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# Palladium-Catalyzed Reaction of Haloarenes with Diarylethynes: Synthesis, Structural Analysis, and Properties of Methylene-Bridged Arenes

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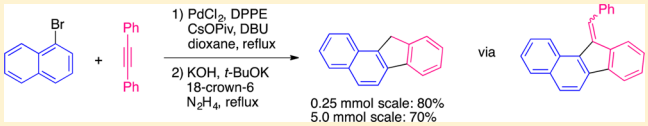
Supporting Information

**ABSTRACT:** Fluorenes and methylene-bridged polyarenes were easily and efficiently synthesized from haloarenes (or aryl triflates) and diarylethynes by a one-pot, two-step procedure. This protocol involves the palladium-catalyzed cycloisomerization and a subsequent base-mediated retro-aldol condensation.



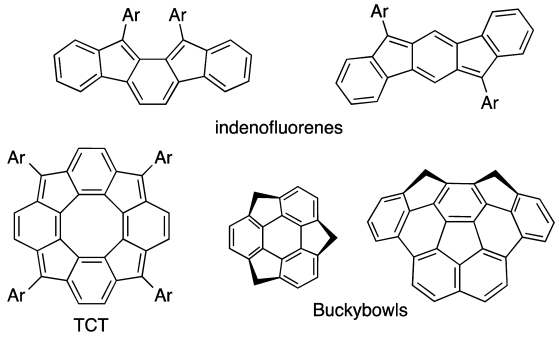

A major advantage is that the starting materials need not have *ortho* functional groups to complete the annulation. The backbone of the designed products was enlarged using dihaloarenes, highly $\pi$-conjugated haloarenes, or diarylalkynes. The mechanism of the formation of benzo[*a*]fluorene was investigated. The bowl-shaped structure of methylene-bridged indenocorannulene was verified by X-ray crystallography. The photophysical and electrochemical properties of the products thus prepared were investigated.

## INTRODUCTION

Fluorene, the simplest methylene-bridged arene (MBA), is an important compound with many interesting physical properties, which enable it and its derivatives to be (potentially) applied in organic materials, including those used in optoelectronics, organic field-effect transistors (OFETs), solar cells, and other devices.[1] Unlike benzonoids, the methylene carbon in an MBA undergoes a wide range of chemical reactions, modifying its physical properties. For example, fluorene can be converted to 9,9-diarylfluorene,[2a] which is used in optoelectronic devices to maintain high color purity owing to its excellent morphological and thermal stabilities.[2b] A fully conjugated hydrocarbon based on an MBA, such as indenofluorenes or tetracyclopentatetraphenylene (TCT), may exhibit biradical (or tetraradical) properties (Chart 1).[3] The five-membered ring in an MBA may increase its curvature to form a buckybowl, which is a fragment of buckminsterfullerene or the end-cap of a carbon nanotube.[4]

Fluorene is generally prepared from biphenyl derivatives.[5] Scheme 1 presents synthetic methods that involve the Friedel–Crafts reaction, metal-catalyzed C–H bond activation,[6] or carbene insertion.[7] 2-Halo-2′-methylbiphenyl is converted to fluorene through the palladium-catalyzed benzylic C–H bond activation and subsequent C–C bond formation (method I).[8] The intermediate 2-methyl-2′-palladabiphenyl in this reaction can also be formed by the cascade coupling of 1,2-dihalobenzenes with 2-tolylboronic acid[9a] or 2,6-dimethylphenylmagnesium bromide.[9b] Biphenyl triazene under acidic conditions (method II)[10a] or (2-biphenyl)methanol in the presence of nanostructured $MoO_3$ (method IV)[10b] forms fluorene, and the latter should be upon intramolecular Friedel–Crafts arylation. The preparation of fluorene from 1-benzyl-2-halobenzene (method III),[11] 2-(chloromethyl)biphenyl,[12a] or 2-phenylbenzyl trifluoroacetate[12b] (method V) involves the palladium-catalyzed activation of the aryl C–H bond. The rhodium-catalyzed cyclization of 2,2-diphenylethanoic acid involves 2-fold aryl C–H bond cleavages and subsequent decarboxylation to produce fluorene (method VI).[13] 2-Cycloheptatrienyl biphenyl and 2-biphenyl *N*-tosylhydrazone (method VII) furnish fluorene via gold carbene[14a] and free carbene,[14b] respectively. Although some of the synthetic methods in Scheme 1 are very effective, their starting materials must have an *ortho* functional group for cyclization or formation of a suitable intermediate. The exception is 2,2-diphenylacetic acid (method VI), but the corresponding precursors for substituted fluorenes have to be prepared by the arylation of phenylacetates.[13] Our recent investigations demonstrated that an MBA is directly generated from a haloarene and a diarylacetylene, and no *ortho* functional groups in both starting materials are required (method VIII). Despite the advantages of such a reaction and the importance of MBAs,

**Chart 1**

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**Scheme 1. Preparations of Fluorene**

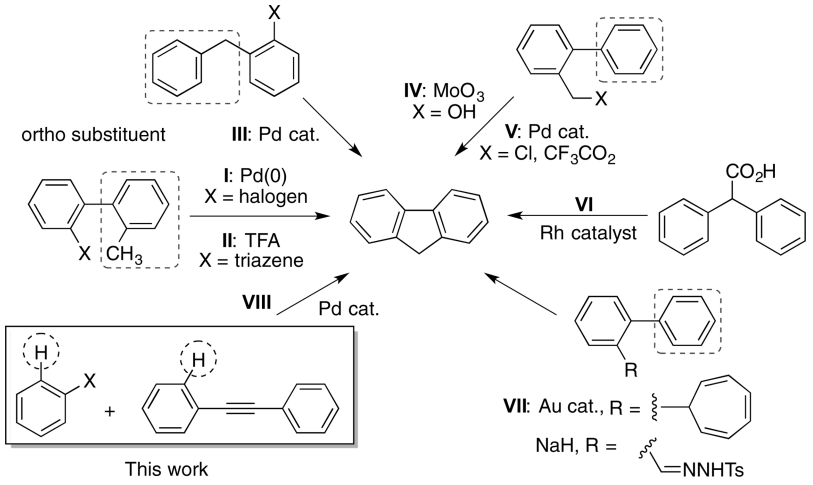
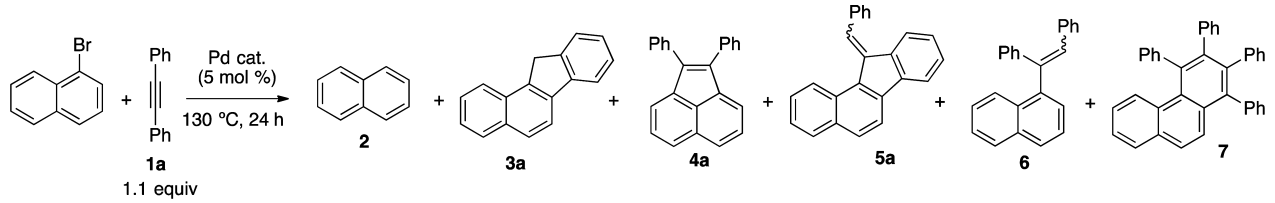



**Table 1. Optimization of Reaction Conditions for the Preparation of 11-(Phenylmethylene)benzo[*a*]fluorene (5a)**




| entry[a] | catalyst | solvent | base (equiv) | additive (equiv) | conversion (%) | ratio of 2/3a/4a/5a/6/7 |
|---|---|---|---|---|---|---|
| 1[b] | $Pd(OAc)_2$ + $PPh_3$ | DMF | NaOAc (2) | *n*-$Bu_4NCl$ (1) | 77 | 0:0:24:61:0:15 |
| 2[b] | $Pd(OAc)_2$ + DPPM | DMF | CsOPiv (2) | | 100 | 5:0:40:50:0:5 |
| 3 | $PdCl_2$(dppf) | dioxane | DBU (3) | CsOPiv (1.1) | 100 | 0:37:63:0:0:0 |
| 4 | $PdCl_2$(dppf) | dioxane | $Cs_2CO_3$ (3) | CsOPiv (1.1) | 100 | 22:0:55:23:0:0 |
| 5 | $PdCl_2$(dppf) | dioxane | *i*$Pr_2NH$ (3) | CsOPiv (1.1) | 0 | |
| 6 | $PdCl_2$(dppf) | dioxane | pyridine (3) | CsOPiv (1.1) | 57 | 28:0:21:51:0:0 |
| 7 | $PdCl_2$(dppf) | dioxane | piperidine (3) | CsOPiv (1.1) | 100 | 22:0:27:18:34:0 |
| 8 | $PdCl_2$(dppf) | dioxane | DABCO (3) | CsOPiv (1.1) | 90 | 0:0:1:0:0:98 |
| 9 | $PdCl_2$(dppf) | dioxane | DBN (3) | CsOPiv (1.1) | 44 | 5:0:95:0:0:0 |
| 10 | $PdCl_2(PPh_3)_2$ | dioxane | DBU (3) | CsOPiv (1.1) | 100 | 0:50:50:0:0:0 |
| 11 | $PdCl_2(PPh_3)_2$ | dioxane | DBU (0.5) | | 25 | 24:0:76:0:0:0 |
| 12 | $PdCl_2(PPh_3)_2$ | dioxane | DBU (0.5) | CsOPiv (1.1) | 100 | 6:0:22:72:0:0 |
| 13 | $PdCl_2(PPh_3)_2$ | dioxane | | CsOPiv (1.5) | 100 | 23:0:20:0:0:57 |
| 14 | $PdCl_2(PPh_3)_2$ | anisole | DBU (3) | CsOPiv (1.1) | 100 | 0:34:66:0:0:0 |
| 15 | $PdCl_2(PPh_3)_2$ | DMF | DBU (3) | CsOPiv (1.1) | 100 | 0:27:73:0:0:0 |
| 16 | $PdCl_2(PPh_3)_2$ | NMP | DBU (3) | CsOPiv (1.1) | 100 | 0:25:75:0:0:0 |
| 17 | $PdCl_2(PPh_3)_2$ | DMAc | DBU (3) | CsOPiv (1.1) | 100 | 0:34:66:0:0:0 |
| 18 | $PdCl_2(PPh_3)_2$ | *p*-xylene | DBU (3) | CsOPiv (1.1) | 100 | 0:40:60:0:0:0 |
| 19 | $Pd(OAc)_2$ + DPPE | dioxane | DBU (3) | CsOPiv (1.1) | 100 | 0:51:49:0:0:0 |
| 20 | $Pd(OAc)_2$ + DPPM | dioxane | DBU (3) | CsOPiv (1.1) | 100 | 0:48:42:10:0:0 |
| 21 | $Pd(OAc)_2$ + CyJohnPhos | dioxane | DBU (3) | CsOPiv (1.1) | 100 | 0:20:60:20:0:0 |
| 22 | $Pd(OAc)_2$ + P(*o*-tol)$_3$ | dioxane | DBU (3) | CsOPiv (1.1) | 100 | 0:44:54:0:2:0 |
| 23 | $Pd(OAc)_2$ + DPPE | dioxane | DBU (0.5) | CsOPiv (1.1) | 96 | 9:0:11:75:0:0 |
| 24 | $Pd(OAc)_2$ + DPPE | dioxane | DBU (0.5) | CsOPiv (2) | 100 | 2:0:13:85:0:0 |
| 25 | $Pd(OAc)_2$ + DPPE | dioxane | | CsOPiv (1.5) | 40 | 0:0:1:0:0:98 |
| 26[c] | $Pd(OAc)_2$ + DPPE | dioxane | DBU (0.5) | CsOPiv (2) | 100 | 0:0:12:88:0:0 |
| 27[c,d] | $PdCl_2$ + DPPE | dioxane | DBU (0.5) | CsOPiv (2) | 100 | 0:0:9:91:0:0 |

[a]A mixture of 1-bromonaphthalene (0.25 mmol), alkyne **1a** (1.1 equiv), palladium catalyst (5 mol %), ligand (10 mol % for $PPh_3$, CyJohnPhos, or P(*o*-tol)$_3$; 5 mol % for DPPE or DPPM), base, and solvent (1.5 mL) in a sealed tube was heated for 24 h. The conversion of 1-bromonaphthalene and the ratio of the compounds was determined by GC MS. Ligands DPPF = 1,1′-bis(diphenylphosphino)ferrocene, DPPE = 1,2-bis(diphenylphosphino)ethane, DPPM = 1,1-bis(diphenylphosphino)methane, CyJohnPhos = (2-biphenyl)dicyclohexylphosphine. [b]The reaction was conducted according to the Larock's protocol at 100 °C. For details, see refs 15a and 19. [c]The reaction was performed in dioxane (6 mL). [d]Under the optimal conditions, an inseparable mixture of **4a** and **5a** (ratio 9:91) was obtained with a combined yield of 90%. A large-scale synthesis (5.0 mmol) gave a total yield of 85% (**4a**:**5a** = 9:91).



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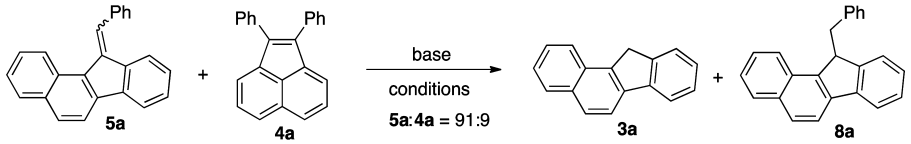
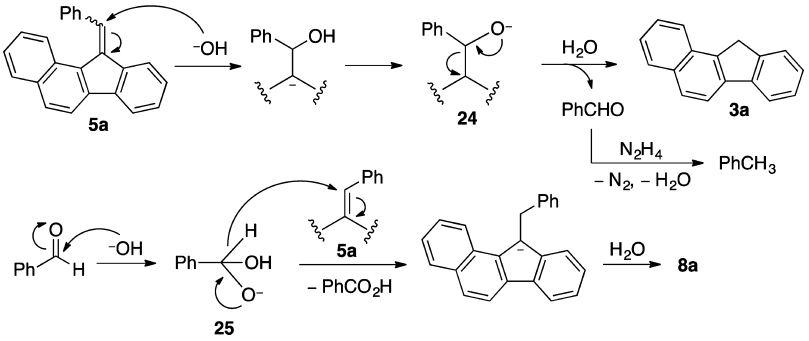
**Table 2. Optimization of Reaction Conditions for the Preparation of Benzo[*a*]fluorene (3a) from 11-(Phenylmethylene)benzo[*a*]fluorene (5a)**




| entry[a] | base (equiv) | solvent (mL) | temp (°C) | time (h) | additive | conversion (%) | ratio of 3a/8a | yield (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | KOH (10) | dioxane (3) | 150 | 24 | | 34 | 100:0 | |
| 2 | NaOH (10) | dioxane (3) | 150 | 24 | A1 | 40 | 100:0 | |
| 3 | LiOH (10) | dioxane (3) | 150 | 24 | A1 | 0 | | |
| 4 | DBU (10) | dioxane (3) | 150 | 24 | A1 | 10 | 100:0 | |
| 5 | KOH (10) | dioxane (3) | 150 | 24 | A1 | 100 | 68:32 | |
| 6 | *t*-BuOK (10) | dioxane (3) | 150 | 6 | A2 | 100 | 67:33 | |
| 7 | *t*-BuOK (10) | dioxane (3) | 150 | 12 | A2 | 100 | 65:35 | |
| 8 | *t*-BuOK (10) | dioxane (3) | 150 | 24 | A2 | 100 | 70:30 | 55 |
| 9 | B1 | dioxane (3) | 150 | 24 | A2 | 100 | 75:25 | 68 |
| 10 | B1 | *p*-xylene (3) | 150 | 24 | A2 | 100 | 70:30 | |
| 11 | B1 | NMP (3) | 150 | 24 | A2 | 100 | 100:0 | 16 |
| 12 | B1 | quinoline (3) | 150 | 24 | A2 | 100 | 68:32 | 64 |
| 13 | B1 | dioxane (6) | 150 | 24 | A3 | 100 | 88:12 | |
| 14 | B1 | dioxane (6) | 110 | 12 | A3 | 100 | 100:0 | 88 |

[a]The reaction was conducted with a mixture of **4a** and **5a** (ratio 9:91, 0.25 mmol) in a sealed tube. The ratio of the compounds was determined by GC−MS. The recovery of **4a** was neglected. Additive A1 = $(n\text{-Bu})_4NBr$ (0.5 equiv); A2 = 18-crown-6 (0.5 equiv); A3 = 18-crown-6 (0.5 equiv) + $N_2H_4$ (3 equiv). Base B1 = *t*-BuOK (5 equiv) + KOH (5 equiv).

**Scheme 2. Proposed Reaction Mechanism for the Formation of 3a from 5a**




this work develops a simple and efficient protocol for synthesizing various MBAs.

## RESULTS AND DISCUSSION

The palladium-catalyzed annulation of 1-bromonaphthalene with diphenylethyne (**1a**) yielded a mixture of naphthalene (**2**), benzo[*a*]fluorene (**3a**), 4,5-diphenylacephenanthrylene (**4a**), 11-(phenylmethylene)benzo[*a*]fluorene (**5a**), 1-naphthyl-1,2-diphenylethene (**6**) and phenanthrene **7** (Table 1). The best result was that benzo[*a*]fluorene (**3a**) and 1,2-diphenylacenaphthrylene (**4a**) were obtained in almost equal amounts, based on GC−MS analysis (entries 10 and 19, Table 1). Owing to the low chemoselectivity between **3a** and **4a**, the one-pot procedure was modified to a two-step protocol. The desired product **3a** was assumed to be generated from the key intermediate **5a** by the base-mediated cleavage of the exocyclic alkenyl moiety. This assumption faces several challenges. Although Larock's method, which is adopted to synthesize 9-(alkylidene)fluorene by the palladium-catalyzed cycloisomerization of an iodobenzene derivative with an arylalkyne,[15] provides useful information concerning the mechanism of formation of **5a**, it could not be utilized herein because the byproduct **4a** was formed in a significant amount (entries 1 and 2, Table 1). More importantly, the efficient generation of a methylene group by the cleavage of an exocyclic alkenyl substituent has not yet been reported.[16]

The palladium-catalyzed reaction of 1-bromonaphthalene with diphenylethyne (**1a**) was systematically examined, and the palladium catalyst, ligand, base, and additive were all critical to affect formations of compounds **2**−**7**. In the preparation of **5a**, a system of DPPE and $PdCl_2$ or $Pd(OAc)_2$ was found to outperform other catalysts $PdCl_2(dppf)$, $PdCl_2(PPh_3)_2$, and catalytic combinations that are listed in Table 1. DBU appeared to be superior to other bases such as $Cs_2CO_3$, *i*-$Pr_2NH$, pyridine, piperidine, DBN, and DABCO; it inhibited the reductive debromination of 1-bromonaphthalene and promoted the selective generation of **4a** (entries 3−9, Table 1). The reaction was conducted with DMF, NMP, DMAc, *p*-xylene, anisole, or 1,4-dioxane as a solvent, and the last was observed to lower the amount of **4a** formed (entries 14−18, Table 1). The absence of the additive cesium pivalate (CsOPiv) greatly reduced the conversion of 1-bromonaphthalene (entry 11, Table 1). A mixture of CsOPiv and DBU with a suitable ratio under dilute conditions strongly improved the formation of **5a**



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**Table 3. One-Pot Synthesis of Methylene-Bridged Arenes through the Palladium-Catalyzed Reaction of Haloarenes with Diarylethynes and the Subsequent Retro-Aldol Condensation**

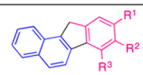
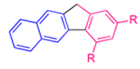
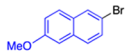
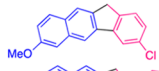
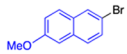
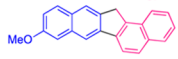
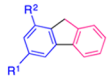
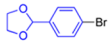
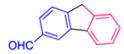
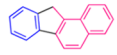
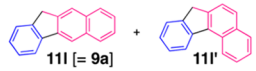
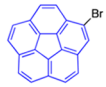
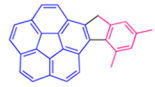
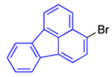
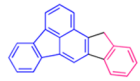
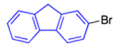
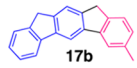
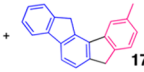
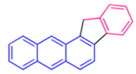
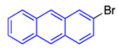
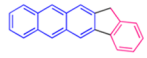
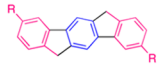
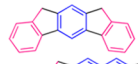
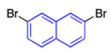
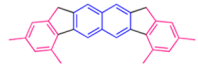
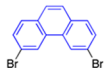
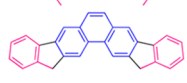
| Entry[a] | Arene | Alkyne | Product | Method (Yield, %) |
|---|---|---|---|---|
| |  | |  | |
| 1 | X = Br | **1a** | **3a** ( $R^1 = R^2 = R^3 = H$) | **A** (80, 70[b]) |
| 2 | X = Cl | **1a** | **3a** | **B** (55) |
| 3 | X = Br | **1b** | **3b** ($R^2$ = Me, $R^1 = R^3 = H$) | **A** (80) |
| 4 | X = I | **1b** | **3b** | **A** (71) |
| 5 | X = Br | **1c** | **3c** ($R^2$ = *n*-Bu, $R^1 = R^3 = H$) | **A** (65) |
| 6 | X = Br | **1d** | **3d** ($R^2$ = *t*-Bu, $R^1 = R^3 = H$) | **A** (70) |
| 7 | X = Br | **1e** | **3e** ($R^2$ = OMe, $R^1 = R^3 = H$) | **A** (66) |
| 8 | X = Br | **1f** | **3f** ($R^2$ = F, $R^1 = R^3 = H$) | **A** (59) |
| 9 | X = Br | **1g** | **3g** ($R^1$ = Me; $R^2 = R^3 = H$)<br>**3g'** ($R^3$ = Me; $R^1 = R^2 = H$) | **A** (61, 72:28) |
| 10 | X = Br | **1h** | **3h** ($R^2 = H$, $R^1 = R^3$ = Me) | **A** (87) |
| 11 | X = Br | **1i** | **3i** ($R^1 = R^2 = R^3$ = OMe) | **A** (61) |
| |  | |  | |
| 12 | X = Br | **1a** | **9a** (R = H) | **A** (85) |
| 13 | X = OTf | **1a** | **9a** | **A** (87) |
| 14 | X = Br | **1h** | **9h** (R = Me) | **A** (82) |
| 15 |  | **1j** |  **10j** | **A** (85) |
| 16 |  | **1k** |  **10k** | **A** (70) |
| |  | |  | |
| 17 | X = Br | **1a** | **11a** ($R^1 = R^2 = H$) | **A** (55), **C** (72) |
| 18 | X = I | **1a** | **11a** ($R^1 = R^2 = H$) | **A** (70), **C** (90) |
| 19 | X = Br | **1a** | **12a** ($R^1$ = Me, $R^2 = H$) | **A** (58), **C** (76) |
| 20 | X = Br | **1a** | **13a** ($R^1 = H$, $R^2$ = Me) | **A** (49), **C** (57) |
| 21 |  | **1a** |  **14a** | **C** (73) |
| 22 |  | **1k** |  **11k [= 3a]** | **A** (80) |
| 23 |  | **1l** |  **11l [= 9a]** + **11l'** | **A** (60, 70:30) |
| 24 |  | **1h** |  **15h** | **A** (63) |
| 25 |  | **1a** |  **16a** | **A** (58) |
| 26 |  | **1b** |  **17b** +  **17b'** | **A** (66, 80:20) |
| 27 |  | **1a** |  **18a** | **A** (55) |
| 28 |  | **1a** |  **19a** | **A** (76) |
| 29 |  | **1a** |  **20a** (R = H) | **A** (50) |
| 30 | | **1b** | **20b** (R = Me) | **A** (63) |
| 31 |  | **1a** |  **21a** | **A** (57) |
| 32 |  | **1h** |  **22h** | **A** (55) |
| 33 |  | **1a** |  **23a** | **A** (88) |



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**Table 3. continued**

[a]Method A: (step 1) $PdCl_2$ (5 mol %), DPPE (5 mol %), bromoarene (0.25 mmol), alkyne (1.1 equiv), DBU (0.5 equiv), CsOPiv (2 equiv), and dioxane (6 mL) in a sealed tube was heated for 24 h; (step 2) a mixture of KOH (5 equiv), *t*-BuOK (5 equiv), $N_2H_4{\cdot}H_2O$ (3 equiv), and 18-crown-6 (0.5 equiv) was heated for 12 h. For the synthesis of a bis(methlyene)-bridged arene from a dibromoarene, the reaction was conducted with 3 equiv of alkyne and 2-fold reagents and catalysts in the same amount of solvent. Method B: similar to method A, but the first step was conducted with a catalytic system that was composed of $PdCl_2(PCy_3)_2$ (10 mol %), $P(t\text{-}Bu)_3{\cdot}HBF_4$ (20 mol %), DBU (2 equiv), and CsOPiv (2 equiv) at 150 °C. Method C: similar to method A, but the palladium-catalyzed cycloisomerization was conducted with a mixture of $Pd(OAc)_2$ (5 mol %), DPPE (5 mol %), bromoarene (0.25 mmol), alkyne (1.2 equiv), CsOPiv (2 equiv), DBU (1 equiv), and dioxane (3 mL) at 130 °C. [b]The reaction was performed with 5.0 mmol of 1-bromonaphthalene. For details, see the Experimental Section.

(entries 26 and 27, Table 1). The use of less CsOPiv or the absence of DBU reduced the reaction efficiency, but an excess of the latter enhanced the amount of byproduct **4a**. Under the optimal conditions, an inseparable mixture of **4a** and **5a** (ratio 9:91) was obtained with a combined yield of 90%. A large-scale synthesis (5.0 mmol) in a flask under reflux gave a yield of 85% (entry 27, Table 1). Unlike diphenylethyne (**1a**), other phenyl-substituted alkynes, such as 1-phenyl-1-propyne and 1-cyclopropyl-2-phenylethyne, yielded unsatisfactory results because they mostly underwent benzannulation with 1-bromonaphthalene to form phenanthrene derivatives.

The cleavage of the exocyclic alkenyl moiety in **5a** was intensively investigated using hydroxyl anions or *tert*-butoxide in dioxane (Table 2). Potassium hydroxide provided better results than the corresponding sodium and lithium salts (entries 2, 3, and 5, Table 2). Although *t*-BuOK is generally regarded as a non-nucleophilic base, its ability to generate hydroxyl anion from water under nonanhydrous conditions should not be ignored (entries 6–8, Table 2). It was observed that more **3a** was formed when a mixed base KOH/*t*-BuOK was employed instead of *t*-BuOK alone (entries 8 and 9, Table 2). The phase-transfer catalysts $N(n\text{-}Bu)_4Br$ and 18-crown-6 increased the reaction efficiency (entries 1, 5, and 9, Table 2). In addition to the desired product **3a**, 11-benzylbenzo[*a*]fluorene (**8a**) was observed as a serious byproduct. This unfavorable outcome was improved upon by the addition of hydrazine (entries 9 and 13, Table 2), whose role in this reaction is described in Scheme 2. Under the optimal conditions, **3a** was obtained with a yield of 88% (entry 14, Table 2). Since both the Pd-catalyzed cycloisomerization and the based-mediated alkene cleavage were performed in dioxane, an attempt was made to conduct this synthetic approach as a one-pot, two-step procedure; in doing so, **3a** was afforded with yields of 80% and 70% on scales of 0.25 and 5.0 mmol, respectively (entry 1, Table 3, method A). This one-pot, two-step protocol can be easily implemented: the reagents for the second step are just added to a flask or Pyrex tube that contains the reaction mixture formed in the first step. When the unacidified crude product was directly exposed to ambient air and stirred at room temperature for 4 h, benzo[*a*]fluoren-11-one was obtained with a yield of 70% (based on 0.25 mmol of 1-bromonaphthalene). Notably, these protocols developed herein are much more efficient than conventional methods,[17] which require many synthetic steps from commercially available starting materials.

The reactivity of alkynes **1** in annulation was examined using 1-bromonaphthalene, and products **3** were obtained with moderate to excellent yields (entries 1–11, Table 3). Reactions with $\pi$-extended haloarenes or diarylalkynes also efficiently generated desired products. Fluorene and its derivatives **11**–**14** were obtained with higher yields (entries 17–21, Table 3) when the reactions were performed with $Pd(OAc)_2$ and more DBU (1.0 equiv) (method C). In contrast to other halobenzenes, sterically congested 2-bromotoluene furnished 1-methylfluorene (**13a**) in a lower yield (57%) with the recovery of 20% of the starting material (entry 20, Table 3).

The regioselectivity of this protocol strongly depends on the aryl halides and the diarylacetylenes. For example, reactions of 2-bromonaphthalenes and 2-bromoanthracene with diarylethynes, such as diphenylethyne (**1a**), bis(3,5-dimethylphenyl)ethyne (**1h**), di(4-chlorophenyl)ethyne (**1j**), and di(1-naphthyl)ethyne (**1k**), yielded corresponding products **9a**–**h**, **10j**,**k**, and **19a** as the sole regioisomers (entries 12–16 and 28, Table 3). In contrast, the combinations 2-bromofluorene/**1a**, bromobenzene/di(2-naphthyl)ethyne (**1l**), and 1-bromonaphthalene/di(3-tolyl)ethyne (**1g**) each generated two regioisomers (entries 9, 23, and 26, Table 3), with the best result obtained in the first case (66% yield, **17b**:**17b**′ = 80:20).

The reaction conditions utilized herein are suitable for not only bromoarenes but also iodoarenes and aryl triflates, with comparable reactivities (entries 4 and 13, Table 3). The use of iodobenzene in the synthesis of fluorene gave a higher yield than bromobenzene (entry 18, Table 3). When the catalytic system that comprised $PdCl_2$ and DPPE was replaced with $PdCl_2(PCy_3)_2$ and $P(t\text{-}Bu)_3{\cdot}HBF_4$ (method B), 1-chloronaphthalene also gave **3a**, but with an unsatisfactory yield (55%, entry 2, Table 3).

The use of potassium hydroxide and hydrazine for alkene cleavage should cause a compatibility issue with carbonyl derivatives. The reaction of 4-bromobenzaldehyde with **1a** was examined. Indeed, the aldehyde group could not tolerate the reaction conditions herein, but this problem was solved by replacing 4-bromobenzaldehyde with 2-(4-bromophenyl)-1,3-dioxolane (entry 21, Table 3).

The reactivity of dibromoarenes and solubility of each product in common organic solvents both critically affect the reaction efficiencies of the 2-fold annulations. Among these dibromoarenes, 3,6-dibromophenanthrene gave the best result with a yield of 88% (entry 33, Table 3) because of its high reactivity and ease of purification (see the Experimental Section). The products that were obtained from 1,4- and 1,3-dibromobenzenes and 2,6-dibromonaphthalene were regioselectively acquired in 50–63% yields (entries 29–32, Table 3). Notably, derivatives of 6,12-dihydroindeno[1,2-*b*]fluorene (**20a**) have been suggested to be suitable candidates for OFETs and OLEDs (organic light-emitting diodes).[18]

The formation of **5a** through 1,4-palladium migration can be easily formulated on the basis of the literature,[15a,19] but the generation of **3a** from **5a** was unknown. In order to gain insight into the mechanism of cleavage of the exocyclic alkenyl moiety, the reaction products were analyzed. In the absence of hydrazine, significant amounts of benzoic acid and a reduced product, 11-benzylbenzo[*a*]fluorene (**8a**), were obtained. When **3i** was prepared under the optimal conditions (method



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A, Table 3), a mixture of 3,4,5-trimethoxybenzaldehyde and 3,4,5-trimethoxytoluene was observed, and the aldehyde was identified by direct comparison with the authentic sample using GC−MS. On the basis of the outcomes of the above experiments, Scheme 2 presents a putative reaction mechanism for the formation of **3a** from **5a**. The reaction is initiated by the nucleophilic attack of a hydroxide ion at an alkenyl carbon in **5a**, followed by proton transfer to yield the adduct **24**, which fragments into a mixture of benzaldehyde and **3a** upon protonation. The base-mediated cleavage of the exocyclic alkenyl moiety can be treated as the retro-aldol condensation. Benzaldehyde enhanced the formation of the reduction product **8a** by a redox process similar to the Cannizzaro reaction, which involves the base-mediated disproportionation of benzaldehyde to yield a mixture of benzyl alcohol and potassium benzoate.[16b,20] Hydroxide attacks the carbonyl moiety in benzaldehyde to yield phenylmethanediol anion **25**, from which a hydride is transferred to **5a** to generate **8a** upon protonation. Adding hydrazine to consume benzaldehyde suppresses the latter undesired process.[21]

X-ray-quality crystals of **15h** were obtained by the slow evaporation of MeOH into the solution in $CH_2Cl_2$.[22] Compound **15h** is a bowl-shaped molecule in a sterically congested environment. The distance of the nonbonded contact between the two carbon atoms shown in Figure 1

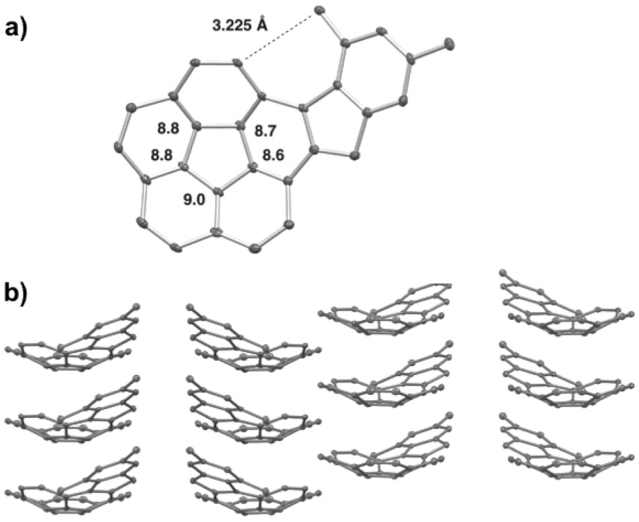


**Figure 1.** (a) Crystallographic structure and the POAV pyramidalization angles (degrees) of buckybowl **15h**. (b) Crystal packing along the *c* axis. Only carbon atoms are shown for clarity.

was determined to be 3.23 Å, which is shorter than the sum of their van der Waals radii (3.70 Å).[23] This bay-region clash leads the methyl carbon atom to be out-of-plane distorted from the *m*-xylyl ring by 0.22 Å. This steric interaction does not strongly affect the bowl curvature. The structure of **15h** is slightly more curved than that of corannulene, as determined by comparing their bowl depths and the maximum POAV ($\pi$-orbital axis vector) pyramidalization angles[24] of the corannulene fragments (0.90 vs 0.87 Å[25] and 9.0 vs 8.2°). Their comparable curvatures also reflect their similar bowl-to-bowl inversion barriers of around 11 kcal/mol.[26] A significant difference between corannulene and **15h** is in their molecular packings. The aggregation of the former is highly disordered, whereas the latter forms bowl-in-bowl stacks. The shortest distance between two **15h** bowls in a column was determined to be 3.85 Å. All of the bowl stacks are aligned in one direction, forming polar crystals, consistent with the polar space group $Pna2_1$. Owing to its uniform packing order, **15h** may have potential applications as an organic material with high electron mobility, piezoelectricity, or pyroelectricity.[27] Notably, 1,2,5,6-tetrabromocorannulene and **15h** have the same space group and very similar structural features.[28]

The photophysical properties of selected compounds in $CH_2Cl_2$ (10 $\mu$M) at room temperature were investigated herein (Table 4 and Supporting Information) and found to be strongly

**Table 4. Physical Properties of Methylene-Bridged Polyarenes**

| entry[a] | compd | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | $E^{red}$ (V) |
|---|---|---|---|---|
| 1 | **3a** | 344 | 354, 366 | −2.66 |
| 2 | **9a** | 340 | 353, 361, 379 | −2.64 |
| 3 | **10k** | 340, 360 | 371, 381 | −2.62, −2.92 |
| 4 | **15h** | 364, 415 | 453 | −2.14, −2.64 |
| 5 | **16a** | 352, 372 | 440, 466 | −2.76 |
| 6 | **17b** | 335 | 415, 430 | |
| 7 | **18a** | 381, 403 | 439 | −2.24, −2.79 |
| 8 | **22h** | 349, 367 | 370, 390, 412 | −2.86 |
| 9 | **23a** | 329, 346 | 382, 393, 404, 458 | −2.77 |

[a]Photophysical properties were measured at a concentration ca. 10 $\mu$M in $CH_2Cl_2$, and absorption bands over 330 nm are listed. Redox properties were investigated with compounds (concentration ca. 10 mM) in background electrolyte solution of 0.1 M $(n\text{-Bu})_4NBF_4$ (tetrabutylammonium tetrafluoroborate) in DMSO with the scan rate of 0.1 V/s and potentials vs the $Fc/Fc^+$ couple.

influenced by the aromatic $\pi$ system in the backbone. In contrast to benzo[*a*]fluorene (**3a**), its benzoannulated derivative, 13*H*-indeno[2,1-*a*]anthracene (**18a**), exhibits significantly red-shifted absorption and emission bands (entries 1 and 7, Table 4), whereas the two "regioisomers" benzo[*a*]fluorene (**3a**) and benzo[*b*]fluorene (**9a**) display very similar photophysical properties (entries 1 and 2, Table 4). Notably, indenocoranuulene **15h** and 13*H*-indeno[1,2-*b*]fluoranthene (**16a**) exhibit an absorption and an emission band, respectively, at the longest wavelength of any of the compounds that are presented in Table 4. Compound **17b** was observed to have the largest Stokes shift (80 nm; entry 6 in Table 4).

The redox properties of selected MBAs were elucidated by cyclic voltammetry and are presented in Table 4 and the Supporting Information. The oxidation waves of all compounds were not observed in this electrochemical window (from +0.45 to −3.25 V vs $Fc/Fc^+$). Reduction signals ($E^{red}$) of most compounds can be detected, but all are irreversible, indicating the low thermodynamic stability of these anionic species. This phenomenon is very similar to the electrochemical properties of fluorene and its derivatives.[29] The reduction of fluorene first yields a fluorenyl radical anion, which then forms a stable fluorenyl anion and 0.5 equiv of the hydrogen molecule through the cleavage of the C−H bond and dimerization of the hydrogen atoms on the electrode surface. The reduction potential(s) of the investigated compounds is sensitive to the aromatic $\pi$ system in the backbone. Indenocoranuulene **15h** displays the lowest reduction potential (−2.14 V) among compounds listed in Table 4. The first reduction potential for **3a** (−2.66 V) is higher than that of its benzoannulated derivative **18a** (−2.24 V) (entries 1 and 7, Table 4). As


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expected, benzo[*a*]fluorene (**3a**) and benzo[*b*]fluorene (**9a**) have similar reduction potentials (−2.66 vs −2.64 V; entries 1 and 2, Table 4). A mono(methylene)-bridged arene exhibits a lower reduction potential than a bis(methylene)-bridged arene. This conclusion is supported by the two facts described as follows: The reduction potentials for bis(methylene)-bridged arenes **22h** and **23a** were determined to be −2.86 and −2.77 V, respectively, and they are the first and second highest values in Table 4 (entries 8 and 9). The redox properties of **17b** cannot be determined, revealing that its reduction potential is higher than that of fluorene (−3.11 V). Unlike 6,12-dihydroindeno-[1,2-*b*]fluorene (**20a**) reported in the literature,[30] the second reduction potentials for bis(methylene)-bridged arenes such as **17b**, **22h**, and **23a** were not observed.

## CONCLUSIONS

Fluorenes and higher $\pi$-conjugated MBAs have been easily and efficiently synthesized by a one-pot, two-step procedure from haloarenes and diarylethynes by the palladium-catalyzed cycloisomerization and a subsequent base-mediated retro-aldol condensation. A major advantage of this protocol is that the starting materials need not have *ortho* functional groups to complete the annulation. The extension of this simple synthetic approach to the preparation of more extended derivatives and investigations of their properties are in progress.

## EXPERIMENTAL SECTION

**General Methods.** $^1$H NMR spectra were recorded on 300, 400, and 500 MHz spectrometers. $^{13}$C NMR spectra were recorded on 75, 100, and 125 MHz NMR spectrometers. MS and HRMS were obtained on a double-focusing sector mass spectrometer (ionization mode: EI or FAB). Melting points were measured by a hot-stage melting point apparatus and are uncorrected. The authentic sample of 3,4,5-trimethoxybenzaldehyde was purchased from a commercial supplier. 1-Phenyl-1-propyne,[31] 1-cyclopropyl-2-phenylethyne,[32] and diarylethynes,[33] including 1,2-di(4-tolyl)ethyne (**1b**), 1,2-di(4-*n*-butylphenyl)ethyne (**1c**), 1,2-di(4-*tert*-butylphenyl)ethyne (**1d**), 1,2-di(4-anisyl)ethyne (**1e**), 1,2-di(4-fluorophenyl)ethyne (**1f**), 1,2-di(3-tolyl)-ethyne (**1g**), 1,2-bis(3,5-dimethylphenyl)ethyne (**1h**), 1,2-bis(3,4,5-trimethoxyphenyl)ethyne (**1i**), 1,2-di(4-chlorophenyl)ethyne (**1j**), 1,2-di(1-naphthyl)ethyne (**1k**), and 1,2-di(2-naphthyl)ethyne (**1l**), were prepared according or similar to the literature procedures. Haloarenes such as 3-bromofluoranthene,[34] bromocorannulene,[35] 1-bromoanthracene,[36] 2-bromoanthracene,[37] 2,7-dibromonaphthalene,[38] 1,5-dibromonaphthalene,[39] 3,6-dibromophenanthrene,[40] 2-naphthyl trifluoromethanesulfonate,[41] and 2-(4-bromophenyl)-1,3-dioxolane[42] were synthesized according to the literature procedures.

General procedures for the Pd-catalyzed annulation of a haloarene with an alkyne:

**Method A (Entries 1−16 and 22−28, Table 3).** A mixture of haloarene (or aryl triflate, 0.25 mmol), alkyne (0.28 mmol), $PdCl_2$ (2.2 mg, 12.5 $\mu$mol, 5 mol %), DPPE (5.0 mg, 12.5 $\mu$mol, 5 mol %), DBU (19.0 mg, 0.125 mmol), CsOPiv (118 mg, 0.50 mmol), and dioxane (6 mL) in a thick-walled Pyrex tube was purged with nitrogen for 5 min. The sealed tube was kept in an oil bath at 130 °C for 24 h. After being cooled to room temperature, the reaction mixture was treated with KOH (70.1 mg, 1.25 mmol), *t*-BuOK (140 mg, 1.25 mmol), 18-crown-6 (33.0 mg, 0.125 mmol), and $N_2H_4{\cdot}H_2O$ (37.5 mg, 0.75 mmol) and purged with nitrogen for 5 min. The sealed tube was placed again in an oil bath at 110 °C for 12 h. The tube was cooled to room temperature and then immersed in an ice bath. Hydrochloric acid (2 N, 2.5 mL) was slowly added, and the aqueous phase was extracted with $CH_2Cl_2$ (2 × 15 mL). The combined extracts were dried over $MgSO_4$, and the solvent of the filtrate was removed under reduced pressure. The residue was subjected to chromatography on silica gel. For the synthesis of a bis(methlyene)-bridged arene from a dibromoarene (entries 29−33, Table 3), the reaction was conducted with 3 equiv of alkyne and 2-fold reagents and catalysts in the same amount of solvent.

**Method B (Entry 2, Table 3).** Similar to method A, but the step for the cycloisomerization was conducted with 1-chloronaphthalene (40.7 mg, 0.25 mmol), diphenylethyne (53.5 mg, 0.30 mmol), $PdCl_2(PCy_3)_2$ (18.5 mg, 25.0 $\mu$mol, 10 mol %), $PtBu_3{\cdot}HBF_4$ (14.5 mg, 50.0 $\mu$mol, 20 mol %), DBU (76 mg, 0.50 mmol), CsOPiv (117 mg, 0.5 mmol), and dioxane (6 mL) at 150 °C for 24 h.

**Method C (Entries 17−21, Table 3).** Similar to method A, but the step for the cycloisomerization was conducted with haloarene (0.25 mmol), alkyne (0.30 mmol), $Pd(OAc)_2$ (2.8 mg, 12.5 $\mu$mol, 5 mol %), DPPE (5.0 mg, 12.5 $\mu$mol, 5 mol %), DBU (38.1 mg, 0.25 mmol), CsOPiv (117 mg, 0.5 mmol), and dioxane (3 mL).

**11*H*-Benzo[*a*]fluorene (3a).** White solid [43.2 mg (80%) from 1-bromonaphthalene; 29.7 mg, (55%) from 1-chloronaphthalene]. The $^1$H NMR spectrum is identical to that reported in the literature.[13] *Procedure for large-scale preparation*: A mixture of 1-bromonaphthalene (1.04 g, 5.00 mmol), **1a** (1.16 g, 6.50 mmol), $PdCl_2$ (44.3 mg, 0.25 $\mu$mol, 5 mol %), DPPE (99.6 mg, 0.25 $\mu$mol, 5 mol %), DBU (380 mg, 2.50 mmol), CsOPiv (2.34 g, 10.0 mmol), and dioxane (120 mL) in a three-neck flask equipped with a reflux condenser was refluxed under nitrogen for 24 h (bath temperature 140 °C). After the mixture was cooled to room temperature, KOH (1.40 g, 25.0 mmol), *t*-BuOK (2.81 g, 25.0 mmol), and $N_2H_4{\cdot}H_2O$ (751 mg, 15.0 mmol) were added, and the reaction mixture was refluxed under nitrogen for 12 h (bath temperature 110 °C). The flask was cooled to room temperature and then immersed into an ice bath. Hydrochloric acid (2 N, 50 mL) was slowly added, and the aqueous phase was extracted with $CH_2Cl_2$ (2 × 30 mL). The combined extracts were dried over $MgSO_4$, and the solvent of the filtrate was removed under reduced pressure. The residue was subjected to chromatography on silica gel, eluting with hexane to give **3a** (0.76 g, 70%) as a white solid.

**8-Methyl-11*H*-benzo[*a*]fluorene (3b).** White solid [46.2 mg (80%) from 1-bromonaphthalene; 40.8 mg (71%) from 1-iodonaphthalene], mp 181.4−182.1 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 2.49 (s, 3H), 4.15 (s, 2H), 7.15 (d, $^3J$ = 7.7 Hz, 1H), 7.43−7.57 (m, 3H), 7.66 (s, 1H), 7.86 (d, $^3J$ = 9.1 Hz, 1H), 7.91 (d, $^3J$ = 8.5 Hz, 2H), 8.02 (d, $^3J$ = 8.3 Hz, 1H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 21.6 ($CH_3$), 35.2 ($CH_2$), 118.7 (CH), 120.3 (CH), 124.1 (CH), 124.6 (CH), 125.2 (CH), 126.4 (CH), 127.2 (CH), 127.7 (CH), 128.9 (CH), 130.8 ($C_{quat}$), 132.8 ($C_{quat}$), 136.4 ($C_{quat}$), 139.0 ($C_{quat}$), 140.2 ($C_{quat}$), 140.4 ($C_{quat}$), 142.8 ($C_{quat}$). EI MS (70 eV), *m*/*z*: 230 (100) [$M^+$], 215 (69) [$M^+ - CH_3$]. HRMS (EI): calcd for $C_{18}H_{14}$ 230.1096, found 230.1097.

**8-(*n*-Butyl)-11*H*-benzo[*a*]fluorene (3c).** White solid [44.2 mg (65%)], mp 127.8−128.2 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 0.97 (t, $^3J$ = 7.5 Hz, 3H), 1.43 (sex, $^3J$ = 7.5 Hz, 2H), 1.70 (quin, $^3J$ = 7.5 Hz, 2H), 2.75 (t, $^3J$ = 7.5 Hz, 2H), 4.15 (br s, 2H), 7.15 (dd, $^3J$ = 7.6, $^4J$ = 1.4 Hz, 1H), 7.46 (td, $^3J$ = 7.6, $^4J$ = 1.4 Hz, 1H), 7.51−7.54 (m, 2H), 7.66 (s, 1H), 7.87 (d, $^3J$ = 8.4 Hz, 1H), 7.91 (d, $^3J$ = 7.4 Hz, 1H), 7.92 (d, $^3J$ = 8.4 Hz, 1H), 8.01 (d, $^3J$ = 8.3 Hz, 1H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 14.0 ($CH_3$), 22.5 ($CH_2$), 34.1 ($CH_2$), 35.3 ($CH_2$), 35.8 ($CH_2$), 118.7 (CH), 119.6 (CH), 124.1 (CH), 124.6 (CH), 125.2 (CH), 126.4 (CH), 126.7 (CH), 127.7 (CH), 128.9 (CH), 130.8 ($C_{quat}$), 132.8 ($C_{quat}$), 139.1 ($C_{quat}$), 140.2 ($C_{quat}$), 140.6 ($C_{quat}$), 141.6 ($C_{quat}$), 142.7 ($C_{quat}$). EI MS (70 eV), *m*/*z*: 272 (65) [$M^+$], 229 (77), 228 (72), 215 (100) [$M^+ - C_4H_9$]. HRMS (EI): calcd for $C_{21}H_{20}$ 272.1565, found 272.1573.

**8-*tert*-Butyl-11*H*-benzo[*a*]fluorene (3d).** White solid [47.6 mg (70%)], mp 157.9−158.3 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 1.44 [s, 9H, $C(CH_3)_3$], 4.15 (s, 2H), 7.39 (dd, $^3J$ = 7.9, $^4J$ = 1.8 Hz, 1H), 7.47 (td, $^3J$ = 7.5, $^4J$ = 1.8 Hz, 1H), 7.54 (td, $^3J$ = 8.0, $^4J$ = 1.5 Hz, 1H), 7.57 (d, $^3J$ = 8.0 Hz, 1H), 7.87 (d, $^3J$ = 8.6 Hz, 1H), 7.88 (d, $^4J$ = 1.5 Hz, 1H), 7.91 (d, $^3J$ = 8.6 Hz, 1H), 7.95 (d, $^3J$ = 8.4 Hz, 1H), 8.02 (d, $^3J$ = 8.1 Hz, 1H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 31.7 [$C(CH_3)_3$], 34.9 [$C(CH_3)_3$], 35.2 ($CH_2$), 116.5 (CH), 118.7 (CH), 123.7 (CH), 124.1 (CH), 124.4 (CH), 125.2 (CH), 126.4 (CH), 127.7 (CH), 128.9 (CH), 130.8 ($C_{quat}$), 132.8 ($C_{quat}$), 139.2 ($C_{quat}$), 140.2 ($C_{quat}$), 140.5 ($C_{quat}$), 142.5 ($C_{quat}$), 150.0 ($C_{quat}$).



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J. Org. Chem. 2015, 80, 10446−10456

EI MS (70 eV), *m*/*z*: 272 (100) [$M^+$], 257 (53), 215 (66) [$M^+ - C_4H_9$]. HRMS (EI): calcd for $C_{21}H_{20}$ 272.1565, found 272.1569.

**8-Methoxy-11*H*-benzo[*a*]fluorene (3e).** White solid [40.6 mg (66%)], mp 152.8−153.3 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 3.93 (s, 3H), 4.12 (s, 2H), 6.89 (dd, $^3J$ = 8.2, $^4J$ = 2.3 Hz, 1H), 7.37 (d, $^4J$ = 2.3 Hz, 1H), 7.44 (d, $^3J$ = 7.4 Hz, 1H), 7.51 (d, $^3J$ = 8.0 Hz, 1H), 7.54 (t, $^3J$ = 7.5 Hz, 1H), 7.88 (s, 2H), 7.91 (d, $^3J$ = 8.1 Hz, 1H), 8.01 (d, $^3J$ = 8.0 Hz, 1H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 34.9 ($CH_2$), 55.6 ($CH_3$), 105.0 (CH), 112.5 (CH), 118.6 (CH), 124.1 (CH), 125.4 (CH × 2), 126.5 (CH), 127.7 (CH), 128.9 (CH), 130.7 ($C_{quat}$), 132.9 ($C_{quat}$), 135.4 ($C_{quat}$), 138.8 ($C_{quat}$), 141.0 ($C_{quat}$), 143.9 ($C_{quat}$), 159.3 ($C_{quat}$). EI MS (70 eV), *m*/*z*: 246 (100) [$M^+$], 202 (46). HRMS (EI): calcd for $C_{18}H_{14}O$ 246.1045, found 246.1051.

**8-Fluoro-11*H*-benzo[*a*]fluorene (3f).** White solid [34.5 mg (59%)], mp 149.8−150.5 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 4.15 (s, 2H), 7.01 (ddd, $^3J$ = 9.3, $^3J$ = 8.2, $^4J$ = 2.4 Hz, 1H), 7.45−7.58 (m, 4H), 7.85 (d, $^3J$ = 8.5 Hz, 1H), 7.89 (d, $^3J$ = 8.8 Hz, 1H), 7.92 (d, $^3J$ = 8.8 Hz, 1H), 8.01 (d, $^3J$ = 8.4 Hz, 1H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): 35.1 ($CH_2$), 106.8 (d, $^2J_{C,F}$ = 23.0 Hz, CH), 113.0 (d, $^2J_{C,F}$ = 23.0 Hz, CH), 118.7 (CH), 124.1 (CH), 125.68 (d, $^3J_{C,F}$ = 8.3 Hz, CH), 125.69 (CH), 126.7 (CH), 128.0 (CH), 129.0 (CH), 130.6 ($C_{quat}$), 133.0 ($C_{quat}$), 138.2 ($C_{quat}$), 138.5 ($C_{quat}$), 141.2 ($C_{quat}$), 144.5 (d, $^3J_{C,F}$ = 9.1 Hz, $C_{quat}$), 162.7 (d, $^1J_{C,F}$ = 243.1 Hz, $C_{quat}$). EI MS (70 eV), *m*/*z*: 234 (100) [$M^+$]. HRMS (EI): calcd for $C_{17}H_{11}F$ 234.0845, found 234.0837.

**9-Methyl-11*H*-benzo[*a*]fluorene (3g) and 7-Methyl-11*H*-benzo[*a*]fluorene (3g′).** White solid [35.1 mg (61%), ratio 72:28]. The $^1$H NMR spectrum of **3g′** is identical to that reported in the literature.[8]

**7,9-Dimethyl-11*H*-benzo[*a*]fluorene (3h).** White solid [53.1 mg (87%)]. The $^1$H NMR spectrum is identical to that reported in the literature.[43]

**7,8,9-Trimethoxy-11*H*-benzo[*a*]fluorene (3i).** White solid [46.7 mg (61%)], mp 142.7−143.2 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 3.96 (s, 6H), 4.10 (s, 3H), 4.13 (s, 2H), 7.00 (s, 1H), 7.43 (t, $^3J$ = 7.4 Hz, 1H), 7.52 (t, $^3J$ = 7.4 Hz, 1H), 7.85 (d, $^3J$ = 8.6 Hz, 1H), 7.89 (d, $^3J$ = 8.4 Hz, 1H), 7.96 (d, $^3J$ = 8.3 Hz, 1H), 8.19 (d, $^3J$ = 8.5 Hz, 1H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 36.2 ($CH_2$), 56.4 ($CH_3$), 61.0 ($CH_3$), 61.2 ($CH_3$), 104.8 (CH), 121.3 (CH), 123.8 (CH), 124.8 (CH), 126.2 (CH), 127.7 (CH), 128.3 ($C_{quat}$), 128.8 (CH), 130.3 ($C_{quat}$), 132.0 ($C_{quat}$), 138.4 ($C_{quat}$), 138.6 ($C_{quat}$), 139.5 ($C_{quat}$), 141.4 ($C_{quat}$), 149.1 ($C_{quat}$), 153.0 ($C_{quat}$). EI MS (70 eV), *m*/*z*: 306 (100) [$M^+$]. HRMS (EI): calcd for $C_{20}H_{18}O_3$ 306.1256, found 306.1250.

**11*H*-Benzo[*b*]fluorene (9a).** White solid [45.9 mg (85%)]. The $^1$H NMR spectrum is identical to that reported in the literature.[8]

**2,4-Dimethyl-11*H*-benzo[*b*]fluorene (9h).** White solid [50.1 mg (82%)], mp 107.2−107.9 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 2.42 (s, 3H), 2.81 (s, 3H), 4.05 (s, 2H), 7.03 (s, 1H), 7.25 (s, 1H), 7.44−7.47 (m, 2H), 7.83−7.86 (m, 1H), 7.92−7.95 (m, 1H), 7.93 (s, 1H), 8.25 (s, 1H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 21.2 ($CH_3$), 21.4 ($CH_3$), 36.4 ($CH_2$), 120.8 (CH), 122.9 (CH), 123.3 (CH), 125.2 (CH × 2), 127.5 (CH), 128.4 (CH), 130.1 (CH), 132.2 ($C_{quat}$), 133.1 ($C_{quat}$), 133.7 ($C_{quat}$), 136.7 ($C_{quat}$), 137.2 ($C_{quat}$), 141.5 ($C_{quat}$), 141.7 ($C_{quat}$), 144.5 ($C_{quat}$). EI MS (70 eV), *m*/*z*: 244 (100) [$M^+$], 229 (85) [$M^+ - CH_3$]. HRMS (EI): calcd for $C_{19}H_{16}$ 244.1252, found 244.1250.

**3-Chloro-7-methoxy-11*H*-benzo[*b*]fluorene (10j).** White solid [59.6 mg (85%)], mp 165.6−166.2 °C. $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ = 3.96 (s, 3H), 4.00 (s, 2H), 7.15 (dd, $^3J$ = 8.9, $^4J$ = 2.4 Hz, 1H), 7.24 (d, $^4J$ = 2.4 Hz, 1H), 7.30 (dd, $^3J$ = 7.8, $^4J$ = 1.8 Hz, 1H), 7.46 (d, $^3J$ = 7.8 Hz, 1H), 7.75 (d, $^3J$ = 8.9 Hz, 1H), 7.85 (d, $^4J$ = 1.8 Hz, 1H), 7.87 (s, 1H), 8.07 (s, 1H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 35.8 ($CH_2$), 55.3 ($CH_3$), 106.2 (CH), 117.2 (CH), 118.6 (CH), 120.7 (CH), 123.4 (CH), 126.2 (CH), 127.3 (CH), 128.9 ($C_{quat}$), 129.2 (CH), 133.0 ($C_{quat}$), 134.1 ($C_{quat}$), 139.0 ($C_{quat}$), 139.8 ($C_{quat}$), 142.2 ($C_{quat}$), 143.0 ($C_{quat}$), 157.5 ($C_{quat}$). EI MS (70 eV), *m*/*z*: 282/280 (22/64) [$M^+$], 245 (100) [$M^+ - Cl$], 202 (56). HRMS (EI): calcd for $C_{18}H_{13}ClO$ 280.0655, found 280.0656.

**9-Methoxy-13*H*-dibenzo[*a*,*h*]fluorene (10k).** Pale yellow solid [51.8 mg (70%)], mp 276.3−277.1 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 3.97 (s, 3H), 4.32 (s, 2H), 7.14 (dd, $^3J$ = 8.9, $^4J$ = 2.5 Hz, 1H), 7.28 (d, $^4J$ = 2.5 Hz, 1H), 7.49 (td, $^3J$ = 7.5, $^4J$ = 1.2 Hz, 1H), 7.57 (td, $^3J$ = 7.5, $^4J$ = 1.2 Hz, 1H), 7.78 (d, $^3J$ = 8.9 Hz, 1H), 7.91 (d, $^3J$ = 8.0 Hz, 1H), 7.94 (d, $^3J$ = 7.0 Hz, 1H), 7.95 (s, 1H), 8.02 (d, $^3J$ = 8.4 Hz, 1H), 8.03 (d, $^3J$ = 8.3 Hz, 1H), 8.14 (s, 1H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 34.9 ($CH_2$), 55.3 ($CH_3$), 106.3 (CH), 116.5 (CH), 117.9 (CH), 119.1 (CH), 123.2 (CH), 124.3 (CH), 125.7 (CH), 126.6 (CH), 128.0 (CH), 128.4 ($C_{quat}$), 128.9 (CH), 129.2 (CH), 130.8 ($C_{quat}$), 133.3 ($C_{quat}$), 134.2 ($C_{quat}$), 138.4 ($C_{quat}$), 139.0 ($C_{quat}$), 140.8 ($C_{quat}$), 141.9 ($C_{quat}$), 157.4 ($C_{quat}$). EI MS (70 eV), *m*/*z*: 296 (100) [$M^+$]. HRMS (EI): calcd for $C_{22}H_{16}O$ 296.1201, found 296.1205.

**Fluorene (11a).** White solid [30.0 mg (72%) from 1-bromobenzene; 37.4 mg (90%) from 1-iodobenzene]. The $^1$H NMR spectrum is identical to that reported in the literature.[44]

**11*H*-Benzo[*b*]fluorene (9a) and 7*H*-Benzo[*c*]fluorene (11l′).** White solid [32.4 mg (60%), ratio 70:30]. The $^1$H NMR spectrum of **11l′** is identical to that reported in the literature.[8]

**3-Methylfluorene (12a).** White solid [34.2 mg (76%)]. The $^1$H NMR spectrum is identical to that reported in the literature.[13]

**1-Methylfluorene (13a).** White solid [25.7 mg (57%)]. The $^1$H NMR spectrum is identical to that reported in the literature.[10a]

**Fluorene-3-carbalaldehyde (14a).** The title compound was prepared similar to method C, but the acidified solution was stirred at room temperature for 1 h (monitored by GC−MS). **14a**. Pale yellow solid [35.4 mg (73%)], mp 248.2−248.8 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 4.00 (s, 2H), 7.36 (td, $^3J$ = 7.6, $^4J$ = 1.5 Hz, 1H), 7.42 (t, $^3J$ = 7.6 Hz, 1H), 7.58 (d, $^3J$ = 7.4 Hz, 1H), 7.70 (d, $^3J$ = 7.7 Hz, 1H), 7.84 (dd, $^3J$ = 7.7, $^4J$ = 1.5 Hz, 1H), 7.88 (d, $^3J$ = 7.0 Hz, 1H), 8.29 (s, 1H), 10.11 (s, 1H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 37.3 ($CH_2$), 120.41 (CH), 120.44 (CH), 125.2 (CH), 125.5 (CH), 127.2 (CH), 127.7 (CH), 129.1 (CH), 135.7 ($C_{quat}$), 140.4 ($C_{quat}$), 142.8 ($C_{quat}$), 143.1 ($C_{quat}$), 150.2 ($C_{quat}$), 192.4 (CHO). FAB MS, *m*/*z*: 194 (31) [$M^+$], 165 (100) [$M^+ - CHO$]. HRMS (FAB): calcd for $C_{14}H_{10}O$ 194.0732, found 194.0739.

**2,4-Dimethyl-13*H*-indeno[1,2-*a*]coranuulene (15h).** Yellow crystals [57.6 mg (63%)], mp 197.3−197.9 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 2.47 (s, 3H, $CH_3$), 3.16 (s, 3H, $CH_3$), 4.24 (s, 2H, $CH_2$), 7.19 (s, 1H), 7.34 (s, 1H), 7.81 (d, $^3J$ = 8.8 Hz, 1H), 7.82 (s, 2H), 7.83 (s, 2H), 7.87 (d, $^3J$ = 8.8 Hz, 1H), 7.94 (d, $^3J$ = 8.7 Hz, 1H), 8.25 (d, $^3J$ = 8.9 Hz, 1H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 21.2 ($CH_3$), 23.5 ($CH_3$), 35.7 ($CH_2$), 123.1 (CH), 125.0 (CH), 126.4 (CH), 126.79 (CH), 126.83 (CH), 126.9 (CH), 127.1 (CH), 127.6 (CH), 127.8 (CH), 128.2 ($C_{quat}$), 128.6 ($C_{quat}$), 130.1 ($C_{quat}$), 130.5 ($C_{quat}$), 130.9 (CH), 131.0 ($C_{quat}$), 131.7 ($C_{quat}$), 135.0 ($C_{quat}$), 135.77 ($C_{quat}$), 135.83 ($C_{quat}$), 135.9 (2 × $C_{quat}$), 136.1 ($C_{quat}$), 139.1 ($C_{quat}$), 140.7 ($C_{quat}$), 142.1 ($C_{quat}$), 145.0 ($C_{quat}$). EI MS (70 eV), *m*/*z*: 366 (100) [$M^+$], 351 (65) [$M^+ - CH_3$]. HRMS (EI): calcd for $C_{29}H_{18}$ 366.1409, found 366.1411.

**13*H*-Indeno[1,2-*b*]fluoranthene (16a).** Pale yellow solid [42.1 mg (58%)], mp 162.1−162.9 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 4.23 (s, 2H), 7.33−7.40 (m, 3H), 7.47 (t, $^3J$ = 7.5 Hz, 1H), 7.64 (d, $^3J$ = 7.1 Hz, 1H), 7.67 (d, $^3J$ = 7.1 Hz, 1H), 7.88−7.98 (m, 5H), 8.30 (s, 1H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 35.2 ($CH_2$), 113.1 (CH), 119.4 (CH), 119.6 (CH), 121.3 (CH), 121.5 (CH), 123.6 (CH), 125.0 (CH), 126.4 (CH), 126.8 (CH), 127.3 (CH), 127.6 (CH), 128.3 (CH), 132.5 ($C_{quat}$), 136.8 ($C_{quat}$), 137.5 ($C_{quat}$), 139.5 ($C_{quat}$), 139.8 ($C_{quat}$), 140.5 ($C_{quat}$), 141.4 ($C_{quat}$), 142.6 ($C_{quat}$), 143.4 ($C_{quat}$). One $C_{quat}$ cannot be observed due to signals overlap. EI MS (70 eV), *m*/*z*: 290 (100) [$M^+$]. HRMS (EI): calcd for $C_{23}H_{14}$ 290.1096, found 290.1098.

**3-Methyl-10,12-dihydroindeno[2,1-*b*]fluorene (17b).** The pure form of **17b** was obtained by crystallization of a mixture of **17b** and **17b′** [44.2 mg (66%), ratio 80:20] from $CH_2Cl_2$/MeOH. **17b**. White solid, mp 202.3−203.1 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 2.49 (s, 3H), 3.91 (s, 2H), 3.95 (s, 2H), 7.13 (dd, $^3J$ = 7.5,



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J. Org. Chem. 2015, 80, 10446−10456

$^4J$ = 1.1 Hz, 1H), 7.31 (t, $^3J$ = 7.4 Hz, 1H), 7.41 (td, $^3J$ = 7.4, $^4J$ = 1.1 Hz, 1H), 7.44 (d, $^3J$ = 7.7 Hz, 1H), 7.56 (d, $^3J$ = 7.5 Hz, 1H), 7.68 (s, 1H), 7.71 (s, 1H), 7.88 (d, $^3J$ = 7.6 Hz, 1H), 8.16 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 21.6 ($CH_3$), 36.4 ($CH_2$), 36.8 ($CH_2$), 110.9 (CH), 119.7 (CH), 120.3 (CH), 121.7 (CH), 124.7 (CH), 125.0 (CH), 126.4 (CH), 126.7 (CH), 127.4 (CH), 136.4 ($C_{quat}$), 140.56 ($C_{quat}$), 140.59 ($C_{quat}$), 140.7 ($C_{quat}$), 141.87 ($C_{quat}$), 141.93 ($C_{quat}$), 142.4 ($C_{quat}$), 143.0 ($C_{quat}$), 143.5 ($C_{quat}$). EI MS (70 eV), *m*/*z*: 268 (100) [$M^+$], 253 (57) [$M^+ - CH_3$]. HRMS (EI): calcd for $C_{21}H_{16}$ 268.1252, found 268.1251.

**13*H*-Indeno[2,1-*a*]anthracene (18a).** Yellow solid [36.6 mg (55%)], mp 248.7−249.5 °C. $^1H$ NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 4.30 (s, 2H), 7.35 (td, $^3J$ = 7.4, $^4J$ = 1.1 Hz, 1H), 7.43 (t, $^3J$ = 7.5 Hz, 1H), 7.46−7.52 (m, 2H), 7.67 (d, $^3J$ = 7.5 Hz, 1H), 7.84 (d, $^3J$ = 7.5 Hz, 1H), 7.92 (d, $^3J$ = 8.7 Hz, 1H), 8.00−8.09 (m, 3H), 8.49 (s, 1H), 8.55 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 36.0 ($CH_2$), 118.9 (CH), 119.5 (CH), 122.1 (CH), 124.8 (CH), 125.2 (CH), 125.7 (CH), 126.2 (CH), 126.8 (CH), 127.6 (CH), 128.4 (CH × 2), 129.3 ($C_{quat}$), 131.4 ($C_{quat}$ × 2), 132.1 ($C_{quat}$), 138.3 ($C_{quat}$), 139.6 ($C_{quat}$), 142.9 ($C_{quat}$), 143.4 ($C_{quat}$). One CH cannot be observed due to signals overlap. EI MS (70 eV), *m*/*z*: 266 (100) [$M^+$]. HRMS (EI): calcd for $C_{21}H_{14}$ 266.1096, found 266.1095.

**13*H*-Indeno[1,2-*b*]anthracene (19a).** Pale yellow solid [50.6 mg (76%)], mp 232.4−233.1 °C. $^1H$ NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 4.16 (s, 2H), 7.37 (td, $^3J$ = 7.4, $^4J$ = 1.5 Hz, 1H), 7.40−7.48 (m, 3H), 7.58 (d, $^3J$ = 7.5 Hz, 1H), 7.97−8.03 (m, 3H), 8.09 (s, 1H), 8.35 (s, 1H), 8.42 (s, 1H), 8.51 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 36.3 ($CH_2$), 117.5 (CH), 120.9 (CH), 123.1 (CH), 125.08 (CH), 125.11 (CH), 125.4 (CH), 125.8 (CH), 126.3 (CH), 127.1 (CH), 127.97 (CH), 128.03 (CH), 128.1 (CH), 131.5 ($C_{quat}$ × 2), 131.6 ($C_{quat}$), 140.5 ($C_{quat}$), 140.9 ($C_{quat}$ × 2), 143.9 ($C_{quat}$). One $C_{quat}$ cannot be observed due to signals overlap. EI MS (70 eV), *m*/*z*: 266 (100) [$M^+$]. HRMS (EI): calcd for $C_{21}H_{14}$ 266.1096, found: 266.1097.

**6,12-Dihydroindeno[1,2-*b*]fluorene (20a).** White solid [31.8 mg (50%)]. The $^1H$ NMR spectrum is identical to that reported in the literature.[8]

**3,9-Dimethyl-6,12-dihydroindeno[1,2-*b*]fluorene (20b).** White solid [44.5 mg (63%)]. The $^1H$ NMR spectrum is identical to that reported in the literature.[9a]

**10,12-Dihydroindeno[2,1-*b*]fluorene (21a).** White solid [36.3 mg (57%)]. The $^1H$ NMR spectrum is identical to that reported in the literature.[8]

**2,4,7,9-Tetramethyl-11,14-dihydrofluoreno[2,3-*b*]fluorene (22h).** White solid [49.6 mg (55%)], mp >300 °C dec. $^1H$ NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 2.43 (s, 6H), 2.85 (s, 6H), 4.06 (s, 4H), 7.03 (s, 2H), 7.25 (s, 2H), 7.92 (s, 2H), 8.35 (s, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 21.3 ($CH_3$), 21.4 ($CH_3$), 36.4 ($CH_2$), 121.4 (CH), 122.6 (CH), 123.3 (CH), 130.1 (CH), 131.0 ($C_{quat}$), 132.8 ($C_{quat}$), 133.5 ($C_{quat}$), 136.8 ($C_{quat}$), 136.9 ($C_{quat}$), 141.0 ($C_{quat}$), 141.3 ($C_{quat}$), 144.5 ($C_{quat}$). EI MS (70 eV), *m*/*z*: 360 (100) [$M^+$], 345 (35) [$M^+ - CH_3$]. HRMS (EI): calcd for $C_{28}H_{24}$ 360.1878, found 360.1872.

**13,16-Dihydrodiindeno[1,2-*b*:2′,1′-*h*]phenanthrene (23a).** The title compound was prepared according to method A, but it was purified using a different method due to its low solubility in common organic solvents. The reaction mixture at 0 °C was treated with hydrochloric acid (2 N, 10 mL), and the collected precipitates were washed with water (5 mL) and methanol (5 mL). The off-white solid was loaded onto the top of a 2 cm thick layer of silica gel. Elution with hexane/$CH_2Cl_2$ (10:1) gave **23a** (78.1 mg, 88%) as a pale yellow solid, mp >295 °C dec. $^1H$ NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 4.18 (s, 4H), 7.37 (t, $^3J$ = 7.1 Hz, 2H), 7.45 (t, $^3J$ = 7.1 Hz, 2H), 7.62 (d, $^3J$ = 7.1 Hz, 2H), 7.85 (s, 2H), 7.97 (d, $^3J$ = 7.1 Hz, 2H), 8.26 (s, 2H), 8.89 (s, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, plus DEPT, ppm): $\delta$ = 37.0 ($CH_2$), 118.7 (CH), 118.9 (CH), 120.5 (CH), 125.2 (CH), 126.9 (CH), 127.0 (CH), 127.3 (CH), 129.8 ($C_{quat}$), 131.5 ($C_{quat}$), 140.6 ($C_{quat}$), 141.3 ($C_{quat}$), 141.9 ($C_{quat}$), 143.8 ($C_{quat}$). EI MS (70 eV), *m*/*z*: 354 (100) [$M^+$]. HRMS (EI): calcd for $C_{28}H_{18}$ 354.1409, found 354.1410.

**Synthesis of Benzo[*a*]fluoren-11-one.** Similar to method A, but the crude product of benzo[*a*]fluorene was exposed to ambient air and stirred at room temperature for 4 h (monitored by TLC) before treatment with hydrochloric acid at 0 °C. The title compound was purified by chromatography on silica gel, eluting with hexane/$CH_2Cl_2$ (10:1), and obtained with a yield of 70% (40.2 mg, based on 0.25 mmol of 1-bromonaphthalene) as orange solid. The $^1H$ NMR spectrum is identical to that reported in the literature.[17g]

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02111.

NMR spectral data of all methylene-bridged arenes, photoabsorption and fluorescence spectra, cyclic voltammograms, and X-ray crystallographic analysis of **15h** (PDF)

crystallographic data of **15h** (CIF)

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### Notes

The authors declare no competing financial interest.

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