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# A Facile Route to Benzo[*a*]fluorenes *via* a Palladium-Catalyzed Reaction of 2-Alkynylbromobenzene with 2-(2-Alkynylphenyl)-malonate

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**Abstract:** A palladium-catalyzed reaction of 2-alkynylbromobenzenes with 2-(2-alkynylphenyl)-malonates gives rise to benzo[*a*]fluorenes in good yields. This tandem process is efficient with the formation of three bonds from easily available starting materials.

**Keywords:** 2-alkynylbromobenzenes; 2-(2-alkynylphenyl)malonates; benzo[*a*]fluorenes; palladium catalyst; tandem reactions

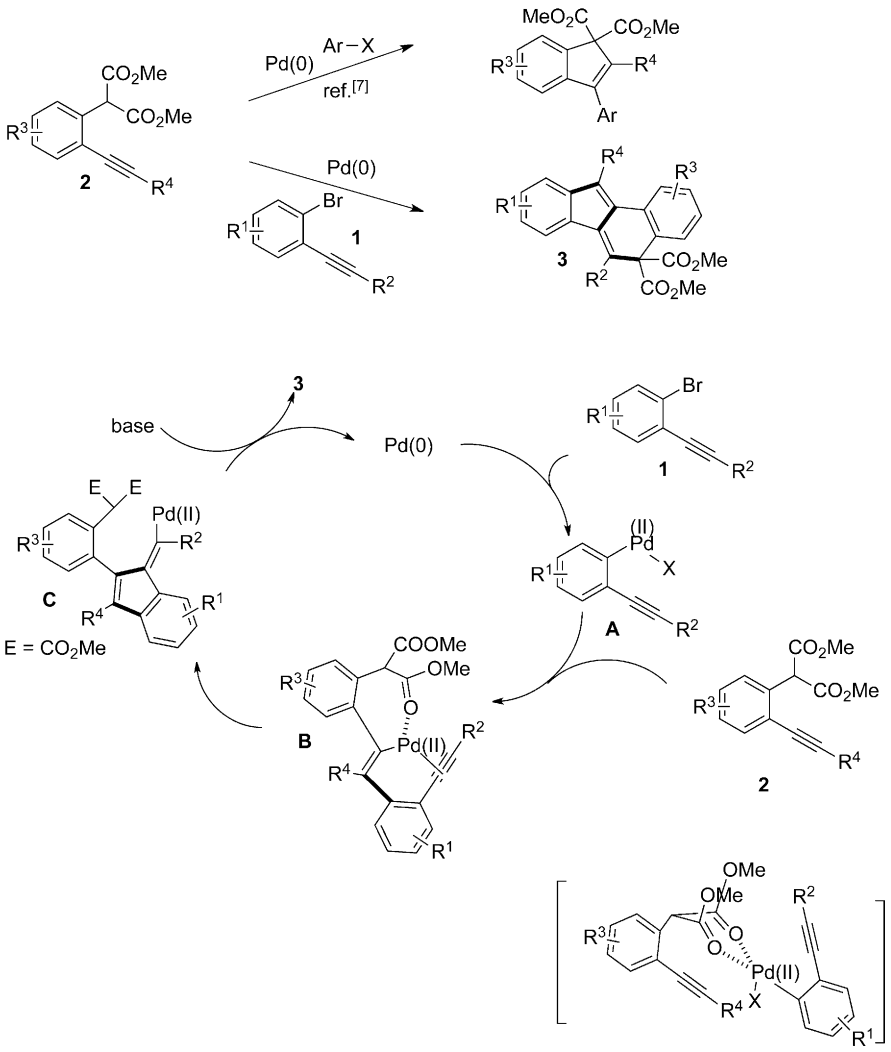
## Introduction

The development of novel routes for the construction of carbocyclic units through a transition metal-catalyzed process has attracted much attention by organic chemists. Although there are developed pathways for the synthesis of carbocycles,[1] utilizing tandem reactions for the generation of polycarbocycles in a one-pot procedure from simple and readily available starting materials is still rare. Among the polycarbocycles, the benzo[*a*]fluorene core as a privileged substructure is attractive. This scaffold (including its reduced and oxidized forms) which has a tetracyclic backbone, can be found widely in natural products[2] and biologically active pharmaceuticals.[3] However, the reported methods for the preparation of this structure typically required multiple steps and toxic reagents.[3a] The lack of a simple, straightforward and efficient synthetic procedure for these polycarbocycles prevents their broader and further applications in chemical biology and medicinal chemistry.[4] Thus, the development of methods for the efficient construction of benzo[*a*]-fluorenes is highly desirable.

A tandem reaction would be the choice for the generation of molecular complexity and diversity.[5] This approach has been successfully utilized in the synthesis of natural product-like compounds. Recently, a powerful strategy using intramolecular or intermolecular double insertion of triple bonds has been applied in the preparation of polyheterocyclic or polycarbocyclic compounds.[6] Prompted by this result and the achievement of tandem reactions, we envisioned that the benzo[*a*]fluorene derivatives could be constructed *via* a palladium-catalyzed reaction of 2-alkynylbromobenzenes with 2-(2-alkynylphenyl)malonates. The proposed synthetic route is illustrated in Scheme 1.

We hypothesized that an oxidative addition of 2-alkynylbromobenzene **1** to Pd(0) would occur first to generate a Pd(II) species **A**. On the basis of our previous work,[6b,c] we believed that the dimethyl malonate group would act as the coupling partner as well as a directing group for control of the regioselectivity. Thus, the regioselectivity of insertion into the triple bond would depend on the coordination of the palladium center with the dimethyl malonate functional group. An impact of the electronic properties of the substitutions is not observed. Therefore, the subsequent coordination and insertion to the triple bond of 2-(2-alkynylphenyl)malonate **2** would result in the formation of intermediate **B**. Then the intramolecular insertion of the triple bond would take place to produce intermediate **C**, which would undergo a C–C coupling to afford the desired benzo[*a*]fluorene **3**. However, there are several significant challenges. Firstly, the generation of indene compounds would be a competitive pathway for the reaction of 2-(2-alkynylphenyl)-malonate **2** in the presence of 2-alkynylbromobenzene




**Scheme 1.** A proposed pathway for the generation of benzo[*a*]fluorenes.

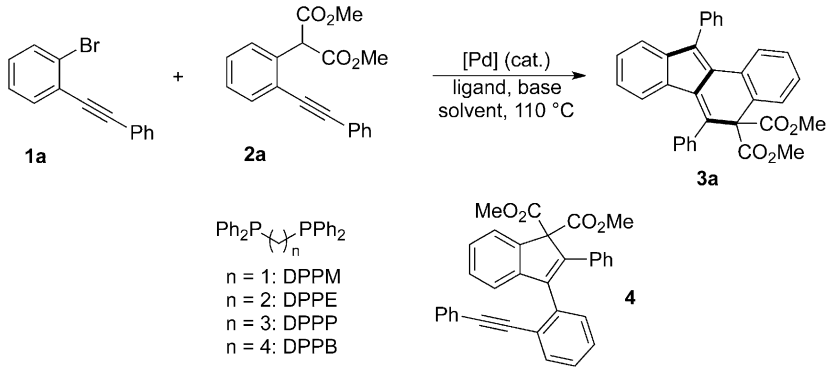
**1** and a palladium catalyst.[7] For instance, Liang reported the preparation of substituted indenes *via* a palladium-catalyzed carboannulation of 2-[2-(1-alkynyl)phenyl]malonate with aryl, benzylic, and alkenyl halides.[7a] Larock described the synthesis of substituted indenes through a palladium-catalyzed cyclization of diethyl 2-[2-(1-alkynyl)phenyl]malonate with organic halides.[7b] Secondly, the coordination between dimethyl malonate and the palladium center is weaker and more complicated compared to other heteroatom nucleophiles, which might hamper the process of insertion of the triple bond. To achieve the proposed synthetic route shown in Scheme 1, we started to explore the feasibility for the construction of benzo[*a*]fluorenes.

## Results and Discussion

To efficiently assemble the benzo[*a*]fluorene scaffold, we first evaluated the reaction using 1-bromo-2-(phenylethynyl)benzene **1a** and dimethyl 2-(2-(phenylethynyl)phenyl)malonate **2a**. To identify the optimal reaction conditions for this reaction, a number of ligands was examined initially in the presence of $Pd(OAc)_2$ (5 mol%) and $K_2CO_3$ in toluene under reflux (Table 1). However, for most cases, the direct carboannulation product **4** dominated, and only a trace amount of benzo[*a*]fluorene **3a** was detected (Table 1, entries 1–5). To our delight, the addition of alkane-tethered bidentate phosphine ligands was proven to be efficient in the reaction, providing the desired product **3a** in low yields (Table 1, entries 6–9). DPPM was the best choice and the corresponding benzo[*a*]fluorene **3a** was isolated in 43% yield (Table 1, entry 9). We further screened various organic and inorganic bases (Table 1, entries 10–13).

**Table 1.** Initial studies for the palladium-catalyzed reaction of 1-bromo-2-(phenylethynyl)benzene **1a** with dimethyl 2-(2-(phenylethynyl)phenyl)malonate **2a**.[a]




| Entry | [Pd] | Ligand | Base | Solvent | Yield [%][b] | |
|---|---|---|---|---|---|---|
| | | | | | **3a** | **4** |
| 1 | $Pd(OAc)_2$ | $PCy_3$ | $K_2CO_3$ | toluene | trace | 64 |
| 2 | $Pd(OAc)_2$ | $(t\text{-}Bu)_3P{\cdot}HBF_4$ | $K_2CO_3$ | toluene | trace | 48 |
| 3 | $Pd(OAc)_2$ | (±)-BINAP | $K_2CO_3$ | toluene | trace | 30 |
| 4 | $Pd(OAc)_2$ | XPhos | $K_2CO_3$ | toluene | trace | 25 |
| 5 | $Pd(OAc)_2$ | $PPh_3$ | $K_2CO_3$ | toluene | trace | 33 |
| 6 | $Pd(OAc)_2$ | DPPB | $K_2CO_3$ | toluene | 30 | 20 |
| 7 | $Pd(OAc)_2$ | DPPP | $K_2CO_3$ | toluene | 24 | 25 |
| 8 | $Pd(OAc)_2$ | DPPE | $K_2CO_3$ | toluene | 25 | 17 |
| 9 | $Pd(OAc)_2$ | DPPM | $K_2CO_3$ | toluene | 43 | 13 |
| 10 | $Pd(OAc)_2$ | DPPM | $Na_2CO_3$ | toluene | N.R. | trace |
| 11 | $Pd(OAc)_2$ | DPPM | $Cs_2CO_3$ | toluene | 40 | trace |
| 12 | $Pd(OAc)_2$ | DPPM | $K_3PO_4$ | toluene | 55 | trace |
| 13 | $Pd(OAc)_2$ | DPPM | $i\text{Pr}_2\text{NEt}$ | toluene | nr | trace |
| 14 | $Pd(OAc)_2$ | DPPM | $K_3PO_4$ | 1,4-dioxane | 30 | 21 |
| 15 | $Pd(OAc)_2$ | DPPM | $K_3PO_4$ | DMF | trace | 30 |
| 16 | $Pd(OAc)_2$ | DPPM | $K_3PO_4$ | DMSO | trace | trace |
| 17 | $Pd(OAc)_2$ | DPPM | $K_3PO_4$ | PhCN | trace | trace |
| 18 | $Pd_2(dba)_3$ | DPPM | $K_3PO_4$ | toluene | trace | 20 |
| 19 | $Pd(PPh_3)_4$ | DPPM | $K_3PO_4$ | toluene | trace | 32 |
| 20 | $Pd(PhCN)_2Cl_2$ | DPPM | $K_3PO_4$ | toluene | trace | 17 |
| 21 | $Pd(CF_3COO)_2$ | DPPM | $K_3PO_4$ | toluene | 20 | 15 |
| 22[c] | $Pd(OAc)_2$ | DPPM | $K_3PO_4$ | toluene | 64 | trace |
| 23[c,d] | $Pd(OAc)_2$ | DPPM | $K_3PO_4$ | toluene | 80 | trace |
| 24[e] | $Pd(OAc)_2$ | DPPM | $K_3PO_4$ | toluene | trace | trace |

[a] *Reaction conditions:* 1-bromo-2-(phenylethynyl)benzene **1a** (0.3 mmol), dimethyl 2-(2-(phenylethynyl)phenyl)malonate **2a** (1.2 equiv.), palladium catalyst (5 mol%), phosphine ligand (10 mol%), base (2.0 equiv.), solvent (2.0 mL), 110 °C.
[b] Isolated yield based on 1-bromo-2-(phenylethynyl)benzene **1a**.
[c] 1.5 equiv. of dimethyl 2-[2-(phenylethynyl)phenyl]malonate **2a** were used.
[d] 6.0 mL of toluene were used.
[e] The reaction was performed at 90 °C.

The transformation worked efficiently in the presence of $K_3PO_4$, leading to the product in 55% yield (Table 1, entry 12). Further investigation indicated that toluene was the best solvent (Table 1, entries 14–17). Other palladium catalysts were examined subsequently, however, the yield was decreased dramatically (Table 1, entries 18–21). Interestingly, the benzo[*a*]fluorene **3a** was obtained in 80% yield when the reaction occurred in toluene at a lower concentration (Table 1, entry 23). The efficiency was retarded when the reaction was run at 90 °C (Table 1, entry 24). The structure of benzo[*a*]fluorene **3a** was unambiguously identified by X-ray diffraction analysis (Figure 1).

After establishing the optimal conditions, we then explored the scope of this palladium-catalyzed tandem reaction of 2-alkynylbromobenzenes **1** with 2-(2-alkynylphenyl)malonates **2**. The results are presented in Scheme 2. All the reactions proceeded smoothly to afford the benzo[*a*]fluorenes **3** in moderate to good yields. Different substituents including

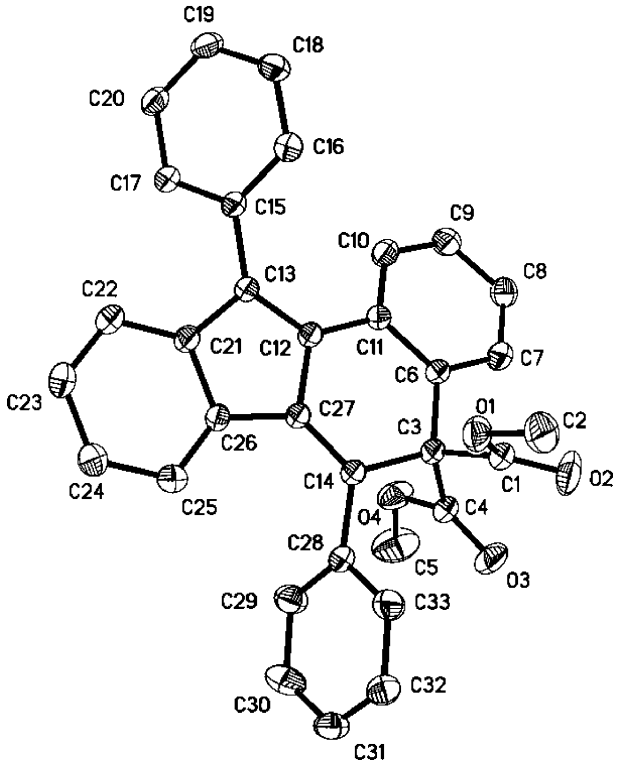



**Figure 1.** ORTEP illustration of benzo[*a*]fluorene **3a** (30% probability ellipsoids).

aryl and alkyl groups attached to the triple bond were all tolerated under the standard conditions. For instance, the 4-acetylphenyl group could be compatible in the reaction, which furnished the expected product **3d** in 88% yield. The thienyl-substituted 2-alkynylbromobenzene was a good reactant as well, although the corresponding product **3g** was formed in 44% yield. Various substrates bearing electron-withdrawing and electron-donating substituents on the aromatic backbone were then examined. As expected, the nature of the substituents did not hamper the efficiency of the conversion.

## Conclusions

In summary, we have described an efficient route for the generation of benzo[*a*]fluorenes *via* a palladium-catalyzed tandem reaction of 2-alkynylbromobenzenes with 2-(2-alkynylphenyl)malonates. A tetracyclic backbone could be constructed in a one-pot procedure with the formation of three C–C bonds. A double insertion of triple bonds is the key step, and the molecular complexity could be easily introduced during the transformation.

## Experimental Section

### General Procedure of the Palladium-Catalyzed Reaction of 2-Alkynylbromobenzene 1 with 2-(2-Alkynylphenyl)malonate 2

2-Alkynylbromobenzene **1** (0.3 mmol), 2-(2-alkynylphenyl)-malonate **2** (0.45 mmol), $Pd(OAc)_2$ (5 mol%), DPPM (5 mol%) and $K_3PO_4$ (0.6 mmol) were placed in the test tube under $N_2$. Toluene (6.0 mL) was added *via* a syringe. The mixture was stirred under reflux. After completion of the reaction as indicated by TLC (usually 10 h), the mixture was cooled to room temperature and the solvent was evaporated. The residue was purified immediately by flash column chromatography on silica gel to give the desired product **3**.

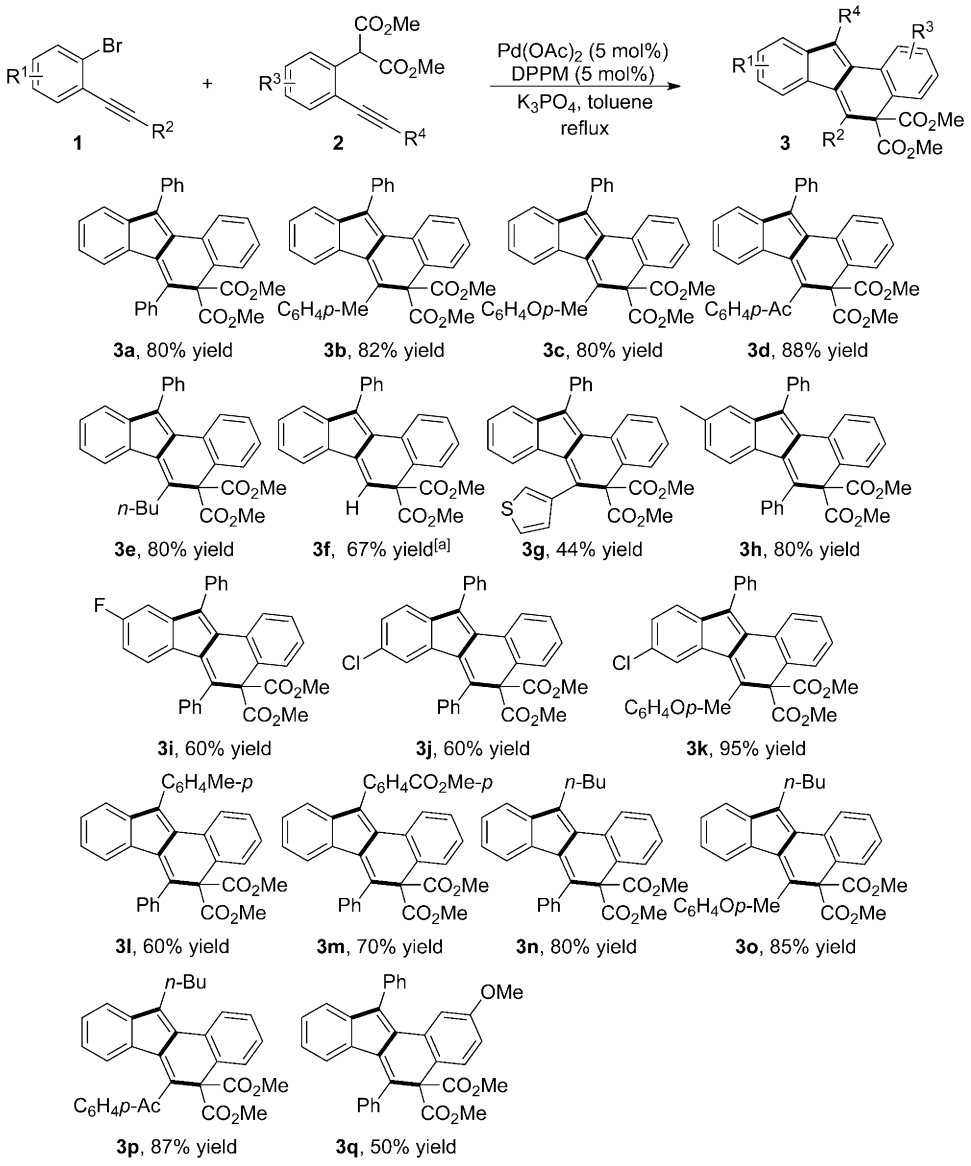
**Dimethyl 6,11-diphenyl-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3a):** yellow solid; mp 175–176 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.54–7.47 (m, 9H), 7.39 (m, 3H), 7.19–7.03 (m, 3H), 6.97 (d, $J$ = 7.2 Hz, 1H), 6.86–6.83 (m, 1H), 6.12 (d, $J$ = 7.2 Hz, 1H), 3.61 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 168.9, 146.3, 139.0, 138.8, 137.5, 136.5, 136.0, 133.5, 132.4, 129.8, 129.2, 129.13, 129.07, 128.9, 128.7, 128.1, 128.05, 127.95, 127.6, 127.0, 125.9, 125.6, 123.5, 120.2, 67.0, 52.8; HR-MS (ESI): $m/z$ = 485.1743, calcd. for $C_{33}H_{25}O_4$ $[M+H]^+$: 485.1753. IR (thin film): $\nu$ = 3060, 2950, 2918, 2849, 1769, 1745, 1596, 1493, 1432, 1218, 1051 cm$^{-1}$.

**Dimethyl 11-phenyl-6-(*p*-tolyl)-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3b):** yellow solid; mp 203–204 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.53–7.49 (m, 6H), 7.37 (d, $J$ = 7.8 Hz, 1H), 7.26 (m, 4H), 7.17–7.09 (m, 2H), 7.06–7.02 (m, 1H), 6.96 (d, $J$ = 7.2 Hz, 1H), 6.88–6.84 (m, 1H), 6.23 (d, $J$ = 7.2 Hz, 1H), 3.61 (s, 6H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 168.9, 146.2, 138.8, 138.6, 138.5, 136.8, 136.0, 134.4, 133.6, 132.5, 129.7, 129.5, 129.1, 129.0, 128.7, 128.0, 127.9, 127.6, 126.9, 125.8, 125.5, 123.5, 120.1, 67.0, 52.8, 21.4; HR-MS (ESI): **m/z** = 499.1916, calcd. for $C_{34}H_{27}O_4$ $[M+H]^+$: 499.1909; IR (thin film): $\nu$ = 3060, 2950, 2926, 1769, 1745, 1591, 1448, 1213, 1051 cm$^{-1}$.

**Dimethyl 6-(4-methoxyphenyl)-11-phenyl-5*H*-benzo[*a*]-fluorene-5,5-dicarboxylate (3c):** yellow solid; mp 219–220 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.53–7.48 (m, 6H), 7.38–7.36 (m, 1H), 7.32–7.30 (m, 2H), 7.18–7.10 (m, 2H), 7.06–7.00 (m, 4H), 6.90–6.87 (m, 1H), 6.29 (d, $J$ = 7.2 Hz, 1H), 3.88 (s, 3H), 3.61 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 169.0, 159.8, 146.2, 138.9, 136.7, 136.0, 133.6, 132.5, 130.5, 129.7, 129.5, 129.1, 128.8, 128.0, 127.9, 127.6, 126.9, 125.8, 125.6, 123.5, 120.1, 114.1, 67.1, 55.2, 52.8; HR-MS (ESI): $m/z$ = 515.1846, calcd. for $C_{34}H_{27}O_5$ $[M+H]^+$: 515.1858; IR (thin film): $\nu$ = 2957, 2911, 2839, 1776, 1745, 1606, 1509, 1242, 1170, 1052 cm$^{-1}$.

**Dimethyl 6-(4-acetylphenyl)-11-phenyl-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3d):** yellow solid; mp 223–224 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.08 (d, $J$ = 6.8 Hz, 2H), 7.55–7.49 (m, 8H), 7.38 (d, $J$ = 7.8 Hz, 1H), 7.20–7.04 (m, 3H), 6.97 (d, $J$ = 7.2 Hz, 1H), 6.86–6.82 (m, 1H), 6.12 (d, $J$ = 7.2 Hz, 1H), 3.62 (s, 6H), 2.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 197.6, 168.7, 146.3, 142.6, 139.5, 139.0, 137.0, 135.6, 135.0, 133.1, 132.0, 129.8, 129.5, 129.1, 128.9, 128.6, 128.4, 128.1, 128.0, 127.4, 127.0, 125.8, 125.7, 123.3, 120.3, 66.9, 52.9, 26.7; HR-MS (ESI): $m/z$ = 527.1858, calcd. for $C_{35}H_{27}O_5$ $[M+H]^+$: 527.1858; IR (thin film): $\nu$ = 3061, 2951, 2926, 1745, 1686, 1602, 1475, 1448, 1400, 1264, 1050 cm$^{-1}$.




[a] Isolated yield based on 2-alkynylbromobenzene **1**.

**Scheme 2.** Investigationof scope for the palladium-catalyzed reaction of 2-alkynylbromobenzenes **1** with 2-(2-alkynylphenyl)-malonates **2**.

**Dimethyl 6-butyl-11-phenyl-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3e):** yellow solid; mp 157–158 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.67$ (d, $J = 6.8$ Hz, 1H), 7.51–7.43 (m, 6H), 7.32–7.23 (m, 3H), 7.15–7.13 (m, 1H), 7.04–7.01 (m, 2H), 3.69 (s, 6H), 2.91–2.90 (m, 2H), 1.59–1.57 (m, 4H), 1.02–1.00 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 169.6$, 146.4, 146.4, 139.5, 137.2, 136.7, 136.2, 132.9, 131.9, 129.7, 129.2, 129.1, 128.7, 127.8, 127.7, 127.6, 126.8, 125.80, 125.75, 123.8, 120.4, 66.3, 53.0, 33.0, 30.9, 23.4, 13.8; HR-MS (ESI): $m/z = 465.2040$, calcd. for $C_{31}H_{29}O_4$ $[M+H]^+$: 465.2066; IR (thin film): $\nu = 3061$, 2954, 2871, 1762, 1736, 1644, 1601, 1451, 1213, 1047 cm$^{-1}$.

**Dimethyl 11-phenyl-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3f):** yellow solidmp 150–151 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.73$–7.71 (m, 2H), 7.53–7.42 (m, 6H), 7.24–7.21 (m, 3H), 7.13 (s, 1H), 7.09–7.02 (m, 2H), 3.78 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 169.7$, 146.1, 140.3, 139.1, 135.7, 133.3, 130.2, 130.1, 129.7, 129.1, 128.9, 128.8, 128.1, 126.9, 126.4, 125.8, 125.7, 121.5, 120.3, 120.1, 61.7, 53.5; HR-MS (ESI): $m/z = 409.1425$, calcd. for $C_{27}H_{21}O_4$ $[M+H]^+$: 409.1440; IR (thin film): $\nu = 3059$, 2952, 2924, 2849, 1735, 1601, 1493, 1474, 1451, 1228, 1041 cm$^{-1}$.

**Dimethyl 11-phenyl-6-(thiophen-3-yl)-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3g):** yellow solid; mp 204–205 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.54$–7.45 (m, 8H), 7.37 (m, 2H), 7.19–7.13 (m, 2H), 7.09–7.05 (m, 2H), 6.99–6.94 (m, 2H), 6.36 (d, $J = 7.8$ Hz, 1H), 3.63 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 169.1$, 146.2, 139.3, 139.2, 137.3, 135.9, 133.4, 132.2, 132.1, 129.7, 129.1, 129.0, 128.3, 128.07, 127.96, 127.4, 126.9, 125.8, 125.1, 123.3, 120.2, 66.8, 53.0;

HR-MS (ESI): $m/z$ = 491.1304, calcd. for $C_{31}H_{23}O_4S$ $[M+H]^+$: 491.1317; IR (thin film): ν = 3065, 2952, 2916, 1766, 1740, 1653, 1596, 1452, 1211, 1052 $cm^{-1}$.

**Dimethyl 9-methyl-6,11-diphenyl-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3h):** yellow solid; mp 206–207 °C; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.54–7.45 (m, 9H), 7.37–7.35 (m, 3H), 7.17–7.13 (m, 1H), 7.05–7.01 (m, 1H), 6.77 (s, 1H), 6.66 (d, $J$ = 7.2 Hz, 1H), 6.01 (d, $J$ = 7.2 Hz, 1H), 3.60 (s, 6H), 2.22 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 169.0, 146.6, 138.9, 138.6, 138.3, 137.6, 136.1, 135.6, 132.4, 130.9, 129.8, 129.2, 129.12, 129.07, 128.8, 128.7, 128.6, 128.0, 127.9, 126.8, 126.3, 125.8, 123.3, 120.9, 66.9, 52.8, 21.5; HR-MS (ESI): $m/z$ = 491.1895; calcd. for $C_{34}H_{27}O_4$ $[M+H]^+$: 499.1909; IR (thin film): ν = 3055, 3024, 2942, 1771, 1745, 1601, 1483, 1437, 1206, 1052 $cm^{-1}$.

**Dimethyl 9-fluoro-6,11-diphenyl-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3i):** yellow solid; mp 193–194 °C; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.54–7.48 (m, 9H), 7.38 (m, 3H), 7.23–7.17 (m, 1H), 7.08–7.04 (m, 1H), 6.67 (d, $J$ = 8.0 Hz, 1H), 6.54–6.49 (m, 1H), 6.05–6.02 (m, 1H), 3.62 (m, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 168.8, 163.3(d, $J$ (C,F) = 245.0 Hz), 148.6 (d, $J$ (C,F) = 8.6 Hz), 137.9, 137.8, 137.2, 136.6, 135.4, 132.6, 129.4, 129.3, 129.2, 128.98, 128.94, 128.85, 128.79, 128.3, 128.0, 127.3, 126.0, 124.6 (d, $J_{C,F}$ = 8.6 Hz), 111.9 (d, $J_{C,F}$ = 22.9 Hz), 107.4 (d, $J_{C,F}$ = 23.8 Hz), 67.0, 52.9; HR-MS (ESI): $m/z$ = 503.1658, calcd. for $C_{33}H_{24}FO_4$ $[M+H]^+$: 503.1659; IR (thin film): ν = 3070, 2947, 2916, 1771, 1730, 1596, 1463, 1216, 1144, 1052 $cm^{-1}$.

**Dimethyl 8-chloro-6,11-diphenyl-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3j):** yellow solid; mp 230–231 °C; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.53–7.48 (m, 8H), 7.37 (m, 3H), 7.20–7.16 (m, 2H), 7.08–7.06 (m, 2H), 6.87 (d, $J$ = 7.8 Hz, 1H), 6.01 (s, 1H), 3.62 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 168.7, 144.6, 138.3, 138.10, 138.06, 136.9, 135.5, 134.9, 132.3, 131.4, 129.5, 129.2, 129.1, 129.0, 128.9, 128.3, 128.0, 127.9, 127.7, 127.2, 125.8, 123.91, 123.87, 120.8, 67.1, 52.9; HR-MS (ESI): $m/z$ = 519.1362, calcd. for $C_{33}H_{24}ClO_4$ $[M+H]^+$: 519.1363. IR (thin film): ν = 3060, 2951, 2849, 1769, 1746, 1601, 1444, 1217, 1047 $cm^{-1}$.

**Dimethyl 8-chloro-6-(4-methoxyphenyl)-11-phenyl-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3k):** yellow solid; mp 202–203 °C; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.52–7.47 (m, 6H), 7.36–7.29 (m, 3H), 7.18–7.15 (m, 1H), 7.09–7.01 (m, 4H), 6.87 (d, $J$ = 7.8 Hz, 1H), 6.23 (s, 1H), 3.88 (s, 3H), 3,61 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 168.8, 160.1, 144.5, 138.3, 138.1, 138.0, 135.5, 135.0, 132.4, 131.3, 130.5, 129.5, 129.2, 129.0, 128.9, 128.2, 128.0, 127.8, 127.1, 125.8, 123.84, 123.80, 120.8, 114.2, 67.2, 55.3, 52.9; HR-MS (ESI): $m/z$ = 549.1469, calcd. for $C_{34}H_{26}ClO_5$ $[M+H]^+$: 549.1469; IR (thin film): ν = 2955, 2925, 2854, 1770, 1730, 1607, 1509, 1445, 1289, 1250, 1046 $cm^{-1}$.

**Dimethyl 6-phenyl-11-(*p*-tolyl)-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3l):** yellow solid; mp 194–195 °C; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.51–7.46 (m, 5H), 7.38–7.33 (m, 6H), 7.18–7.04 (m, 3H), 7.00–6.98 (m, 1H), 6.85–6.81 (m, 1H), 6.12 (d, $J$ = 7.4 Hz, 1H), 3.60 (s, 6H), 2.47 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 169.0, 146.4, 139.2, 138.8, 137.8, 137.6, 136.3, 133.5, 132.8, 132.3, 129.9, 129.8, 129.2, 128.9, 128.8, 128.7, 128.1, 127.9, 127.4, 126.9, 125.9, 125.5, 123.4, 120.2, 67.0, 52.8, 21.4; HR-MS (ESI): $m/z$ = 499.1905, calcd. $C_{34}H_{27}O_4$ $[M+H]^+$: 499.1909; IR (thin film): ν = 3065, 2952, 2916, 1766, 1745, 1596, 1483, 1442, 1432, 1216, 1047 $cm^{-1}$.

**Dimethyl 11-(4-(methoxycarbonyl)phenyl)-6-phenyl-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3m):** yellow solid; mp 189–190 °C; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, $J$ = 7.4 Hz, 2H), 7.60 (d, $J$ = 7.4 Hz, 2H), 7.53–7.47 (m, 4H), 7.38 (m, 2H), 7.31–7.04 (m, 4H), 6.94–6.84 (m, 2H), 6.14 (d, $J$ = 7.4 Hz, 1H), 3.98 (s, 3H), 3.61 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 168.8, 166.9, 145.7, 141.1, 138.6, 137.6, 137.4, 133.4, 132.5, 130.4, 129.8, 129.3, 129.1, 129.0, 128.82, 128.77, 128.2, 128.1, 127.2, 125.8, 123.6, 119.9, 67.1, 52.9, 52.2; HR-MS (ESI): $m/z$ = 543.1807, calcd. for $C_{35}H_{27}O_6$ $[M+H]^+$: 543.1808; IR (thin film): ν = 3065, 2952, 2849, 1766, 1724, 1606, 1437, 1278, 1221, 1057 $cm^{-1}$.

**Dimethyl 11-butyl-6-phenyl-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3n):** yellow solid; mp 121–122 °C; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, $J$ = 7.8 Hz, 1H), 7.53 (d, $J$ = 7.8 Hz, 1H), 7.41 (m, 4H), 7.30–7.16 (m, 5H), 6.83–6.79 (m, 1H), 6.03 (d, $J$ = 7.4 Hz, 1H), 3.55 (s, 6H), 3.00 (t, $J$ = 7.8 Hz, 2H), 1.75–1.73 (m, 2H), 1.60–1.55 (m, 2H), 1.02 (t, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 169.1, 145.8, 140.0, 138.9, 137.6, 134.3, 133.8, 132.1, 130.7, 129.3, 129.1, 128.61, 128.55, 128.48, 127.9, 126.50, 126.46, 125.5, 125.4, 123.3, 118.7, 67.0, 52.7, 30.0, 26.6, 23.3, 14.0; HR-MS (ESI): $m/z$ = 465.2076, calcd. for $C_{31}H_{29}O_4$ $[M+H]^+$: 465.2066; IR (thin film): ν = 3075, 2952, 2865, 1766, 1740, 1591, 1447, 1216, 1047 $cm^{-1}$.

**Dimethyl 11-butyl-6-(4-methoxyphenyl)-5*H*-benzo[*a*]-fluorene-5,5-dicarboxylate (3o):** yellow solid; mp 206–207 °C; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, $J$ = 7.8 Hz, 1H), 7.54 (d, $J$ = 7.8 Hz, 1H), 7.44–7.41 (m, 1H), 7.32–7.21 (m, 5H), 6.95 (d, $J$ = 8.2 Hz, 2H), 6.89–6.85 (m, 1H), 6.20 (d, $J$ = 7.2 Hz, 1H), 3.86 (s, 3H), 3.58 (s, 6H), 3.02 (t, $J$ = 6.8 Hz, 2H), 1.77 (m, 2H), 1.60–1.59 (m, 2H), 1.04 (d, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 169.2, 159.7, 145.7, 139.9, 139.1, 134.4, 133.9, 132.1, 130.7, 130.6, 129.7, 129.0, 128.4, 127.8, 126.6, 126.4, 125.45, 125.38, 123.3, 118.6, 114.0, 67.0, 55.1, 52.7, 30.0, 26.6, 23.3, 14.0; HR-MS (ESI): $m/z$ = 495.2163, calcd. for $C_{32}H_{31}O_5$ $[M+H]^+$: 495.2171; IR (thin film): ν = 3060, 2952, 2870, 1771, 1745, 1601, 1509, 1477, 1288, 1242, 1052 $cm^{-1}$.

**Dimethyl 6-(4-acetylphenyl)-11-butyl-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3p):** yellow solid; mp 180–181 °C; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.05–7.97 (m, 3H), 7.55–7.43 (m, 4H), 7.33–7.19 (m, 3H), 6.84–6.81 (m, 1H), 6.05 (d, $J$ = 7.2 Hz, 1H), 3.59 (s, 6H), 3.02 (t, $J$ = 7.2 Hz, 2H), 2.67 (s, 3H), 1.77 (m, 2H), 1.62–1.57 (m, 2H), 1.04 (t, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 197.7, 168.9, 145.8, 142.7, 140.6, 139.2, 136.8, 133.4, 132.7, 131.7, 130.5, 129.9, 129.1, 128.6, 128.5, 128.3, 126.5, 126.3, 125.5, 125.4, 123.2, 118.9, 66.8, 52.8, 29.9, 26.6, 23.3, 13.9; HR-MS (ESI); $m/z$ = 507.2164, calcd. for $C_{33}H_{31}O_5$ $[M+H]^+$: 507.2171; IR (thin film): ν = 3060, 2957, 2859, 1771, 1745, 1596, 1452, 1401, 1267, 1216, 1047 $cm^{-1}$.

**Dimethyl 2-methoxy-6,11-diphenyl-5*H*-benzo[*a*]fluorene-5,5-dicarboxylate (3q):** yellow solid; mp 191–192 °C; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.55–7.37 (m, 11H), 7.14–7.10 (m, 1H), 6.99–6.97 (m, 1H), 6.89–6.83 (m, 2H), 6.74 (d, $J$ = 8.3 Hz, 1H), 6.12 (d, $J$ = 7.8 Hz, 1H), 3.61 (s, 6H), 3.33 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 169.1, 158.8, 146.2, 139.0, 138.6, 137.6, 136.8, 136.1, 133.5, 130.8, 130.0, 129.3, 129.2, 129.1, 128.7, 128.13, 128.05, 127.9, 125.6, 124.8, 123.6,

120.2, 115.4, 108.6, 66.6, 54.5, 52.8; HR-MS (ESI): $m/z$ = 515.1849, calcd. for $C_{34}H_{27}O_5$ $[M+H]^+$: 515.1858; IR (thin film): $\nu$ = 3057, 2993, 2951, 2835, 1766, 1745, 1604, 1484, 1244, 1049 $cm^{-1}$.

**Dimethyl 2-phenyl-3-(2-(phenylethynyl)phenyl)-1*H*-indene-1,1-dicarboxylate (4):** white solid; mp 56–57 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.69 (m, 1H), 7.61–7.59 (m, 1H), 7.30–7.14 (m, 14H), 6.94–6.93 (m, 2H), 3.75 (s, 3H), 3.28 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 169.0, 168.6, 145.1,144.8, 141.3, 140.4, 137.5, 134.3, 131.9, 131.3, 129.9, 129.5, 128.6, 128.5, 128.0, 127.9, 127.8, 127.6, 127.4, 126.4, 123.9, 123.3, 123.0, 121.8, 93.8, 88.3, 72.3, 53.0, 52.5; HR-MS (ESI): $m/z$ = 485.1749, calcd. for $C_{33}H_{25}O_4$ $[M+H]^+$: 485.1747; IR (thin film): $\nu$ = 3055, 3029, 2947, 2212, 1740, 1596, 1493, 1463, 1226, 1052 $cm^{-1}$.

Crystallographic data for the structure **3a** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 887903. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (internat.): +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

### Supporting Information

Experimental procedures, characterization data, $^1H$ and $^{13}C$ NMR spectra of compounds **3** and **4** re available in the Supporting Information.

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