and then treated with H_2O (15 mL). After the solution was warmed to room temperature the CH_2Cl_2 layer was separated, the aqueous layer extracted with an additional portion of CH_2Cl_2 and the combined organic layers dried over Na_2SO_4. Flash chromatography on silica gel eluting with 7% EtOAc/hexanes afforded the trilfate **8** as an oil which solidified on standing: 350 mg (87% yield); mp 115–116 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.79 (m, 2), 7.96 (dd, 1, J = 7.5, 1.6), 7.79 (s, 1), 7.75–7.66 (m, 3), 7.64–7.54 (m, 6); ^{13}C-NMR δ 148.2 (u), 134.7 (u), 133.8 (d), 132.3 (u), 131.6 (u), 131.2 (u) 131.0 (u), 130.2 (d), 129.8 (d), 129.4 (d), 128.9 (d), 127.8 (d), 127.5 (d), 127.4 (u), 127.3 (d, 2 C), 126.8 (d), 123.5 (d), 123.2 (d), 122.3 (d), 118.7 (u) (q, J_{CF3} = 319 Hz). Anal. Calcd for $C_{21}H_{13}F_3O_3S$: C, 62.68; H, 3.26. Found: C, 62.75; H, 3.25.

9-(2-Hydroxyphenyl)anthracene Triflate (11). Prepared from **10** in 96% yield as described above for **8**: solid; mp 130–131 °C (EtOAc/hexanes).

8-Hydroxy-1-(1-naphthyl)naphthalene Triflate (14). Prepared from **13** as a white solid in 87% yield as described above for **8**; mp 106–107 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.05–7.93 (m, 3), 7.71–7.38 (m, 8), 7.30–7.26 (m, 2). Anal. Calcd for $C_{21}H_{13}F_3O_3S$: C, 62.69; H, 3.23. Found: C, 62.48; H, 3.29.

8-Hydroxy-1-(2-naphthyl)naphthalene Triflate (17). Prepared from **16** in 82% yield as described above for **8**: white solid; mp 162–164 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.03–7.89 (m, 6), 7.68–7.46 (m, 7). Anal. Calcd for $C_{21}H_{13}F_3O_3S$: C, 62.69; H, 3.23. Found: C, 62.56; H, 3.29.

2-Hydroxy-3-(1-naphthyl)naphthalene Triflate (21). Prepared from **20** as a semisolid in 79% yield as described above for **8**.

9-(2-Hydroxy-5-methoxyphenyl)phenanthrene Triflate (24). Prepared from **23** as a semisolid in 92% yield as described above for **8**: ^{1}H-NMR δ 8.77 (m, 2), 7.94 (dd, 1, J = 7.4, 1.6), 7.77–7.56 (m, 6), 7.42 (d, 1, J = 9.9), 7.07 (d, 1, J = 3.1), 7.06 (dd, 1), 3.86 (s, 3). Anal. Calcd for $C_{22}H_{15}F_3O_3S$: C, 61.11; H, 3.47. Found: C, 61.09; H, 3.49.

9-(2-Hydroxy-4-methoxyphenyl)phenanthrene Triflate (28). Prepared from **27** in 88% yield as described above for **8**: solid; mp 90–92 °C (EtOAc/hexanes).

9-(5-Fluoro-2-hydroxyphenyl)phenanthrene Triflate (32). Prepared from **31** as an oil in 82% yield as described above for **8**.

9-(2-Fluoro-6-hydroxyphenyl)phenanthrene Triflate (38). Prepared from **37** as an off-white solid in 95% yield as described above for **8**: mp 114–116 °C (EtOAc/hexanes).

9-(2-Hydroxy-6-methoxyphenyl)phenanthrene Triflate (43). Prepared from **42** as an oil in 85% yield as described above for **8**.

1-(2-Fluoro-6-hydroxyphenyl)phenanthrene Triflate (50). Prepared from **49** as a white solid in quantitative yield as described above for **8**: mp 125–126 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.95 (d, 1, J = 8.3), 8.84 (d, 1, J = 8.1), 7.98 (dd, 1, J = 7.2, 1.9), 7.80 (m, 5), 7.45 (m, 4). Anal. Calcd for $C_{21}H_{12}F_4O_3S$: C, 60.00; H, 2.86. Found: C, 59.94; H, 2.88.

1-(5-Fluoro-2-hydroxyphenyl)phenanthrene Triflate (54). Prepared from **53** as a white solid in 93% yield as described above for **8**: mp 99–100 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.88 (d, 1, J = 8.4), 8.80 (d, 1, J = 9.0), 7.95 (dd, 1, J = 7.4, 1.9), 7.68 (m, 7), 7.29 (m, 2). Anal. Calcd for $C_{21}H_{12}F_4O_3S$: C, 60.00; H, 2.86. Found: C, 59.91; H, 2.89.

9-(4-Fluoro-2-hydroxyphenyl)phenanthrene Triflate (59). Prepared from **57** as a white solid in 89% overall yield for the two steps as described above for **8**: mp 81–82 °C; (EtOAc/hexanes); ^{1}H-NMR δ 8.81 (d, 1, J = 8.4), 8.77 (d, 1, J = 8.5), 7.95 (dd, 1, J = 7.5, 1.8), 7.73 (m, 4), 7.58 (m, 3), 7.31 (m, 2). Anal. Calcd for $C_{21}H_{12}F_4O_3S$: C, 60.00; H, 2.86. Found: C, 59.91; H, 2.90.

General Procedure for Intramolecular Triflate–Arene Coupling. Benzo[*b*]fluoranthene (1). A solution of the triflate **8** (80.5 mg, 0.2 mmol), bis(triphenylphosphine)palladium(II) chloride (14 mg, 0.02 mmol), LiCl (25 mg, 0.6 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 36.5 mg, 0.24 mmol) in DMF (2 mL) was heated under N_2 at 140 °C for 10 h. After the solution was cooled to room temperature H_2O (5 mL) was added and the solution extracted with EtOAc. The organic layer was washed with H_2O, dried over Na_2SO_4, and evaporated. Flash chromatography on silica gel eluting with 2% EtOAc/hexanes afforded **1** as an off-white solid: 43 mg (85% yield); mp 167–168 °C (MeOH/benzene) (lit.[30] mp 168.3 °C); ^{1}H-NMR δ 8.65 (m, 1), 8.45 (d, 1, J = 8.1), 8.21 (s, 1), 8.07–7.91 (m, 4), 7.78 (d, 1, J = 8.0), 7.72–7.63 (m, 2), 7.46–7.41 (m, 2); ^{13}C-NMR δ 141.2 (u), 139.0 (u), 137.5 (u), 135.6 (u), 134.5 (u), 132.6 (u), 131.2 (u), 130.7 (d), 128.7 (d), 128.6 (d), 128.1 (u), 128.0 (d), 127.5 (d), 127.3 (d), 123.7 (d), 122.4 (d), 122.2 (d), 122.0 (d), 121.9 (d), 120.1 (d).

Benzo[*a*]fluoranthene (2). Prepared from **11** in 84% yield as described for **1** (15 h reaction time): solid; mp 145–146 °C (MeOH/benzene) (lit.[31] mp 146.3 °C); ^{1}H-NMR δ 8.78 (d, 1, J = 8.8), 8.49 (s, 1), 8.40 (d, 1, J = 7.7), 8.16 (d, 1, J = 8.8), 8.05–8.01 (m, 3), 7.68 (m, 2), 7.57–7.38 (m, 3); ^{13}C-NMR δ 141.9 (u), 140.9 (u), 139.5 (u), 137.4 (u), 135.0 (u), 131.9 (u), 131.1 (d), 129.5 (u), 128.4 (d), 128.0 (d), 127.9 (d), 127.8 (d), 127.7 (d), 127.0 (d), 125.4 (d), 124.8 (d), 124.2 (d), 122.2 (d), 120.7 (d).

Benzo[*j*]fluoranthene (3). Prepared from **14** in 93% yield (120 °C for 10 h) as described for **1**: mp 164–165 °C (MeOH/benzene) (lit.[32] mp 165.4 °C); ^{1}H-NMR δ 8.70 (d, 1, J = 8.4), 8.42 (d, 1, J = 7.0), 8.02 (d, 1, J = 8.3), 7.97 (d, 1, J = 6.9), 7.95 (m, 1), 7.86 (d, 2, J = 7.4), 7.72–7.59 (m, 3), 7.51 (ddd, 1, J = 8.2, 6.8,

(30) *Spectral Atlas of Polycyclic Aromatic Compounds*; Karcher, W., Fordham, R. J., Dubois, J. J., Glaude, P. G. J. M., Ligthart, J. A. M., Eds.; Reidel, D.: Dordrecht, Holland, 1985; p 489.
(31) Reference 29, 471.
(32) Reference 29, 507.

1.3); ^{13}C-NMR δ 138.3 (u), 138.2 (u), 137.6 (u), 134.8 (u), 134.5 (u), 132.5 (u), 131.1 (u), 130.1 (u), 129.8 (d), 128.8 (d), 128.7 (d), 128.3 (d), 127.8 (d), 127.5 (d), 127.4 (d), 125.8 (d), 124.8 (d), 124.6 (d), 121.4 (d), 120.4 (d).

Benzo[*k*]fluoranthene (4). Prepared from **21** in 64% yield (120 °C, 3 h) as described above for **1**: mp 214–215 °C (lit.[33] mp 215.7 °C) ^{1}H-NMR δ 8.33 (s, $H_{7,12}$), 8.03 (d, $H_{1,6}$, J = 7.0), 7.96 (dd, $H_{8,11}$, J = 6.2, 3.3), 7.87 (d, $H_{3,4}$, J = 8.4), 7.68 (dd, $H_{2,5}$, J = 8.1, 7.0), 7.50 (dd, $H_{9,10}$, J = 6.2, 3.3); ^{13}C-NMR δ 138.3 (u), 137.4 (u), 134.0 (u), 131.0 (u), 129.2 (d), 128.7 (d), 126.5 (d), 120.7 (d), 119.7 (d).

6-Methoxybenzo[*b*]fluoranthene (25). Prepared from **24** as a white solid in 62% yield as described for **1** with the inclusion of 0.4 equiv of triphenylphosphine in the reaction mixture: mp 145–146 °C (EtOAc/hexanes) (lit.[6a] mp 145–146 °C); ^{1}H-NMR δ 8.66 (dd, 1, J = 7.3, 1.8), 8.39 (d, 1, J = 8.2), 8.21 (s, 1), 8.05 (m, 1), 7.88 (d, 1, J = 7.2), 7.81 (d, 1, J = 8.1), 7.75 (d, 1, J = 7.9), 7.71–7.63 (m, 2), 7.56 (d, H_7, $J_{5,7}$ = 2.5), 6.97 (dd, H_5, $J_{4,5}$ = 8.2), 3.97 (s, 3); ^{13}C-NMR δ 160.5 (u), 140.9 (u), 137.7 (u), 135.7 (u), 134.5 (u), 134.4 (u), 133.0 (u), 131.4 (u), 130.8 (d), 128.8 (d), 128.0 (u), 127.6 (d), 127.3 (d), 123.7 (d), 122.6 (d), 122.0 (d), 121.0 (d), 119.1 (d), 114.4 (d), 108.2 (d), 56.0 (d).

5-Methoxybenzo[*b*]fluoranthene (29). Prepared from **28** as a white solid in 73% yield as described above for **1** with the inclusion of 0.4 equiv of triphenylphosphine in the reaction mixture and a reaction time of 14 h: mp 189–190 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.65 (dd, 1, J = 7.1, 2.4), 8.46 (d, 1, J = 8.1), 8.10 (s, 1), 8.04–7.87 (m, 3), 7.75 (dd, 1, J = 8.1), 7.68–7.61 (m, 2), 7.48 (d, H_4, $J_{4,6}$ = 2.3), 6.96 (dd, H_6, $J_{6,7}$ = 8.3, $J_{4,6}$ = 2.3), 3.96 (s, 3); ^{13}C-NMR δ 160.9, 143.0, 137.4, 135.5, 134.8, 133.4, 132.0, 130.7, 130.4, 128.5, 128.1, 127.3, 127.1, 123.6, 123.2, 122.4, 120.7, 120.0, 113.7, 107.7, 56.2. Anal. Calcd for $C_{21}H_{14}O$: C, 89.36; H, 4.97. Found: C, 89.25; H, 5.05.

6-Fluorobenzo[*b*]fluoranthene (33). Prepared from **32** in 72% yield (8 h) as described above for **1**. In the presence of PPh_3 (0.4 equiv) for 8 h the yield was 68%; white solid; mp 130–131 °C (benzene/MeOH) (lit.[34] mp 115–116 °C); ^{1}H-NMR δ 8.60 (m, 1), 8.36 (d, 1, J = 8.2), 8.06 (s, H_8), 7.98 (dd, 1, J = 7.4, 1.7), 7.84 (d, 1, J = 7.0), 7.77 (dd, 1, J = 8.1, 4.9), 7.73–7.55 (m, 4), 7.14–7.04 (m, 1); ^{13}C-NMR δ 163.4 (u) (d, J_{CF} = 243.4), 141.0 (u) (d, J_{CF} = 9.4), 137.1 (u) (d, J_{CF} = 2.3), 136.6 (u), 134.6 (u), 134.6 (u), 134.2 (u), 131.4 (u), 130.8 (d), 128.7 (d), 128.0 (u), 127.8 (d), 127.3 (d), 123.6 (d), 122.6 (d) (d, J_{CF} = 8.9), 122.6 (d), 121.7 (d), 119.7 (d), 115.2 (d) (d, J_{CF} = 23.3), 109.7 (d) (d, J_{CF} = 23.6). Anal. Calcd for $C_{20}H_{11}F$: C, 88.89; H, 4.07. Found: C, 88.61; H, 4.11.

7-Fluorobenzo[*b*]fluoranthene (39). Prepared from **38** in 60% yield (15 h) as described above for **1**: mp 148–149 °C (benzene/MeOH) (lit.[35] mp 148–149 °C); ^{1}H-NMR δ 8.63 (dd, 1, J = 7.2, 1.5), 8.45 (d, 1, J = 8.2), 8.34 (s, 1), 8.05 (dd, 1, J = 7.2, 1.9), 7.97 (d, 1, J = 7.2), 7.71 (m, 4), 7.37 (m, 1), 7.10 (m, 1); ^{13}C-NMR δ 160.1 (u) (d, J_{CF} = 249.5), 143.7 (u) (d, J_{CF} = 6.3), 137.0 (u), 136.9 (u) (d, J_{CF} = 2.5), 134.6 (u), 132.4 (u), 132.3 (u), 132.2 (u), 130.9 (d), 130.0 (d) (d, J_{CF} = 7.3), 128.6 (d), 127.8 (d), 127.4 (d), 125.9 (d) (d, J_{CF} = 4.5), 123.6 (d), 122.7 (d), 120.7 (d), 117.8 (d) (d, J_{CF} = 2.9), 115.1 (d) (d, J_{CF} = 20.0).

7-Methoxybenzo[*b*]fluoranthene (44). Prepared from **43** as an ivory colored solid in 42% yield as described above for **1** with the inclusion of 0.4 equiv of triphenylphosphine in the reaction mixture (6 h reaction time): mp 170–171 °C (EtOAc/hexanes); ^{1}H-NMR δ 8.65 (dd, 1, J = 8.6, 2.0), 8.47 (d, 1, J = 8.3), 8.46 (s, 1), 8.07 (dd, 1, J = 7.0, 2.1), 7.99 (d, 1, J = 6.8), 7.65 (m, 4), 7.40 (dd, 1, J = 8.1, 7.5), 6.98 (d, 1, J = 8.3); ^{13}C-NMR δ 157.6 (u), 142.7 (u), 137.4 (u), 135.1 (u), 134.5 (u), 132.4 (u), 130.8 (d), 129.9 (d), 128.3 (d), 127.8 (u), 127.3 (d), 127.2 (d), 126.2 (u), 125.7 (d), 123.5 (d), 122.3 (d), 120.4 (d), 114.8 (d), 112.8 (u), 110.6 (d), 56.0 (d). Anal. Calcd for $C_{21}H_{14}O$: C, 89.36; H, 4.97. Found: C, 89.15; H, 5.04.

4-Fluorobenzo[*b*]fluoranthene (51). Prepared from **50** as a white solid in 52% yield (15 h) as described above for **1**: mp 145–146 °C (benzene/MeOH); ^{1}H-NMR δ 8.59 (dd, 1, J = 7.3, 1.3), 8.38 (d, 1, J = 8.3), 8.09 (s, 1), 8.07 (d, 1, J = 6.6), 7.97 (dd, 1, J = 7.0, 2.0), 7.70 (m, 4), 7.32 (m, 1), 7.10 (m, 1); ^{13}C-NMR δ 159.5 (u) (d, J_{CF} = 249), 141.7 (u) (d, J_{CF} = 6.6), 134.9 (u) (d, J_{CF} = 2), 134.3 (u), 134.3 (u), 134.2 (u), 131.9 (u), 131.3 (u), 130.8 (d), 129.2 (d) (d, J_{CF} = 7.2), 128.9 (d), 127.8 (d), 127.3 (d), 123.6 (d), 123.5 (d) (d, J_{CF} = 4.2), 122.9 (d), 122.2 (d), 118.2 (d) (d, J_{CF} = 2.9), 115.7 (d) (d, J_{CF} = 20). Anal. Calcd for $C_{20}H_{11}F$: C, 88.89; H, 4.07. Found: C, 88.77; H, 4.18.

5-Fluorobenzo[*b*]fluoranthene (55). Method A: Prepared from **54** in 58% yield as a 1:1 mixture with **39** (5 h reaction time). Method B: Prepared from **59** as a pure compound in 55% yield as described above: white solid; mp 159–160 °C (benzene/MeOH); ^{1}H-NMR δ 8.62 (dd, 1, J = 7.2, 1.6), 8.44 (d, 1, J = 8.1), 8.08 (s, 1), 8.00 (dd, 1, J = 7.2, 2.0), 7.89 (m, 2), 7.65 (m, 4), 7.08 (m, 1); ^{13}C-NMR δ 163.8 (u) (d, J_{CF} = 244.6), 143.2 (u) (d, J_{CF} = 9.0), 136.5 (u) (d, J_{CF} = 3.0), 134.9 (u) (d, J_{CF} = 2.6), 134.6 (u), 134.5 (u), 133.1 (u), 130.9 (u), 130.6 (d), 128.6 (d), 128.1 (u), 127.6 (d), 127.4 (d), 123.6 (d), 123.3 (d) (d, J_{CF} = 9.2), 122.8 (d), 121.8 (d) (d, J_{CF} = 1.8), 120.4 (d), 114.6 (d) (d, J_{CF} = 23.2), 109.2 (d) (d, J_{CF} = 23.6). Anal. Calcd for $C_{20}H_{11}F$: C, 88.89; H, 4.07. Found: C, 88.61; H, 4.26.

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Supplementary Material Available: Tabulated ^{13}C-NMR spectra for **10, 13, 14, 16, 17, 20, 23, 24, 27, 31, 37, 42, 49, 50, 53, 54, 58,** and **59** and ^{1}H-NMR, ^{13}C-NMR, and APT spectra for compounds **11, 15, 18, 19, 21, 22, 28, 30, 32, 34, 38, 40, 43, 47, 52,** and **56** (46 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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