JOC The Journal of Organic Chemistry

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# Bi(III)-Catalyzed Intermolecular Reactions of (*Z*)-Pent-2-en-4-yl Acetates with Ethynylarenes for the Construction of Multisubstituted Fluorene Skeletons through a Cascade Electrophilic Addition/Cycloisomerization Sequence

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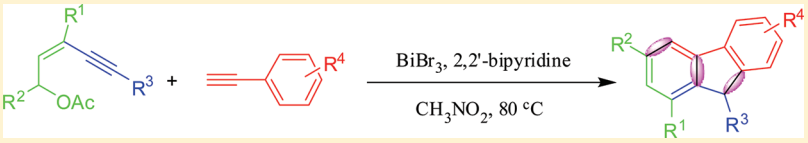
Supporting Information




**ABSTRACT:** A Bi(III)-catalyzed method for the synthesis of highly conjugated aromatic multisubstituted fluorene with (*Z*)-pent-2-en-4-yl acetates and ethynylarenes via domino reaction is described. In this process, the reaction appears to be very general and suitable for a variety of multisubstituted fluorene.

Polycyclic aromatic hydrocarbons (PAHs) have been of great interest especially in materials science because of their utility in organic electronics, such as light-emitting diodes, field-effect transistors, and solar cells.[1] In particular, fluorene derivatives are notable structural motifs for the diverse PAH derivatives having various applications as dyes or optical brightening agents.[2] In addition, while some types of fluorene-bearing compounds exhibit interesting bioactivities,[3] they are also frequently utilized as effective ligands in organometallic chemistry.[4] Consequently, they have drawn considerable interest for synthetic chemists. The classical method for the synthesis of fluorenes includes addition of organometals to 9-fluorenones;[5] Friedel−Crafts ring closure of biarylmethanols, which utilizes a large excess of strong Brønsted acids such as HCl/HOAc1k[6] or PPA at refluxing temperatures,[7] or an equal or excess amount of $BF_3{\cdot}Et_2O$;[8] Friedel−Crafts alkylation of fluorenes;[9] metal-catalyzed or -mediated reactions including Pd-catalyzed rearrangement reactions;[10] Pd-catalyzed annulative reaction of dihalobenzenes with hindered Grignard reagents;[11] activation of C−F/C−H bonds of *o*-arylated *α*,*α*,*α*-trifluorotoluene derivatives,[12] etc. Although these methods are effective for the synthesis of fluorenes, they have certain drawbacks, for example, a strong acid medium or a stoichiometric amount of Lewis acid sometimes is required. For these reasons, a direct and preparative method for functionalized PAHs is considered to be highly urgent.

In the context of our ongoing efforts to synthesis PAHs derivatives,[13] we found that (*Z*)-pent-2-en-4-yl acetates might be perfect substrates in a domino process.[14] We envision that (*Z*)-1,3,5-triphenylpent-2-en-4-ynyl acetated derivatives could realize an isomerization/Friedel−Crafts type reaction to afford highly conjugated carbon-rich fluorene in the presence of Lewis acid. Herein, we report Bi(III)-catalyzed[15] tandem isomerization/Friedel−Crafts reaction to synthesize multisubstituted fluorene via carbon−carbon bond formation.

We started by treating (*Z*)-1,3,5-triphenylpent-2-en-4-ynyl acetate **1a** (0.3 mmol) and 1-ethynyl-4-methylbenzene **2a** (2.0 equiv) with 5 mol % of $Bi(OTf)_3$ in $CH_3NO_2$ (5 mL), and the desired product **3aa** was formed in 15% yield after 7 h. It is worth mentioning that we confirmed the structure of **3la** unambiguously through an X-ray crystal analysis.[16] Further investigations demonstrated that the addition of certain ligands dramatically changed the reaction progress and the 2,2′-bipyridine was the best choice (entry 2) in all ligands we examined, which would change the strength of the Lewis acid and make the reaction proceed efficiently. Compared with $BiBr_3$, other Bi salts as catalysts were less effective (Table 1, entries 8−10). In addition, other Lewis acids and Brønsted acids as catalyst did not give better results (entries 11−15). Other solvents such as $CH_3CN$, $CH_2Cl_2$, and toluene were also evaluated in the presence of $BiBr_3$, and no superior result was obtained (entries 16−18). The polar solvent of $MeNO_2$ may have good solubility with metal complexes. Thus, (*Z*)-pent-2-en-4-yl acetates **1** (0.3 mmol), aryl acetylenes (0.6 mmol), $BiBr_3$ (10 mol %), 2,2′-bipyridine (20 mol %), and $CH_3NO_2$ (5 mL) at 80 °C were chosen as the standard conditions.

Encouraged by our initial results, we sought to examine the scope and the generality of the method under the optimized reaction conditions. The reactions of **1a** with various aryl acetylenes

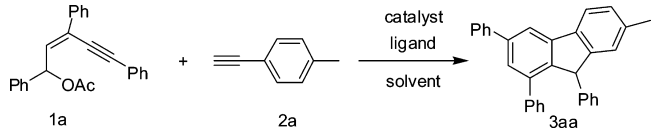
**Received:** December 19, 2011
**Published:** January 11, 2012





dx.doi.org/10.1021/jo202607z | *J. Org. Chem.* 2012, 77, 2064−2068

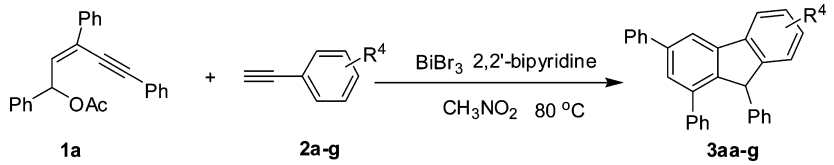
**Table 1. Optimization Conditions**[a]




| entry | catalyst | solvent | ligand | time (h) | yield (%) |
|---|---|---|---|---|---|
| 1 | $Bi(OTf)_3$ | $CH_3NO_2$ | none | 7 | 15 |
| 2 | $Bi(OTf)_3$ | $CH_3NO_2$ | 2,2′-bipyridine | 9 | 61 |
| 3 | $Bi(OTf)_3$ | $CH_3NO_2$ | 2,2′:6′,2″-terpyridine | 12 | 51 |
| 4 | $Bi(OTf)_3$ | $CH_3NO_2$ | TMEDA | 18 | 42 |
| 5 | $Bi(OTf)_3$ | $CH_3NO_2$ | 1,10-phenanthroline | 13 | 39 |
| 8 | $BiCl_3$ | $CH_3NO_2$ | 2,2′-bipyridine | 10 | 72 |
| 9 | $BiBr_3$ | $CH_3NO_2$ | 2,2′-bipyridine | 9 | 78 |
| 10 | $BiI_3$ | $CH_3NO_2$ | 2,2′-bipyridine | 9 | 65 |
| 11 | $FeCl_3$ | $CH_3NO_2$ | 2,2′-bipyridine | 6 | 32 |
| 12 | $CuBr_2$ | $CH_3NO_2$ | 2,2′-bipyridine | 10 | |
| 14 | $BF_3{\cdot}Et_2O$ | $CH_3NO_2$ | 2,2′-bipyridine | 6 | trace |
| 15 | TsOH | $CH_3NO_2$ | 2,2′-bipyridine | 11 | trace |
| 16 | $BiBr_3$ | $CH_3CN$ | 2,2′-bipyridine | 12 | 48 |
| 17 | $BiBr_3$ | $CH_2Cl_2$ | 2,2′-bipyridine | 14 | trace |
| 18 | $BiBr_3$ | Toluene | 2,2′-bipyridine | 14 | 13 |

[a]Reactions were carried out at 80 °C using **1a** (0.3 mmol), **2a** (0.6 mmol), 10 mol % of catalyst, and 20 mol % of ligand.

**Table 2. Test of Ethynylarene Scope**[a]




| entry | $R^4$ | product | time (h) | yield (%) |
|---|---|---|---|---|
| 1 | 4-$CH_3$ | **3aa** | 9 | 78 |
| 2 | H | **3ab** | 10 | 69 |
| 3 | 4-$OCH_3$ | **3ac** | 6 | 65 |
| 4 | 2,4-di$CH_3$ | **3ad** | 8 | 61 |
| 5 | 4-Ph | **3ae** | 11 | 59 |
| 6 | 4-F | **3af** | 12 | 51 |
| 7 | **2g**[b] | **3ag** | 8 | 76 |

[a]General conditions: **1a** (0.3 mmol) and **2** (0.6 mmol), $BiBr_3$ (10 mol %), 2,2′-bipyridine(20 mol %), $CH_3NO_2$ (5 mL) at 80 °C. [b]**2g** = 2-ethynylnaphthalene.

**2a−g** were investigated. The results are summarized in Table 2. The reactions of **1a** with **2a−e** resulted in 3**aa-ae** in good yields (entries 2−5). When the ethynylarene with electron-withdrawing substituent such as **2f** was used, the yield decreased in 51% (entry 6). Notably, the 2-ethynylnaphthalene also showed good reaction activity and result in 76% (entry 7).

To study the scope of this formation of (*Z*)-pent-2-en-4-yl acetates, various acetates bearing different aryl substituents were examined using **2a** as the electrophilic addition component. It was found that the differently substituted (*Z*)-pent-2-en-4-yl acetates **1a−g** gave good yields. It should be noted that the current condensation reaction of (*Z*)-pent-2-en-4-yl acetates was dependent, to some degree, upon the electronic properties of the aryl substituents $R^1$−$R^3$ in **1**. For example, as a $R^1$ group when substrates bearing electron-withdrawing aryl substituents (Table 3, entries 1−4) or weakly electron-donating substituents (entries 5 and 6) were employed, this reaction could proceed to give the expected products in good yields. When either $R^2$ or $R^3$ in **1** was electron-withdrawing (entries 7−11), the desired products were afforded in good yields.

On the basis of the above experimental results, a possible mechanism for the Bi(III)-catalyzed tandem reactions is proposed (Scheme 1). Initially, $BiBr_3$-promoted deacetoxylation of (*Z*)-pent-2-en-4-yl acetates **1** forms the allylic cation center of **4**. Subsequently, the intermediate **4** is followed by electrophilic addition of ethynylarenes to give the propargylic carbocation **5** and $BiBr_3$ is released for the next catalytic cycle. Then the propargylic carbocation **7** is generated from the intermediate **5** through tandem intramolecular electrophilic addition reaction. Finally, the intermediate **7** undergoes proton elimination to give the intermediate **8** and the subsequent aromatization reaction to afford product **3**.[17]

In summary, we have developed a straightforward method for the synthesis of multisubstituted fluorene with (*Z*)-pent-2-en-4-yl acetates and ethynylarenes catalyzed by $BiBr_3$ via domino reaction, which involved intermolecular electrophilic addition and cycloisomerization aromatization. Variation of substituted


dx.doi.org/10.1021/jo202607z | J. Org. Chem. 2012, 77, 2064−2068

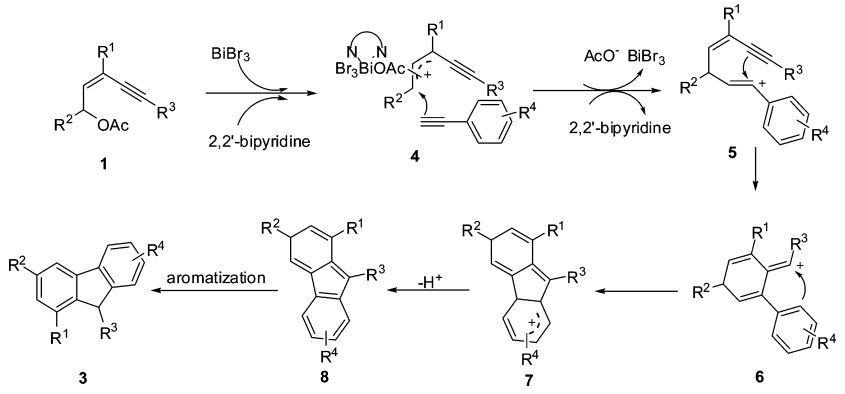
**Table 3. Bi(III)-Catalyzed Synthesis of Fluorene**[a]


1 2a 3

| entry | 1 | $R^1$ | $R^2$ | $R^3$ | product | time (h) | yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | **1b** | 4-F-Ph | Ph | Ph | **3ba** | 9 | 72 |
| 2 | **1c** | 4-Cl-Ph | Ph | Ph | **3ca** | 8 | 71 |
| 3 | **1d** | 4-Br-Ph | Ph | Ph | **3da** | 8 | 73 |
| 4 | **1e** | 4-CN-Ph | Ph | Ph | **3ea** | 8 | 82 |
| 5 | **1f** | 4-$CH_3$-Ph | Ph | Ph | **3fa** | 11 | 61 |
| 6 | **1g** | 2-naphthal | Ph | Ph | **3ga** | 8 | 62 |
| 7 | **1h** | Ph | 4-Cl-Ph | 4-Cl-Ph | **3ha** | 12 | 70 |
| 8 | **1i** | Ph | 4-Br-Ph | 4-Br-Ph | **3ia** | 11 | 69 |
| 9 | **1j** | Ph | 4-CN-Ph | H | **3ja** | 9 | 78 |
| 10 | **1k** | Ph | 4-$NO_2$-Ph | H | **3ka** | 8 | 76 |
| 11 | **1l** | Ph | 4-CN-Ph | 4-$OCH_3$-Ph | **3la** | 9 | 73 |

[a]General conditions: **1** (0.3 mmol), **2a** (0.6 mmol), $BiBr_3$ (10 mol %), 2,2′-bipyridine (20 mol %), $CH_3NO_2$ (5 mL) at 80 °C.

**Scheme 1. Proposed Mechanism**




groups was proven possible and this reaction can proceed smoothly in moderate to good yields.

## EXPERIMENTAL SECTION

**General Procedure 1: Synthesis of (*Z*)-Pent-2-en-4-yl Acetates.** (*Z*)-Pent-2-en-4-yl acetates were prepared according to the literature[18]

**General Procedure for Synthesis of Multisubstituted Fluorene.** To a solution of (*Z*)-pent-2-en-4-yl acetates **1** (0.30 mmol) and ethynylarenes **2** (0.60 mmol) in $CH_3NO_2$ (5.0 mL) were added 10 mmol % of $BiBr_3$ and 20 mmol % of 2,2′-bipyridine at 80 °C. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was quenched by addition of saturated aqueous $NH_4Cl$, diluted with ethyl ether (40 mL), washed with water, and saturated brine, dried over $Na_2SO_4$, and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford the corresponding **3**.

**7-Methyl-1,3,9-triphenyl-9*H*-fluorene (3aa).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.57 (s, 1H), 8.56−8.24 (m, 1H), 8.23−8.22 (m, 2H), 7.80−7.78 (m, 1H), 7.66−7.59 (m, 2H), 7.36−7.34 (m, 2H), 7.27−7.06 (m, 4H), 7.03−6.97 (m, 6H), 6.65−6.30 (m, 2H), 5.16 (s, 1H), 2.33 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 149.2, 148.8, 146.1, 143.3, 142.8, 140.3, 139.8, 138.7, 138.6, 138.2, 137.1, 133.2, 133.1, 129.8, 129.7, 128.4, 128.1, 126.8, 126.3, 125.9, 122.2, 122.1, 119.9, 117.4, 53.7, 21.6. IR (neat, $cm^{-1}$): 3398, 3057, 1601, 1026, 757. Anal. Calcd for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 94.12; H, 5.87.

**1,3,9-Triphenyl-9*H*-fluorene (3ab).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.06 (s, 1H), 7.76−7.74 (m, 2H), 7.50−7.40 (m, 5H), 7.27−7.19 (m, 8H), 6.97−6.95 (m, 3H), 6.67−6.52 (m, 2H), 5.30 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 149.7, 144.9, 142.5, 141.2, 141.2, 140.6, 140.6, 140.4, 128.8, 128.6, 128.4, 128.1, 127.9, 127.7, 127.6, 127.4, 127.3, 127.3, 127.0, 126.0, 125.3, 119.9, 117.4, 53.8. IR (neat, $cm^{-1}$): 3399, 2361, 1508, 1068, 696. Anal. Calcd for $C_{31}H_{22}$: C, 94.38; H, 5.62. Found: C, 94.41; H, 5.58.

**7-Methoxy-1,3,9-triphenyl-9*H*-fluorene (3ac).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.97 (s, 1H), 7.71−7.70 (m, 3H), 7.48−7.34 (m, 4H), 7.25−7.01 (m, 5H), 6.96−6.91 (m, 4H), 6.76−6.74 (m, 1H), 6.66−6.62 (m, 2H), 5.21 (s, 1H), 3.74 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 159.9, 151.0, 142.5, 140.4, 133.4, 129.6, 128.8, 128.8, 128.6, 128.1, 128.1, 127.9, 127.9, 127.8, 127.3, 126.8, 126.5, 126.0, 120.7, 116.6, 113.5, 113.3, 110.6, 55.4, 53.8. IR (neat, $cm^{-1}$): 3369, 2361, 1384, 1066, 756. Anal. Calcd for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 90.49; H, 5.74.

**5,7-Dimethyl-1,3,9-triphenyl-9*H*-fluorene (3ad).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.26 (s, 1H), 7.76−7.74 (m, 2H), 7.51−7.40 (m, 4H), 7.22−7.07 (m, 6H), 6.97−6.92 (m, 4H), 6.61−6.60 (m, 2H), 5.16 (s, 1H), 2.81 (s, 3H), 2.43 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 147.6, 145.8, 143.8, 141.7, 141.3, 140.9, 140.9, 131.7, 129.3, 128.8, 128.6, 128.1, 127.8, 127.8, 127.4, 127.3, 126.8, 126.7, 125.7, 122.3, 121.1, 53.2, 20.3, 16.6. IR (neat, $cm^{-1}$): 3062, 1708, 1592, 1076, 755. Anal. Calcd for $C_{33}H_{26}$: C, 93.80; H, 6.20. Found: C, 93.71; H, 6.29.

**1,3,7,9-Tetraphenyl-9*H*-fluorene (3ae).** $^1$H NMR (400 MHz, $CDCl_3$, ppm):$\delta$ 8.04 (s, 1H), 7.95−7.88 (m, 1H), 7.75−7.73 (m, 2H), 7.60−7.36 (m, 9H), 7.25−7.18 (m, 5H), 6.95−6.92 (m, 3H), 6.68−6.66 (m, 2H), 5.29 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$


dx.doi.org/10.1021/jo202607z | J. Org. Chem. 2012, 77, 2064−2068

149.2, 145.0, 141.2, 141.2, 140.6, 140.2, 139.7, 129.0, 128.8, 128.8, 128.7, 128.6, 128.2, 127.9, 127.7, 127.4, 127.3, 127.3, 127.1, 127.1, 126.6, 126.0, 125.3, 124.0, 119.9, 117.5, 53.9. IR (neat, $cm^{-1}$): 3396, 2361, 1384, 1076, 695. Anal. Calcd for $C_{37}H_{26}$: C, 94.43; H, 5.57. Found: C, 94.51; H, 5.50.

**7-Fluoro-1,3,9-triphenyl-9*H*-fluorene (3af).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.02 (s, 1H), 7.71−7.70 (m, 2H), 7.50−7.37 (m, 5H), 7.25−7.22 (m, 3H), 7.11−7.08 (m, 2H), 6.98−6.65 (m, 5H), 6.64−6.63 (m, 2H), 5.20 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 149.1, 144.9, 142.6, 141.3, 141.1, 140.5, 140.3, 139.6, 130.2, 130.1, 128.8, 128.5, 128.1, 128.0, 127.9, 127.7, 127.6, 127.4, 127.3, 126.1, 125.3, 120.0, 117.6, 114.8, 53.8. IR (neat, $cm^{-1}$): 3398, 2362, 1488, 1089, 696. Anal. Calcd for $C_{31}H_{21}F$: C, 90.26; H, 5.13. Found: C, 90.31; H, 5.08.

**7,8,10-Triphenyl-7*H*-benzo[*c*]fluorene (3ag).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.06−8.03 (m, 2H), 7.95−7.85 (m, 2H), 7.74−7.68 (m, 3H), 7.47−7.45 (m, 2H), 7.37−7.15 (m, 10H), 6.91−6.85 (m, 2H), 6.59−6.57 (m, 2H), 5.60 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 146.6, 144.4, 142.6, 141.2, 141.0, 140.8, 140.4, 140.1, 138.6, 133.7, 128.9, 128.9, 128.8, 128.7, 128.3, 128.0, 127.9, 127.3, 127.3, 127.0, 126.4, 125.8, 125.3, 124.2, 118.5, 117.3, 53.2. IR (neat, $cm^{-1}$): 3405, 2921, 1383, 1075, 697. Anal. Calcd for $C_{35}H_{24}$: C, 94.56; H, 5.44. Found: C, 94.51; H,5.49.

**1-(4-Fluorophenyl)-7-methyl-3,9-diphenyl-9*H*-fluorene (3ba).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$8.02 (s, 1H), 7.80−7.73 (m, 3H), 7.54−7.21 (m, 8H), 7.11−7.01 (m, 5H), 6.71−6.69 (m, 2H), 5.20 (s, 1H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 149.3, 144.8, 142.7, 141.2, 140.8, 139.5, 137.7, 130.8, 128.9, 128.8, 128.2, 128.0, 127.4, 127.3, 127.1, 126.1, 125.9, 119.7, 117.3, 114.8, 53.7, 21.3. IR (neat, $cm^{-1}$): 3408, 2923, 1452, 1026, 697 Anal. Calcd for $C_{32}H_{23}F$: C, 90.11; H, 5.44. Found: C, 90.17; H,5.38.

**1-(4-Chlorophenyl)-7-methyl-3,9-diphenyl-9*H*-fluorene (3ca).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.04 (s, 1H), 7.81−7.74 (m, 3H), 7.52−7.48 (m, 2H), 7.42−7.22 (m, 6H), 7.14−6.89 (m, 5H), 6.69−6.68 (m, 2H), 5.18 (s, 1H), 2.35 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 149.3, 144.8, 142.8, 141.2, 141.1, 140.7, 139.3, 139.2, 137.5, 137.6, 132.8, 129.9, 128.6, 128.3, 128.2, 128.1, 128.0, 127.5, 127.3, 127.0, 126.2, 125.9, 119.8, 117.5, 53.7, 21.6. IR (neat, $cm^{-1}$): 3408, 2920, 1512, 813, 701. Anal. Calcd for: $C_{32}H_{23}Cl$: C, 86.76; H, 5.23. Found: C, 86.69; H,5.28.

**1-(4-Bromophenyl)-7-methyl-3,9-diphenyl-9*H*-fluorene (3da).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.98 (s, 1H), 7.75−7.68 (m, 3H), 7.47−7.44 (m, 2H), 7.37−7.17 (m, 5H), 7.07−6.97 (m, 6H), 6.65−6.63 (m, 2H), 5.13 (s, 1H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 149.2, 144.7, 142.8, 141.2, 141.1, 140.7, 139.6, 139.2, 137.8, 137.6, 130.9, 130.2, 128.8, 128.2, 128.1, 128.0, 127.4, 127.3, 126.8, 126.2, 125.9, 121.0, 119.7, 117.4, 53.6, 21.6. IR (neat, $cm^{-1}$): 3437, 2361, 1634, 1068, 695. Anal. Calcd for: $C_{32}H_{23}Br$: C, 78.85; H, 4.76. Found: C, 78.79; H, 4.85.

**4-(7-Methyl-3,9-diphenyl-9*H*-fluoren-1-yl)benzonitrile (3ea).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.06 (s, 1H), 7.81−7.73 (m, 3H), 7.54−7.36 (m, 5H), 7.28−7.25 (m, 3H), 7.06−6.99 (m, 5H), 6.67−6.65 (m, 2H), 5.17 (s, 1H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): 149.0, 145.5, 144.5, 141.5, 140.3, 138.5, 138.0, 137.3, 131.6, 129.3, 128.9, 128.8, 128.4, 128.1, 128.1, 127.6, 127.3, 126.5, 126.3, 125.8, 119.8, 118.0, 110.7, 53.6, 21.6. IR (neat, $cm^{-1}$): 3398, 2360, 1382, 1067, 695. Anal. Calcd for $C_{33}H_{23}N$: C, 91.42; H, 5.35; N, 3.23. Found: C, 91.35; H,5.42; N, 3.18.

**7-Methyl-3,9-diphenyl-1-*p*-toyl-9*H*-fluorene (3fa).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.96 (s, 1H), 7.78−7.70 (m, 2H), 7.48−7.44 (m, 2H), 7.37−7.25 (m, 2H), 7.24−7.17 (m, 3H), 7.05−6.94 (m, 7H), 6.67−6.65 (m, 2H), 5.21 (s, 1H), 2.31 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 149.4, 144.8, 142.6, 141.3, 141.0, 140.5, 137.8, 137.8, 137.5, 136.4, 129.5, 128.7, 128.6, 128.4, 128.4, 128.2, 127.8, 127.3, 127.3, 125.9, 125.9, 119.6, 116.9, 53.7, 21.6, 21.1. IR (neat, $cm^{-1}$): 3400, 2923, 1450, 1071,758, 695. Anal. Calcd for $C_{33}H_{26}$: C, 93.80; H, 6.20. Found: C, 93.75; H, 6.24.

**7-Methyl-1-(naphthalen-2-yl)-3,9-diphenyl-9*H*-fluorene (3ga).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.05−8.03 (m, 2H), 7.94−7.85 (m, 2H), 7.70−7.68 (m, 2H), 7.48−7.45 (m, 2H), 7.36−7.24 (m, 6H), 7.12−7.05 (m, 3H), 6.89−6.85 (m, 3H), 6.60−6.58 (m, 2H), 5.60 (s, 1H), 2.41(s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 146.7, 142.5, 141.0, 138.6, 137.9, 136.6, 133.6, 130.2, 129.5, 128.9, 128.8, 128.8, 128.7, 128.6, 128.4, 128.3, 128.0, 127.8, 127.4, 127.3, 127.1, 126.9, 126.4, 125.8, 125.2, 124.2, 118.5, 117.1, 53.2, 21.2. IR (neat, $cm^{-1}$): 3396, 2924, 1425, 1066, 670. Anal. Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.31; H, 5.66.

**3,9-Bis(4-chlorophenyl)-7-methyl-1-phenyl-9*H*-fluorene (3ha).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.91 (s, 1H), 7.63−7.61 (m, 2H), 7.44−7.04 (m, 11H), 6.91−6.87 (m, 2H), 6.56−6.51 (m, 2H), 5.18 (s, 1H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 149.3, 144.8, 142.8, 141.3, 141.1, 140.7, 139.3, 139.2, 137.8, 137.6, 132.8, 129.9, 128.9, 128.6, 128.3, 128.2, 128.1, 128.0, 127.2, 127.3, 127.0, 126.2, 125.9, 119.8, 117.5, 53.7, 21.6. IR (neat, $cm^{-1}$): 3399, 2921, 1384, 1024, 757. Anal. Calcd for $C_{32}H_{22}Cl_2$: C, 80.50; H, 4.64. Found: C, 80.49; H, 4.68.

**3,9-Bis(4-bromophenyl)-7-methyl-1-phenyl-9*H*-fluorene (3ia).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.94 (s, 1H), 7.91−7.84 (m, 1H), 7.57 (s, 2H), 7.35−6.97 (m, 12H), 6.50−6.45 (m, 2H), 5.16 (s, 1H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 148.78, 144.7, 140.7, 140.3, 140.1, 139.8, 137.9, 137.6, 131.1, 130.9, 130.2, 129.8, 129.7, 129.6, 128.9, 128.7, 128.5, 128.3, 128.0, 127.8, 127.1, 127.1, 126.8, 125.8, 119.8, 116.9, 53.0, 21.7. IR (neat, $cm^{-1}$): 3398, 2920, 1384, 1021, 757. Anal. Calcd for $C_{32}H_{22}Br_2$: C, 67.87; H, 3.92. Found: C, 67.79; H, 3.88.

**4-(7-Methyl-1,9-diphenyl-9*H*-fluoren-3-yl)benzonitrile (3ga).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.94 (s, 1H), 7.63−7.58 (m, 4H), 7.46−7.37 (m, 1H), 7.28−7.27 (m, 2H), 7.21−7.02 (m, 5H), 6.95−6.92 (m, 4H), 6.63−6.60 (m, 2H), 5.20 (s, 1H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 149.3, 146.2, 145.7, 143.0, 140.9, 140.4, 140.1, 138.9, 138.0, 137.3, 132.5, 131.6, 129.6, 129.3, 128.4, 128.1, 127.9, 127.8, 127.0, 126.0, 125.9, 119.7, 118.9, 117.0, 110.8, 53.7, 21.6. IR (neat, $cm^{-1}$): 3398, 2923, 1601, 1026, 697. Anal. Calcd for $C_{33}H_{23}N$: C, 91.42; H, 5.35; N: 3.23 Found: C, 91.36; H, 5.41; N, 3.19.

**7-Methyl-3-(4-nitrophenyl)-1,9-diphenyl-9*H*-fluorene (3ka).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.29 (s, 2H), 8.05−8.01 (m, 1H), 7.98−7.83 (m, 2H), 7.40−7.02 (m, 9H), 6.97−6.91 (m, 3H), 6.64−6.60 (m, 2H), 5.22 (s, 1H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 149.3, 147.7, 146.5, 143.1, 141.0, 140.3, 140.1, 138.6, 138.1, 137.2, 129.6, 128.6, 128.5, 128.3, 128.1, 128.0, 128.0, 127.9, 127.9, 127.1, 126.0, 124.1, 119.8, 117.2, 53.7, 21.7. IR (neat, $cm^{-1}$): 3396, 2361, 1384, 1075, 698. Anal. Calcd for $C_{32}H_{23}NO_2$: C, 84.74; H, 5.11; N, 3.09. Found: C, 84.66; H, 5.18; N, 3.11.

**4-(9-(4-Methoxyphenyl)-7-methyl-1-phenyl-9*H*-fluoren-3-yl)benzonitrile (3la).** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.97 (s, 1H), 7.84−7.75 (m, 5H), 7.40−7.36 (m, 1H), 7.26−7.15 (m, 5H), 7.06−7.05 (m, 2H), 6.51−6.48 (m, 4H), 5.20 (s, 1H), 3.68 (s, 3H), 2.35 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 157.8, 149.6, 146.5, 145.8, 142.9, 140.9, 140.3, 138.9, 138.0, 137.2, 132.6, 129.0, 128.6, 128.5, 128.4, 128.2, 128.0, 127.8, 127.1, 125.9, 119.7, 117.0, 113.4, 110.9, 55.1, 52.9, 21.6. IR (neat, $cm^{-1}$): 3405, 2923, 1450, 1072, 758, 698. Anal. Calcd for $C_{34}H_{25}NO$: C, 88.09; H, 5.44; N, 3.02. Found: C, 88.03; H,5.41; N, 3.09.

## ■ ASSOCIATED CONTENT

### Supporting Information

$^1$H NMR and $^{13}$C NMR spectra of all products and X-ray data of **3la** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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## ■ ACKNOWLEDGMENTS

We thank the National Basic Research Program of China (973 Program) 2010CB8- 33203 for financial support. We thank the

National Basic Research Program of China (973 Program) (No. 2010CB8-33203) for financial support. We also acknowledge support by the "111" Project.

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