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# Synthesis of Polycyclic Aromatics and Heteroaromatics via Electrophilic Cyclization

Tuanli Yao, Marino A. Campo, and Richard C. Larock*

*Department of Chemistry, Iowa State University, Ames, Iowa 50011*

*larock@iastate.edu*

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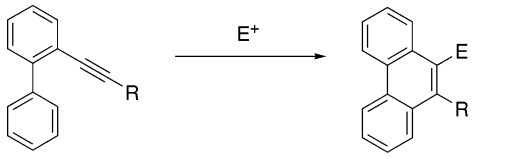
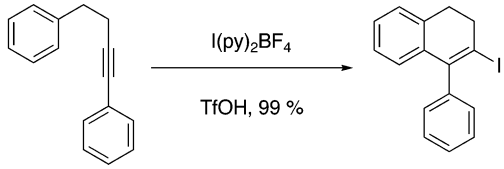



A variety of substituted polycyclic aromatics are readily prepared in good to excellent yields under very mild reaction conditions by the reaction of 2-(1-alkynyl)biphenyls with ICl, $I_2$, NBS, and $p$-$O_2NC_6H_4SCl$. This methodology readily accommodates various functional groups and has been successfully extended to systems containing a variety of polycyclic and heterocyclic rings.

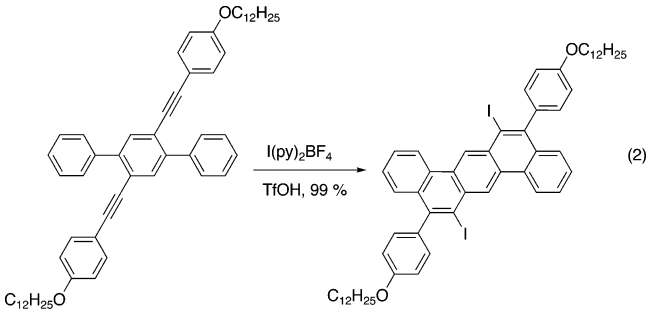
## Introduction

The electrophilic cyclization of alkenes has been studied extensively, and utilized as a key step in a variety of syntheses,[1] particularly the biomimic cyclization of polyenes.[2] Various electrophiles have been reported to effect C−C bond formation in such ring closures.[1−3] Relatively little attention has been paid to the electrophile-induced carbocyclization of alkynes. Nevertheless, the electrophilic addition to carbon−carbon triple bonds can generate cationic species capable of undergoing intramolecular cyclization onto an aromatic ring.[4] Thus, Barluenga first used $I(py)_2BF_4$, a highly electrophilic source of iodonium ions, in the presence of a very strong acid to cyclize 1,4-diphenyl-1-butyne to the corresponding iododihydronaphthalene (eq 1).[5] Swager employed this same reagent



(1)

system to prepare fused polycyclic aromatics (eq 2).[6] Unfortunately, the presence of a $p$-alkoxy group on the phenylethynyl moiety was apparently critical to the success of that methodology. No other applications of this type of carbocyclization have been reported despite its tremendous synthetic potential.



(2)

Polycyclic aromatics are critical to advances in a number of areas of chemical research. For example, polycyclic aromatic iodides are very useful starting materials in organic synthetic methodology, particularly palladium-catalyzed annulation,[7] cyclization,[8] and carbonylation

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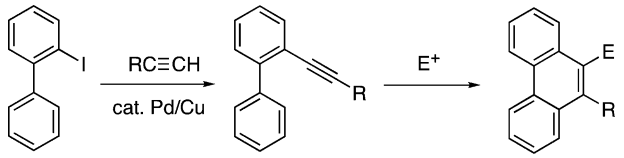
processes.[9] Polycyclic aromatics can also be used as rigid molecular platforms in various areas of chemical research, such as host−guest chemistry,[10] liquid crystal chemistry,[11] and biochemical studies of synthetic peptides.[12] Furthermore, these rigid conjugated materials can serve as key components in many advanced technologies utilizing nonlinear optical,[13] photo- and electroluminescent,[14] and molecule-based sensory devices.[15] They can transfer an applied bias or optical input to a desired response through their highly conjugated $\pi$ electron systems. Polycyclic aromatics obviously possess the degree of conjugation and rigidity necessary to eliminate conformational disorder, which lowers the effective conjugation.[16]

We and others have developed methods for the synthesis of benzo[*b*]thiophenes,[17] isoquinolines and naphthyridines,[18] isocoumarins and α-pyrones,[19] benzofurans,[20] furans,[21] indoles,[22] furopyridines,[23] cyclic carbonates,[24] 2,3-dihydropyrroles and pyrroles,[25] pyrilium salts,[26] bicyclic $\beta$-lactams,[27] isochromenes,[28,26a] phosphaisocoumarins,[29] and isoindolin-1-ones[30] via electrophilic cyclization of functionally substituted alkynes. This successful electrophilic cyclization strategy has encouraged us to develop a more general methodology for the synthesis of polycyclic aromatics.[31] Herein, we report the successful electrophilic cyclization of arene-containing acetylenes to polycyclic aromatics. This chemistry generally produces good to excellent yields of polycyclic aromatics under very mild reaction conditions, accommodates various functional groups, and has been successfully extended to systems containing a variety of polycyclic and heterocyclic rings.

**SCHEME 1**




$E^+$ = ICl, $I_2$, NBS, $p$-$O_2NC_6H_4SCl$, PhSeCl

## Results and Discussion

A two-step approach to polycyclic aromatics has been examined involving (i) preparation of 2-(1-alkynyl)biaryls by the Sonagashira coupling reaction[32] and (ii) electrophilic cyclization (Scheme 1).

The 2-(1-alkynyl)biaryls required for our approach are readily prepared by Sonogashira coupling[32] of the corresponding 2-iodobiaryls with terminal alkynes by using 2% $PdCl_2(PPh_3)_2$ and 1% CuI in $Et_3N$ solvent at 55 °C. The yields of this process range from 55% to 99% and this procedure readily accommodates considerable functionality.

To explore the scope of our electrophilic cyclization strategy, the reactions of alkynyl biphenyl **1** with various electrophiles (ICl, $I_2$, NBS, $p$-$O_2NC_6H_4SCl$, and PhSeCl)

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in $CH_2Cl_2$ at room temperature have been studied (Table 1, entries 1−5). Excellent 99% and 92% yields of the expected iodo- and sulfur-containing phenanthrenes have been obtained in only 30 min when ICl and *p*-$O_2NC_6H_4SCl$ were used as electrophiles, respectively (entries 1 and 4). $I_2$ can also be employed as the electrophile, but the reaction took 24 h at room temperature to afford the corresponding product in only an 80% yield (entry 2). It should be noted that $NaHCO_3$ is indispensable in this reaction. Otherwise, an inseparable mixture of unidentified products was obtained. The structure of compound **2** was confirmed by comparison with 9-iodo-10-phenylphenanthrene prepared by the palladium-catalyzed annulation of (phenylacetylenyl)trimethylsilane by 2-iodobiphenyl, followed by subsequent iododesilylation by ICl.[9a] NBS itself did not react with 2-(1-phenylethynyl)biphenyl (**1**). Interestingly, a mixture of NBS and silica gel provided the cyclized bromine-containing product **3** in an 86% yield after 6 d. Unfortunately, none of the desired selenium-containing product was observed when using PhSeCl. Only 1,2-adducts formed by PhSeCl addition to the carbon−carbon triple bond were obtained.

We next examined the reaction of 2-(*p*-methoxyphenylethynyl)biphenyl (**6**) and ICl (Table 1, entry 6). We first examined the reaction of **6** with 1.2 equiv of ICl in $CH_2Cl_2$ at room temperature. This reaction afforded a mixture of the corresponding iodocyclization product **7** and a side-product, which is believed to be 10-iodo-9-(3-iodo-4-methoxyphenyl)phenanthrene. Fortunately, when the same reaction was carried out at −78 °C, the desired 10-iodo-9-(*p*-methoxyphenyl)phenanthrene (**7**) was the only product formed in a 99% yield. Thus, our standard reaction conditions employ 0.30 mmol of acetylene, 1.2 equiv of ICl in $CH_2Cl_2$ at −78 °C.

By employing this standard protocol, the reaction of 2-(*p*-tolylethynyl)biphenyl (**8**) with ICl afforded the desired 10-iodophenanthrene **9** in a 98% yield (entry 7). The presence of a modest electron-withdrawing group, like a *p*-$CO_2Et$ group, on the phenylethynyl moiety, as in **10**, still provided the cyclization product **11** in a quantitative yield (entry 8). Surprisingly, even the presence of a strong electron-withdrawing *p*-$NO_2$ group on the phenylethynyl moiety (**12**) afforded the corresponding cyclization product **13** in a 57% yield, along with a 42% combined yield of side-products presumed to be 1,2-adducts formed by ICl addition to the carbon−carbon triple bond (entry 9). Thus, the *p*-alkoxy group on the phenylethynyl moiety, which was critical to the success of Swager's cyclization methodology, is obviously not necessary in our chemistry. A notable feature in this chemistry is the preference for the 6-*endo*-dig cyclization to give phenanthrenes over the alternative 5-*exo* mode of cyclization.

Encouraged by our success with the above substrates, we next investigated the cyclization of analogous acetylenes in which various substituents have been attached to the arene undergoing substitution. Treatment of *p*-[2-(phenylethynyl)phenyl]benzaldehyde (**14**) with ICl under our standard reaction conditions afforded cyclization product **15** in a 71% yield. A 17% yield of products from ICl addition to the alkyne was also obtained (entry 10). Substrate **16** containing a strong electron-withdrawing *p*-$NO_2$ group afforded the desired iodophenanthrene **17** in a 55% yield, along with a 31% yield of ICl alkyne adducts (entry 11). The lower yields for these substrates in which the aromatic ring undergoing cyclization is electron-poor is consistent with our proposed mechanism (see the later mechanistic discussion). Substrate **18**, which also contains a nitro group, undergoes cyclization smoothly to produce the desired product **19** in an 88% yield (compare entries 11 and 12). Obviously, moving the nitro group from the ring undergoing substitution to the central arene facilitates electrophilic aromatic substitution.

To further investigate the scope of this methodology, we have examined the effect of various substituents on the remote end of the alkyne moiety. An olefin-substituted alkyne **20** is readily accommodated (entries 13). However, the reaction of alkynes bearing a saturated alkyl or TMS group with ICl under our standard reaction conditions failed to produce the desired phenanthrene products (entries 14 and 15). Interestingly, the (trimethylsilyl)methyl-substituted alkyne **26** underwent smooth iodocyclization to afford the desired phenanthrene **27** in a 50% yield. This favorable result can be attributed to the fact that a silyl group can stabilize a carbocation located in the $\beta$ position,[33] which favors cyclization onto the neighboring phenyl group (see the later mechanistic discussion). The desilylation of product **27** will afford a 9-alkyl-substituted phenanthrene, which means that 9-alkyl phenanthrenes can be prepared by this electrophilic cyclization method in two steps.

This cyclization chemistry has been successfully extended to other biaryl systems. For instance, 1-phenyl-2-(phenylethynyl)naphthalene (**28**) afforded the cyclization product **29** in a 48% yield (entry 17). Changing the phenyl group of the phenylethynyl moiety to a *p*-methoxyphenyl group dramatically increased the yield to 97% (compare entries 17 and 18). The thiophene-containing acetylene **32** afforded the expected cyclization product **33** in a 96% yield (entry19), despite our concern that electrophilic substitution in the very reactive thiophene ring might prove competitive. Obviously it is not. In a similar manner, the isocoumarin-containing alkyne **34** provided a 65% yield of the corresponding polycycle **35**. Treatment of the benzofuran-containing acetylene **36** with ICl afforded the cyclization product **37** in a 91% yield (entry 21). Again, direct substitution of the electron-rich benzofuran does not appear to be competitive with iodocyclization. However, the benzofuran-containing acetylene **38** failed to afford the desired product (entry 22). This may be the result of inductive electron-withdrawal by the oxygen moiety disfavoring cation formation or it may be the unfavorable geometry present when the alkyne and arene undergoing substitution are placed on an unsaturated five-membered ring, rather than the more usual six-membered benzene ring. Treatment of the benzothiophene-containing acetylene **40** with NBS and *p*-$O_2NC_6H_4SCl$ afforded the anticipated cyclization products **41** and **42** in 88% and 91% yields, respectively, with no indication of any products being formed by direct substitution of the benzothiophene (entries 23 and 24).

The regioselectivity in this electrophilic cyclization chemistry has also been investigated. The iodocyclization of biphenyl **43** afforded approximately a 3:1 regiochemical

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**TABLE 1. Synthesis of Polycyclic Aromatics via Electrophilic Cyclization**[a]

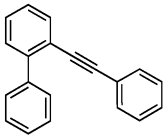
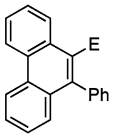
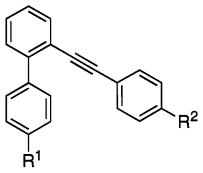
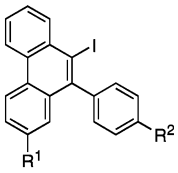
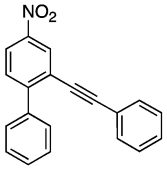
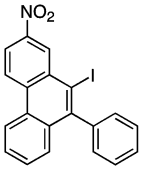
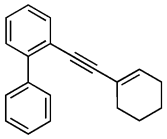
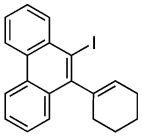
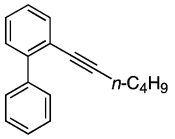
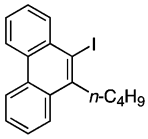
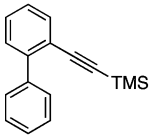
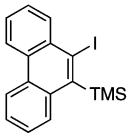
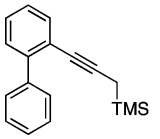
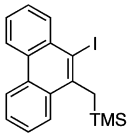
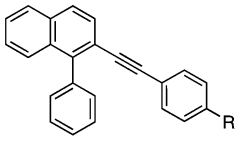
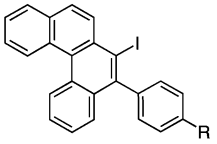
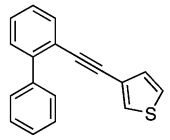
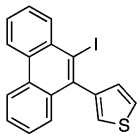
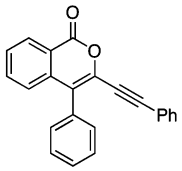
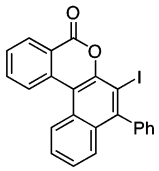
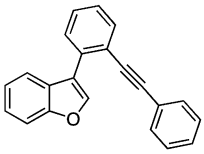
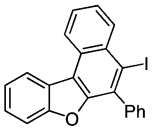
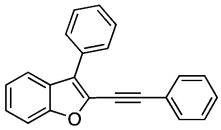
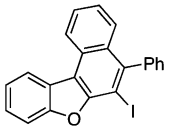
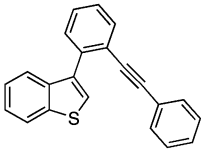
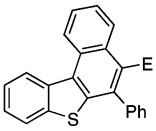
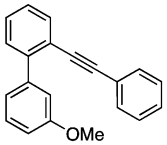
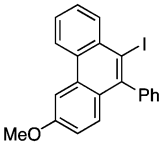
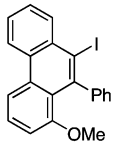
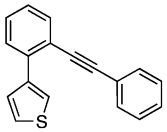
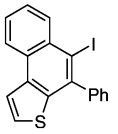
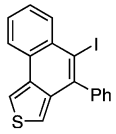
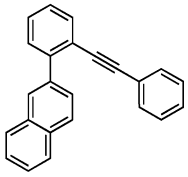
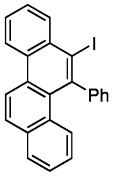
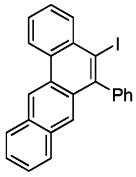
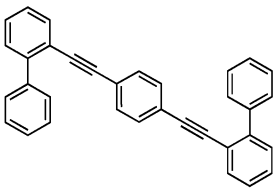
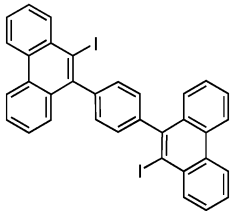
| entry | alkyne | | | electrophile | time (h) | product(s) | | % isolated yield |
|---|---|---|---|---|---|---|---|---|
| 1 |  | | **1** | ICl | 0.5 |  E = I | **2** | 99[b] |
| 2 | | | | $I_2$/$NaHCO_3$ | 24 | E = I | **2** | 80[b,c] |
| 3 | | | | NBS | 144 | E = Br | **3** | 86[b,d] |
| 4 | | | | *p*-$O_2NC_6H_4SCl$ | 0.5 | E = *p*-$O_2NC_6H_4S$ | **4** | 92[b] |
| 5 | | | | PhSeCl | 0.5 | E = PhSe | **5** | 0[b] |
| |  | | | ICl | |  | | |
| | $R^1$ | $R^2$ | | | | | | |
| 6 | H | OMe | **6** | | 0.5 | | **7** | 99 |
| 7 | H | Me | **8** | | 0.5 | | **9** | 98 |
| 8 | H | $CO_2Et$ | **10** | | 3 | | **11** | 99 |
| 9 | H | $NO_2$ | **12** | | 3 | | **13** | 57[e] |
| 10 | CHO | H | **14** | | 1 | | **15** | 71[f] |
| 11 | $NO_2$ | H | **16** | | 3 | | **17** | 55[g] |
| 12 |  | | **18** | ICl | 0.5 |  | **19** | 88 |
| 13 |  | | **20** | ICl | 3 |  | **21** | 70 |
| 14 |  | | **22** | ICl | 0.5 |  | **23** | 0[h] |
| 15 |  | | **24** | ICl | 0.5 |  | **25** | 0[h] |
| 16 |  | | **26** | ICl | 0.5 |  | **27** | 50 |
| |  | | | ICl | 0.5 |  | | |
| 17 | R = H | | **28** | | | | **29** | 48 |
| 18 | R = OMe | | **30** | | | | **31** | 97 |

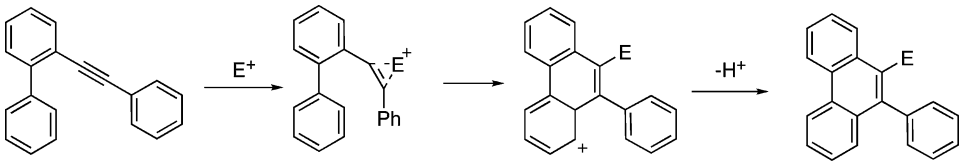
**Table 1 (Continued)**

| entry | alkyne | | electrophile | time (h) | product(s) | | % isolated yield |
|---|---|---|---|---|---|---|---|
| 19 |  | **32** | ICl | 0.5 |  | **33** | 96 |
| 20 |  | **34** | ICl | 0.5 |  | **35** | 65 |
| 21 |  | **36** | ICl | 0.5 |  | **37** | 91 |
| 22 |  | **38** | ICl | 0.5 |  | **39** | 0[h] |
| 23 |  | **40** | NBS | 72 |  | E = Br | **41** | 88[b,d] |
| 24 | | | *p*-$O_2NC_6H_4SCl$ | 0.5 | | E = *p*-$O_2NC_6H_4S$ | **42** | 91[b] |
| 25 |  | **43** | ICl | 0.5 |  | **44**  | **45** | 66 + 20 |
| 26 |  | **46** | ICl | 0.5 |  | **47**  | **48** | 50 + 37 |
| 27 |  | **49** | ICl | 0.5 |  | **50**  | **51** | 76 + 14 |
| 28 |  | **52** | ICl | 0.5 |  | **53** | 90 |

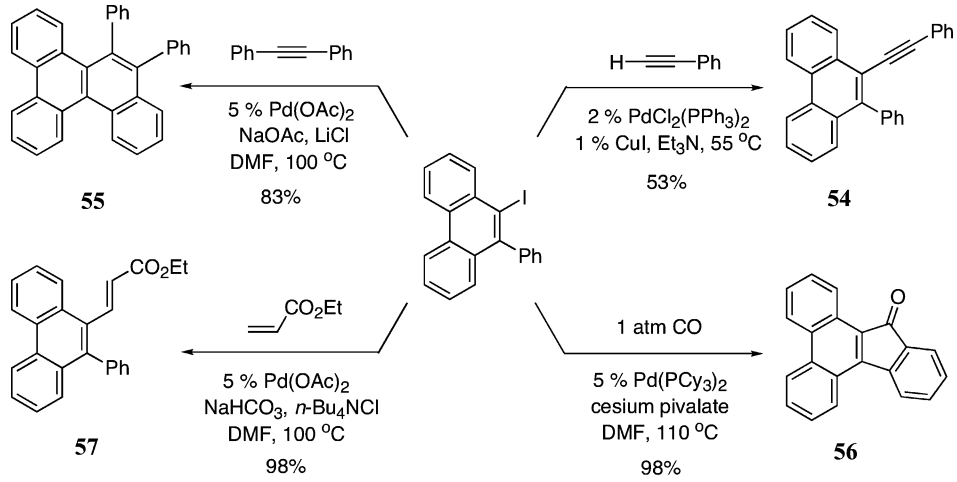
[a] All reactions were run under the following conditions, unless otherwise specified: 0.30 mmol of the acetylene in 3 mL of $CH_2Cl_2$ was placed in a 4-dram vial under $N_2$ and 1.2 equiv of electrophile was added at −78 °C. [b] The reaction was run at room temperature. [c] 3.0 equiv of electrophile and 3.0 equiv of $NaHCO_3$ were used. [d] Silica gel (50 mg) was added. [e] Contains a 42% yield of addition products. [f] Contains a 17% yield of alkyne addition products. [g] Contains a 31% yield of alkyne addition products. [h] Only alkyne addition products were obtained.

mixture of **44** and **45**, with cyclization to the less hindered position being favored (entry 25). In the cyclization of thiophene **46**, electronic effects control the regioselectivity, affording product **47** as the major isomer by cycliza-

**SCHEME 2**




**SCHEME 3**




tion to the more electron-rich α-position of the thiophene (entry 26). However, substantial amounts of the product of substitution in the 4-position are also observed. The iodocyclization of the naphthalene-containing acetylene **49** afforded approximately a 5:1 regiochemical mixture of **50** and **51** in an excellent overall yield (entry 27). The predominant isomer is **50**, which arises by cyclization onto the 1-position of the naphthalene moiety. Clearly, electronic effects favor cyclization to **50** over cyclization to the less hindered 3-position of the naphthalene, which affords **51**.

The facility with which this carbocyclization process occurs encouraged us to attempt a double cyclization. The double cyclization of diyne **52** afforded the desired product **53** in a 90% yield (entry 28).

We propose a mechanism for this electrophilic cyclization chemistry that involves (1) formation of an electrophile acetylene complex, (2) electrophilic attack of this intermediate on the neighboring aromatic ring of the biaryl moiety, and (3) deprotonation to generate the desired polycyclic aromatic (Scheme 2).

An interesting feature of this chemistry is the fact that the polycyclic aromatic iodides produced can be further elaborated by using a variety of palladium-catalyzed processes. For example, palladium-catalyzed Sonogashira coupling,[32] alkyne annulation,[7] cyclocarbonylation,[9] and the Heck reaction[34] have afforded the corresponding products **54**−**57** in 53%, 83%, 98%, and 98% yields, respectively (Scheme 3). The Sonogashira reaction nicely provides products which can again be subjected to electrophilic cyclization to generate still further aromatic rings in an iterative process.

In conclusion, an efficient synthesis of polycyclic aromatics under very mild reaction conditions has been developed. This methodology accommodates various functional groups and affords the anticipated substituted polycyclic aromatics in good to excellent yields. It can be applied to the synthesis of simple polycyclic aromatic hydrocarbons and heterocyclic systems. Finally, the resulting iodine-containing products can be readily elaborated to more complex products by using known organopalladium chemistry.

## Experimental Section

**General Procedure for Preparation of the 2-(1-Alkynyl)biphenyls.** To a solution of the corresponding aryl iodide (1.0 mmol) and the terminal alkyne (1.2 mmol, 1.2 equiv) in $Et_3N$ (4 mL) were added $PdCl_2(PPh_3)_2$ (14 mg, 2 mol %) and CuI (2 mg, 1 mol %). The resulting mixture was then heated under a $N_2$ atmosphere at 55 °C for 3 h. The mixture was allowed to cool to room temperature, and the ammonium salt was removed by filtration. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford the corresponding product.

**2-[(4-Methoxyphenyl)ethynyl]biphenyl (6).** 2-Ethynylbiphenyl and 4-iodoanisole were employed. Purification by flash chromatography (30:1 hexane/EtOAc) afforded 211 mg (74%) of the product as a clear liquid: $^1$H NMR ($CDCl_3$) $\delta$ 3.80 (s, 3H), 6.84 (dd, $J$ = 2.4, 6.9 Hz, 2H), 7.30 (dd, $J$ = 2.1, 6.9 Hz, 2H), 7.34−7.50 (m, 6H), 7.64−7.73 (m, 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 55.5, 88.4, 92.5, 114.2, 115.9, 122.2, 127.3, 127.6, 128.1, 128.4, 129.6, 129.7, 132.9, 133.1, 140.9, 143.9, 159.8; IR (neat, cm$^{-1}$) 3059, 3017, 2214, 1605; HRMS calcd for $C_{21}H_{16}O$ 284.1201, found 284.1205.

**General Procedure for the Electrophilic Cyclization of 2-(1-Alkynyl)biphenyls by ICl.** To a solution of 2-(1-alkynyl)biphenyl (0.30 mmol) in $CH_2Cl_2$ (3 mL) under $N_2$ was added ICl (1.2 equiv) in $CH_2Cl_2$ (0.5 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 0.5 h unless otherwise indicated. The reaction mixture was then diluted with diethyl ether (50 mL), washed with satd aq $Na_2S_2O_3$ (25

(34) For leading reviews of the Heck reaction, see: (a) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379. (b) Shibasaki, M.; Boden, C. D. J.; Kojima, A. *Tetrahedron* **1997**, *53*, *7371.* (c) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2. (d) Overman, L. E. *Pure Appl. Chem.* **1994**, *66*, 1423.

mL), dried ($MgSO_4$), and filtered. The solvent was evaporated under reduced pressure and the product was purified by chromatography on a silica gel column.

**9-Iodo-10-(4-methoxyphenyl)phenanthrene (7).** Purification by flash chromatography (30:1 hexane/EtOAc) afforded 122 mg (99%) of the product as a white solid: mp 170−171 °C; $^1$H NMR ($CDCl_3$) $\delta$ 3.94 (s, 3H), 7.09 (dd, $J$ = 2.1, 6.6 Hz, 2H), 7.21 (dd, $J$ = 2.1, 6.6 Hz, 2H), 7.40−7.49 (m, 2H), 7.64−7.72 (m, 3H), 8.45−8.49 (m, 1H), 8.67−8.78 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 55.6, 107.7, 114.0, 122.8, 122.9, 127.2, 127.3, 127.7, 128.3, 129.0, 130.5, 130.8, 131.3, 132.7, 132.9, 135.0, 138.2, 145.3, 159.4; IR (neat, cm$^{-1}$) 3066, 3024, 2834, 1610; HRMS calcd for $C_{21}H_{15}IO$ 410.0168, found 410.0172.

**General Procedure for the Electrophilic Cyclization of 2-(1-Alkynyl)biphenyls by $I_2$.** To a solution of 2-(1-alkynyl)biphenyl (0.30 mmol) in $CH_2Cl_2$ (3 mL) was added $I_2$ (3.0 equiv) and $NaHCO_3$ (3.0 equiv) at room temperature. The reaction mixture was stirred at room temperature for 24 h unless otherwise indicated. The reaction mixture was then diluted with diethyl ether (50 mL), washed with satd aq $Na_2S_2O_3$ (25 mL), dried ($MgSO_4$), and filtered. The solvent was evaporated under reduced pressure and the product was purified by chromatography on a silica gel column.

**9-Iodo-10-phenylphenanthrene (2).** Purification by flash chromatography (50:1 hexane/EtOAc) afforded 92 mg (80%) of the product as a white solid with a melting point and spectral properties identical with those previously reported.[9a]

**General Procedure for the Electrophilic Cyclization of 2-(1-Alkynyl)biphenyls by NBS.** To a solution of 2-(1-alkynyl)biphenyl (0.30 mmol) in $CH_2Cl_2$ (3 mL) was added NBS (1.2 equiv) and silica gel (50 mg) at room temperature. The reaction mixture was stirred at room tempature for 144 h unless otherwise indicated. The reaction mixture was then diluted with diethyl ether (50 mL), washed with satd aq $Na_2S_2O_3$ (25 mL), dried ($MgSO_4$), and filtered. The solvent was evaporated under reduced pressure and the product was purified by chromatography on a silica gel column.

**9-Bromo-10-phenylphenanthrene (3).** Purification by flash chromatography (40:1 hexane/EtOAc) afforded 86 mg (86%) of the product as a white solid: mp 108−109 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.34−7.38 (m, 2H), 7.41−7.47 (m, 2H), 7.50−7.60 (m, 3H), 7.64−7.77 (m, 3H), 8.53−8.57 (m, 1H), 8.72−8.77 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 122.9, 123.8, 127.1, 127.3, 127.7, 127.9, 128.0, 128.2, 128.7, 129.2, 129.3, 130.2, 130.7, 131.2, 132.9, 139.9, 141.3; IR (neat, cm$^{-1}$) 3071, 3058, 3026, 1583, 1567, 1484; HRMS calcd for $C_{20}H_{15}Br$ 332.0201, found 332.0209.

**General Procedure for the Electrophilic Cyclization of 2-(1-Alkynyl)biphenyls by *p*-$O_2NC_6H_4SCl$.** To a solution of 2-(1-alkynyl)biphenyl (0.30 mmol) in $CH_2Cl_2$ (3 mL) was added *p*-$O_2NC_6H_4SCl$ (1.2 equiv) at room temperature. The reaction mixture was stirred for 0.5 h unless otherwise indicated. The reaction mixture was then diluted with diethyl ether (50 mL), washed with satd aq $NH_4Cl$ (25 mL), dried ($MgSO_4$), and filtered. The solvent was evaporated under reduced pressure and the product was purified by chromatography on a silica gel column.

**9-(4-Nitrophenylsulfenyl)-10-phenylphenanthrene (4).** Purification by flash chromatography (30:1 hexane/EtOAc) afforded 112 mg (92%) of the product as a yellow solid: mp 192−193 °C; $^1$H NMR ($CDCl_3$) $\delta$ 6.94−6.98 (m, 2H), 7.20−7.24 (m, 2H), 7.39−7.47 (m, 3H), 7.50−7.54 (m, 2H), 7.71−7.64 (m, 1H), 7.72−7.79 (m, 2H), 7.93 (dt, $J$ = 9.3, 2.1 Hz, 2H), 8.46 (dd, $J$ = 8.4, 0.9 Hz, 1H), 8.83 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 123.0, 123.4, 124.1, 125.0, 125.9, 127.3, 127.4, 127.8, 128.1, 128.3, 128.4, 128.6, 129.2, 129.4, 131.3, 131.6, 131.7, 132.3, 139.9, 145.1, 148.0, 149.2; IR (neat, cm$^{-1}$) 3066, 3024, 2834, 1610; HRMS calcd for $C_{26}H_7NO_2S$ 407.0980, found 407.0989.

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**Supporting Information Available:** Characterization data for the compounds listed in Table 1 and experimental procedures and characterization data for the reactions summarized in Scheme 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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