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PAPER

Palladium(0)-catalyzed cyclization of 1,6-diyn-3-yl carbonates with a nucleophilic functionality: efficient synthesis of polycyclic benzo[*b*]fluorene derivatives *via* allene intermediates†

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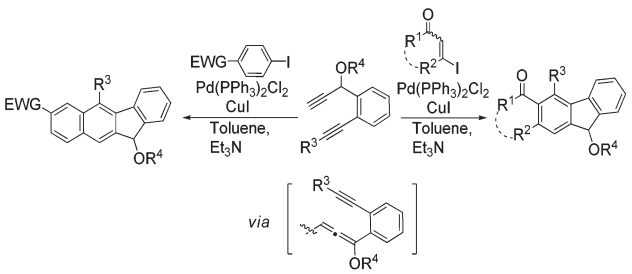
We report in this paper an interesting tandem reaction involving sequential palladium(0)-catalyzed decarboxylation of diynylic carbonates, intramolecular nucleophilic cyclization and Schmittel reaction, which provides a facile method for the synthesis of a variety of polycyclic benzo[*b*]fluorene derivatives from easily accessible starting materials.

Introduction

Construction of polycyclic aromatic ring skeletons has attracted considerable attention in recent years due to their increasing importance in organic material science.[1] The utility of polycyclic aromatic hydrocarbons (PAHs) as organic optoelectronic devices such as light-emitting diodes, field-effect transistors, photovoltaics, acenes, nanographenes and discotic liquid crystals is also important.[2] 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.[3] Therefore, new methods for the efficient synthesis of benzo[*b*]fluorenes are still highly desired.

In the past decades, many novel and useful reactions have been developed based on the chemistry of allenes for the synthesis of useful molecules,[4,5] and some of these reactions have been successfully applied for the synthesis of natural products.[6] It is obvious that the chemistry of allenes will further be extensively explored to show their potential in organic chemistry. The development of novel cascade reactions involving *in situ*-generated reactive functional groups such as allene intermediates is an intensively pursued goal in our group. In this aspect, we previously established a series of sequential reactions wherein an allene intermediate, generated *in situ*, would undergo [4 + 2] cycloaddition reaction under mild conditions, providing an efficient synthesis of structurally complex polycycles with 2,3-dihydrofuran units,[7] structurally diverse fused dihydroisobenzofuran derivatives,[8] and other structurally complex polycycles.[9] Recently we also developed a convenient sequential palladium (0)-catalyzed coupling, propargyl–allenyl isomerization and Schmittel cyclization reaction, leading to polycyclic fluorene derivatives from easily accessible starting materials under mild conditions (Scheme 1).[10]

Based on these studies, we envisioned that palladium(0) catalyst may initially promote decarboxylation of diynylic carbonates **1** to generate an allenylpalladium complex **3**, which would undergo an intramolecular nucleophilic attack by the carbanion to form an allene intermediate **4**. This intermediate **4** may preferentially cyclize to produce a benzofulvene diradical **5** *via* Schmittel reaction; then an intramolecular 1,6-diradical coupling reaction and 1,5-H shift may proceed to furnish benzo[*b*]fluorene derivatives **2** (Scheme 2). By this strategy three new carbon–carbon bonds can be formed to construct the benzene ring in a single stroke meanwhile five rings could be efficiently assembled, affording an attractive synthesis of benzo[*b*]fluorene derivatives. In this paper we wish to report the realization of



Scheme 1 Palladium-catalyzed coupling, propargyl–allenyl isomerization, and Schmittel cyclization reaction for the synthesis of polycyclic fluorene derivatives.

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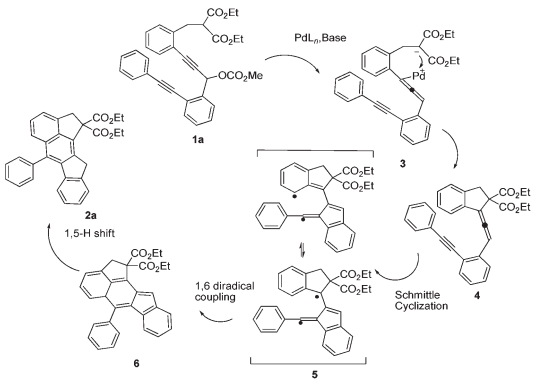
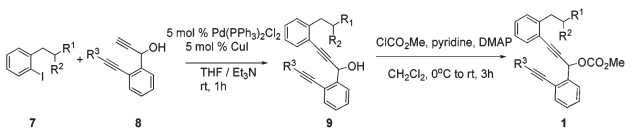
‡Professor Huang passed away on March 6, 2010. He was fully in charge of this project. Professor Luling Wu is helping to finish all the projects with assistance from Professor Shengming Ma.



Scheme 2 Concept of tandem Pd-catalyzed cyclization, and Schmittel cyclization reaction for the synthesis of benzo[*b*]fluorene derivatives.

Table 1 Preparation of acyclic precursors **1**[a]



	9				
Entry	R^1	R^2	R^3		Yield of **1** (%)[b]
1	CO_2Et	CO_2Et	C_6H_5	**9a**	82 (**1a**)
2	CO_2Et	CO_2Et	*p*-MeC_6H_4	**9b**	85 (**1b**)
3	CO_2Et	CO_2Et	*p*-$MeOC_6H_4$	**9c**	90 (**1c**)
4	CO_2Et	CO_2Et	*p*-ClC_6H_4	**9d**	76 (**1d**)
5	CO_2Et	CO_2Et	*p*-FC_6H_4	**9e**	82 (**1e**)
6	CO_2Me	CO_2Me	C_6H_5	**9f**	70 (**1f**)
7	COMe	CO_2Et	C_6H_5	**9g**	60 (**1g**)
8	CN	CO_2Et	C_6H_5	**9h**	65 (**1h**)
9	CO_2Me	CO_2Me	*p*-$MeOC_6H_4$	**9j**	80 (**1j**)
10	CO_2Et	CO_2Et	Cyclohex-2-enyl	**9l**	85 (**1l**)
11	CO_2Et	COMe	Cyclohex-2-enyl	**9m**	88 (**1m**)
12	CO_2Et	CO_2Et	Cyclopent-2-enyl	**9n**	75 (**1n**)
13	CO_2Me	CO_2Me	Cyclopent-2-enyl	**9o**	78 (**1o**)

[a] Reactions were carried out using propargylic alcohol (1.0 mmol), pyridine (4.0 mmol), and DMAP (0.2 mmol) in CH_2Cl_2 (10 mL), ethyl chloroformate (4.0 mmol) was added at 0 °C, then stirred for 2 h at room temperature. [b] Isolated yields.

such a synthesis for benzo[*b*]fluorene derivatives from diynylic carbonates **1**.

Results and discussion

Malonates **9** could be conveniently prepared *via* Sonogashira coupling of iodo-derivatives **7** with propargylic alcohols **8**. Treatment of **9** with ethyl chloroformate afforded propargylic compounds **1** in moderate yields (Table 1).

Our initial study began with the reaction of diethyl 2-(2-(3-(methoxycarbonyloxy)-3-(2-(phenylethynyl)phenyl)prop-1-ynyl)benzyl)malonate (**1a**, 0.2 mmol) using $Pd_2(dba)_3{\cdot}CHCl_3$ (0.05 equiv) as a catalyst in DMF at room temperature. However, no reaction occurred and 78% of **1a** was recovered (entry 1). When PPh_3 was added, no expected product was observed at room temperature and 64% of **1a** was recovered (entry 2). When the reaction was performed at 60 °C, a trace amount of **2a** was detected (entry 3). In the presence of Cs_2CO_3, the expected product **2a** was isolated in 35% yield (entry 4). With the additional study using different catalyst precursors (entries 5 and 6), we found that $Pd(PPh_3)_4$ provided better product yield. Furthermore, K_2CO_3 was also investigated as the base, although lower yield was obtained, while Et_3N was totally ineffective (entries 7 and 8). THF was less effective (entry 9). When the reaction was performed at 60 °C, the yield was improved to 75% (entry 10). Although 1 mol% of $Pd(PPh_3)_4$ was proved to be effective, the yield was slightly lower (entry 11). Thus, we chose the following reaction conditions as optimum for further study: **1a**, 2.0 equiv of Cs_2CO_3, and 5 mol% of $Pd(PPh_3)_4$ in DMF at 60 °C in N_2).

With the optimal conditions in hand, we next examined the reaction scope. Typical results are summarized in Table 2. As for propargylic carbonate **1** wherein R^3 is an aromatic group such as phenyl, *p*-methylphenyl, *p*-methoxyphenyl, *p*-chlorophenyl and *p*-fluorophenyl group, the reactions proceeded smoothly under the established conditions, delivering the benzo[*b*]fluorenes **2** in good yields (Table 3, entries 1–5). However, when R^3 is an alkyl group, *e.g.* **1i**, the reaction did not give the expected product, instead, an unidentified mixture was formed (Scheme 3). Furthermore, diynylic carbonates with different electron withdrawing groups (**1f**), (**1g**) and (**1h**), have also been subjected to the standard conditions, affording the corresponding products **2f**, **2g** and **2h** in moderate yields (Table 3, entries 6, 7 and 8). The substituents R have significant effect on this reaction. When R = CO_2Me, the reaction proceeded smoothly to afford the corresponding product **2j** in 70% yield (Table 3, entry 9). However, when R was acetate, the reaction gave the product **2j** very poor yield (Scheme 3). All of the products were characterized by spectroscopic methods, and **2j** was further confirmed by X-ray crystallography§ (Fig. 1).

To further expand the scope of this reaction, the group of R^3 (eqn in Table 4), the benzene ring (R^3) in **1a** was replaced by a cyclic double bond. The reaction afforded several polycyclic benzo[*b*]fluorene derivatives in satisfactory yields.

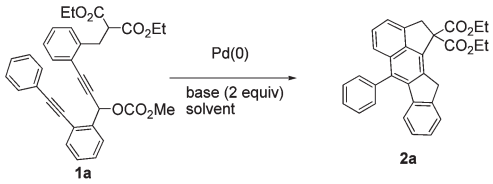
Finally, a control experiment for the current Pd-catalyzed cyclization of **1a** was also carried out under the standard conditions as described above except with the use of additional radical scavenger. It was found that the presence of a radical scavenger, 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl (TEMPO) or hydroquinone, led to an obvious decrease in the yield of cyclized product **2a** (Scheme 4). This result may account for the proposed reaction pathway involving radical intermediates as described in Scheme 2.

Conclusions

In conclusion, we have developed a convenient sequential Pd-catalyzed decarboxylation of propargylic carbonate,

§ X-ray crystal data for **2j**: $C_{30}H_{24}O_5$; M = 464.49; crystal system: monoclinic; space group: *C*2/c; final R indices ($I > 2\sigma(I)$) R_1 = 0.0465, wR_2 = 0.1154, R indices (all data) R_1 = 0.0613, wR_2 = 0.1252; a = 8.3183(2) Å, b = 25.3594(6) Å, c = 10.8216(2) Å; α = 90.00, β = 90.076, γ = 90.00, V = 2282.78(9) Å^3, T = 293(2) K, Z = 4; reflections collected/unique: 21 130/4165 (R(int) = 0.0291); number of observations (>2$\sigma(I)$): 3338; parameters: 319.

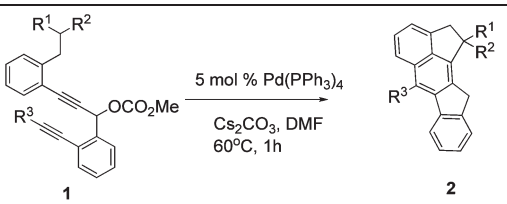
Table 2 Optimization of the Pd-catalyzed cyclization of propargylic carbonate **1a**[a]



Entry	Catalyst (mol%)	Base	Solvent	Temp T (°C)	Time	Yield of **2a**[b] (%)
1	$Pd_2(dba)_3{\cdot}CHCl_3$ (5)		DMF	rt	48 h	0
2	$Pd_2(dba)_3{\cdot}CHCl_3/PPh_3$ (5)		DMF	rt	48 h	0
3	$Pd_2(dba)_3{\cdot}CHCl_3/PPh_3$ (5)		DMF	60	6 h	Trace
4	$Pd_2(dba)_3{\cdot}CHCl_3$ (5)	Cs_2CO_3	DMF	rt	48 h	35
5	$Pd(PPh_3)_4$ (5)	Cs_2CO_3	DMF	rt	16 h	72
6	$Pd(OAc)_2/PPh_3$ (5)	Cs_2CO_3	DMF	rt	24 h	38
7	$Pd(PPh_3)_4$ (5)	K_2CO_3	DMF	rt	12 h	22
8	$Pd(PPh_3)_4$ (5)	Et_3N	DMF	rt	48 h	—
9	$Pd(PPh_3)_4$ (5)	Cs_2CO_3	THF	rt	24 h	19
10	$Pd(PPh_3)_4$ (5)	Cs_2CO_3	DMF	60	1 h	75
11	$Pd(PPh_3)_4$ (1)	Cs_2CO_3	DMF	60	3 h	65

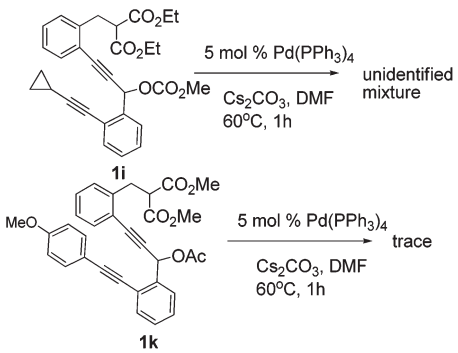
[a] Reactions were carried out on a 0.2 mmol scale in 3.0 mL of solvent at 60 °C in N_2 for the specified period of time with 1.0 equiv of **1a**, 2.0 equiv of base, and [Pd]. [b] Isolated yields.

Table 3 Pd-catalyzed cyclization of propargylic carbonate **1**[a]



	1				
Entry	R^1	R^2	R^3		Yield of **2**[b] (%)
1	CO_2Et	CO_2Et	C_6H_5	**1a**	75 (**2a**)
2	CO_2Et	CO_2Et	p-MeC_6H_4	**1b**	72 (**2b**)
3	CO_2Et	CO_2Et	p-$MeOC_6H_4$	**1c**	73 (**2c**)
4	CO_2Et	CO_2Et	p-ClC_6H_4	**1d**	78 (**2d**)
5	CO_2Et	CO_2Et	p-FC_6H_4	**1e**	65 (**2e**)
6	CO_2Me	CO_2Me	C_6H_5	**1f**	72 (**2f**)
7	COMe	CO_2Et	C_6H_5	**1g**	62 (**2g**)
8	CN	CO_2Et	C_6H_5	**1h**	45 (**2h**)
9	CO_2Me	CO_2Me	p-$MeOC_6H_4$	**1j**	70 (**2j**)

[a] Reactions were carried out using **1** (0.2 mmol), Cs_2CO_3 (2.0 equiv), and $Pd(PPh_3)_4$ (5 mol%) in DMF (3 mL) at 60 °C in N_2. [b] Isolated yields.



Scheme 3

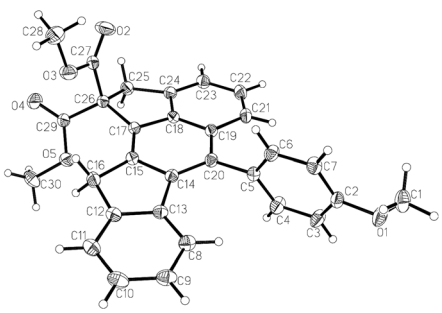


Fig. 1 ORTEP representation of **2j**.

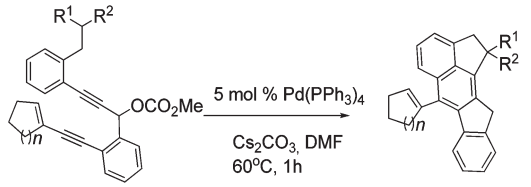
intramolecular nucleophilic attack and Schmittel cyclization, leading to a facile and efficient synthesis of polycyclic benzo[*b*]-fluorene derivatives from easily accessible starting materials under mild conditions.

Experimental section

General

All reactions were performed under an N_2 atmosphere. Anhydrous solvents were distilled prior to use: THF was distilled from sodium–benzophenone; DMF was distilled from CaH_2. Petroleum ether refers to the fraction with the boiling point in the range 60–90 °C. All ^1H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ with TMS as the internal standard. Chemical shifts are expressed in ppm and J values are given in Hz. Starting materials: Propargylic alcohols were prepared according to the literature.

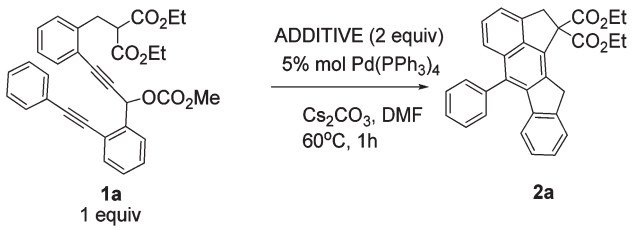
Table 4 Sequential reaction for the synthesis of polycyclic benzo[*b*]-fluorene derivatives **2a**[a]



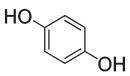
1 2

	1				
Entry	R^1	R^2	*n*		Yield of **2**[b] (%)
1	CO_2Et	CO_2Et	2	**1l**	80 (**2l**)
2	CO_2Et	COMe	2	**1m**	64 (**2m**)
3	CO_2Et	CO_2Et	1	**1n**	75 (**2n**)
4	CO_2Me	CO_2Me	1	**1o**	78 (**2o**)

[a] Reactions were carried out using **1** (0.2 mmol), Cs_2CO_3 (2.0 equiv), and $Pd(PPh_3)_4$ (5 mol%) in DMF (3 mL) at 60 °C in N_2. [b] Isolated yields.



1a 1 equiv **2a**

addtive	yield
	5%
	8%

Scheme 4

Typical procedure: diethyl 2-(2-(3-hydroxy-3-(2-(phenylethynyl)-phenyl)prop-1-ynyl)benzyl)malonate (9a)

An oven-dried Schlenk tube containing a Teflon-coated stirring bar was charged with $Pd(PPh_3)_2Cl_2$ (70 mg, 5 mol%), CuI (19 mg, 5 mol%), and diethyl 2-(2-iodobenzyl)malonate (2 mmol, 0.75 g). The Schlenk tube was sealed, evacuated and backfilled with N_2 (3 cycles). A solution of 1-(2-(phenylethynyl)phenyl)prop-2-yn-1-ol (2.4 mmol, 0.56 g) in 10 mL of THF and 3 mL of Et_3N was subsequently injected to the Schlenk tube. The reaction mixture was stirred for 1 h at room temperature. After 1 h the reaction was complete as monitored by TLC, the reaction was quenched with an aqueous saturated solution of NH_4Cl and extracted with diethyl ether (3 × 20 mL). The combined organic phase was washed with brine and dried over Na_2SO_4. Filtration, evaporation and column chromatography on silica gel (petroleum ether–ethyl acetate 4 : 1) afforded 0.78 g (82%) of diethyl 2-(2-(3-hydroxy-3-(2-(phenylethynyl)phenyl)-prop-1-ynyl)benzyl)malonate as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 7.6 Hz, 1H), 7.58–7.55 (m, 3H), 7.39–7.14 (m, 9H), 6.21 (d, J = 5.2 Hz, 1H), 4.15–4.10 (m, 4H), 3.86 (t, J = 8.0 Hz, 1H), 3.76 (d, J = 5.6 Hz, 1H), 3.37 (d, J = 7.2 Hz, 2H), 1.19–1.15 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.2, 169.1, 142.3, 140.0, 132.3, 132.0, 131.5, 129.9, 128.8, 128.5, 128.4, 128.3, 128.0, 126.7, 126.4, 122.9, 122.2, 121.4, 94.8, 94.1, 86.6, 84.0, 63.2, 61.5, 61.5, 52.4, 33.8, 13.9 ppm; MS: m/z (%) = 480 (M^+, 12.79), 262 (100); IR (neat): 3468, 2981, 1726, 1490, 1370, 1153 cm^{-1}; HRMS calcd for $C_{31}H_{28}O_5$ (M^+): 480.1937; found: 480.1993.

Compounds **9b–o** were prepared according to this typical procedure, and used directly after column purification.

General procedure for the preparation of propargylic compounds 1a–o

To a solution of propargylic alcohol (1.0 mmol), pyridine (0.32 g, 4.0 mmol), and DMAP (22.4 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) was added at 0 °C ethyl chloroformate (0.44 g, 4.0 mmol). After being stirred for 2 h at room temperature, the reaction mixture was diluted with CH_2Cl_2. The CH_2Cl_2 solution was washed with a saturated aqueous copper sulfate solution, water, dried over anhydrous sodium sulfate, filtered and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether–ethyl acetate 20 : 1) to afford the corresponding propargylic compounds.

(1) Diethyl 2-(2-(3-(methoxycarbonyloxy)-3-(2-(phenylethynyl)phenyl)prop-1-ynyl)benzyl)malonate (1a). The reaction of diethyl 2-(2-(3-hydroxy-3-(2-(phenylethynyl)phenyl)prop-1-ynyl)benzyl)malonate (0.48 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.43 g (80%) of **1a** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.88 (m, 1H), 7.60–7.58 (m, 3H), 7.40 (m, 1H), 7.37–7.35 (m, 5H), 7.26–7.22 (m, 3H), 7.10 (s, 1H), 4.12–4.08 (m, 4H), 3.85 (t, J = 8.0 Hz, 1H), 3.78 (s, 3H), 3.37 (d, J = 8.0 Hz, 2H), 1.17–1.13 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.8, 168.7, 154.8, 140.2, 137.3, 132.8, 132.3, 131.7, 129.8, 129.1, 129.0, 128.7, 128.6, 128.3, 128.1, 126.7, 122.8, 122.7, 121.6, 95.1, 89.1, 86.2, 86.0, 68.3, 61.3, 55.0, 52.1, 33.5, 13.9 ppm; MS: m/z (%) = 538 (M^+, 5.56), 315 (100); IR (neat): 2927, 1748, 1494, 1256, 1105, 948, 857, 756 cm^{-1}; HRMS calcd for $C_{33}H_{30}O_7$ (M^+): 538.1992; found: 538.1998.

(2) Diethyl 2-(2-(3-(methoxycarbonyloxy)-3-(2-(*p*-tolylethynyl)phenyl)prop-1-ynyl)benzyl)malonate (1b). The reaction of diethyl 2-(2-(3-hydroxy-3-(2-(*p*-tolylethynyl)phenyl)prop-1-ynyl)benzyl)malonate (0.49 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.47 g (85%) of **1b** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.88 (m, 1H), 7.58–7.56 (m, 1H), 7.50–7.47 (m, 3H), 7.40–7.36 (m, 2H), 7.24–7.12 (m, 6H), 4.12–4.08 (m, 4H), 3.87 (m, 1H), 3.77 (s, 3H), 3.38 (d, J = 8.4 Hz, 2H), 2.35 (s, 3H), 1.17–1.12 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 168.6, 154.7, 140.1, 138.7, 137.1, 132.7, 132.1, 131.5, 129.7, 129.0, 129.0, 128.9, 128.4, 128.0, 126.7, 122.9, 121.6,

119.6, 95.3, 89.1, 86.0, 85.3, 68.3, 61.2, 54.9, 52.0, 33.5, 21.4, 13.8 ppm; MS: *m/z* (%) = 552 (M^+, 11.52), 333 (100); IR (neat): 2981, 2216, 1748, 1484, 1150, 948, 788 cm^{-1}; HRMS calcd for $C_{34}H_{32}O_7$ (M^+): 552.2148; found: 552.2142.

(3) Diethyl 2-(2-(3-(methoxycarbonyloxy)-3-(2-((4-methoxyphenyl)ethynyl)phenyl)prop-1-ynyl)benzyl)malonate (1c). The reaction of diethyl 2-(2-(3-hydroxy-3-(2-((4-methoxyphenyl) ethynyl)phenyl)prop-1-ynyl)benzyl)malonate (0.51 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.51 g (90%) of **1c** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.87 (m, 1H), 7.57–7.48 (m, 4H), 7.40–7.35 (m, 2H), 7.26–7.19 (m, 3H), 7.11–7.10 (m, 1H), 6.90–6.87 (m, 2H), 4.15–4.07 (m, 4H), 3.87 (t, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.38 (d, *J* = 7.6 Hz, 2H), 1.17–1.13 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 168.7, 159.8, 154.8, 140.1, 137.0, 133.2, 132.8, 132.0, 129.8, 129.1, 129.0, 128.3, 128.0, 126.7, 123.2, 121.6, 114.8, 113.9, 95.2, 89.1, 86.1, 84.8, 68.3, 61.3, 55.2, 55.0, 52.1, 33.5, 13.9 ppm; MS: *m/z* (%) = 568 (M^+, 11.81), 349 (100); IR (neat): 2980, 2214, 1747, 1441, 1029, 784 cm^{-1}; HRMS calcd for $C_{34}H_{32}O_8$ (M^+): 568.2097; found: 568.2095.

(4) Diethyl 2-(2-(3-(2-((4-chlorophenyl)ethynyl)phenyl)-3-(methoxycarbonyloxy)prop-1-ynyl)benzyl)malonate (1d). The reaction of diethyl 2-(2-(3-(2-((4-chlorophenyl)ethynyl)phenyl)-3-hydroxyprop-1-ynyl)benzyl)malonate (0.51 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.44 g (76%) of **1d** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.88 (m, 1H), 7.58–7.32 (m, 8H), 7.26–7.19 (m, 3H), 7.09 (s, 1H), 4.15–4.07 (m, 4H), 3.85 (t, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.37 (d, *J* = 8.0 Hz, 2H), 1.17–1.13 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 168.7, 154.8, 140.1, 137.4, 134.6, 132.9, 132.8, 132.2, 129.8, 129.2, 129.1, 128.9, 128.6, 128.1, 126.8, 122.4, 121.6, 121.2, 93.9, 88.9, 87.0, 86.2, 68.2, 61.3, 55.0, 52.1, 33.5, 13.9 ppm; MS: *m/z* (%) = 572 (M^+, 6.30), 43 (100); IR (neat): 2955, 1746, 1440, 1090, 948, 758 cm^{-1}; HRMS calcd for $C_{33}H_{29}O_7{}^{35}Cl$ (M^+): 572.1602; found: 572.1605.

(5) Diethyl 2-(2-(3-(2-((4-fluorophenyl)ethynyl)phenyl)-3-(methoxycarbonyloxy)prop-1-ynyl)benzyl)malonate (1e). The reaction of diethyl 2-(2-(3-(2-((4-fluorophenyl)ethynyl)phenyl)-3-hydroxyprop-1-ynyl)benzyl)malonate (0.50 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.46 g (82%) of **1e** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.88 (m, 1H), 7.60–7.56 (m, 3H), 7.50–7.38 (m, 3H), 7.26–7.17 (m, 3H), 7.09–7.04 (m, 3H), 4.14–4.06 (m, 4H), 3.85 (t, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 3.37 (d, *J* = 7.6 Hz, 2H), 1.18–1.13 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.8, 168.7, 163.9, 161.4, 154.8, 140.1, 137.3, 133.7,133.6, 132.8, 132.2, 129.8, 129.2, 129.1, 128.8, 128.1, 126.8, 122.6, 121.6, 118.8, 115.7, 115.5, 94.0, 89.0, 86.2, 85.7, 68.3, 61.3, 55.0, 52.1, 33.5, 13.9 ppm; MS: *m/z* (%) = 556 (M^+, 15.43), 481 (100); IR (neat): 2982, 1747, 1596, 1369, 1257, 1094, 948 cm^{-1}; HRMS calcd for $C_{33}H_{29}O_7F$ (M^+): 556.1897; found: 556.1898.

(6) Dimethyl 2-(2-(3-(methoxycarbonyloxy)-3-(2-(phenylethynyl)phenyl)prop-1-ynyl)benzyl)malonate (1f). The reaction of dimethyl 2-(2-(3-hydroxy-3-(2-(phenylethynyl)phenyl)prop-1-ynyl)benzyl)malonate (0.45 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.36 g (70%) of **1f** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.87 (m, 1H), 7.60–7.58 (m, 3H), 7.49–7.34 (m, 6H), 7.26–7.12 (m, 3H), 7.11 (s, 1H), 3.90 (t, *J* = 7.6 Hz, 1H), 3.77 (s, 3H), 3.63–3.62 (m, 6H), 3.38 (d, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 169.0, 154.8, 140.0, 137.3, 132.7,132.2, 131.6, 129.7, 129.1, 129.0, 128.7, 128.5, 128.3, 128.0, 126.8, 122.7, 122.6, 121.5, 95.1, 89.2, 86.0, 85.9, 68.2, 55.0, 52.3, 51.8, 33.6 ppm; MS: *m/z* (%) = 510 (M^+, 8.58), 43 (100); IR (neat): 1749, 1701, 1492, 1441, 1102, 922 cm^{-1}; HRMS calcd for $C_{31}H_{26}O_7$ (M^+): 510.1679; found: 510.1674.

(7) Ethyl 2-(2-(3-(methoxycarbonyloxy)-3-(2-(phenylethynyl)-phenyl)prop-1-ynyl)benzyl)-3-oxobutanoate (1g). The reaction of ethyl 2-(2-(3-hydroxy-3-(2-(phenylethynyl)phenyl)prop-1-ynyl)benzyl)-3-oxobutanoate (0.45 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.31 g (60%) of **1g** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.84 (m, 1H), 7.58–7.57 (m, 3H), 7.48–7.34 (m, 6H), 7.25–7.16 (m, 3H), 7.10 (s, 1H), 4.12–3.98 (m, 3H), 3.77 (m, 3H), 3.36–3.20 (m, 2H), 2.15–2.12 (m, 3H), 1.15–1.11 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.3, 202.3, 168.9, 154.8, 140.6, 140.5, 137.4, 137.4, 132.8, 132.8, 132.3, 131.6, 130.0, 129.1, 129.1, 129.1, 128.8, 128.7, 128.6, 128.3, 127.8, 127.8, 126.7, 122.7, 121.4, 95.2, 95.2, 89.2, 86.3, 86.0, 68.3, 61.2, 59.5, 55.0, 32.8, 29.3, 29.3, 13.9 ppm; MS: *m/z* (%) = 508 (M^+, 7.68), 319 (100); IR (neat): 1746, 1715, 1492, 1442, 1103, 923 cm^{-1}; HRMS calcd for $C_{32}H_{28}O_6$ (M^+): 508.1886; found: 508.1887.

(8) Ethyl 2-(2-(3-(methoxycarbonyloxy)-3-(2-(phenylethynyl)-phenyl)prop-1-ynyl)benzyl)-3-oxobutanoate (1i). The reaction of diethyl 2-(2-(3-(2-(cyclopropylethynyl)phenyl)-3-hydroxyprop-1-ynyl)benzyl)malonate (0.44 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.34 g (68%) of **1i** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.79 (m, 1H), 7.48–7.46 (m, 2H), 7.42–7.18 (m, 5H), 6.94 (s, 1H), 4.12–4.09 (m, 4H), 3.88–3.83 (m, 4H), 3.37 (d, *J* = 8.4 Hz, 2H), 1.48–1.47(m, 1H), 1.18–1.13 (m, 6H), 0.88–0.86 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 154.6, 140.0, 137.2, 132.5, 132.0, 129.6, 128.8, 127.7, 127.6, 127.5, 126.6, 123.3, 121.5, 99.5, 89.2, 85.7, 72.3, 68.1, 61.0, 54.7, 51.9, 33.4, 13.7, 8.55, 8.49, 0.10 ppm; MS: *m/z* (%) = 502 (M^+, 2.36), 239 (100); IR (neat): 2984, 2228, 1748, 1443, 1152, 951, 754 cm^{-1}; HRMS calcd for $C_{30}H_{30}O_7$ (M^+): 502.1992; found: 502.1992.

(9) Ethyl 2-(2-(3-(methoxycarbonyloxy)-3-(2-(phenylethynyl)-phenyl)prop-1-ynyl)benzyl)-3-oxobutanoate (1j). The reaction of dimethyl 2-(2-(3-hydroxy-3-(2-((4-methoxyphenyl)ethynyl) phenyl)prop-1-ynyl)benzyl)malonate (0.48 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded

0.43 g (80%) of **1j** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.85 (m, 1H), 7.57–7.48 (m, 4H), 7.40–7.37 (m, 2H), 7.26–7.19 (m, 3H), 7.10 (s, 1H), 6.90–6.88 (m, 2H), 3.89 (t, J = 8.0 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.64–6.63 (m, 6H), 3.38 (d, J = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 169.1, 159.9, 154.8, 140.0, 137.1, 133.2, 132.8, 132.0, 129.7, 129.1, 129.1, 128.3, 128.0, 126.9, 123.2, 121.6, 114.8, 114.0, 95.3, 89.3, 86.0, 84.8, 68.4, 55.3, 55.0, 52.4, 51.9, 33.6 ppm; MS: m/z (%) = 540 (M^+, 10.50), 59 (100); IR (neat): 2954, 2214, 1958, 1512, 1245, 1027, 785 cm^{-1}; HRMS calcd for $C_{32}H_{28}O_8$ (M^+): 540.1874; found: 540.1873.

(10) Dimethyl 2-(2-(3-acetoxy-3-(2-((4-methoxyphenyl)-ethynyl)phenyl)prop-1-ynyl)benzyl)malonate (1k). The reaction of dimethyl 2-(2-(3-acetoxy-3-(2-((4-methoxyphenyl)ethynyl) phenyl)prop-1-ynyl)benzyl)malonate (0.48 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and acetic anhydride (0.41 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.32 g (60%) of **1k** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.87 (m, 1H), 7.58–7.47 (m, 4H), 7.40–7.37 (m, 2H), 7.26–7.19 (m, 4H), 6.90–6.87 (m, 2H), 3.91 (t, J = 8.0 Hz, 1H), 3.82 (s, 3H), 3.65–6.63 (m, 6H), 3.38 (d, J = 7.6 Hz, 2H), 2.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 169.1, 159.8, 139.9, 137.5, 133.2, 132.7, 132.1, 129.7, 128.9, 128.2, 128.1, 126.8, 123.2, 121.8, 114.8, 114.0, 95.2, 89.9, 85.1, 84.9, 64.5, 55.2, 52.4, 52.4, 51.9, 33.7, 20.8 ppm; MS: m/z (%) = 524 (M^+, 24.18), 43 (100); IR (neat): 2952, 2214, 1735, 1486, 1150, 953, 757 cm^{-1}; HRMS calcd for $C_{32}H_{28}O_7$ (M^+): 524.1835; found: 524.1829.

(11) Diethyl 2-(2-(3-(2-(cyclohexenylethynyl)phenyl)-3-(methoxycarbonyloxy)prop-1-ynyl)benzyl)malonate (1l). The reaction of diethyl 2-(2-(3-(2-(cyclohexenylethynyl)phenyl)-3-hydroxyprop-1-ynyl)benzyl)malonate (0.48 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.46 g (85%) of **1l** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.82 (m, 1H), 7.49–7.45 (m, 2H), 7.36–7.32 (m, 2H), 7.27–7.19 (m, 3H), 6.97 (s, 1H), 6.28–6.27 (m, 1H), 4.14–4.09 (m, 4H), 3.85–3.82 (m, 4H), 3.36 (d, J = 8.4 Hz, 2H), 2.24–2.15 (m, 4H), 1.68–1.61 (m, 4H), 1.19–1.14 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 168.7, 154.7, 140.0, 136.9, 135.9, 132.7, 132.0, 129.7, 128.9, 128.9, 128.1, 127.9, 126.7, 123.2, 121.6, 120.4, 97.0, 89.2, 85.9, 83.3, 68.2, 61.2, 54.9, 52.0, 33.5, 28.8, 25.7, 22.2, 21.4, 13.9 ppm; MS: m/z (%) = 542 (M^+, 3.49), 466 (100); IR (neat): 2935, 1748, 1483, 1256, 1008, 788 cm^{-1}; HRMS calcd for $C_{33}H_{34}O_7$ (M^+): 542.2305; found: 542.2316.

(12) Ethyl 2-(2-(3-(2-(cyclohexenylethynyl)phenyl)-3-(methoxycarbonyloxy)prop-1-ynyl)benzyl)-3-oxobutanoate (1m). The reaction of ethyl 2-(2-(3-(2-(cyclohexenylethynyl)phenyl)-3-hydroxyprop-1-ynyl)benzyl)-3-oxobutanoate (0.45 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.45 g (88%) of **1m** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.78 (m, 1H), 7.48–7.45 (m, 2H), 7.36–7.32 (m, 2H), 7.27–7.18 (m, 3H), 6.96 (s, 1H), 6.27 (s, 1H), 4.10–4.00 (m, 3H), 3.82 (s, 3H), 3.31–3.22 (m, 2H), 2.24 (m, 2H), 2.17–2.15 (m, 5H), 1.69–1.60 (m, 4H), 1.17–1.12 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.3, 202.3, 168.8, 154.7, 140.4, 140.4, 136.9, 136.9, 135.9, 132.7, 132.6, 132.0, 130.0, 129.0, 128.1, 128.1, 127.6, 126.6, 123.1, 123.1, 121.4, 120.4, 97.1, 89.2, 85.9, 83.3, 68.2, 61.1, 59.3, 54.9, 32.7, 29.3, 29.2, 28.8, 25.7, 22.1, 21.3, 13.8 ppm; MS: m/z (%) = 512 (M^+, 1.52), 43 (100); IR (neat): 2934, 1745, 1715, 1483, 1442, 1256, 1147, 1101, 1009 cm^{-1}; HRMS calcd for $C_{32}H_{32}O_6$ (M^+): 512.2199; found: 512.2206.

(13) Diethyl 2-(2-(3-(2-(cyclopentenylethynyl)phenyl)-3-(methoxycarbonyloxy)prop-1-ynyl)benzyl)malonate (1n). The reaction of diethyl 2-(2-(3-(2-(cyclopentenylethynyl)phenyl)-3-hydroxyprop-1-ynyl)benzyl)malonate (0.47 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.40 g (75%) of **1n** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.84 (m, 1H), 7.49–7.47 (m, 2H), 7.37–7.32 (m, 2H), 7.22–7.18 (m, 3H), 6.98 (s, 1H), 6.21–6.20 (m, 1H), 4.15–4.08 (m, 4H), 3.88–3.81 (m, 4H), 3.37 (d, J = 8.0 Hz, 2H), 2.58–2.47 (m, 4H), 1.98–1.91 (m, 2H), 1.18–1.13 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 168.6, 154.6, 140.0, 139.0, 137.0, 132.7, 131.9, 129.7, 128.9, 128.9, 128.3, 127.8, 126.6, 124.1, 123.0, 121.6, 92.5, 89.1, 86.9, 85.9, 68.2, 61.3, 54.8, 52.0, 36.1, 33.4, 33.3, 23.2, 13.8 ppm; MS: m/z (%) = 528 (M^+, 8.67), 305 (100); IR (neat): 2958, 1748, 1370, 1257, 1102, 915 cm^{-1}; HRMS calcd for $C_{32}H_{32}O_7$ (M^+): 528.2148; found: 528.2155.

(14) Dimethyl 2-(2-(3-(2-(cyclopentenylethynyl)phenyl)-3-(methoxycarbonyloxy)prop-1-ynyl)benzyl)malonate (1o). The reaction of dimethyl 2-(2-(3-(2-(cyclopentenylethynyl)phenyl)-3-hydroxyprop-1-ynyl)benzyl)malonate (0.44 g, 1 mmol), pyridine (0.32 g, 4.0 mmol), DMAP (22.4 mg, 0.2 mmol), and ethyl chloroformate (0.44 g, 4.0 mmol) in 10 mL of CH_2Cl_2 afforded 0.39 g (78%) of **1o** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.82 (m, 1H), 7.49–7.47 (m, 2H), 7.39–7.19 (m, 5H), 6.98 (s, 1H), 6.21 (s, 1H), 3.90–3.82 (m, 4H), 3.65–3.64 (m, 6H), 3.37 (d, J = 7.6 Hz, 2H), 2.57–2.47 (m, 4H), 1.99–1.91 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 169.0, 154.7, 139.9, 139.1, 137.1, 132.7, 132.0, 129.6, 129.0, 128.3, 127.8, 126.8, 124.1, 123.0, 121.6, 92.6, 89.3, 86.9, 85.8, 68.2, 54.9, 52.3, 51.8, 36.1, 33.5, 33.4, 23.2 ppm; MS: m/z (%) = 500 (M^+, 8.64), 59 (100); IR (neat): 2954, 1749, 1486, 1153, 1009, 853 cm^{-1}; HRMS calcd for $C_{30}H_{28}O_7$ (M^+): 500.1835; found: 500.1829.

Typical procedure for the preparation of fluorene derivatives 2

General experimental procedure: (1) Diethyl 6-phenyl-1*H*-indeno[1,7-*ab*]fluorene-1,1(2*H*,11*H*)-dicarboxylate (2a). An oven-dried Schlenk tube containing a Teflon-coated stirring bar was charged with $Pd(PPh_3)_4$ (10 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol). The Schlenk tube was sealed, evacuated and backfilled with N_2 (3 cycles). A solution of propargylic compound **1a** (108 mg, 0.2 mmol) in DMF (3.0 mL) was subsequently injected to the Schlenk tube. The reaction mixture was stirred at 60 °C. When the reaction was complete as determined by TLC analysis, the resulting mixture was allowed to cool to room temperature and quenched with a saturated aqueous

solution of ammonium chloride, and the mixture was extracted with EtOAc. The combined organic extracts were washed with water and saturated brine. The organic layers were dried over Na_2SO_4 and filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford 69 mg (75%) of **2a**. Solid; m.p. 128–131 °C (petroleum ether–ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.50 (m, 4H), 7.44–7.41 (m, 2H), 7.38–7.26 (m, 3H), 7.24–7.19 (m, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 4.34–4.26 (m, 4H), 4.26 (s, 2H), 4.18 (s, 2H), 1.31 (t, J = 7.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.8, 144.5, 141.1, 140.2, 138.3, 138.1, 137.1, 134.3, 132.7, 131.1, 129.9, 129.0, 127.7, 127.4, 127.0, 126.2, 124.7, 123.7, 122.0, 119.2, 65.0, 62.0, 41.5, 35.3, 14.1 ppm; MS: m/z (%) = 462 (M^+, 95.64), 315 (100); IR (neat): 2977, 1721, 1468, 1251, 1122, 915, 769 cm^{-1}; HRMS calcd for $C_{31}H_{26}O_4$ (M^+): 462.1831; found: 462.1837.

The following compounds were prepared according to this procedure.

(2) Diethyl 6-*p*-tolyl-1*H*-indeno[1,7-*ab*]fluorene-1,1(2*H*,11*H*)-dicarboxylate (2b). The reaction of **1b** (110 mg, 0.2 mmol), Pd(PPh_3)$_4$ (10 mg, 5 mol%), and Cs_2CO_3 (130 mg, 0.4 mmol) in DMF (3.0 mL) afforded 68 mg (72%) of **2b**. Solid; m.p. 142–145 °C (petroleum ether–ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.6 Hz, 1H), 7.42–7.28 (m, 7H), 7.23 (t, J = 7.4 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 4.37–4.25 (m, 4H), 4.24 (s, 2H), 4.18 (s, 2H), 2.54 (s, 3H), 1.32 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 144.5, 141.2, 140.24, 140.16, 138.1, 137.4, 137.1, 135.2, 134.2, 132.8, 131.2, 129.7, 127.3, 127.0, 126.2, 124.7, 123.7, 122.1, 119.2, 65.0, 62.0, 41.6, 35.3, 21.5, 14.2 ppm; MS: m/z (%) = 476 (M^+, 40.79), 84 (100); IR (neat): 2980, 1729, 1466, 1243, 1121, 910, 728 cm^{-1}; HRMS calcd for $C_{32}H_{28}O_4$ (M^+): 476.1988; found: 476.1980.

(3) Diethyl 6-(4-methoxyphenyl)-1*H*-indeno[1,7-*ab*]fluorene-1,1(2*H*,11*H*)-dicarboxylate (2c). The reaction of **1c** (114 mg, 0.2 mmol), Pd(PPh_3)$_4$ (10 mg, 5 mol%), and Cs_2CO_3 (130 mg, 0.4 mmol) in DMF (3.0 mL) afforded 72 mg (73%) of **2c**. Solid; m.p. 135–138 °C (petroleum ether–ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.6 Hz, 1H), 7.40–7.29 (m, 5H), 7.25–7.20 (m, 1H), 7.12 (d, J = 8.8 Hz, 2H), 7.04 (t, J = 7.6 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 4.32–4.25 (m, 4H), 4.25 (s, 2H), 4.18 (s, 2H), 3.94 (s, 3H), 1.32 (t, J = 7.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 159.2, 144.5, 141.2, 140.5, 140.2, 138.1, 137.1, 134.2, 132.4, 131.4, 131.0, 130.3, 127.3, 127.0, 126.3, 124.7, 123.7, 122.1, 119.1, 114.4, 65.0, 62.0, 55.3, 41.5, 35.3, 14.2 ppm; MS: m/z (%) = 492 (M^+, 29.48), 84 (100); IR (neat): 2980, 1728, 1607, 1242, 1049, 852, 729 cm^{-1}; HRMS calcd for $C_{32}H_{28}O_5$ (M^+): 492.1937; found: 492.1933.

(4) Diethyl 6-(4-chlorophenyl)-1*H*-indeno[1,7-*ab*]fluorene-1,1-(2*H*,11*H*)-dicarboxylate (2d). The reaction of **1d** (114 mg, 0.2 mmol), Pd(PPh_3)$_4$ (10 mg, 5 mol%), and Cs_2CO_3 (130 mg, 0.4 mmol) in DMF (3.0 mL) afforded 77 mg (78%) of **2d**. Solid; m.p. 141–144 °C (petroleum ether–ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (t, J = 9.8 Hz, 3H), 7.41–7.30 (m, 4H), 7.25 (t, J = 7.6 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H), 4.36–4.26 (m, 4H), 4.25 (s, 2H), 4.18 (s, 2H), 1.32 (t, J = 7.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 144.6, 140.8, 140.3, 140.2, 138.1, 137.0, 136.8, 134.7, 133.8, 131.4, 131.1, 130.9, 129.3, 127.6, 127.2, 126.3, 124.9, 123.5, 121.7, 119.3, 65.0, 62.1, 41.5, 35.3, 14.1 ppm; MS: m/z (%) = 498 (M^+(^{37}Cl), 15.73), 496 (M^+(^{35}Cl), 40.35), 84 (100); IR (neat): 2981, 1728, 1482, 1244, 1013, 911, 773 cm^{-1}; HRMS calcd for $C_{31}H_{25}O_4{}^{35}Cl$ (M^+): 496.1441; found: 496.1440.

(5) Diethyl 6-(4-fluorophenyl)-1*H*-indeno[1,7-*ab*]fluorene-1,1-(2*H*,11*H*)-dicarboxylate (2e). The reaction of **1e** (112 mg, 0.2 mmol), Pd(PPh_3)$_4$ (10 mg, 5 mol%), and Cs_2CO_3 (130 mg, 0.4 mmol) in DMF (3.0 mL) afforded 62 mg (65%) of **2e**. Solid; m.p. 126–129 °C (petroleum ether–ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.0 Hz, 1H), 7.42–7.35 (m, 3H), 7.34–7.22 (m, 5H), 7.05 (t, J = 7.6 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 4.37–4.27 (m, 4H), 4.25 (s, 2H), 4.18 (s, 2H), 1.32 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.8, 162.5 (d, J = 244 Hz), 144.6, 140.9, 140.4 (d, J = 19.5 Hz), 138.1, 137.1, 134.6, 134.1 (d, J = 2.6 Hz), 131.7 (d, J = 7.9 Hz), 131.5, 131.1, 127.5, 127.2, 126.3, 124.9, 123.5, 121.7, 119.3, 116.2, 116.0, 65.0, 62.1, 41.5, 35.3, 14.2 ppm; MS: m/z (%) = 480 (M^+, 14.34), 84 (100); IR (neat): 2964, 1728, 1599, 1467, 1177, 911 cm^{-1}; HRMS calcd for $C_{31}H_{25}O_4F$ (M^+): 480.1737; found: 480.1732.

(6)Dimethyl 6-phenyl-1*H*-indeno[1,7-*ab*]fluorene-1,1(2*H*,11*H*)-dicarboxylate (2f). The reaction of **1f** (102 mg, 0.2 mmol, Pd(PPh_3)$_4$ (10 mg, 5 mol%), and Cs_2CO_3 (130 mg, 0.4 mmol) in DMF (3.0 mL) afforded 62 mg (72%) of **2f**. Solid; m.p. 168–171 °C (petroleum ether–ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.52 (m, 4H), 7.43–7.21 (m, 6H), 7.01 (t, J = 7.8 Hz, 1H), 6.59 (d, J = 7.6 Hz, 1H), 4.20 (s, 2H), 4.19 (s, 2H), 3.82 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 144.5, 141.0, 140.2, 140.0, 138.2, 138.0, 137.0, 134.2, 132.8, 131.1, 129.9, 129.0, 127.8, 127.4, 127.1, 126.3, 124.8, 123.7, 122.1, 119.3, 64.7, 53.0, 41.6, 35.1 ppm; MS: m/z (%) = 434 (M^+, 52.54), 315 (100); IR (neat): 2954, 1745, 1492, 1255, 1105, 922, 752, cm^{-1}; HRMS calcd for $C_{29}H_{22}O_4$ (M^+): 434.1518; found: 434.1510.

(7) Ethyl 1-acetyl-6-phenyl-2,11-dihydro-1*H*-indeno[1,7-*ab*]-fluorene-1-carboxylate (2g). The reaction of **1g** (102 mg, 0.2 mmol), Pd(PPh_3)$_4$ (10 mg, 5 mol%), and Cs_2CO_3 (130 mg, 0.4 mmol) in DMF (3.0 mL) afforded 54 mg (62%) of **2g**. Solid; m.p. 116–119 °C (petroleum ether–ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.48 (m, 4H), 7.45–7.28 (m, 5H), 7.22 (t, J = 7.4 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 4.38–4.27 (m, 4H), 4.00 (d, J = 23.2 Hz, 1H), 3.85 (d, J = 18.0 Hz, 1H), 2.18 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.9, 170.4, 144.5, 140.9, 140.3, 139.9, 138.3, 138.2, 137.7, 134.4, 132.7, 131.3, 130.0, 129.9, 129.1, 129.0, 127.8, 127.5, 127.2, 126.3, 124.8, 123.7, 122.3, 119.4, 72.0, 62.0, 40.3, 35.3, 26.0, 14.2 ppm; MS: m/z (%) = 432 (M^+, 65.64), 317 (100); IR (neat): 2981, 1712, 1465, 1246, 1123, 1074, 908, 775 cm^{-1}; HRMS calcd for $C_{30}H_{24}O_3$ (M^+): 432.1725; found: 432.1733.

(8) Methyl 1-cyano-6-phenyl-2,11-dihydro-1*H*-indeno[1,7-*ab*]-fluorene-1-carboxylate (2h). The reaction of **1h** (95 mg,

0.2 mmol), $Pd(PPh_3)_4$ (10 mg, 5 mol%), and Cs_2CO_3 (130 mg, 0.4 mmol) in DMF (3.0 mL) afforded 36 mg (45%) of **2h**. Solid; m.p. 216–219 °C (petroleum ether–ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.56 (m, 4H), 7.46–7.24 (m, 6H), 7.05 (t, J = 7.6 Hz, 1H), 6.61 (d, J = 8.4 Hz, 1H), 4.41 (d, J = 16.8 Hz, 1H), 4.38 (d, J = 22.0 Hz, 1H), 4.14 (d, J = 17.2 Hz, 1H), 4.07 (d, J = 22.0 Hz, 1H), 3.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 143.8, 140.6, 140.5, 138.6, 137.6, 136.8, 135.9, 133.6, 132.1, 131.6, 129.8, 129.7, 129.2, 129.1, 128.1, 127.6, 126.7, 125.1, 123.8, 122.8, 119.9, 117.7, 54.0, 50.4, 43.6, 33.7, 29.7 ppm; MS: m/z (%) = 401 (M^+, 37.77), 342 (100); IR (neat): 2978, 2240, 1754, 1430, 1247, 903 cm^{-1}; HRMS calcd for $C_{28}H_{19}NO_2$ (M^+): 401.1416; found: 401.1417.

(9) Dimethyl 6-(4-methoxyphenyl)-1*H*-indeno[1,7-*ab*]fluorene-1,1(2*H*,11*H*)-dicarboxylate (2j). The reaction of **1j** (108 mg, 0.2 mmol), $Pd(PPh_3)_4$ (10 mg, 5 mol%), and Cs_2CO_3 (130 mg, 0.4 mmol) in DMF (3.0 mL) afforded 65 mg (70%) of **2j**. Solid; m.p. 210–213 °C (petroleum ether–ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.6 Hz, 1H), 7.41–7.29 (m, 5H), 7.24 (t, J = 7.2 Hz, 1H), 7.13 (d, J = 8.8 Hz, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 4.19 (s, 4H), 3.95 (s, 3H), 3.82 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 159.2, 144.5, 141.2, 140.6, 140.0, 138.1, 137.0, 134.1, 132.6, 131.5, 131.0, 130.3, 127.4, 127.1, 126.3, 124.8, 123.8, 122.2, 119.2, 114.4, 64.7, 55.3, 53.0, 41.6, 35.2 ppm; cm^{-1}; MS: m/z (%) = 464 (M^+, 100); IR (neat): 2980, 2903, 1732, 1403, 1247, 1055, 894 cm^{-1}; HRMS calcd for $C_{30}H_{24}O_5$ (M^+): 464.1624; found: 464.1629.

(10) Diethyl 6-cyclohexenyl-1*H*-indeno[1,7-*ab*]fluorene-1,1-(2*H*,11*H*)-dicarboxylate (2l). The reaction of **1l** (108 mg, 0.2 mmol), $Pd(PPh_3)_4$ (10 mg, 5 mol%), and Cs_2CO_3 (130 mg, 0.4 mmol) in DMF (3.0 mL) afforded 75 mg (80%) of **2l** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.39–7.28 (m, 3H), 5.86 (d, J = 1.2 Hz, 1H), 4.34–4.21 (m, 4H), 4.20 (s, 2H), 4.14 (s, 2H), 2.44–2.21 (m, 4H), 2.04–1.80 (m, 4H), 1.34–1.26 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 144.4, 141.3, 140.3, 138.8, 138.2, 137.3, 135.2, 134.9, 133.4, 130.2, 127.5, 127.1, 126.9, 126.5, 124.8, 123.7, 121.6, 119.0, 64.9, 61.9, 41.5, 35.3, 29.3, 25.6, 23.2, 22.2, 14.1 ppm; MS: m/z (%) = 466 (M^+, 29.48), 43 (100); IR (neat): 2928, 1729, 1445, 1336, 1094, 908, 726 cm^{-1}; HRMS calcd for $C_{31}H_{30}O_4$ (M^+): 466.2144; found: 466.2141.

(11) Ethyl 1-acetyl-6-cyclohexenyl-2,11-dihydro-1*H*-indeno-[1,7-*ab*]fluorene-1-carboxylate (2m). The reaction of **1m** (102 mg, 0.2 mmol), $Pd(PPh_3)_4$ (10 mg, 5 mol%), and Cs_2CO_3 (130 mg, 0.4 mmol) in DMF (3.0 mL) afforded 55 mg (64%) of **2m** (dr = 1 : 1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 7.6 Hz, 1H), 7.80–7.77 (m, 1H), 7.55 (d, J = 6.8 Hz, 1H), 7.48 (d, J = 7.4 Hz, 2H), 7.40–7.30 (m, 3H), 5.86 (s, 1H), 4.37–4.20 (m, 4H), 3.94 (dd, J_1 = 22.4 Hz, J_2 = 4.4 Hz, 1H), 3.81 (dd, J_1 = 17.6 Hz, J_2 = 2.8 Hz, 1H), 2.50–2.30 (m, 4H), 2.13 (d, J = 9.6 Hz, 3H), 2.05–1.89 (m, 4H), 1.36–1.25 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.2, 202.1, 170.5, 144.4, 141.1, 140.0, 139.0, 138.4, 138.0, 137.9, 135.3, 135.2, 134.9, 134.8, 133.4, 130.54, 130.51, 127.7, 127.2, 127.1, 126.6, 124.9, 123.8, 121.8, 119.25, 119.22, 71.9, 61.9, 40.3, 35.3, 29.4, 29.3, 26.0, 25.9, 25.6, 23.3, 22.2, 14.2 ppm; cm^{-1}; MS: m/z (%) = 436 (M^+, 8.06), 43 (100); IR (neat): 2923, 1719, 1377, 1242, 1159, 1072 cm^{-1}; HRMS calcd for $C_{30}H_{28}O_3$ (M^+): 436.2038; found: 436.2036.

(12) Diethyl 6-cyclopentenyl-1*H*-indeno[1,7-*ab*]fluorene-1,1-(2*H*,11*H*)-dicarboxylate (2n). The reaction of **1n** (106 mg, 0.2 mmol), $Pd(PPh_3)_4$ (10 mg, 5 mol%), and Cs_2CO_3 (130 mg, 0.4 mmol) in DMF (3.0 mL) afforded 68 mg (75%) of **2n** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (t, J = 4.0 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 5.6 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.38–7.28 (m, 3H), 5.89 (s, 1H), 4.34–4.22 (m, 4H), 4.20 (s, 2H), 4.14 (s, 2H), 2.89–2.64 (m, 4H), 2.32–2.24 (m, 2H), 1.30 (t, J = 7.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 144.4, 141.2, 140.4, 139.3, 138.1, 137.2, 133.7, 130.6, 130.3, 130.2, 127.2, 127.0, 126.6, 124.8, 123.5, 121.6, 119.1, 64.9, 62.0, 41.5, 36.8, 35.2, 33.7, 24.0, 14.1 ppm; MS: m/z (%) = 452 (M^+, 16.87), 43 (100); IR (neat): 2981, 1723, 1428, 1249, 1176, 1051, 948, 767 cm^{-1}; HRMS calcd for $C_{30}H_{28}O_4$ (M^+): 452.1988; found: 452.1979.

(13) Dimethyl 6-cyclopentenyl-1*H*-indeno[1,7-*ab*]fluorene-1,1-(2*H*,11*H*)-dicarboxylate (2o). The reaction of **1o** (100 mg, 0.2 mmol), $Pd(PPh_3)_4$ (10 mg, 5 mol%), and Cs_2CO_3 (130 mg, 0.4 mmol) in DMF (3.0 mL) afforded 66 mg (78%) of **2o** as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 6.4 Hz,1H), 7.46 (t, J = 7.8 Hz, 1H), 7.39–7.30 (m, 3H), 5.89 (s, 1H), 4.15 (s, 4H), 3.80 (s, 6H), 2.91–2.66 (m, 4H), 2.34–2.22 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 144.4, 141.2, 140.3, 140.2, 139.3, 138.1, 137.1, 133.6, 130.7, 130.2, 130.28, 127.3, 127.1, 126.7, 124.9, 123.5, 121.7, 119.2, 64.7, 53.0, 41.6, 36.8, 35.1, 33.8, 24.0 ppm; MS: m/z (%) = 424 (M^+, 13.37), 43 (100); IR (neat): 2950, 1732, 1608, 1115, 950, 772 cm^{-1}; HRMS calcd for $C_{28}H_{24}O_4$ (M^+): 424.1675; found: 424.1667.

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