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A New Suzuki−Heck-Type Coupling Cascade: Indeno[1,2,3]-Annelation of Polycyclic Aromatic Hydrocarbons

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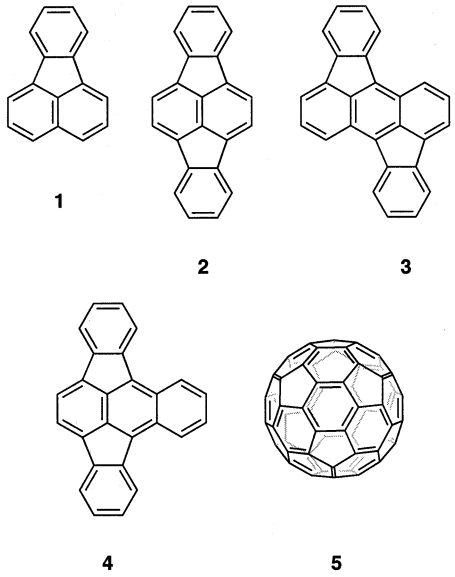
Under palladium catalysis, *o*-bromobenzeneboronic acid can be coupled with 1-bromonaphthalene (**6**) and with oligocyclic bromoarenes to furnish indeno-annelated polycyclic aromatic hydrocarbons **1**−**4** and **25** in a single operation in moderate to good yields (27−87%). Alternatively, *o*-dibromoarenes and 1,2-dibromocycloalkenes can be cross-coupled with 1-naphthaleneboronic acid under the same conditions to yield analogous products (6−87%), and indenocorannulene (**19**) can be prepared likewise in a single step from pinacol corannuleneboronate (**18**) (40%).

Introduction

Significant effort has been directed recently toward the synthesis of polycylic aromatic hydrocarbons (PAHs) containing fully unsaturated five-membered rings that are externally fused to six-membered ring perimeters (CP-PAHs) and indeno-annelated polycyclic aromatic hydrocarbons (indeno-PAHs).[1,2] The latter class includes such compounds as fluoranthene (**1**), indeno[1,2,3-*cd*]-fluoranthene (**2**), rubicene (**3**), and isorubicene (**4**). Special interest in these nonalternant hydrocarbons stems from their resemblance to partial structures of C_{60}-fullerene (**5**) and its higher analogues, their unusual (photo)-physical properties, e.g., anomalous fluorescence and high electron affinities,[3,4] and the carcinogenicity exhibited by several representatives of this family of hydrocarbons.[5,6]

Recently Dang et al. published a one-step palladium-catalyzed cyclopentannelation of 9-bromoanthracene with terminal acetylenes.[7] In this paper we present a new one-step synthesis of a variety of indeno[1,2,3]-annelated PAHs. Our strategy relies on the Suzuki coupling reaction to join two ring systems together initially and then on an intramolecular Heck-type arylation to close the five-membered ring. Since both steps are catalyzed by palladium, our goal was to find conditions under which the entire indeno-annelation sequence could be effected in a single operation. The early work of Rice and Cai,[2] who used aryl triflates, showed that Heck-type arylations are able to close the five-membered ring of the fluoranthene ring system.



Results and Discussion

The first execution of this strategy began with a bromo-PAH and used *o*-bromobenzeneboronic acid (**7**) as the annelation partner (Figure 1). A variety of palladium catalysts and conditions were evaluated (Table 1). The best results were obtained with the combination of

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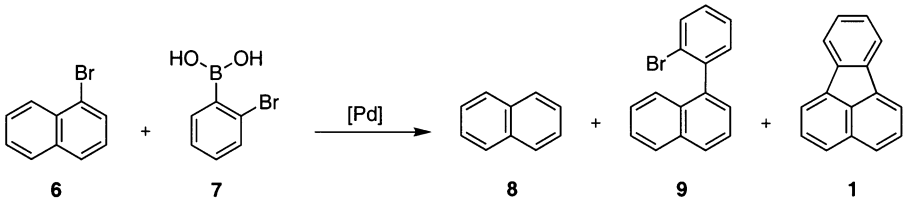


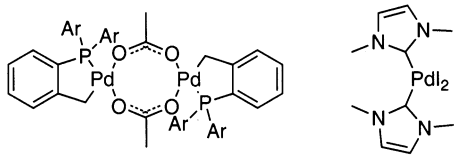
6 7 8 9 1

FIGURE 1. Suzuki−Heck-type coupling cascade of **6** and **7** to form **1**. see Table 1 for conditions.

TABLE 1. Optimization of the Conditions for the Suzuki−Heck-type Coupling Cascade Shown in Figure 1

entry	catalyst (mol %)	additive	base	solvent	temp (°C)	time (h)	products	yield[a] (%) (ratio)
1	$Pd(OAc)_2$, 20		DBU	DMF	155	48	**8**	43
2	$Pd(OAc)_2$, 20	$P(Cy)_3$	DBU	DMF	155	48	**8, 9, 1**	95 (3:1:2.6)
3	$Pd(PPh_3)_2Cl_2$, 20		DBU	DMF	150	48	**9, 1**	81 (1.2:1)
4	**10**, 20		DBU	DMF	155	48	**8**	65
5	$Pd(MeCN)_2Cl_2$, 20		DBU	DMF	155	48	**8, 9**	95 (1:18)
6	**11**, 20		DBU	DMF	155	48	**1**	43
7	$Pd(PPh_3)_4$, 20		K_2CO_3	DMF	110	14	**9**	95[b]
8	$Pd_2(dba)_3$, 20	$P(Ph)_3$	DBU	DMF	155	48	**9, 1**	99 (1:3)
9	$Pd_2(dba)_3$, 20	$P(p\text{-tol})_3$	DBU	DMF	155	48	**9, 1**	98 (1:2.6)
10	$Pd_2(dba)_3$, 20	$P(n\text{-Bu})_3$	DBU	DMF	155	48	**8, 9, 1**	94 (1:2:4.5)
11	$Pd_2(dba)_3$, 20	dppe	DBU	DMF	155	48	**9, 1**	22:65
12	$Pd_2(dba)_3$, 20	$P(Cy)_3$	DBU	DMF	155	48	**1**	97
13	$Pd_2(dba)_3$, 10	$P(Cy)_3$	DBU	DMF	155	48	**1**	95
14	$Pd_2(dba)_3$, 5	$P(Cy)_3$	DBU	DMF	155	48	**9, 1**	81 (1:1.6)
15	$Pd_2(dba)_3$, 2	$P(Cy)_3$	DBU	DMF	155	48	**9, 1**	62 (1,5:1)

[a] If not otherwise noted, the yields were determined by NMR. [b] Isolated yield.



10 Ar = *o*-Tolyl **11**

$Pd_2(dba)_3$ and $P(Cy)_3$. The amount of catalyst could be reduced to 10 mol %, but with lower catalyst loadings the yield dropped dramatically (Table 1, entries 13−15). With $Pd(PPh_3)_4$ as a catalyst at 110 °C, only the Suzuki coupling product **9** was isolated (Table 1, entry 7).

It is noteworthy that none of the catalytic systems promoted any detectable coupling of **7** with itself. We anticipated that the conjugate base of the boronic acid would sterically and electronically retard oxidative addition of the *ortho* C−Br bond to Pd(0), and our results are consistent with this prediction.

In view of the fact that simple areneboronic acids are more easily prepared than *o*-bromoareneboronic acids, we decided to examine a variant of this annelation by applying the same reaction conditions to 1-naphthaleneboronic acid (**12**) and 1,2-dibromobenzene (**13**). Indeed, **1** is also formed by this method and could be isolated in 87% yield (Figure 2).

The same reaction conditions were also examined for the coupling of 1,2-dibromocycloalkenes with **12**. From the reaction of 1,2-dibromocyclohexene (**14b**) with **12**, the ring-closed product **16b** could be isolated in 58% yield. The 2-fold Suzuki coupling product **17b**, a product type which was never observed in the reactions of *o*-dibromobenzene (**13**), was obtained as a side product in 6% yield (Figure 3). When 1,2-dibromcyclopentene (**14a**) was used, the yield of the cyclization product **16a** dropped to 33%, and that of the 2-fold Suzuki coupling product **17a**

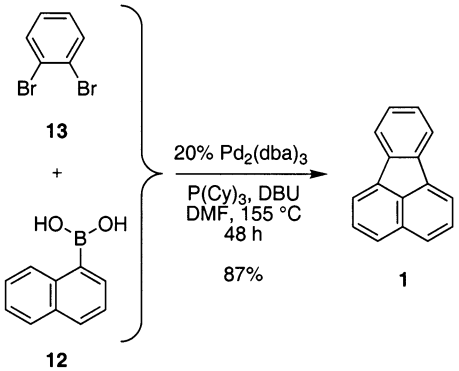
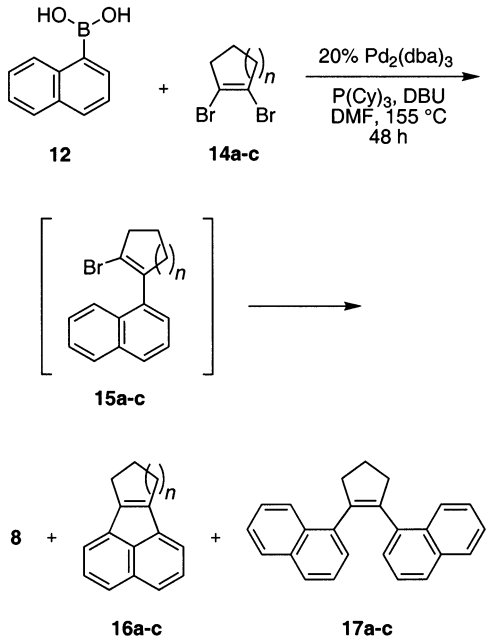


FIGURE 2. Application of the optimized conditions to **12** and **13**.

increased to 19%. 1,2-Dibromocycloheptene (**14c**) gave the cyclized product **16c** in only 6% yield.

Monitoring the reaction of **14b** by NMR spectroscopy revealed that the reaction is complete after 5 h. We therefore repeated this reaction, adding the boronic acid by syringe pump over 5 h. Unfortunately, no significant change in the ratio of cyclized **16b** to 2-fold Suzuki product **17b** was observed. The same result was obtained for **14a**. This led to the conclusion that the second Suzuki coupling step is about as fast as the first one and successfully competes with the Heck-type intramolecular coupling.



	n+4	8	16	17
a	5	-	33%	19%
b	6	4%	58%	6%
c	7	18%	6%	-

FIGURE 3. Suzuki−Heck-type coupling cascade of dibromocycloalkenes **14** with **12**.

As a preliminary probe into the scope and limitations of these cross-coupling−cyclization cascades, the reactions of pinacol corannuleneboronate (**18**) with 1,2-dibromobenzene (**14**) and of 1,4-dibromonaphthalene (**20**), 9,10-dibromoanthracene (**21**), and 1,8-dibromophenanthrene (**24**) with **7** were performed under the optimized conditions. Gratifyingly, the otherwise difficultly accessible indenocorannulene (**19**)[8] was obtained in this single-operation procedure in 40% isolated yield (Figure 4). **2** was isolated in 51% yield from **20**, along with **1** (35%). An inseparable mixture of **3** and **4** was isolated in 28% yield from **21** (1:1 ratio by ^{1}H NMR analysis), along with benzo[*a*]fluoranthene (**22**) (27%) and anthracene (**23**) (19%). The reaction of **24** gave the desired **25** and the byproduct **26** both in 27% yield. In this case, 12% starting material **24** was also recovered (Figure 4).

As these first examples demonstrate, a new Suzuki−Heck-type coupling cascade to build indeno[1,2,3]-PAHs quickly in moderate to good yields has now been found. A search for improved conditions to diminish the formation of side products is currently in progress.

Experimental Section

General Procedures. ^{1}H NMR spectra (250 MHz) were recorded at ambient temperature in $CDCl_3$, using $CHCl_3$ (δ = 7.26) or tetramethylsilane (δ = 0.00) as internal standard. Chemical shifts (δ) are quoted in parts per million, and coupling constants (J) are given in absolute values in hertz to the nearest 0.1 Hz. The following abbreviations are used for the signal multiplicities: s (singlet), d (doublet), m (multiplet). ^{13}C NMR spectra (62.9 MHz) were recorded at ambient temperature in $CDCl_3$, with $\delta(CDCl_3)$ = 77.0 as internal standard. Mass spectra were recorded using electron impact ionization at 70 eV. High-resolution mass spectroscopy (HRMS) was performed using preselected ion peak matching at $R \approx$ 10000 to be within ±2 ppm. Elemental analyses were performed at the University of Göttingen, Germany. All solvents were distilled before use. Chromatography: for standard chromatography, silica gel of 230−400 mesh (0.063−0.200 mm) was used, and for flash chromatography, silica gel of 70−230 mesh (0.040−0.063 mm) was used. Unless specified otherwise, solutions of $NaHCO_3$ were saturated aqueous solutions. An-

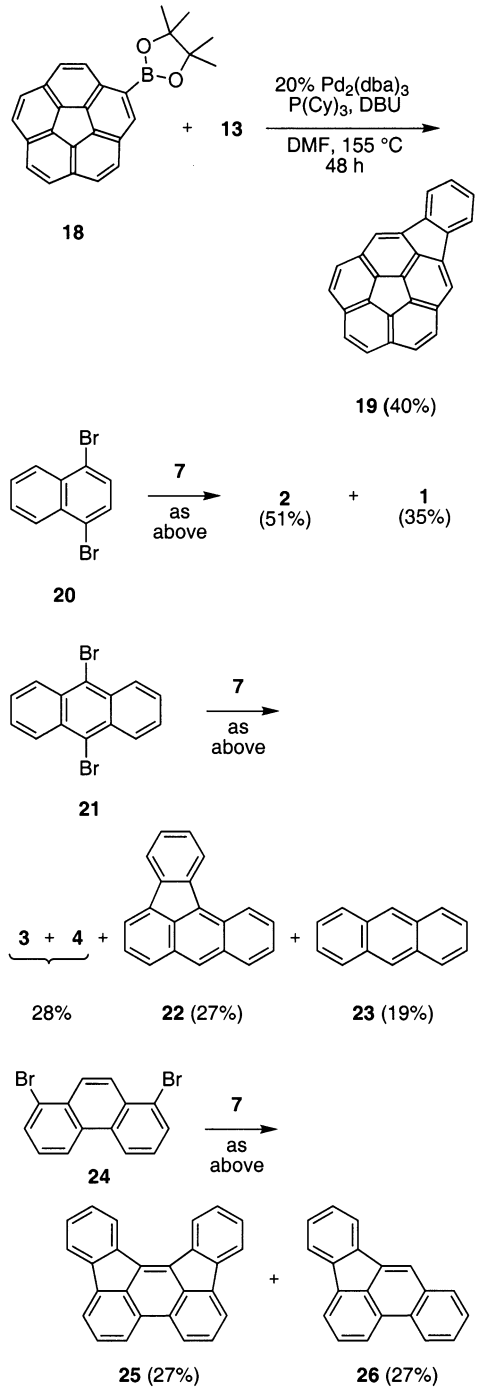


FIGURE 4. Synthesis of indeno-annelated PAHs with the new Suzuki−Heck-type coupling cascade.

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hydrous solvents were prepared according to standard laboratory techniques. All reactions with organometallic substances were performed under argon. All chemicals were used as commercially available, unless otherwise noted.

General Procedure for the Suzuki−Heck-Type Coupling Cascade (GP 1). A 10 mL Schlenk flask was equipped with a magnetic stirring bar, $Pd_2(dba)_3$ (10−20 mol %), $P(Cy)_3$ (40−80 mol %), the bromoarene (0.24 mmol), the areneboronic acid (0.29 mmol), and DBU (0.25 mL) in DMF (4 mL). The resulting mixture was stirred at 155 °C overnight. After dilution with 50 mL of CH_2Cl_2, the mixture was washed twice with 50 mL each of HCl (10%) and once each with 50 mL of $NaHCO_3$ and 50 mL of H_2O. Drying of the organic phase over $MgSO_4$ and evaporation of the solvent gave the crude product, which was subjected to chromatography on silica gel, eluting with pentane/CH_2Cl_2 mixtures.

Fluoranthene (1). According to GP 1, a mixture of 1-bromonaphthalene (**6**) (50 mg, 0.24 mmol), *o*-bromobenzeneboronic acid (**7**) (58 mg, 0.29 mmol), $Pd_2(dba)_3$ (50 mg, 0.048 mmol), $P(Cy)_3$ (54 mg, 0.19 mmol), and DBU (0.25 mL) in DMF (4 mL) was stirred at 155 °C for 2 d. Column chromatography on silica gel (30 g, column 2.0 × 39 cm, pentane/CH_2Cl_2, 19:1) yielded 42 mg (87%) of **1** as colorless crystals, mp 106−108 °C. The spectroscopic data agreed with those of a commercially available sample.

1-(2′-Bromophenyl)naphthalene (9). A 10 mL Schlenk flask was equipped with a magnetic stirring bar, $Pd(PPh_3)_4$ (0.23 g, 0.20 mmol), **6** (0.21 g, 1.0 mmol), **7** (0.24 g, 1.2 mmol), and K_2CO_3 (1.4 g, 10 mmol) in DMF (5 mL). The resulting mixture was stirred at 110 °C overnight. After dilution with 50 mL of CH_2Cl_2, the mixture was washed twice with 50 mL each of HCl (10%) and once each with 50 mL of $NaHCO_3$ and 50 mL of H_2O. Drying of the organic phase over $MgSO_4$ and evaporation of the solvent gave the crude product. Column chromatography on silica gel (80 g, column 3.5 × 45 cm, pentane/CH_2Cl_2, 10:1) yielded 0.27 g (95%) of **9** as colorless crystals, mp 82−84 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.27−7.60 (m, 8 H), 7.75 (d, ^3J = 8.2 Hz, 1 H), 7.92 (d, ^3J = 8.2 Hz, 2 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 124.35, 125.14, 125.84, 125.91, 126.11, 126.97, 127.13, 128.17, 128.23, 129.07, 131.53, 131.60, 131.97, 132.71, 133.41, 141.33. MS (70 eV) *m*/*z* (rel intens): 285/284/283/282 (48) [M$^+$], 204/203/202/201/199 (100), 101 (31). Correct HRMS (*m*/*z*) as calcd for $C_{16}H_{11}Br$: 282.0044. Anal. Calcd for $C_{16}H_{11}Br$: C, 67.87; H, 3.92. Found: C, 68.17; H, 3.75.

8,9-Tetrahydro-7*H*-cyclopent[*a*]acenaphthylene (16a). According to GP 1, a mixture of 1-naphthaleneboronic acid (**12**) (55 mg, 0.32 mmol), 1,2-dibromocyclopentene (**14a**) (60 mg, 0.27 mmol), $Pd_2(dba)_3$ (55 mg, 0.053 mmol), $P(Cy)_3$ (60 mg, 0.21 mmol), and DBU (0.30 mL) in DMF (4 mL) was stirred at 155 °C for 2 d. Column chromatography on silica gel (30 g, column 2.0 × 39 cm, pentane/CH_2Cl_2, 19:1) yielded 17 mg (33%) of **16a** as yellow crystals, mp 64−67 °C (lit.[9] mp 67−68 °C). The spectroscopic data agreed with those reported in the literature.[9]

7,8,9,10-Tetrahydrofluoranthene (16b). According to GP 1, a mixture of **12** (50 mg, 0.29 mmol), 1,2-dibromocyclohexene (**14b**) (57 mg, 0.29 mmol), $Pd_2(dba)_3$ (50 mg, 0.048 mmol), $P(Cy)_3$ (54 mg, 0.19 mmol), and DBU (0.25 mL) in DMF (4 mL) was stirred at 155 °C for 2 d. Column chromatography on silica gel (30 g, column 2.0 × 39 cm, pentane/CH_2Cl_2, 9:1) yielded 29 mg (58%) of **16b** as an orange oil. The spectroscopic data corresponded with those reported in the literature.[10]

8,9,10,11-Tetrahydro-7*H*-cyclohept[*a*]acenaphthylene (16c). According to GP 1, a mixture of **12** (55 mg, 0.32 mmol), 1,2-dibromocycloheptene (**14c**) (68 mg, 0.27 mmol), $Pd_2(dba)_3$ (55 mg, 0.053 mmol), $P(Cy)_3$ (60 mg, 0.21 mmol), and DBU (0.30 mL) in DMF (4 mL) was stirred at 155 °C for 2 d. Column chromatography on silica gel (30 g, column 2.0 × 39 cm, pentane/CH_2Cl_2, 19:1) yielded 10 mg of a mixture of naphthalene **8** and **16c** (6%) in a ratio of 3:1 (according to ^{1}H NMR). The spectroscopic data agreed with those reported in the literature.[10]

Pinacol Corannuleneboronate (18). A 10 mL Schlenk flask equipped with a magnetic stirring bar was charged with $PdCl_2(dppf)$ (2.2 mg, 3.0 μmol), bromocorannulene (**6**)[11] (33 mg, 0.10 mmol), triethylamine (42 μL, 0.30 mmol), pinacolborane (22 μL, 0.15 mmol), and dioxane (0.4 mL). The resulting mixture was stirred at 105 °C for 24 h. After dilution with 50 mL of CH_2Cl_2, the mixture was washed twice with 50 mL of H_2O. Drying of the organic phase over $MgSO_4$ and evaporation of the solvent gave the crude product. Recrystallization from pentane/CH_2Cl_2 yielded 41.6 mg (95%) of **18** as yellow crystals, mp 67−70 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.27 (s, 12 H), 7.63−7.96 (m, 7 H), 8.46 (d, ^3J = 8.8 Hz, 1 H), 8.50 (s, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 25.0, 83.9, 126.77, 126.84, 126.9, 127.0, 127.1, 127.5, 128.9, 130.6, 130.8, 131.4, 134.9, 135.4, 135.7, 135.8, 136.0, 136.9, 137.4. MS (70 eV) *m*/*z* (rel intens): 376 (45) [M$^+$], 303 (12), 276 (38), 250 (100). Correct HRMS (*m*/*z*) as calcd for $C_{26}H_{21}BO_2$: 376.1635.

Indenocorannulene (19). According to GP 1, a mixture of **18** (0.11 g, 0.29 mmol), 1,2-dibromobenzene (**13**) (57 mg, 0.24 mmol), $Pd_2(dba)_3$ (50 mg, 0.048 mmol), $P(Cy)_3$ (54 mg, 0.19 mmol), and DBU (0.25 mL) in DMF (4 mL) was stirred at 155 °C for 2 d. Column chromatography on silica gel (80 g, column 3.5 × 45 cm, pentane/CH_2Cl_2, 9:1) yielded 31 mg (40%) of **19** as yellow crystals, mp 192−194 °C (lit.[8] mp 194−196 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, ^3J = 8.4 Hz, 2H), 7.64 (s, 2H), 7.65−7.63 (m, 2H), 7.57 (d, ^3J = 8.4 Hz, 2H), 7.53 (s, 2H), 7.21−7.19 (m, 2H). The spectroscopic data agreed with those reported previously.[8]

Indeno[1,2,3-*cd*]fluoranthene (2). According to GP 1, a mixture of 1,4-dibromonaphthalene (**20**) (86 mg, 0.30 mmol), **7** (0.14 g, 0.71 mmol), $Pd_2(dba)_3$ (62 mg, 0.060 mmol), $P(Cy)_3$ (67 mg, 0.24 mmol), and DBU (0.50 mL) in DMF (4 mL) was stirred at 155 °C for 2 d. Column chromatography on silica gel (80 g, column 3.5 × 45 cm, pentane/CH_2Cl_2, 19:1) yielded 42 mg (51%) of **2** as yellow crystals, mp 255−258 °C (lit.[12] mp 261−262 °C) and 21 mg (35%) of **1**. ^{1}H NMR of **2** (400 MHz, $CDCl_3$): δ 7.61−7.55 (m, 4H), 7.53 (s, 4H), 7.20−7.14 (m, 4H). The spectroscopic data of **2** agreed with those reported previously.[12]

Rubicene (3) and Isorubicene (4). According to GP 1, a mixture of 9,10-dibromoanthracene (**21**) (0.10 g, 0.30 mmol), **7** (0.14 g, 0.71 mmol), $Pd_2(dba)_3$ (62 mg, 0.060 mmol), $P(Cy)_3$ (67 mg, 0.24 mmol), and DBU (0.50 mL) in DMF (4 mL) was stirred at 155 °C for 2 d. Column chromatography on silica gel (80 g, column 3.5 × 45 cm, pentane/CH_2Cl_2, 9:1) yielded 27 mg (28%) of an inseparable mixture of **3** and **4** as red crystals. An ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of the mixture showed well-separated two-proton doublets at δ 8.57, 8.31, and 8.00 ppm for **3** and well-separated two-proton multiplets at δ 8.43 and 6.98 ppm for **4**, the integration of which indicated a **3**:**4** ratio of 1:1. The spectroscopic data agreed with those reported for materials from alternative syntheses.[13,14]

Benz[*e*]indeno[1,2,3-*hi*]acephenanthrylene (25). According to GP 1, a mixture of 1,8-dibromophenanthrene (**24**) (0.10 g, 0.30 mmol), **7** (0.14 g, 0.71 mmol), $Pd_2(dba)_3$ (62 mg, 60 μmol), $P(Cy)_3$ (67 mg, 0.24 mmol), and DBU (0.50 mL) in DMF (4 mL) was stirred at 155 °C for 1.5 d. Column chromatography on silica gel (80 g, column 3.5 × 45 cm,

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pentane/CH_2Cl_2, 19:1) yielded 26 mg (27%) of **25** as yellow crystals, mp 272−276 °C (lit.[15] mp 277−278 °C) and 20 mg (27%) of benz[*e*]acephenanthrylene (**26**). The spectroscopic data agreed with those reported in the literature.[15]

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Supporting Information Available: ^{1}H NMR spectrum of compound **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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