## Palladium-Catalyzed [3+2] Cycloaddition Reaction of (Diarylmethylene)cyclopropa[b]naphthalenes with Arynes: An Efficient Synthesis of 11-(Diarylmethylene)-11*H*-benzo[b]fluorenes

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A Pd-catalyzed [3+2] cycloaddition reaction of (diarylmethylene)cyclopropa[b]naphthalenes with arynes provided an efficient approach for the synthesis of 11-(diarylmethylene)-  $11H\mbox{-}benzo[b]\mbox{fluorenes}$  with good to excellent yields under mild conditions.

### Introduction

The chemistry of polycyclic aromatic hydrocarbons (PAHs) has become a field of increasing interest during the past decades due to their unique properties in material science.<sup>[1]</sup> For example, the charge transport properties of PAHs make them potential candidates for organic optoelectronic devices such as light-emitting diodes, field-effect transistors, photovoltaics, acenes, nanographenes and discotic liquid crystals.<sup>[2]</sup> In addition, PAHs with benzo[b]fluorene skeletons are also of considerable interest due to their applications as bioactive compounds and synthetic intermediates in organic synthesis.<sup>[3]</sup> Thus, much attention has been focused on the synthesis of benzo[b]fluorenes in recent years. Although some known methods provide reliable routes, most of them require multiple steps or harsh conditions.<sup>[4]</sup> Thus, there is high demand for development of efficient methods for their synthesis.

During our recent systematic study of methylenecyclopropane (MCP) chemistry,<sup>[5]</sup> we became interested in the chemistry of the analogous (diarylmethylene)cyclopropa-[*b*]naphthalenes. Because of their unusual structure, which contains a triafulvene, a [3]radialene, and a cycloproparene, they have attracted much attention from physical, theoretical, and synthetic viewpoints.<sup>[6]</sup> However, for transitionmetal-mediated reactions, only one example of the reactions of (diarylmethylene)cyclopropa[*b*]naphthalenes **1** with stoichiometric rhodium(I) and platinum(0) reagents has been reported.<sup>[7]</sup> We first reported a catalytic, highly regioselec-

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tive palladium-catalyzed [3+2] cycloaddition reaction of (diarylmethylene)cyclopropa[b]naphthalenes 1 with alkenes and alkynes in 2008, which provided an efficient method for the synthesis of 1(3)-alkylidene-2,3-dihydro-1H-cyclopenta[b]naphthalenes and 1-alkylidene-1H-cyclopenta-[b]naphthalenes under mild conditions<sup>[8]</sup> (Scheme 1).



Scheme 1. Previous work and our proposal.

Arynes are highly reactive intermediates.<sup>[9]</sup> Since the innovation of  $F^-$ -induced in-situ generation of aryne from 2-(trimethylsilyl)phenyl triflate in 1983,<sup>[10]</sup> the application of arynes under mild conditions in organic synthesis has attracted increasing attention.

The transition-metal-catalyzed reactions of arynes, especially the transition-metal-catalyzed annulation of arynes, have proved to be very useful in organic synthesis.<sup>[11]</sup> It was reported that arvnes readily undergo cyclotrimerization under palladium catalysis to form polycyclic aromatic hydrocarbons.<sup>[12]</sup> Related studies demonstrated that in the presence of transition-metal catalysts, cocyclizations of arynes could be performed with a variety of alkynes,<sup>[13]</sup> divnes,<sup>[14]</sup> allenes,<sup>[15]</sup> allyl derivatives,<sup>[16]</sup> CO<sub>2</sub><sup>[17]</sup> and CO.<sup>[18]</sup> To the best of our knowledge, there are few reports of the cocyclization of arynes and methylenecyclopropanes.<sup>[19]</sup> In this paper, we wish to report a highly efficient palladium-catalyzed [3+2] cycloaddition reaction of (diarylmethylene)cyclopropa[b]naphthalenes with arynes, providing an easy access to 11-(diarylmethylene)-11H-benzo[b]fluorenes in good to excellent yields under mild conditions.



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<sup>[‡]</sup> Professor Huang passed away on March 6, 2010. He was fully in charge of this project. Professor Luling Wu is helping to finish all the projects with assistance from Professor Shengming Ma.

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### **Results and Discussion**

We first employed 1-(diphenylmethylene)-1H-cyclopropa-[b]naphthalene (1a)<sup>[20]</sup> to react with 2.0 equiv. of 2-(trimethylsilyl)phenyl triflate 2a in the presence of 5 mol-% of Pd(dba)<sub>2</sub> and 4.0 equiv. of CsF in MeCN at 25 °C. The desired [3+2] cycloaddition product **3a** was obtained in 88% yield (entry 2, Table 1). The structure of the product 3a was confirmed by X-ray diffraction studies (Figure 1). The reaction was further investigated to optimize the reaction conditions, and the results are summarized in Table 1. We found that Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> was almost as effective as Pd(dba)<sub>2</sub> in furnishing 3a, while the use of PdCl<sub>2</sub> gave an inferior yield (entries 3 and 4, Table 1). When we used  $Pd(PPh_3)_4$  as the catalyst, the reaction was complete within 3 h, and the yield of 3a was improved to 98% (entry 5, Table 1). Gratifyingly, upon using a combination of  $Pd(dba)_2$  and  $PPh_3$ , we could obtain the expected product 3a within 1.5 h with the same excellent yield (entry 6, Table 1). However, when we decreased the amount of  $Pd(dba)_2$  to 1 mol-%, the starting material **1a** was not completely consumed (entry 7, Table 1). When we reduced the amount of 2a from 2.0 equiv. to 1.2 equiv., the yield dropped to 75% (entry 8, Table 1). Among the solvents examined, MeCN was the best (entries 6 and 9–10, Table 1). Therefore, the reaction in the presence of 5 mol-% of Pd(dba)<sub>2</sub>, 10 mol-% of PPh<sub>3</sub> and 4 equiv. of CsF in MeCN at 25 °C was established as standard conditions to explore the reaction scope (entry 6, Table 1). Here it should also be noted that the reaction did not occur in the absence of the palladium catalyst (entry 1, Table 1).

Table 1. Optimization of reaction conditions for the Pd-catalyzed [3+2] cycloaddition reaction of 1-(diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene (1a) with 2-(trimethylsilyl)phenyl triflate (2a).<sup>[a]</sup>

	Ph Ph 1a	TMS OTf 2a	catalyst solvent, rt	Ph CCCC 3a	Ph
Entry	Catalyst	1a/2a	Solvent	Time [h]	Yield of <b>3a</b> [%] <sup>[b]</sup>
1	_	1:2	MeCN	24	0
2	Pd(dba) <sub>2</sub>	1:2	MeCN	1	88
3	Pd <sub>2</sub> (dba) <sub>3</sub> ·CHCl <sub>3</sub>	1:2	MeCN	1	87
4	PdCl <sub>2</sub>	1:2	MeCN	2.5	70
5	Pd(PPh <sub>3</sub> ) <sub>4</sub>	1:2	MeCN	3	98
6	Pd(dba) <sub>2</sub> /PPh <sub>3</sub>	1:2	MeCN	1.5	98
7	Pd(dba) <sub>2</sub> /PPh <sub>3</sub>	1:2	MeCN	24	40 <sup>[c]</sup>
8	Pd(dba) <sub>2</sub> /PPh <sub>3</sub>	1:1.2	MeCN	2	75
9	Pd(dba) <sub>2</sub> /PPh <sub>3</sub>	1:2	THF	24	12
10	Pd(dba) <sub>2</sub> /PPh <sub>3</sub>	1:2	MeCN/toluene	e 12	85 <sup>[d]</sup>

[a] The reactions were conducted with 1a (0.2 mmol), CsF (4.0 equiv.), catalyst (5 mol-%), and ligand (10 mol-%) in 5 mL of solvent. [b] Isolated yield. [c] 1 mol-% of catalyst and 2 mol-% of ligand were used, and 32% of 1a was recovered. [d] The reaction was conducted in MeCN (2.5 mL) and toluene (2.5 mL).

Under the optimized reaction conditions, we next examined the scope of this reaction with various substrates. In addition to 1a, (diarylmethylene)cyclopropa[b]naphthalenes



Figure 1. ORTEP representation of 3a.

**1b–1h**, which bear substituted phenyl rings as the Ar group in 1, all efficiently underwent annulation to generate the corresponding products in high to excellent yields (entries 2-8, Table 2): The reaction of 1b with 2a gave a 98% yield of the desired compound 3b (entry 2, Table 2). (Diarylmethylene)cyclopropa[b]naphthalenes with m-tolyl (1c) and otolyl (1d) as the aryl groups gave their corresponding products in 84 and 85% yields, respectively (entries 3 and 4, Table 2). The reduced yield may result from the steric hindrance of the methyl groups. Substrate 1e, which incorporated two electron-donating *p*-methoxy groups, gave a yield of 93% (entry 5, Table 2). Electron-withdrawing groups such as fluorine (1f) were tolerated in the reaction to give 3f in 96% yield (entry 6, Table 2). The substrate 1i, upon reacting with the aryne precursor 2a, gave the desired compounds 3i and 3j as a 1:1 mixture of inseparable isomers in an 81% overall yield (entry 9, Table 2).

Table 2. Pd-catalyzed [3+2] cycloaddition reaction of (diarylmethylene)cyclopropa[*b*]naphthalenes 1 with 2a.<sup>[a]</sup>

Ĺ	Ar + 1	TMS OTf CsF, CH <sub>3</sub> CN, r.t. 2a	<b></b> (	
Entry	1 Ar	- Product	Time [h]	Yield of <b>3</b> [%] <sup>[b]</sup>
1	Ph (1a)	3a	1.5	98
2	$4-MeC_{6}H_{4}(1b)$	3b	2.5	98
3	$3-MeC_{6}H_{4}(1c)$	3c	3	84
4	2-MeC <sub>6</sub> H <sub>4</sub> (1d)	3d	4.5	85
5	$4\text{-}MeOC_{6}H_{4}\left(\mathbf{1e}\right)$	3e	3	93
6	4-FC <sub>6</sub> H <sub>4</sub> (1f)	3f	2	96
7	4-ClC <sub>6</sub> H <sub>4</sub> (1g)	3g	2	96
8	$4\text{-BrC}_{6}\text{H}_{4}\left(\mathbf{1h}\right)$	3h	2	94
9	Ii		2	81 <sup>[c]</sup> (1:1)

[a] The reactions were conducted with **1** (0.2 mmol), **2a** (2.0 equiv.), CsF (4.0 equiv.), Pd(dba)<sub>2</sub> (5 mol-%), and PPh<sub>3</sub> (10 mol-%) in CH<sub>3</sub>CN (5 mL) at room temp. [b] Isolated yield. [c] The ratio of products was determined by <sup>1</sup>H NMR spectral analysis.



Scheme 2. The synthetic utilities of 3g and 3h.

The reactions of substrates bearing other halogen atoms (1g and 1h) with 2a also proceeded smoothly to afford excellent yields of the corresponding compounds 3g and 3h, providing opportunities for further elaboration (entries 7 and 8, Table 2). Our further experiments have applied the HBF<sub>4</sub> salt of a monophosphane ligand, that is, dicyclohexyl-(2,4,6-trimethoxyphenyl)phosphane, to the Suzuki coupling reaction of 3g and 3h with different organoboronic acids in high yields.<sup>[21]</sup> Furthermore, the combination of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and AuCl(PPh<sub>3</sub>) made a unique catalytic system that allowed Sonogashira-type cross-coupling of 3h with 1-ethynylbenzene to afford 4d in a yield of 90%.<sup>[22]</sup> The reaction of 3h with hex-1-yne afforded 4e in 86% yield by using an efficient catalytic system of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and CuI in piperidine<sup>[23]</sup> (Scheme 2).

We further examined the reaction of 1a by using a variety of substituted aryne precursors. Treatment of aryne precursor 2b with 1a gave the targeted product 11-(diphenylmethylene)-2,3-dimethyl-11*H*-benzo[*b*]fluorene (3k) smoothly in a 90% isolated yield (entry 1, Table 3). When 2c and 2d were used as aryne precursors under the established reaction conditions, the reaction led to lower yields, and a large amount of an unknown mixture was detected. Thus, in order to optimize the reaction further, a mixture of the two substrates (1a and aryne precursor) in MeCN was added slowly to the reaction system by a micro infusion pump over 1 h at 80 °C. To our delight, the yields of 3l and 3m were dramatically increased to 70% and 85%, respectively (entries 2 and 3, Table 3). When an unsymmetrical aryne precursor 2-methyl-6-(trimethylsilyl)phenyl triflate 2e was used to react with **1a**, a mixture of inseparable isomers **3n** and **3o** was obtained in an 92% overall yield, with an isomeric ratio of 1:1 (entry 4, Table 3 < xtabr3 pos="x22">).

On the basis of the known organopalladium chemistry of arynes and our previous work on Pd-catalyzed [3+2] cycloaddition reactions of (diarylmethylene)cyclopropa[*b*]naphthalenes with alkenes and alkynes,<sup>[8]</sup> a possible mechanism for the reaction of **1** with aryne precursors **2** catalyzed by Pd(dba)<sub>2</sub> and PPh<sub>3</sub> is shown in (Scheme 3). First, oxidative addition of palladium(0) with the highly strained threemembered ring in (diarylmethylene)cyclopropa[*b*]naphthalenes **1** leads to the palladacyclobutene compound **A**. Subsequently, the insertion reaction of **A** with aryne **B**, which is generated from the triflate **2** in the presence of the fluoride source, gives the palladacyclohexene compound **C** or **D**. Then, reductive elimination gives the [3+2] cycloadduct **3**, and regenerates the catalytically active Pd<sup>0</sup> catalyst.

### Conclusions

In conclusion, we have disclosed a Pd-catalyzed [3+2] cycloaddition reaction of (diarylmethylene)cyclopropa[b]naphthalenes 1 with arynes, providing an efficient method for the synthesis of 11-(diarylmethylene)-11*H*-benzo[b]fluorenes 3 in good to excellent yields under mild conditions. Further studies on the reaction mechanism and the scope of the reaction are in progress. 1a

Entry Aryne precursor

Table 3. Pd-catalyzed [3+2] cycloaddition reaction of 1a with substituted aryne precursor 2.[a]

2

Pd(dba)<sub>2</sub> (5 mol-%) PPh<sub>3</sub> (10 mol-%)

CsF, CH<sub>3</sub>CN

Product(s)

3

Time

[h]

Yield of 3

[%]<sup>[b]</sup>

[a] Unless otherwise specified, the reactions were conducted with **1a** (0.2 mmol), **2** (2.0 equiv.), CsF (4.0 equiv.), Pd(dba)<sub>2</sub> (5 mol-%), and PPh<sub>3</sub> (10 mol-%) in 5 mL of CH<sub>3</sub>CN at room temp. [b] Isolated yield. [c] A mixture of 1 and 2 was added by a micro infusion pump over 1 h at 80 °C. [d] The ratio of products was determined by <sup>1</sup>H



### **Experimental Section**

General Experimental Procedures: All reactions were performed under a N<sub>2</sub> atmosphere. Dry solvents were distilled prior to use: THF, toluene and dioxane were distilled from sodium-benzophenone; MeCN was distilled from CaH<sub>2</sub>; DMF was distilled from MgSO<sub>4</sub>. Petroleum ether refers to the fraction with a boiling range of 60-90 °C. Unless otherwise specified, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra were measured in CDCl<sub>3</sub> with TMS as the internal standard. Chemical shifts are expressed in ppm and J values are given in Hz. Melting points were uncorrected. Starting materials: 1a-1i<sup>[20]</sup> and 2a-2e<sup>[24]</sup> were prepared following the known procedures.

Synthesis of 11-(Diphenylmethylene)-11H-benzo[b]fluorene (3a) as a Representative General Procedure for the Preparation of 11-(Diarylmethylene)-11H-benzo[b]fluorenes 3a-3k, 3n and 3o: A rubbercapped Schlenk vessel containing CsF (121 mg, 0.8 mmol) was flame-dried under vacuum and backfilled with nitrogen three times, then 1-(diphenylmethylene)-1H-cyclopropa[b]naphthalene (1a) (61 mg, 0.2 mmol), PPh<sub>3</sub> (6 mg, 0.02 mmol), 2-(trimethylsilyl)phenyl triflate (2a) (119 mg, 0.4 mmol), and dry MeCN (2 mL) were added sequentially to the Schlenk vessel. After being stirred for about 1 min at room temperature, Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol), and another portion of dry MeCN (3 mL) were added sequentially in one portion. The resulting mixture was then allowed to stir at room temperature. After 1.5 h, the reaction was complete as monitored by TLC. The reaction mixture was filtered through a shot pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether) to afford 3a (74 mg, 98%) as a yellow solid; m.p. 208-210 °C (petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 8.05$  (s, 1 H), 7.84–7.78 (m, 2 H), 7.44–7.34 (m, 12 H), 7.28– 7.24 (m, 2 H), 7.00–6.94 (m, 2 H), 6.69 (d, J = 8.0 Hz, 1 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 144.1, 143.3, 143.0, 140.2, 140.1, 138.5, 137.3, 133.6, 133.1, 132.7, 129.5, 129.4, 129.1, 129.0, 128.9, 128.1, 128.0, 127.9, 127.8, 127.1, 126.0, 125.1, 125.0, 124.4, 120.0, 117.0 ppm. MS: m/z (%) = 380 (100) [M<sup>+</sup>]. IR (neat):  $\tilde{v}$  = 3054, 1592, 1493, 1465, 1436, 1264, 1073, 1026, 884 cm<sup>-1</sup>. HRMS: calcd. for C<sub>30</sub>H<sub>20</sub> (M<sup>+</sup>) 380.1565; found 380.1563.

The following compounds were prepared according to this procedure.

11-[Bis(p-tolvl)methylene]-11H-benzo[b]fluorene (3b): The reaction of 1b (66 mg, 0.2 mmol), 2a (119 mg, 0.4 mmol), PPh<sub>3</sub> (6 mg, 0.02 mmol), CsF (121 mg, 0.8 mmol), and Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol) in MeCN (5 mL) afforded 3b (80 mg, 98%) as a yellow solid (eluent: petroleum ether); m.p. 236-238 °C (petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.07 (s, 1 H), 7.85–7.79 (m, 2 H), 7.40–7.19 (m, 12 H), 7.13 (s, 1 H), 6.99 (t, J = 7.6 Hz, 1 H), 6.80 (d, J = 8.0 Hz, 1 H), 2.46 (s, 3 H), 2.41 (s, 3 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 144.5, 140.5, 140.4, 140.3, 140.0, 138.5, 138.0, 137.9, 137.6, 133.1, 133.0, 132.7, 129.8, 129.7, 129.6, 129.5, 129.1, 127.8, 127.6, 127.0, 125.9, 125.0, 124.9, 124.1, 120.0, 116.9 ppm. MS: m/z (%) = 408 (67) [M<sup>+</sup>], 55 (100). IR (neat):  $\tilde{v} = 2916, 1908, 1592, 1502, 1464, 1427, 1272, 1182, 1109, 1019,$ 950, 887 cm<sup>-1</sup>. HRMS: calcd. for  $C_{32}H_{24}$  (M<sup>+</sup>) 408.1878; found 408.1871.

11-[Bis(m-tolyl)methylene]-11H-benzo[b]fluorene (3c): The reaction of 1c (66 mg, 0.2 mmol), 2a (119 mg, 0.4 mmol), PPh<sub>3</sub> (6 mg, 0.02 mmol), CsF (121 mg, 0.8 mmol) and Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol) in MeCN (5 mL) afforded 3c (69 mg, 84%) as a yellow solid (eluent: petroleum ether); m.p. 210-212 °C (petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.06 (s, 1 H), 7.85–7.79 (m, 2 H), 7.39–7.19 (m, 12 H), 7.01–6.69 (m, 2 H), 6.69 (d, J =8.0 Hz, 1 H), 2.37-2.36 (m, 6 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): *δ* = 144.6, 143.2, 143.0, 140.2, 140.1, 138.8, 138.7, 138.7, 138.6, 138.6, 138.5, 137.4, 133.3, 133.1, 132.8, 129.8, 129.7, 129.1, 128.9, 128.8, 127.8, 127.7, 127.1, 126.5, 126.4, 126.0, 125.1, 124.5, 120.0, 116.9, 21.5, 21.4 ppm. MS: m/z (%) = 408 (100) [M<sup>+</sup>].

TMS





IR (neat):  $\tilde{\nu}$  = 2982, 1595, 1429, 1268, 1165, 1050, 889 cm  $^{-1}.$  HRMS: calcd. for  $C_{32}H_{24}~(M^+)$  408.1878; found 408.1875.

11-[Bis(o-tolyl)methylene]-11H-benzo[b]fluorene (3d): The reaction of 1d (66 mg, 0.2 mmol), 2a (119 mg, 0.4 mmol), PPh<sub>3</sub> (6 mg, 0.02 mmol), CsF (121 mg, 0.8 mmol) and Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol) in MeCN (5 mL) afforded of 3d (70 mg, 85%) as a yellow oil (eluent: petroleum ether). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]-DMSO, 80 °C):  $\delta$  = 8.31 (s, 1 H), 7.98 (d, J = 7.0 Hz, 1 H), 7.89 (d, J = 8.5 Hz, 1 H), 7.44–7.21 (m, 12 H), 7.02 (t, J = 8.0 Hz, 1 H), 6.78 (s, 0.4 H), 6.71 (s, 0.6 H), 6.51 (d, J = 8.0 Hz, 0.4 H), 6.45 (d, J = 8.0 Hz, 0.6 H), 2.30 (s, 1.7 H), 2.29 (s, 1.7 H), 2.17 (s, 1.3 H)H), 2.16 (s, 1.3 H) ppm. <sup>13</sup>C NMR (125 MHz, [D<sub>6</sub>]DMSO, 80 °C):  $\delta = 142.4, 142.4, 142.1, 141.5, 141.1, 140.5, 140.0, 139.8, 139.5,$ 138.3, 138.3, 137.1, 136.8, 136.4, 136.4, 135.3, 134.7, 134.5, 133.4, 133.3, 132.9, 132.9, 131.6, 131.5, 131.3, 131.2, 130.3, 129.1, 129.0, 128.9, 128.9, 128.7, 128.7, 128.6, 128.6, 128.4, 128.3, 128.2, 127.5, 127.3, 127.2, 127.1, 126.9, 126.9, 126.2, 126.2, 124.2, 123.9, 123.5, 123.2, 121.0, 118.0, 117.9, 20.2, 20.2, 20.1, 20.0 ppm. MS: m/z (%) = 408 (100) [M<sup>+</sup>]. IR (neat):  $\tilde{v}$  = 3054, 2920, 1578, 1428, 1377, 1264, 1114, 1035, 949, 886 cm<sup>-1</sup>. HRMS: calcd. for  $C_{32}H_{24}$  (M<sup>+</sup>) 408.1878; found 408.1882.

**11-[Bis(4-methoxyphenyl)methylene]-11***H*-benzo[*b*]fluorene (3e): The reaction of **1e** (73 mg, 0.2 mmol), **2a** (119 mg, 0.4 mmol), PPh<sub>3</sub> (6 mg, 0.02 mmol), CsF (121 mg, 0.8 mmol), and Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol) in MeCN (5 mL) afforded **3e** (82 mg, 93%) as a yellow solid (eluent: petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 10:1); m.p. 238–239 °C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.08 (s, 1 H), 7.87–7.80 (m, 2 H), 7.45–7.24 (m, 9 H), 7.02–6.84 (m, 6 H), 3.88 (s, 3 H), 3.85 (s, 3 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 159.8, 159.7, 144.1, 140.7, 139.9, 138.5, 137.8, 135.9, 135.7, 132.9, 132.8, 131.7, 131.6, 129.1, 127.8, 127.4, 127.0, 125.8, 125.0, 124.7, 123.7, 120.0, 116.9, 114.2, 114.1, 55.4, 55.3 ppm. MS: *m/z* (%) = 440 (100) [M<sup>+</sup>]. IR (neat):  $\tilde{v}$  = 2919, 2849, 1601, 1505, 1459, 1365, 1283, 1245, 1178, 1107, 1027, 892 cm<sup>-1</sup>. HRMS: calcd. for C<sub>32</sub>H<sub>24</sub>O<sub>2</sub> (M<sup>+</sup>) 440.1776; found 440.1781.

11-[Bis(4-fluorophenyl)methylene]-11H-benzo[b]fluorene (3f): The reaction of 1f (68 mg, 0.2 mmol), 2a (119 mg, 0.4 mmol), PPh<sub>3</sub> (6 mg, 0.02 mmol), CsF (121 mg, 0.8 mmol) and Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol) in MeCN (5 mL) afforded 3f (80 mg, 96%) as a yellow solid (eluent: petroleum ether); m.p. 224-226 °C (petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.06 (s, 1 H), 7.85–7.80 (m, 2 H), 7.43–7.27 (m, 8 H), 7.17–7.07 (m, 5 H), 7.00 (t, J =7.6 Hz, 1 H), 6.71 (d, J = 8.0 Hz, 1 H) ppm. <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ , 25 °C):  $\delta = 162.8$  (d, J = 246.7 Hz), 162.7 (d, J = 246.7 Hz), 141.4, 140.3, 139.9, 139.0 (d, J = 3.2 Hz), 138.8 (d, J = 2.8 Hz), 138.5, 137.1, 134.3, 133.2, 132.7 (d, J = 9.0 Hz), 131.6 (d, J =8.9 Hz), 131.5, 129.1, 128.2, 127.9, 127.2, 126.3, 125.4, 124.8, 124.2, 120.2, 117.2, 116.1 (d, J = 21.3 Hz), 116.0 (d, J = 21.3 Hz) ppm. MS: m/z (%) = 416 (100) [M<sup>+</sup>]. IR (neat):  $\tilde{v}$  = 3050, 1594, 1499, 1428, 1274, 1217, 1155, 1092, 1015, 950, 891 cm<sup>-1</sup>. HRMS: calcd. for C<sub>30</sub>H<sub>18</sub>F<sub>2</sub> (M<sup>+</sup>) 416.1377; found 416.1371.

**11-[Bis(4-chlorophenyl)methylene]-11***H***-benzo[***b***]fluorene (3g): The reaction of 1g (75 mg, 0.2 mmol), 2a (119 mg, 0.4 mmol), PPh<sub>3</sub> (6 mg, 0.02 mmol), CsF (121 mg, 0.8 mmol) and Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol) in MeCN (5 mL) afforded 3g (86 mg, 96%) as a yellow solid (eluent: petroleum ether); m.p. 210–211 °C (petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): \delta = 8.07 (s, 1 H), 7.86–7.81 (m, 2 H), 7.45–7.24 (m, 12 H), 7.12 (s, 1 H), 7.02 (t, J = 7.6 Hz, 1 H), 6.76 (d, J = 8.0 Hz, 1 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): \delta = 141.3, 141.1, 140.7, 140.4, 139.7, 138.5, 136.8, 134.6, 134.4, 134.3, 133.3, 132.7, 131.4, 131.3, 129.3, 129.3, 129.2, 128.4, 127.9, 127.3, 126.4, 125.4, 124.9, 124.4, 120.2, 117.3 ppm. MS:** *m/z* 

(%) = 448 (<sup>35,35</sup>Cl, 100) [M<sup>+</sup>], 450 (<sup>35,37</sup>Cl, 73) [M<sup>+</sup>], 452 (<sup>37,37</sup>Cl, 16) [M<sup>+</sup>]. IR (neat):  $\tilde{v} = 2922$ , 1586, 1484, 1428, 1395, 1270, 1089, 1013, 957, 891 cm<sup>-1</sup>. HRMS: calcd. for C<sub>30</sub>H<sub>18</sub><sup>35</sup>Cl<sub>2</sub> (M<sup>+</sup>) 448.0786; found 448.0778.

**11-[Bis(4-bromophenyl)methylene]-11***H***-benzo[***b***]fluorene (3h): The reaction of <b>1h** (92 mg, 0.2 mmol), **2a** (119 mg, 0.4 mmol), PPh<sub>3</sub> (6 mg, 0.02 mmol), CsF (121 mg, 0.8 mmol) and Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol) in MeCN (5 mL) afforded **3h** (101 mg, 94%) as a yellow solid (eluent: petroleum ether); m.p. 198–199 °C (petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 8.05$  (s, 1 H), 7.84–7.80 (m, 2 H), 7.59–7.23 (m, 12 H), 7.10 (s, 1 H), 7.02 (t, J = 7.6 Hz, 1 H), 6.76 (d, J = 8.0 Hz, 1 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 141.7$ , 141.4, 140.7, 140.4, 139.6, 138.4, 136.8, 134.6, 133.3, 132.7, 132.3, 132.2, 131.6, 131.5, 129.2, 128.4, 127.9, 127.3, 126.4, 125.5, 124.9, 124.4, 122.6, 122.6, 120.2, 117.3 ppm. MS: *m/z* (%) = 536 (<sup>79,79</sup>Br, 50) [M<sup>+</sup>], 538 (<sup>79,81</sup>Br, 100) [M<sup>+</sup>], 540 (<sup>81.81</sup>Br, 53) [M<sup>+</sup>]. IR (neat):  $\tilde{v} = 2910$ , 1576, 1482, 1390, 1273, 1069, 1008, 882 cm<sup>-1</sup>. HRMS: calcd. for C<sub>30</sub>H<sub>18</sub><sup>79</sup>Br<sub>2</sub> (M<sup>+</sup>) 535.9775; found 535.9758.

(*Z*)-11-(1-Phenylethylidene)-11*H*-benzo[*b*]fluorene (3i) and (*E*)-11-(1-Phenylethylidene)-11*H*-benzo[*b*]fluorene (3j): The reaction of 1i (49 mg, 0.2 mmol), 2a (119 mg, 0.4 mmol), of PPh<sub>3</sub> (6 mg, 0.02 mmol), CsF (121 mg, 0.8 mmol) and Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol) in MeCN (5 mL) afforded a mixture of 3i and 3j (1:1) (52 mg, 81%) as a yellow oil (eluent: petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.32 (s, 1 H), 8.11 (s, 1 H), 8.01– 7.74 (m, 7 H), 7.49–7.17 (m, 19 H), 6.88 (t, *J* = 7.6 Hz, 1 H), 6.57 (s, 1 H), 6.30 (d, *J* = 8.0 Hz, 1 H), 2.80 (s, 3 H), 2.72 (s, 3 H) ppm.

**11-(Diphenylmethylene)-2,3-dimethyl-11***H***-benzo[***b***]fluorene (3k): The reaction of <b>1a** (61 mg, 0.2 mmol), **2b** (130 mg, 0.4 mmol), PPh<sub>3</sub> (6 mg, 0.02 mmol), CsF (121 mg, 0.8 mmol) and Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol) in MeCN (5 mL) afforded **3k** (73 mg, 90%) as a yellow solid (eluent: petroleum ether); m.p. 220–222 °C (petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.00 (s, 1 H), 7.79 (d, *J* = 8.4 Hz, 1 H), 7.61 (s, 1 H), 7.45–7.23 (m, 13 H), 6.89 (s, 1 H), 6.39 (s, 1 H), 2.30 (s, 3 H), 2.01 (s, 3 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 143.3, 143.2, 142.8, 138.9, 138.3, 138.2, 137.7, 136.8, 135.6, 133.7, 133.2, 132.5, 129.6, 129.5, 129.1, 128.9, 128.8, 128.0, 127.9, 127.7, 126.2, 125.9, 124.9, 124.3, 121.0, 116.3, 20.4, 20.1 ppm. MS: *m/z* (%) = 408 (100) [M<sup>+</sup>]. IR (neat):  $\tilde{v}$  = 3052, 2918, 1595, 1501, 1488, 1441, 1264, 1073, 1018, 874 cm<sup>-1</sup>. HRMS: calcd. for C<sub>32</sub>H<sub>24</sub> (M<sup>+</sup>) 408.1878; found 408.1873.

**11-(Diphenylmethylene)-4-methyl-11***H*-benzo[*b*]fluorene (3n) and 11-(**Diphenylmethylene)-1-methyl-11***H*-benzo[*b*]fluorene (3o): The reaction of 1a (61 mg, 0.2 mmol), 2e (125 mg, 0.4 mmol), PPh<sub>3</sub> (6 mg, 0.02 mmol), CsF (121 mg, 0.8 mmol) and Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol) in MeCN (5 mL) afforded a mixture of 3n and 3o (1:1, 72 mg, 92%) as a yellow solid (eluent: petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.21 (s, 1 H), 8.06 (s, 1 H), 7.83–7.73 (m, 3 H), 7.54–7.05 (m, 31 H), 6.92–6.85 (m, 2 H), 6.70 (s, 1 H), 6.63 (d, *J* = 8.0 Hz, 1 H), 2.79 (s, 3 H), 1.53 (s, 3 H) ppm.

Synthesis of 11-(Diphenylmethylene)-2,3-difluoro-11*H*-benzo[*b*]fluorene (3l) as a Representative General Procedure for the Preparation of 11-(Diarylmethylene)-11*H*-benzo[*b*]fluorenes 3l and 3m: A rubber-capped Schlenk vessel containing CsF (121 mg, 0.8 mmol) was flame-dried under vacuum and backfilled with nitrogen three times. PPh<sub>3</sub> (6 mg, 0.02 mmol), Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol), and dry MeCN (2 mL) were added sequentially to the Schlenk vessel. After being stirred for about 1 min at 80 °C, a mixture of 1a (61 mg, 0.2 mmol) and 2c (134 mg, 0.4 mmol) in dry MeCN (5 mL) was added by a micro infusion pump over 1 h at 80 °C. The reaction was complete as monitored by TLC. The reaction mixture was fil-

tered through a shot pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (eluent: petroleum ether) to afford **31** (58 mg, 70%) as a yellow solid; m.p. 215–217 °C (petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.93 (s, 1 H), 7.80 (d, *J* = 8.4 Hz, 1 H), 7.56–7.24 (m, 14 H), 7.00 (s, 1 H), 6.40–6.35 (m, 1 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 150.7 (dd, *J* = 248.2, 14.2 Hz), 149.6 (dd, *J* = 243.5, 12.7 Hz), 144.8, 144.7, 142.7, 142.2, 137.1, 137.0, 136.7 (dd, *J* = 7.0, 2.1 Hz), 136.2 (dd, *J* = 6.8, 2.9 Hz), 133.1, 132.6, 132.3, 129.4, 129.3, 129.2, 129.1, 128.6, 128.4, 127.8, 126.4, 125.5, 124.5, 117.1, 113.9, 113.7, 108.2, 108.0 ppm. MS: *m*/*z* (%) = 416 (100) [M<sup>+</sup>]. IR (neat):  $\tilde{v}$  = 2922, 1592, 1474, 1446, 1415, 1345, 1315, 1272, 1155, 1054, 1027, 881 cm<sup>-1</sup>. HRMS: calcd. for C<sub>30</sub>H<sub>18</sub>F<sub>2</sub> (M<sup>+</sup>) 416.1377; found 416.1376.

**9-(Diphenylmethylene)-9***H***-tribenzo[***a***,***c***,***h***]fluorene (3m): According to this procedure, the reaction of <b>1a** (61 mg, 0.2 mmol), **2d** (159 mg, 0.4 mmol), PPh<sub>3</sub> (6 mg, 0.02 mmol), CsF (121 mg, 0.8 mmol) and Pd(dba)<sub>2</sub> (6 mg, 0.01 mmol) in MeCN (5 mL) afforded **3m** (82 mg, 85%) as a yellow solid (eluent: petroleum ether); m.p. 240–242 °C (petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.99 (d, *J* = 8.0 Hz, 1 H), 8.69–8.64 (m, 2 H), 8.47 (d, *J* = 8.4 Hz, 1 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.76–7.25 (m, 12 H), 7.07–6.93 (m, 6 H), 6.83 (s, 1 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 145.4, 143.6, 143.5, 139.5, 138.6, 137.3, 135.5, 135.3, 133.0, 132.4, 132.1, 131.8, 131.2, 130.4, 128.9, 128.8, 128.7, 128.5, 128.2, 127.9, 127.8, 127.2, 127.1, 126.5, 125.8, 125.4, 125.3, 125.2, 124.8, 123.6, 122.8, 121.7, 120.5 ppm. MS: *m/z* (%) = 480 (100) [M<sup>+</sup>]. IR (neat):  $\tilde{v}$  = 3052, 1562, 1488, 1441, 1404, 1264, 1159, 1074, 947, 872 cm<sup>-1</sup>. HRMS: calcd. for C<sub>38</sub>H<sub>24</sub> (M<sup>+</sup>) 480.1878; found 480.1869.

### Suzuki Coupling of C-Br Bonds and C-Cl Bonds in 3g and 3h

11-{Bis[4-(p-tolyl)phenyl]methylene}-11H-benzo[b]fluorene (4a): A rubber-capped Schlenk vessel containing K<sub>3</sub>PO<sub>4</sub> (111 mg, 0.525 mmol) was flame-dried under vacuum and backfilled with nitrogen three times.  $Pd(OAc)_2$  (1 mg, 0.0045 mmol),  $L^{[21]}$  (4 mg, 0.009 mmol), p-tolylboronic acid (88 mg, 0.6 mmol), 3h (81 mg, 0.15 mmol), dioxane (1 mL) and water (8 µL, 8 mg, 0.45 mmol) were added sequentially to the Schlenk vessel. The resulting mixture was heated at 110 °C for 10 h. After the reaction was complete as monitored by TLC, the reaction mixture was filtered through a shot pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 10:1) to afford 4a (77 mg, 92%) as a yellow solid; m.p. 290-291 °C (petroleum ether/CH2Cl2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.06 (s, 1 H), 7.84–7.77 (m, 2 H), 7.66-7.54 (m, 8 H), 7.48-7.44 (m, 4 H), 7.36-7.18 (m, 9 H), 6.98 (t, J = 7.4 Hz, 1 H), 6.90 (d, J = 8.0 Hz, 1 H) ppm. <sup>13</sup>C NMR  $(100 \text{ MHz}, \text{ CDCl}_3, 25 \text{ °C})$ :  $\delta = 143.6, 141.9, 141.6, 140.8, 140.7,$ 140.2, 138.6, 137.7, 137.5, 137.4, 137.3, 133.8, 133.1, 132.8, 130.4, 130.3, 129.6, 129.5, 129.2, 127.9, 127.8, 127.3, 127.2, 126.9, 126.8, 126.0, 125.1, 125.0, 124.4, 120.1, 117.0, 21.1 ppm. MS: m/z (%) = 560 (100) [M<sup>+</sup>]. IR (neat):  $\tilde{v} = 2982, 2905, 1360, 1910, 1493, 1394,$ 1260, 1050, 1004, 887 cm<sup>-1</sup>. HRMS: calcd. for  $C_{44}H_{32}$  (M<sup>+</sup>) 560.2504; found 560.2505.

The following compounds were prepared according to this procedure.

**11-[Bis(4-butylphenyl)methylene]-11***H***-benzo[***b***]fluorene (4b):** The reaction of **3h** (81 mg, 0.15 mmol), butylboronic acid (61 mg, 0.6 mmol), Pd(OAc)<sub>2</sub> (1 mg, 0.0045 mmol), L (4 mg, 0.009 mmol), K<sub>3</sub>PO<sub>4</sub> (111 mg, 0.525 mmol) and water (8 mg, 0.45 mmol) in dioxane (1 mL) afforded **4b** (59 mg, 80%) as a yellow oil (eluent: petroleum). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 8.04$  (s, 1 H), 7.83–7.77 (m, 2 H), 7.43–7.18 (m, 12 H), 7.00–6.94 (m, 2 H), 6.74 (d, *J* 

= 8.0 Hz, 1 H), 2.73–2.64 (m, 4 H), 1.74–1.61 (m, 4 H), 1.48–1.36 (m, 4 H), 1.02–0.94 (m, 6 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 144.8, 143.0, 142.9, 140.8, 140.4, 140.3, 140.1, 138.6, 137.6, 133.3, 133.0, 132.8, 129.5, 129.4, 129.0, 129.0, 128.8, 127.8, 127.6, 127.0, 125.8, 125.0, 124.9, 124.3, 120.0, 116.8, 35.5, 33.7, 33.5, 22.4, 22.3, 14.0, 14.0 ppm. MS: *mlz* (%) = 492 (73) [M<sup>+</sup>], 363 (100). IR (neat):  $\tilde{v}$  = 2954, 2925, 2855, 1580, 1501, 1461, 1427, 1267, 1182, 1108, 1019, 955, 884 cm<sup>-1</sup>. HRMS: calcd. for C<sub>38</sub>H<sub>36</sub> (M<sup>+</sup>) 492.2817; found 492.2820.

11-{Bis[4-(2-phenylethynyl)phenyl]methylene}-11H-benzo[b]fluorene (4c): The reaction of 3h (81 mg, 0.15 mmol), (E)-styrylboronic acid (88 mg, 0.6 mmol), Pd(OAc)<sub>2</sub> (1 mg, 0.02 mmol), L (4 mg, 0.009 mmol), K<sub>3</sub>PO<sub>4</sub> (111 mg, 0.525 mmol) and water (8 mg, 0.45 mmol) in dioxane (1 mL) afforded 4c (79 mg, 90%) as a yellow solid (eluent: petroleum ether/ $CH_2Cl_2 = 10:1$ ); m.p. 245–246 °C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ = 8.07 (s, 1 H), 7.86–7.80 (m, 2 H), 7.58–7.52 (m, 8 H), 7.43–7.34 (m, 10 H), 7.30–7.25 (m, 5 H), 7.21–7.16 (m, 4 H), 7.01 (t, J =7.8 Hz, 1 H), 6.91 (d, J = 8.0 Hz, 1 H) ppm. <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 143.4, 142.4, 142.2, 140.3, 140.2, 138.5, 137.4, 137.3, 137.2, 137.1, 133.9, 133.1, 132.8, 130.6, 130.5, 129.3, 129.3, 129.2, 128.7, 128.2, 128.1, 127.9, 127.8, 127.8, 127.1, 127.0, 126.9, 126.6, 126.1, 125.2, 125.0, 124.4, 120.1, 117.1 ppm. MS: m/z (%) = 584 (38) [M<sup>+</sup>], 580 (100). IR (neat):  $\tilde{v} = 2983$ , 2903, 1595, 1502, 1406, 1262, 1072, 964, 885 cm<sup>-1</sup>. HRMS: calcd. for C<sub>46</sub>H<sub>32</sub> (M<sup>+</sup>) 584.2504; found 584.2512.

11-{Bis[4-(3-methoxyphenyl)phenyl]methylene}-11H-benzo[b]fluorene (4f): The reaction of 3h (67 mg, 0.15 mmol), 3-methoxyphenylboronic acid (109 mg, 0.6 mmol), Pd(OAc)<sub>2</sub> (1 mg, 0.0045 mmol), L (4 mg, 0.009 mmol), K<sub>3</sub>PO<sub>4</sub> (111 mg, 0.525 mmol) and water (8 mg, 0.45 mmol) in dioxane (1 mL) afforded 4f (81 mg, 83%) as a yellow solid (eluent: petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 5:1); m.p. 135–137 °C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 8.06 (s, 1 H), 7.85–7.78 (m, 2 H), 7.69–7.64 (m, 4 H), 7.52–7.47 (m, 4 H), 7.41–7.18 (m, 11 H), 6.99 (t, J = 8.0 Hz, 1 H), 6.94–6.90 (m, 3 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 160.1, 160.0, 143.2, 142.4, 142.1, 142.0, 141.9, 140.8, 140.7, 140.3, 140.1, 138.5, 137.3, 134.0, 133.1, 132.8, 130.3, 130.2, 129.9, 129.8, 129.1, 128.0, 127.8, 127.6, 127.5, 127.2, 126.1, 125.2, 125.0, 124.5, 120.1, 119.6, 119.5, 117.1, 112.9, 112.9, 112.8, 55.3, 55.3 ppm. MS: m/z (%) = 592 (100) [M<sup>+</sup>]. IR (neat):  $\tilde{v}$  = 2985, 2903, 1594, 1478, 1427, 1395, 1295, 1217, 1051, 866 cm<sup>-1</sup>. HRMS: calcd. for C44H32O2 (M<sup>+</sup>) 592.2402; found 592.2405.

### Sonogashira Coupling of the C-Br Bonds in 3h

11-{Bis[4-(*E*)-styrylphenyl]methylene}-11*H*-benzo[*b*]fluorene (4d):<sup>[22]</sup> A rubber-capped Schlenk vessel containing 3h (81 mg, 0.15 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (6 mg, 0.01 mmol) and AuCl(PPh<sub>3</sub>) (6 mg, 0.01 mmol) was dried under vacuum and backfilled with nitrogen three times. Et<sub>3</sub>N (92 mg, 0.9 mmol), 1-ethynylbenzene (34 mg, 0.33 mmol), and dry DMF (1 mL) were added sequentially to the Schlenk vessel. The resulting mixture was then allowed to stir at 80 °C. After 12 h, the reaction was complete as monitored by TLC. The reaction mixture was then cooled to room temp. and diluted with diethyl ether (5 mL). The mixture was poured into water, and the aqueous layer was extracted with diethyl ether (10 mL  $\times$  3). The combined organic layer was dried with anhydrous MgSO<sub>4</sub>, and the solvent was evaporated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/ $CH_2Cl_2$  = 10:1) to afford 4d (78 mg, 90%) as a yellow solid; m.p. 240-241 °C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ = 8.07 (s, 1 H), 7.85–7.80 (m, 2 H), 7.63–7.55 (m, 8 H), 7.46–7.28 (m, 14 H), 7.22 (s, 1 H), 7.01 (t, J = 7.8 Hz, 1 H), 6.84 (d, J =



7.6 Hz, 1 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 142.8, 142.6, 142.2, 140.4, 139.9, 138.5, 137.0, 134.5, 133.3, 132.8, 132.2, 132.1, 131.7, 131.6, 130.3, 130.2, 129.3, 128.4, 128.4, 128.3, 127.9, 127.2, 126.3, 125.3, 125.1, 124.5, 123.3, 123.2, 123.1, 123.0, 120.1, 117.2, 90.6, 90.5, 89.3, 89.2 ppm. MS: *m*/*z* (%) = 580 (100) [M<sup>+</sup>]. IR (neat):  $\tilde{v}$  = 2982, 1596, 1503, 1426, 1399, 1266, 1069, 1019, 955, 879 cm<sup>-1</sup>. HRMS: calcd. for C<sub>46</sub>H<sub>28</sub> (M<sup>+</sup>) 580.2191; found 580.2193.

11-{Bis[4-(hex-1-ynyl)phenyl]methylene}-11H-benzo[b]fluorene (4e):<sup>[23]</sup> A rubber-capped Schlenk vessel containing 3h (81 mg, 0.15 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (5 mg, 0.075 mmol) and CuI (3 mg, 0.015 mmol) was dried under vacuum and backfilled with nitrogen three times. Piperdine (1 mL) and hex-1-yne (49 mg, 0.6 mmol) were added sequentially to the Schlenk vessel. The resulting mixture was then allowed to stir at 60 °C. After 7 h, the reaction was complete as monitored by TLC. The reaction mixture was cooled to room temp. and diluted with diethyl ether (5 mL). The mixture was poured into water, and the aqueous layer was extracted with diethyl ether (10 mL  $\times$  3). The combined organic layer was dried with anhydrous MgSO<sub>4</sub>, and the solvent was evaporated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether) to afford 4e (63 mg, 86%) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.07 (s, 1 H), 7.85–7.81 (m, 2 H), 7.48–7.27 (m, 12 H), 7.20 (s, 2 H), 6.99 (t, J = 7.8 Hz, 1 H), 6.81 (d, J = 8.0 Hz, 1 H), 2.49–2.44 (m, 4 H), 1.68–1.61 (m, 4 H), 1.55–1.48 (m, 4 H), 1.00–0.95 (m, 6 H) ppm. <sup>13</sup>C NMR  $(100 \text{ MHz}, \text{ CDCl}_3, 25 \text{ °C})$ :  $\delta = 142.7, 142.1, 142.0, 140.3, 140.0,$ 138.5, 137.1, 134.1, 133.2, 132.8, 132.1, 132.0, 130.1, 130.0, 129.3, 128.1, 127.8, 127.2, 126.2, 125.2, 125.1, 124.4, 124.1, 124.0, 120.1, 117.1, 91.7, 91.7, 80.5, 80.4, 30.8, 30.8, 22.1, 22.0, 19.2, 19.1, 13.7, 13.6 ppm. MS: m/z (%) = 540 (28) [M<sup>+</sup>], 185 (100). IR (neat):  $\tilde{v}$  = 3054, 2956, 2928, 2865, 1501, 1462, 1428, 1325, 1104, 1017, 885 cm<sup>-1</sup>. HRMS: calcd. for  $C_{42}H_{36}$  (M<sup>+</sup>) 540.2817; found 540.2820.

**X-ray Crystal Data for 3a:**  $C_{30}H_{20}$ ,  $M_r = 380.46$ , crystal system: orthorhombic, space group: *Pca21*, final *R* indices  $[I > 2\sigma(I)]$ : *R1* = 0.0446, *wR2* = 0.0843, *R* indices (all data): *R1* = 0.0800, *wR2* = 0.1005, *a* = 18.7779(13) Å, *b* = 13.4178(7) Å, *c* = 8.1839(5) Å, *a* = 90.00°,  $\beta$  = 90.00°,  $\gamma$  = 90.00°, *V* = 2062.0(2) Å<sup>3</sup>, *T* = 293(2) K, *Z* = 4, reflections collected/unique: 9118/2029 [*R*(int) = 0.0556], number of observations [ $I > 2\sigma(I)$ ]:1372, parameters: 271.

CCDC-807039 (for **3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Supporting Information** (see footnote on the first page of this article): <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all the products.

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