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Iron-Catalyzed Tandem Conia–Ene/Friedel–Crafts Reactions of *o*-Alkynyldihydrochalcones: Access to Benzo[*b*]fluorenes

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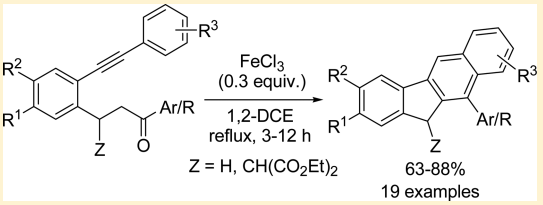
Supporting Information

ABSTRACT: *o*-Alkynyldihydrochalcones when treated with a catalytic amount of anhydrous $FeCl_3$ in refluxing 1,2-dichloroethane underwent tandem Conia–ene and Friedel–Crafts reactions to yield benzo[*b*]-fluorene derivatives in good yields.

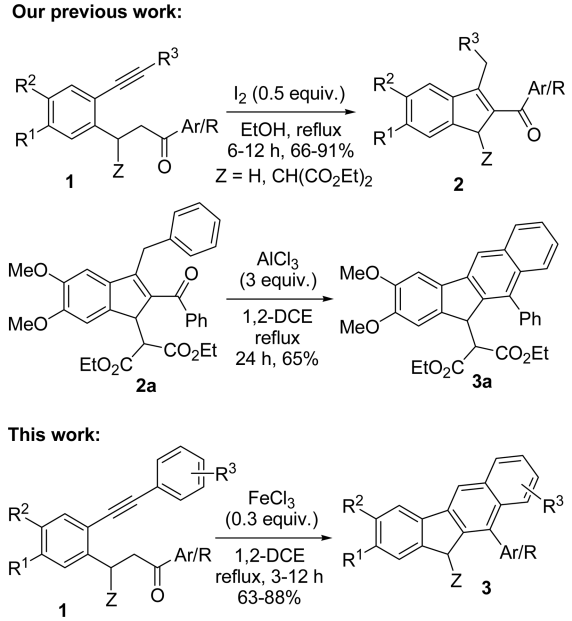


Benzo[*b*]fluorenes are important polycyclic aromatic hydrocarbons (PAHs)[1] that have potential applications in multiple fields. The benzo[*b*]fluorene core is featured in the kinamycin family of secondary metabolites, which possess significant antibiotic and cytotoxic activities.[2] Certain benzo-[*b*]fluorene derivatives have been proposed as nonsteroidal drug candidates for the estrogen receptor related medical treatments.[3] Benzo[*b*]fluorenes also serve as precursors for other PAHs including buck bowls.[4] Many functional materials with promising applications in organic electronics also contain a benzo[*b*]fluorene core.[5] Therefore, a handful of methods have been developed for the access of benzo[*b*]fluorene derivatives. Some notable methods are the cycloaromatization of non-conjugated benzotriynes,[6] thermal intramolecular [4 + 2] cycloaddition of 2-propynyldiarylacetylenes,[7] intramolecular arylalkyne–allene or arylalkyne–alkyne cycloaddition,[8] tandem biscyclization of propargylic compounds with terminal alkynes,[9] selenium-mediated carbocyclization of stilbene derivatives[10] and gold-catalyzed cascade cyclization of 1,6-diynyl carbonates.[11]

Recently, we reported an iodine-catalyzed Conia–ene reaction of *o*-alkynyldihydrochalcones **1** for the synthesis of indene derivatives **2** (Scheme 1).[12] Further, we showed that an indene derivative **2a** could be converted into the benzo[*b*]-fluorene **3a** by an aluminum chloride promoted Friedel–Crafts reaction.[12] We envisaged that a single Lewis acid could promote both the Conia–ene and Friedel–Crafts steps in a tandem manner and thus the benzo[*b*]fluorene derivatives **3** could be obtained directly from **1** in a single step. We herein report that iron(III) choride is capable of efficiently catalyzing the transformation of **1** to **3** via a tandem Conia–ene/Friedel–Crafts reaction (Scheme 1). It is worth noting that tandem strategies have received a great deal of attention in recent years owing to their economical and environmental benefits.[13] It may also be noted that iron-based catalysts and reagents are becoming increasingly popular in organic synthesis due to their ready availability, low cost, greenness and versatility.[14]

The starting *o*-alkynyldihydrochalcones **1** required for the present study were prepared as reported earlier by us (Scheme 2).[12] Thus, the *o*-alkynyldihydrochalcones **1a–o** were obtained by the Michael addition of diethylmalonate to the respective *o*-alkynylchalcones **4** (which were in turn prepared by the condensation of the corresponding *o*-alkynylarenecarbaldehydes with acetophenones). The *o*-alkynyldihydrochalcone **1p** was prepared by reducing the iodochalcone **5** to the corresponding dihydrochalcone using tosylhydrazide and base[15] and then subjecting the product to the standard Sonogashira coupling with phenylacetylene. We preferred the former route for the saturation of the double bond simply because we were already working on the synthetic applications of *o*-alkynylchalcones **4**.[16] It may therefore be noted that the

Scheme 1. Synthesis of Benzo[*b*]fluorenes



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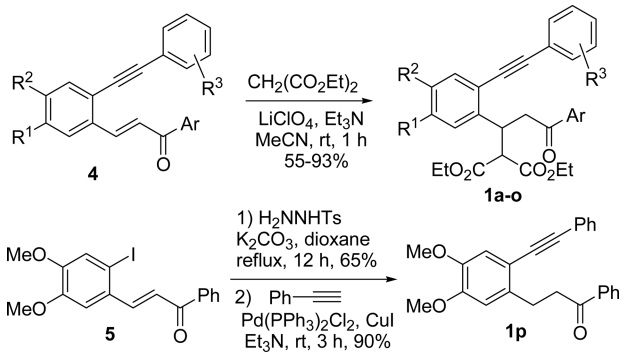
Scheme 2. Preparation of *o*-Alkynyldihydrochalcones

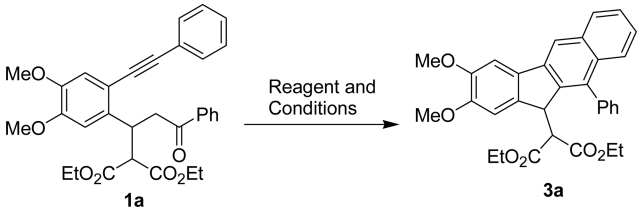


presence of malonate moiety in the starting materials is not a prerequisite for the success of the current methodology.

With the availability of a variety of *o*-alkynyldihydrochalcones in hand, we selected **1a** as a model substrate for optimizing the reaction conditions (Table 1). Since iron(III) halides are known to catalyze Conia–ene reaction[17] as well as Friedel–Crafts cyclization,[18] we first studied the suitability of anhydrous $FeCl_3$ as a catalyst to effect the tandem transformation. When **1a** was heated under reflux with 0.1 equiv of $FeCl_3$ in dichloromethane (DCM) for 24 h, the starting material did not undergo any change (entry 1). However, the reaction when carried out under identical reaction conditions in 1,2-dichloroethane (1,2-DCE) afforded the expected benzo[*b*]fluorene **3a** in 40% yield (entry 2). To improve the yield, we conducted the reaction using more amounts of the catalyst. Thus, the use of 0.3 equiv of $FeCl_3$ gave the best result with in 12 h and **3a** was produced in 87% yield (entry 3). When 0.5 or 1 equiv of $FeCl_3$ was used, the yield of **3a** was decreased mainly because of the formation of copious amounts of precipitates during workup which made the isolation difficult (entries 4 and 5). We also screened other solvents such as THF, toluene and CH_3CN for the reaction, but they gave only poor results (entries 6–8). When $FeCl_3{\cdot}6H_2O$ was used in the place of anhydrous reagent, the yield of **3a** decreased to 57% (entry 9). We also investigated other Lewis acids such as $FeBr_3$, $InCl_3$, $GaCl_3$, $AuCl_3$, $AlCl_3$, $SnCl_4$ and $TiCl_4$ in the reaction, but no encouraging results could be obtained (entries 10–16). Thus, we identified the optimal reaction conditions for the reaction as refluxing **1a** with 0.3 equiv of anhydrous $FeCl_3$ in 1,2-DCE for 12 h.

Under the optimized reaction conditions, we investigated the scope of the reaction for various *o*-alkynyldihydrochalcones and the results are summarized in Table 2. We first examined substrates **1a–f** having electron-rich or deficient and halogenated aromatic rings (Ar) attached to the carbonyl group (entries 1–6). Except **1f** which is having *para*-nitrophenyl ring (entry 6), all other substrates gave the respective benzo[*b*]fluorenes **3a–e** in yields ranging from 63–87% (entries 1–5). The failure of the reaction in the case of **1f** may be attributed to the coordination of the Lewis acid to the nitro group. The reaction tolerated the *o*-alkynyldihydrochalcones **1g** and **1h** having 2-thienyl and 2-furyl rings as Ar and the corresponding benzo[*b*]fluorenes **3g** and **3h** were produced in reasonable yields (entries 7 and 8). The yields are slightly lower possibly because of the high reactivity of these heteroaromatic rings. Next, we studied the substrates **1i–l** having electron donating and halogen substituents (R^3) on the aromatic ring attached to the alkyne unit (entries 9–12). The

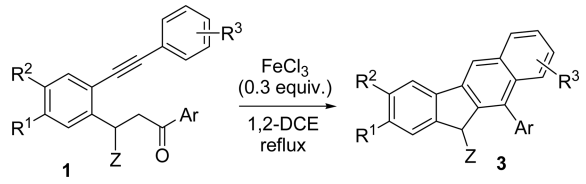
Table 1. Optimization of Reaction Conditions



entry	catalyst (equiv), solvent and conditions[a]	yield[b] (%)
1	$FeCl_3$ (0.1), DCM, reflux, 24 h	NR[c]
2	$FeCl_3$ (0.1), 1,2-DCE, reflux, 24 h	40
3	$FeCl_3$ (0.3), 1,2-DCE, reflux, 12 h	87
4	$FeCl_3$ (0.5), 1,2-DCE, reflux, 12 h	78[d]
5	$FeCl_3$ (1.0), 1,2-DCE, reflux, 12 h	53[d]
6	$FeCl_3$ (0.3), THF, reflux, 24 h	NR[c]
7	$FeCl_3$ (0.3), Toluene, reflux, 24 h	5
8	$FeCl_3$ (0.3), CH_3CN reflux, 24 h	12
9	$FeCl_3{\cdot}6H_2O$ (0.3), 1,2-DCE, reflux, 24 h	57
10	$FeBr_3$ (0.3), 1,2-DCE, reflux, 24 h	55
11	$InCl_3$ (0.3), 1,2-DCE, reflux, 24 h	50
12	$GaCl_3$ (0.3), 1,2-DCE, reflux, 24 h	56
13	$AuCl_3$ (0.3), 1,2-DCE, reflux, 24 h	67
14	$AlCl_3$ (0.3), 1,2-DCE, reflux, 24 h	20
15	$SnCl_4$ (0.3), 1,2-DCE, reflux, 24 h	NR[c]
16	$TiCl_4$ (0.3), 1,2-DCE, reflux, 24 h	NR[c]

[a]No reaction takes place at room temperature. [b]Isolated yields. [c]No reaction. [d]Copious amounts of precipitates formed during workup as well as byproducts reduce the yield.

Table 2. Synthesis of Various Benzo[*b*]fluorenes from *o*-Alkynyldihydrochalcones[a]



entry	R^1, R^2, Ar, R^3, Z	time (h)	yield[a] (%)
1	OMe, OMe, Ph, H, $CH(CO_2Et)_2$ (**1a**)	12	87 (**3a**)
2	OMe, OMe, 4-MeC_6H_4, H, $CH(CO_2Et)_2$ (**1b**)	12	82 (**3b**)
3	OMe, OMe, 4-$MeOC_6H_4$, H, $CH(CO_2Et)_2$ (**1c**)	9	78 (**3c**)
4	OMe, OMe, 4-ClC_6H_4, H, $CH(CO_2Et)_2$ (**1d**)	7	75 (**3d**)
5	OMe, OMe, 4-$CF_3C_6H_4$, H, $CH(CO_2Et)_2$ (**1e**)	12	63 (**3e**)
6	OMe, OMe, 4-$NO_2C_6H_4$, H, $CH(CO_2Et)_2$ (**1f**)	12	–[b]
7	OMe, OMe, 2-thienyl, H, $CH(CO_2Et)_2$ (**1g**)	8	65 (**3g**)
8	OMe, OMe, 2-furyl, H, $CH(CO_2Et)_2$ (**1h**)	10	63 (**3h**)
9	OMe, OMe, Ph, 4-Me, $CH(CO_2Et)_2$ (**1i**)	8	77 (**3i**)
10	OMe, OMe, Ph, 4-Cl, $CH(CO_2Et)_2$ (**1j**)	10	76 (**3j**)
11	OMe, OMe, Ph, 4-OMe, $CH(CO_2Et)_2$ (**1k**)	12	–[c]
12	OMe, OMe, Ph, 3-OMe, $CH(CO_2Et)_2$ (**1l**)	3	83 (**3l**)
13	OMe, OMe, 4-MeC_6H_4, 4-Me, $CH(CO_2Et)_2$ (**1m**)	8	84 (**3m**)
14	$-OCH_2O-$ (R^1, R^2), Ph, H, $CH(CO_2Et)_2$ (**1n**)	9	88 (**3n**)
15	OMe, H, Ph, H, $CH(CO_2Et)_2$ (**1o**)	12	78 (**3o**)
16	H, H, Ph, H, $CH(CO_2Et)_2$ (**1p**)	12	65 (**3p**)
17	OMe, OMe, Ph, H, H (**1q**)	5	64 (**3q**)

[a]Isolated yields. [b]No reaction. [c]Complicated mixture.

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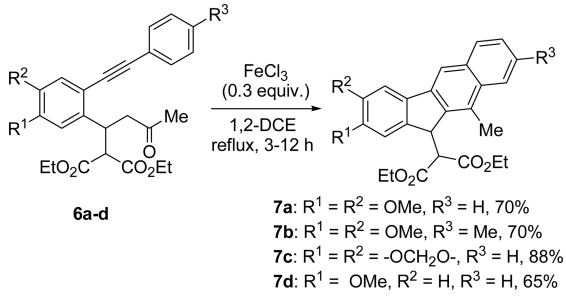
presence of weak *ortho,para*-directing methyl and chloro substituents in the *p*-position of the aromatic ring did not hamper the reaction despite the fact that the Friedel–Crafts reaction would occur at the position which is *meta* to these substituents (entries 9 and 10). On the other hand, the strong *ortho,para*-directing methoxy substituent in the *para*-position of the aromatic ring gave a complicated mixture of products (entry 11). At the same time, a methoxy substituent in the *meta*-position of the aromatic ring facilitated the reaction (entry 12). These observations support the presence of Friedel–Crafts reaction in the tandem process. The reaction was also successful for the substrate **1m** in which both the aromatic rings are *para*-tolyl (entry 13). We also tested substrates **1n–p** having methylenedioxy, single methoxy and no methoxy groups on the main aryl ring and they too furnished the corresponding benzo[*b*]fluorenes **3n–p** in good yields (entries 13–16). As mentioned earlier, the presence of malonate moiety is not critical for the success of the methodology as exemplified by the formation of benzo[*b*]fluorene **3q** from the substrate **1q** (entry 17).

We also explored the scope of the reaction for substrates **6a–d** which are having a methyl group in the place of Ar. These substrates were prepared by the condensation of the respective *o*-alkynylarenecarbaldehydes with 1 equiv of acetone followed by the routine Michael addition with diethylmalonate. Pleasingly, all these substrates furnished the corresponding benzo[*b*]fluorenes **7a–d** in good yields (Scheme 3). For one of the products, **7a**, the structure was unequivocally confirmed by X-ray analysis.[19]

Scheme 3. Further Investigation of the Scope of the Reaction



We propose a mechanism depicted in Scheme 4 for the formation of benzo[*b*]fluorenes **3** from *o*-alkynyldihydrochalcones **1**. The enol **A** is generated from **1** with the assistance of $FeCl_3$. Both the triple and double bonds of **A** coordinate to $FeCl_3$ and this brings the alkyne and enol units closer for a Conia–ene reaction.[17,18] The product **B** formed during the reaction undergoes isomerization to yield the more stable indene derivative **2**. The Friedel–Crafts reaction of **2** promoted by $FeCl_3$ affords benzo[*b*]fluorene **3** via the arenium ion intermediate **C**. The byproduct, $FeCl_2(OH)$ may catalyze the subsequent cycle of transformation or may get converted into $FeCl_3$ under the reaction conditions. The real catalytic species involved in the transformation might be $FeCl_2^+$, as in cases of certain reactions catalyzed by $InCl_3$ and $GaCl_3$.[20] To obtain evidence for the mechanism, we prepared the indene derivative **2a** ($R^1 = R^2 = OMe$, $R^3 = H$, Ar = Ph) independently (yield: 86%)[12] and subjected it to the Friedel–Crafts reaction using $FeCl_3$ (0.3 equiv), which produced **3a** in 86% yield (the overall yield is 74%).

In summary, we have developed an efficient procedure for the synthesis of a variety of benzo[*b*]fluorene derivatives from *o*-alkynyldihydrochalcones. The transformation proceeds in a tandem manner through 5-*exo*-*dig* Conia–ene reaction followed by Friedel–Crafts cyclization. The reactions require only readily available iron catalyst and are easy to perform and applicable to a wide array of substrates.

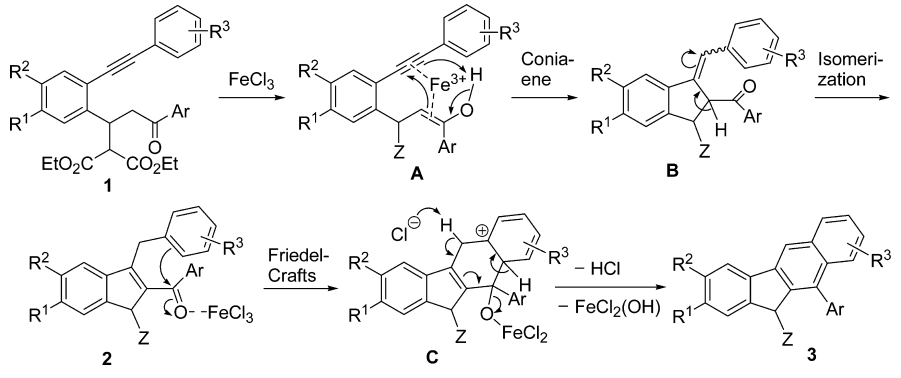
EXPERIMENTAL SECTION

General Remarks. Melting points were determined using an apparatus by the open capillary tube method and are uncorrected. The ^1H and ^{13}C NMR spectra were recorded on a 400 or 500 MHz NMR spectrometer. HRMS (ESI) were recorded on Q-TOF mass spectrometers. Low resolution mass spectra (ESI) were recorded on LC–MS spectrometers. Elemental analyses were performed on a CHN analyzer. X-ray crystallographic data were collected on a CCD diffractometer using graphite-monochromated Mo Ka radiation. Thin layer chromatography (TLC) was performed on precoated alumina sheets and detected under UV light. Silica gel (100–200 mesh) was used for column chromatography.

General Procedure for the Synthesis of *o*-Alkynyldihydrochalcones 1 (or 6). To a stirred mixture of diethyl malonate (176 mg; 1.1 mmol) and lithium perchloarte (5.3 mg; 5 mol %) in acetonitrile (5 mL) was added *o*-alkynylarene chalcone **4** (1.0 mmol) followed by addition of triethylamine (0.14 mL; 1.0 mmol). The reaction mixture was stirred for 60 min at rt to give an yellow oil and then diluted with water. The product was extracted with ethyl acetate and the organic layer was washed with water, dried over anhydrous Na_2SO_4 and filtered. The crude product obtained was purified by column chromatography (SiO_2; EtOAc:hexane, 1:3 v/v) to afford pure **1** (or **6**).

*Diethyl 2-(1-(4,5-dimethoxy-2-phenylethynyl-phenyl)-3-oxo-3-phenyl-propyl)-malonate (**1a**).* Brown oil. Yield: 90% (475 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.2 Hz, 2H), 7.48–7.45 (m,

Scheme 4. Plausible Mechanism for the Formation of Benzo[*b*]fluorenes



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2H), 7.39 (t, J = 7.2 Hz, 1H), 7.31−7.26 (m, 5H), 6.88 (s, 1H), 6.76 (s, 1H), 4.60−4.55 (m, 1H), 4.23 (d, J = 9.2 Hz, 1H), 4.14−4.03 (m, 2H), 3.95 (q, J = 7.2 Hz, 2H), 3.81−3.69 (m, 7H), 3.53 (dd, J = 16.4, 4.8 Hz, 1H), 1.14 (t, J = 7.2 Hz, 3H), 1.00 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 167.5, 167.0, 148.1, 146.5, 135.9, 134.3, 131.9, 130.3, 127.5, 127.3, 127.1, 122.4, 113.9, 92.4, 86.9, 60.5, 60.4, 54.89, 54.86, 54.8, 39.9, 38.5, 13.0, 12.9 ppm. MS (ESI) m/z 529 [M + H$^+$]. Anal. Calcd for $C_{32}H_{32}O_7$: C 72.71, H 6.10. Found: C 72.89, H 6.22.

*Diethyl 2-(1-(4,5-Dimethoxy-2-phenylethynyl-phenyl)-3-oxo-3-p-tolyl-propyl)-malonate (**1b**).* Brown oil. Yield: 77% (417 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 7.2 Hz, 2H), 7.35 (t, J = 6.0 Hz, 3H), 7.16 (d, J = 8.0 Hz, 2H), 6.95 (s, 1H), 6.84 (s, 1H), 4.68−4.62 (m, 1H), 4.28 (d, J = 8.8 Hz, 1H), 4.22−4.09 (m, 3H), 4.02 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.66 (dd, J = 16.0, 9.2 Hz, 1H), 3.57 (dd, J = 16.4, 4.8 Hz, 1H), 2.32 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 168.5, 168.0, 149.1, 147.5, 143.7, 135.5, 134.5, 131.4, 129.2, 128.3, 128.1, 123.5, 114.9, 114.4, 112.1, 93.3, 88.0, 61.5, 61.4, 60.4, 55.92, 55.89, 40.9, 39.6, 21.6, 21.0, 14.2, 14.0, 13.9 ppm. MS (ESI) m/z 543 [M + H$^+$]. Anal. Calcd for $C_{33}H_{34}O_7$: C 73.04, H 6.32. Found: C 73.21, H 6.19.

*Diethyl 2-(1-(4,5-dimethoxy-2-phenylethynyl-phenyl)-3-(4-methoxy-phenyl)-3-oxo-propyl)-malonate (**1c**).* Brown oil. Yield: 75% (419 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 5.6 Hz, 2H), 7.34 (t, J = 5.6 Hz, 3H), 6.95 (s, 1H), 6.84 (s, 2H), 6.82 (s, 1H), 4.71−4.65 (m, 1H), 4.29−4.09 (m, 3H), 4.02 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 3.77 (s, 3H), 3.67 (dd, J = 16.0,10.0 Hz, 1H), 3.55 (dd, J = 16.0,4.8 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 168.5, 168.0, 163.4, 149.1, 147.5, 135.4, 131.4, 130.5, 130.0, 128.3, 128.1, 123.5, 114.8, 113.7, 93.2, 88.0, 61.5, 61.4, 56.0, 55.92, 55.88, 55.4, 40.9, 14.0, 13.9 ppm. MS (ESI) m/z 559 [M + H$^+$]. Anal. Calcd for $C_{33}H_{34}O_8$: C 70.95, H 6.13. Found: C 70.89, H 6.24.

*Diethyl 2-(3-(4-chloro-phenyl)-1-(4,5-dimethoxy-2-phenylethynyl-phenyl)-3-oxo-propyl)-malonate (**1d**).* Brown oil. Yield: 81% (455 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.51−7.49 (m, 2H), 7.37−7.34 (m, 3H), 7.32 (d, J = 8.4 Hz, 2H), 6.94 (s, 1H), 6.82 (s, 1H), 4.66−4.61 (m, 1H), 4.25−4.13 (m, 3H), 4.02 (q, J = 7.2 Hz, 2H), 3.85 (s, 6H), 3.69−3.57 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 168.5, 167.8, 149.2, 147.6, 19.4, 135.2, 135.0, 131.3, 129.7, 128.9, 128.4, 128.2, 123.3, 114.8, 114.6, 93.4, 87.8, 61.6, 61.5, 56.0, 55.9, 41.3, 14.0, 13.9 ppm. MS (ESI) m/z 563 [M + H$^+$]. Anal. Calcd for $C_{32}H_{31}ClO_7$: C 68.26, H 5.55. Found: C 68.48, H 5.66.

*Diethyl 2-(1-(4,5-dimethoxy-2-phenylethynyl-phenyl)-3-oxo-3-(4-trifluoromethyl-phenyl)-propyl)-malonate (**1e**).* Yellow oil. Yield: 55% (330 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.35−7.34 (m, 3H), 6.95 (s, 1H), 6.82 (s, 1H), 4.27−4.09 (m, 1H), 4.03 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.68 (d, J = 6.8 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 168.5, 167.8, 149.2, 147.6, 139.5, 134.7, 134.3, 134.0, 131.3, 128.6, 128.3, 125.62, 125.59, 124.9, 123.2, 122.2, 114.8, 114.5, 93.4, 87.7, 61.7, 61.5, 56.0, 55.91, 55.88, 41.8, 14.0, 13.9 ppm. MS (ESI) m/z 619 [M + Na$^+$]. Anal. Calcd for $C_{33}H_{31}F_3O_7$: C 66.44, H 5.24. Found: C 66.57, H 5.31.

*Diethyl 2-(1-(4,5-dimethoxy-2-phenylethynyl-phenyl)-3-(4-nitro-phenyl)-3-oxo-propyl)-malonate (**1f**).* Brown oil. Yield: 56% (321 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 7.2 Hz, 4H), 7.35 (d, J = 6.0 Hz, 3H), 6.94 (s, 1H), 6.82 (s, 1H), 4.67−4.63 (m, 1H), 4.25−4.17 (m, 3H), 4.02 (q, J = 6.8 Hz, 2H), 3.87 (s, 6H), 3.64−3.60 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 168.5, 167.8, 149.2, 147.7, 135.7, 15.0, 131.8, 131.3, 129.8, 128.4, 128.2, 128.1, 123.3, 114.9, 93.4, 87.8, 61.6, 61.5, 56.0, 55.94, 55.91, 41.3, 14.0, 13.9 ppm. MS (ESI) m/z 574 [M + H$^+$]. Anal. Calcd for $C_{32}H_{31}NO_9$: C 67.01, H 5.45, N 2.44. Found: C 67.19, H 5.51, N 2.59.

*Diethyl 2-(1-(4,5-dimethoxy-2-phenylethynyl-phenyl)-3-oxo-3-thiophen-2-yl-propyl)-malonate (**1g**).* Brown oil. Yield: 57% (304 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 3.6 Hz, 1H), 7.57−7.54 (m, 2H), 7.53 (d, J = 5.2 Hz, 1H), 7.38−7.33 (m, 3H), 7.00 (t, J = 6.0 Hz, 1H), 6.96 (s, 1H), 6.85 (s, 1H), 4.67−4.61(m, 1H), 4.33−4.13 (m, 3H), 4.02 (q, J = 7.2 Hz, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.75 (dd, J = 15.6, 9.2 Hz, 1H), 3.51 (dd, J = 15.6, 4.8 Hz, 1H), 1.24 (t, J = 6.8 Hz, 3H), 1.07 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 168.4, 167.9, 149.1, 147.5, 144.3, 135.0, 133.7, 132.2, 131.4, 128.4, 128.2, 128.1, 123.4, 114.9, 114.4, 93.4, 87.9, 61.6, 61.50, 61.45, 55.92, 55.88, 55.7, 41.7, 14.0, 13.9 ppm. MS (ESI) m/z 535 [M + H$^+$]. Anal. Calcd for $C_{30}H_{30}O_7S$: C 67.40, H 5.66. Found: C 67.55, H 5.70.

*Diethyl 2-(1-(4,5-dimethoxy-2-phenylethynyl-phenyl)-3-furan-2-yl-3-oxo-propyl)-malonate (**1h**).* Yellow oil. Yield: 67% (347 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.56 (m, 2H), 7.48 (s, 1H), 7.39−7.34 (m, 3H), 7.19 (d, J = 3.6 Hz, 1H), 6.95 (s, 1H), 6.86 (s, 1H) 6.43−6.41(m, 1H), 4.65−4.59 (m, 1H), 4.30 (d, J = 9.6 Hz, 1H), 4.23−4.14 (m, 2H), 4.02 (q, J = 7.2 Hz, 2H), 3.90−3.83 (m, 6H), 3.66 (dd, J = 16.0, 9.2 Hz, 1H), 3.39 (dd, J = 16.0, 4.8 Hz, 1H), 1.24 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 186.9, 168.4, 167.8, 152.6, 149.1, 147.6, 146.3, 135.1, 131.4, 128.4, 128.1, 123.5, 117.4, 115.0, 112.2, 93.4, 87.9, 61.6, 61.4, 55.93, 55.90, 55.7, 40.8, 14.0, 13.9 ppm. MS (ESI) m/z 519 [M + H$^+$]. Anal. Calcd for $C_{30}H_{30}O_8$: C 69.49, H 5.83. Found: C 69.60, H 5.70.

*Diethyl 2-(1-(4,5-dimethoxy-2-p-tolylethynyl-phenyl)-3-oxo-3-phenyl-propyl)-malonate (**1i**).* Yellow oil. Yield: 69% (374 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 2H), 7.47−7.43 (m, 3H), 7.37 (t, J = 7.2 Hz, 2H), 7.16 (d, J = 7.6 Hz, 2H), 6.94 (s, 1H), 6.83 (s, 1H), 4.63−4.60 (m, 1H), 4.33 (d, J = 8.8 Hz, 1H), 4.22−4.12 (m, 2H), 4.03(q, J = 7.2 Hz, 2H),), 3.84 (s, 3H), 3.82−3.79 (m, 4H), 3.61 (dd, J = 16.0,10.0 Hz, 1H), 2.38 (s, 3H), 1.25(t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 168.4, 167.9, 148.9, 147.5, 138.2, 136.9, 135.2, 133.0, 131.2, 129.1, 128.5, 128.1, 120.4, 115.0, 93.6, 87.3, 61.4, 61.3, 55.9, 55.88,55.85, 55.7, 40.9, 21.4, 14.0, 13.8 ppm. MS (ESI) m/z 543 [M + H$^+$]. Anal. Calcd for $C_{33}H_{34}O_7$: C 73.04, H 6.32. Found: C 73.23, H 6.23.

*Diethyl 2-(1-(2-(4-chloro-phenylethynyl)-4,5-dimethoxy-phenyl)-3-oxo-3-phenyl-propyl)-malonate (**1j**).* Yellow oil. Yield: 73% (413 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 8.0 Hz, 3H), 7.30 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 6.86 (s, 1H), 6.75 (s, 1H), 4.59−4.56 (m, 1H), 4.16−4.04 (m, 3H), 3.95 (q, J = 7.2 Hz, 2H), 3.77 (s, 3H), 3.75 (s, 3H), 3.64 (dd, J = 16.4, 9.2 Hz 1H), 3.53 (dd, J = 16.4, 4.8 Hz 1H), 1.15 (t, J = 6.8 Hz, 3H), 1.00 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 168.5, 167.9, 149.3, 147.5, 136.9, 135.5, 134.1, 133.0, 132.6, 128.7, 128.6, 128.2, 122.0, 114.8, 114.2, 92.2, 88.5, 61.6, 61.5, 55.93, 55.90, 41.1, 14.0, 13.9 ppm. MS (ESI) m/z 563 [M + H$^+$]. Anal. Calcd for $C_{32}H_{31}ClO_7$: C 68.26, H 5.55. Found: C 68.42, H 5.70.

*Diethyl 2-(1-(4,5-Dimethoxy-2-(4-methoxy-phenylethynyl)-phenyl)-3-oxo-3-phenyl-propyl)-malonate (**1k**).* Brown oil. Yield: 71% (392 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.50−7.45 (m, 3H), 7.37−7.36 (m, 2H), 6.95 (s, 1H), 6.89−6.85 (m, 3H), 4.68−4.66 (m, 1H), 4.33 (d, J = 8.8 Hz, 1H), 4.21−4.08 (m, 2H), 4.03 (q, J = 7.2 Hz, 2H), 3.82−3.77 (m, 10H), 3.61 (dd, J = 16.4, 11.0 Hz, 1H), 1.22 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 168.5, 168.0, 159.6, 148.9, 147.5, 137.0, 135.1, 132.9, 132.8, 128.5, 128.1, 115.6, 114.84, 114.78, 114.0, 93.4, 86.6, 61.5, 61.3, 55.9, 55.84, 55.75, 55.3, 40.9, 14.0, 13.9 ppm. MS (ESI) m/z 559 [M + H$^+$]. Anal. Calcd for $C_{33}H_{34}O_8$: C 70.95, H 6.13. Found: C 70.99, H 6.20.

*Diethyl 2-(1-(4,5-dimethoxy-2-(3-methoxy-phenylethynyl)-phenyl)-3-oxo-3-phenyl-propyl)-malonate (**1l**).* Brown oil. Yield: 88% (489 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 7.6 Hz, 1H), 7.17−7.13 (m, 2H), 6.98 (s, 1H), 6.92−6.89 (m, 1H), 6.86 (s, 1H), 4.71−4.62 (m, 1H), 4.32 (d, J = 8.8 Hz, 1H), 4.23−4.13 (m, 2H), 4.05 (q, J = 7.2 Hz, 2H), 3.85−3.78 (m, 10H), 3.62 (dd, J = 16.4, 4.8 Hz, 1H), 1.26 (t, J = 6.8 Hz, 3H), 1.08 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 168.5, 168.0, 159.4, 149.1, 147.5, 136.9, 135.5, 133.0, 129.4, 128.5, 128.1, 124.4, 123.9, 116.3, 114.9, 114.7, 114.3, 112.1, 93.4, 87.8, 61.5, 61.4, 55.90, 55.88, 55.8, 55.3, 40.9,

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39.5, 14.1, 13.9 ppm. MS (ESI) m/z 559 [M + H$^+$]. Anal. Calcd for $C_{33}H_{34}O_8$: C 70.95, H 6.13. Found: C 70.81, H 6.17.

*Diethyl 2-(1-(4,5-dimethoxy-2-p-tolylethynyl-phenyl)-3-oxo-3-p-tolyl-propyl)-malonate (**1m**).* Brown oil. Yield: 73% (406 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 4H), 6.94 (s, 1H), 6.84 (s, 1H), 4.72−4.61 (m, 1H), 4.31 (d, J = 9.2 Hz, 1H), 4.24−4.12 (m, 2H) 4.02 (q, J = 7.2 Hz, 2H), 3.86−3.73 (m, 7H), 3.56 (dd, J = 16.0, 4.4 Hz, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 1.22(t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 168.5, 168.0, 148.9, 147.4, 143.7, 138.2, 135.3, 134.5, 131.3, 129.2, 129.1, 128.3, 120.4, 114.9, 114.6, 93.5, 87.3, 61.5, 61.4, 55.90, 55.86, 40.9, 21.6, 21.5, 14.0, 13.9 ppm. MS (ESI) m/z 557 [M + H$^+$]. Anal. Calcd for $C_{34}H_{36}O_7$: C 73.36, H 6.52. Found: C 73.49, H 6.61.

*Diethyl 2-(3-oxo-3-phenyl-1-(6-phenylethynyl-benzo(1,3)dioxol-5-yl)-propyl)-malonate (**1n**).* Yellow oil. Yield: 93% (476 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.2 Hz, 2H), 7.94−7.44 (m, 3H), 7.39−7.25 (m, 5H), 6.91 (s, 1H), 6.83 (s, 1H), 5.91 (d, J = 4.4 Hz, 2H), 4.73−4.70 (m, 1H), 4.21−4.18 (m, 3H), 4.04 (q, J = 7.2 Hz, 2H), 3.70−3.60 (m, 2H), 1.22 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 168.4, 167.9, 148.1, 146.3, 137.2, 136.8, 133.0, 131.5, 128.6, 128.3, 128.2, 128.1, 123.4, 111.9, 101.5, 93.4, 87.8, 61.52, 61.49, 56.0, 40.9, 14.0, 13.9 ppm. MS (ESI) m/z 513 [M + H$^+$]. Anal. Calcd for $C_{31}H_{28}O_7$: C 72.64, H 5.51. Found: C 72.83, H 5.65.

*Diethyl 2-(1-(5-methoxy-2-phenylethynyl-phenyl)-3-oxo-3-phenyl-propyl)-malonate (**1o**).* Brown oil. Yield: 81% (403 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 7.2 Hz, 2H), 7.46−7.41 (m, 2H), 7.36−7.29 (m, 5H), 6.89 (s, 1H), 6.70 (d, J = 8.8 Hz, 1H), 4.76−4.73 (m, 1H), 4.30 (d, J = 8.4 Hz, 1H), 4.18−4.12 (m, 2H), 4.03 (q, J = 7.2 Hz, 2H), 3.84−3.63 (m, 5H), 1.18 (t, J = 7.2 Hz, 3H), 1.06 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 168.4, 168.0, 159.6, 144.0, 137.0, 134.2, 133.0, 131.4, 128.6, 128.3, 128.2, 128.14 128.06, 123.7, 114.8, 114.6, 112.5, 93.5, 87.9, 61.5, 61.4, 55.7, 55.3, 40.6, 14.0, 13.9 ppm. MS (ESI) m/z 513 [M + H$^+$]. Anal. Calcd for $C_{31}H_{30}O_6$: C 74.68, H 6.07. Found: C 74.77, H 6.15.

*Diethyl 2-(3-oxo-3-phenyl-1-(2-phenylethynyl-phenyl)-propyl)-malonate (**1p**).* Brown oil. Yield: 85% (398 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 4.8 Hz, 2H), 7.50−7.45 (m, 2H), 7.39−7.31 (m, 6H), 7.26−7.15 (m, 2H), 4.79−4.74 (m, 1H), 4.27 (d, J = 8.8 Hz, 1H), 4.22−4.10 (m, 2H), 4.04 (q, J = 7.2 Hz, 2H), 3.81 (dd, J = 16.4, 9.2 Hz, 1H), 3.65 (dd, J = 16.4, 4.4 Hz, 1H), 1.20 (t, J = 7.2 Hz, 3H), 1.05 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 168.4, 168.0, 159.6, 144.0, 137.0, 134.2, 133.0, 131.4, 128.6, 128.3, 128.2, 128.14, 128.06, 123.7, 114.8, 114.6, 112.5, 93.5, 87.9, 61.5, 61.4, 55.7, 55.3, 40.6, 14.0, 13.9 ppm. MS (ESI) m/z 569 [M + H$^+$]. Anal. Calcd for $C_{30}H_{28}O_5$: C 76.90, H 6.02. Found: C 76.79, H 6.13.

*Diethyl 2-(1-(4,5-dimethoxy-2-phenylethynyl-phenyl)-3-oxo-butyl)-malonate (**6a**).* Yellow oil. Yield: 70% (326 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2H), 7.59−7.35 (m, 3H) 6.98 (s, 1H), 6.82 (s, 1H), 4.49−4.21 (m, 1H) 4.20−4.12 (m, 3H) 4.02 (q, J = 6.8 Hz, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 3.20 (dd, J = 16.8, 8.4 Hz, 1H), 3.05 (dd, J = 16.4, 8.4 Hz, 1H), 2.09 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.0 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5,168.4, 167.9, 149.2, 147.6, 135.4, 131.3, 128.4, 128.2, 123.4, 114.9, 93.4, 87.8, 61.5, 61.4, 56.0, 55.9, 55.7, 46.0, 30.1, 14.0, 13.9 ppm. MS (ESI) m/z 467 [M + H$^+$]. Anal. Calcd for $C_{27}H_{30}O_7$: C 69.51, H 6.48. Found: C 69.66, H 6.51.

*Diethyl 2-(1-(4,5-dimethoxy-2-p-tolylethynyl-phenyl)-3-oxo-butyl)-malonate (**6b**).* Yellow oil. Yield 80% (384 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 6.97 (s, 1H), 6.82 (s, 1H), 4.45−4.30 (m, 1H) 4.20−4.16 (m, 3H), 4.02 (q, J = 6.8 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 3.21(dd, J = 16.4, 8.8 Hz, 1H), 3.04 (dd, J = 16.4, 4.4 Hz, 1H), 2.38, (s, 3H), 2.08 (s, 3H), 1.24 (t, J = 6.8 Hz, 3H), 1.08 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 168.4, 67.9, 149.0, 147.6, 138.4, 135.2, 131.2, 129.2, 120.3, 114.9, 93.6, 87.1, 61.5, 61.4, 56.0, 55.9, 55.6, 46.0, 30.0, 21.5, 14.0, 13.9 ppm. MS (ESI) m/z 481 [M + H$^+$]. Anal. Calcd for $C_{28}H_{32}O_7$: C 69.98, H 6.71. Found: C 70.17, H 6.77.

*Diethyl 2-(1-(5-methoxy-2-phenylethynyl-phenyl)-3-oxo-butyl)-malonate (**6c**).* Yellow oil. Yield 77% (347 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.56 (m, 2H), 7.37−7.30 (m, 3H), 6.93 (s, 1H), 6.78 (s, 1H), 5.93 (s, 2H), 4.61−4.55 (m, 1H), 4.20−4.10 (m, 3H), 4.05 (q, J = 7.2 Hz, 2H), 3.16−3.02 (m, 2H), 2.10, (s, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.00 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 168.3, 167.8, 148.1, 146.4, 137.1, 131.6, 131.5, 131.4, 128.4, 128.3, 123.3, 115.7, 111.9, 101.6, 93.4, 87.7, 61.50, 61.47, 60.4, 55.8, 45.91, 38.4, 30.0, 14.0, 13.9 ppm. MS (ESI) m/z 451 [M + H$^+$]. Anal. Calcd for $C_{26}H_{26}O_7$: C 69.32, H 5.82. Found: C 69.49, H 5.93.

*Diethyl 2-(3-oxo-1-(6-phenylethynyl-benzo[1,3]dioxol-5-yl)-butyl)-malonate (**6d**).* Yellow oil. Yield 68% (296 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.4 Hz, 1H), 7.38−7.32 (m, 3H), 6.83 (d, J = 2.4 Hz, 1H), 6.74 (dd, J = 8.8, 2.8 Hz, 1H), 4.55−4.49 (m, 1H), 4.19−4.14 (m, 3H), 4.03 (q, J = 7.2 Hz, 2H), 3.79 (s, 3H), 3.20 (dd, J = 16.8, 8.8 Hz, 1H), 3.07 (dd, J = 16.8, 5.2 Hz, 1H), 2.09, (s, 3H), 1.23 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 168.3, 167.9, 159.6, 143.8, 134.2, 131.3, 128.4, 128.1, 123.6, 114.7, 112.5, 93.4, 87.7, 61.5, 61.4, 55.5, 55.3, 45.7, 30.1, 14.0, 13.8 ppm. MS (ESI) m/z 435 [M-H$^+$]. Anal. Calcd for $C_{26}H_{28}O_6$: C 71.54, H 6.47. Found: C 71.62, H 6.55.

Procedure for the Synthesis of 3-(4,5-Dimethoxy-2-phenylethynyl-phenyl)-1-phenyl-propan-1-one (1q). To a solution of *o*-iodochalcone **5** (394 mg; 1.0 mmol) in 1,4-dioxane (6 mL) were added tosylhydrazide (205 mg; 1.1 mmol) and K_2CO_3 (207 mg; 1.5 mmol). The reaction mixture was heated under reflux for 24 h. After completion of the reaction, the reaction mixture was cooled to room temperature, filtered and dried. The crude product was purified by column using hexane/ethyl acetate to give pure iododihydrochalcone (257 mg; 65%). To a mixture of the pure iododihydrochalcone (198 mg, 0.5 mmol), phenylacetylene (0.1 mL; 1 mmol) and $Pd(PPh_3)_2Cl_2$ (18 mg; 5 mol %) in triethylamine (5 mL) was added copper(I) iodide (1 mg; 1 mol %) under nitrogen atmosphere and allowed to stir at room temperature for 3 h. The reaction mixture was concentrated under reduced pressure, and the residue was extracted with ethyl acetate. The organic layer was washed with water, dried (anhydrous Na_2SO_4), and the solvent was removed. The crude product was purified by column chromatography (SiO_2; EtOAc:hexane, 1:9 v/v) to afford pure **1q**. Brown oil. Yield: 90% (167 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 6.4 Hz, 2H), 7.51−7.46 (m, 3H), 7.39 (t, J = 6.4 Hz, 2H), 7.35−7.31 (m, 3H), 7.03 (s, 1H), 6.82 (s, 1H), 3.89 (s, 6H), 3.63 (t, J = 8.0 Hz, 2H), 3.25 (t, J = 8.0 Hz, 2H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 149.5, 147.2, 136.90, 136.86, 133.1, 131.4, 128.6, 128.4, 128.2, 128.1, 123.5, 114.7, 114.2, 112.3, 92.0, 88.1, 56.1, 56.0, 39.9, 29.7 ppm. MS (ESI) m/z = 371 [M + H$^+$]. Anal. Calcd for $C_{25}H_{22}O_3$: C 81.06, H 5.99. Found: C 81.24, H 5.87.

General Procedure for the Synthesis of Benzo[*b*]fluorene. To a solution of *o*-alkynyldihydrochalcones **1** (or **6**) (0.25 mmol) in 1,2-dichloroethane (6 mL) was added anhydrous $FeCl_3$ (12 mg; 0.075 mmol) and the reaction mixture was heated under reflux for 3−12 h. After completion of the reaction, the reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was diluted with water and extracted with dichloromethane. The combined organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product obtained was purified by column chromatography (SiO_2; EtOAc:hexane, 1:9 v/v) to afford pure **3** (or **7**). The compound **3a** could also be obtained in 56% overall yield over two steps using 0.5 equiv of I_2 and 3.0 equiv of $AlCl_3$ as described earlier.[12]

*Diethyl 2-(2,3-dimethoxy-10-phenyl-11H-benzo[b]fluoren-11-yl)-malonate (**3a**).* Colorless solid. Yield: 87% (111 mg). mp 140−142 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H) 7.93 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.59−7.46 (m, 6H), 7.37−7.33(m, 2H), 7.22 (s, 1H), 4.86 (d, J = 2.4 Hz, 1H), 4.19−4.13 (m, 2H), 4.02 (s, 3H), 3.90 (s, 3H), 3.64 (d, J = 2.8 Hz, 1H), 3.60−3.48 (m, 2H), 1.21 (t, J = 7.0 Hz, 3H), 0.61 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 166.9, 149.6, 149.5, 140.7, 137.9, 136.7, 135.5,

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134.1, 133.7, 131.5, 130.8, 129.5, 128.5, 128.0, 127.9, 125.9, 125.7, 125.1, 116.0, 109.3, 102.8, 61.3, 60.5, 56.11,56.06, 51.9, 45.5, 14.1, 13.4 ppm. HRMS (ESI) Calcd for $C_{32}H_{30}O_6$ 511.2115 [M + H^+], found 511.2134. This compound could also be obatined in two steps as described earlier.

*Diethyl 2-(2,3-dimethoxy-10-p-tolyl-11H-benzo[b]fluoren-11-yl)-malonate (**3b**).* Colorless solid. Yield: 82% (107 mg). mp 127−129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H) 7.92 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.48−7.44 (m, 1H), 7.40 (s, 2H), 7.37−7.32 (m, 4H), 7.21 (s, 1H), 4.86 (d, J = 2.4 Hz, 1H), 4.23−4.12 (m, 2H), 4.02 (s, 3H), 3.90 (s, 3H), 3.67 (d, J = 2.4 Hz, 1H), 3.62−3.46 (m, 2H), 2.48 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H), 0.61 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 199.9, 149.5, 140.7, 140.1, 137.5, 136.7, 135.6, 134.8. 134.1, 133.8, 131.7, 130.6, 130.1, 129.3, 129.2, 128.0, 126.0, 125.6, 125.6, 125.0, 115.8, 109.3, 102.8, 61.3, 60.5, 56.11, 56.06, 51.9, 45.6, 21.34, 14.1, 13.4 ppm. HRMS (ESI) Calcd for $C_{33}H_{32}O_6$ 525.2272 [M + H^+], found 525.2279.

*Diethyl 2-(2,3-dimethoxy-10-(4-methoxy-phenyl)-11H-benzo[b]-fluoren-11-yl)-malonate (**3c**).* Colorless solid. Yield: 78% (105 mg). mp 153−155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H) 7.92 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.48−7.32 (m, 5H), 7.21 (s, 1H), 7.13(dd, J = 8.4, 2.8 Hz, 1H), 7.06 (dd, J = 8.4, 2.4 Hz, 1H), 4.86 (d, J = 2.4 Hz, 1H), 4.24−4.13 (m, 2H), 4.02 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H), 3.70 (d, J = 2.8 Hz, 1H), 3.62−3.46 (m, 2H), 1.22 (t, J = 7.0 Hz, 3H), 0.6 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 166.9, 159.3, 149.53, 149.46, 140.9, 140.1, 136.7, 135.3, 134.1, 133.8, 131.9, 131.8, 130.5, 129.9, 128.0, 125.9, 125.7, 125.0, 115.8, 114.8, 114.1, 109.3, 102.8, 61.4, 60.5, 56.1, 56.1, 55.3, 51.9, 45.6, 14.0, 13.4 ppm. HRMS (ESI) Calcd for $C_{33}H_{32}O_7$ 541.2221 [M + H^+], found 541.2236.

*Diethyl 2-(10-(4-chloro-phenyl)-2,3-dimethoxy-11H-benzo[b]-fluoren-11-yl)-malonate (**3d**).* Colorless solid. Yield: 75% (102 mg). mp 117−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.61−7.56 (m, 2H), 7.54−7.46 (m, 3H), 7.43−7.40 (m, 1H), 7.38−7.34 (m, 2H), 7.22 (s, 1H), 4.83 (d, J = 2.4 Hz, 1H), 4.24−4.13 (m, 2H), 4.02 (s, 3H), 3.90 (s, 3H), 3.62 (d, J = 2.8 Hz, 1H), 3.60−3.49 (m, 2H), 1.25 (t, J = 7.0 Hz, 3H), 0.61 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.47, 166.73, 149.6, 140.9, 140.2, 136.5, 136.4, 134.2, 134.1, 134.0, 133.6, 132.2, 131.3, 130.9, 129.7, 128.9, 128.1, 125.9, 125.6, 125.3, 116.3, 109.3, 102.8, 61.6, 60.6, 56.1, 52.1, 45.4, 14.1, 13.4 ppm. HRMS (ESI) Calcd for $C_{32}H_{29}ClO_6$ 545.1725 [M + H^+], found 545.1718.

*Diethyl 2-(2,3-dimethoxy-10-(4-trifluoromethyl-phenyl)-11H-benzo[b]fluoren-11-yl)-malonate (**3e**).* Yellow oil. Yield: 63% (91 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H) 7.95 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.40−7.35 (m, 2H), 7.25 (s, 1H), 4.83 (d, J = 2.0 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 4.03 (s, 3H), 3.91 (s, 3H), 3.63−3.47 (m, 3H), 1.91 (t, J = 7.2 Hz, 3H), 0.61 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$)169.1, 166.6, 149.7, 142.0, 141.0, 140.2, 136.3, 134.0, 133.9, 133.4, 131.3, 130.04, 129.97, 128.9, 128.2, 126.42, 126.39, 126.0, 125.9, 125.5, 125.4, 116.6, 109.3, 102.7, 61.6, 60.8, 56.2, 51.9, 45.4, 13.9, 12.9 ppm. MS (ESI) m/z 601 [M + Na^+]. Anal. Calcd for $C_{33}H_{29}F_3O_6$: C 68.51, H 5.05. Found: C 68.72, H 5.17.

*Diethyl 2-(2,3-dimethoxy-10-thiophen-2-yl-11H-benzo[b]fluoren-11-yl)-malonate (**3g**).* Yellow solid. Yield: 65% (84 mg). mp 101−103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.91 (d, J = 9.2 Hz, 2H), 7.55 (dd, J = 4.8, 1.2 Hz, 1H), 7.50−7.46 (m, 1H), 7.41−7.37 (m, 1H), 7.35 (s, 1H), 7.27−7.23 (m, 3H), 4.99 (d, J = 2.4 Hz, 1H), 4.29−4.17 (m, 2H), 4.01 (s, 3H), 3.91 (s, 3H), 3.86 (d, J = 2.8 Hz, 1H), 3.63−3.46 (m, 2H), 1.26 (t, J = 7.0 Hz, 3H), 0.60 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 166.9, 149.6, 142.7, 140.2, 137.8, 136.6, 134.0, 133.5, 132.3, 128.8, 128.0, 127.9, 127.6, 126.9, 126.0, 125.7, 125.5, 116.9, 109.3, 102.7, 61.5, 60.6, 56.11, 56.07, 51.7, 46.2, 14.2, 13.4 ppm. MS (ESI) m/z 539 [M + Na^+]. Anal. Calcd for $C_{30}H_{28}O_6S$: C 69.75, H 5.46. Found: C 69.88, H 5.58.

*Diethyl 2-(2,3-dimethoxy-10-furan-2-yl-11H-benzo[b]fluoren-11-yl)-malonate (**3h**).* Yellow solid. Yield: 63% (79 mg). mp 115−117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11(d, J = 8.4 Hz, 1H), 8.03 (s, 1H) 7.82 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 1.6 Hz, 1H), 7.51−7.42 (m, 2H), 7.35 (s, 1H), 7.31(s, 1H), 6.77 (d, J = 3.2 Hz, 1H), 6.67 (dd, J = 3.4, 1.8 Hz, 1H), 5.13 (d, J = 2.0 Hz, 1H), 4.37−4.24 (m, 2H), 4.01 (s, 3H), 3.93 (s, 3H), 3.60−3.42 (m, 3H), 1.32 (t, J = 7.0 Hz, 3H), 0.58 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 166.9, 149.9, 149.61, 149.57, 143.04, 142.6, 140.3, 136.7, 134.1, 133.4, 130.9, 128.2, 125.9, m125.6, 125.4, 124.2, 117.1, 111.8, 111.4, 109.5, 102.8, 61.5, 60.5, 65.12, 56.10, 52.0, 46.0, 14.2, 13.3 ppm. . MS (ESI) m/z 501 [M + H^+]. Anal. Calcd for $C_{30}H_{28}O_7$: C 71.99, H 5.64. Found: C 72.14, H 5.56.

*Diethyl 2-(2,3-dimethoxy-8-methyl-10-phenyl-11H-benzo[b]-fluoren-11-yl)-malonate (**3i**).* Colorless solid. Yield: 77% (101 mg). mp 162−164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H) 7.83 (d, J = 8.4 Hz, 1H), 7.61−7.44 (m, 5H), 7.42 (s, 1H), 7.35 (s, 1H), 7.32−7.29 (m, 1H), 7.21(s, 1H), 4.83 (d, J = 2.4 Hz, 1H), 4.21−4.07 (m, 2H), 4.00 (s, 3H), 3.89 (s, 3H), 3.61 (d, J = 2.4 Hz, 1H), 3.60−3.46 (m, 2H), 2.40 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H), 0.60 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 166.9, 149.5, 149.2, 140.8, 139.3, 138.1, 136.4, 134.9, 134.8, 133.9, 132.2, 131.6, 130.8, 129.48, 129.45, 128.5, 127.94, 127.92, 127.81, 124.9, 115.9, 109.3, 102.7, 61.4, 60.5, 56.10, 56.06, 51.945.5, 21.9, 14.1, 13.4 ppm. HRMS (ESI) Calcd for $C_{33}H_{32}O_6$ 525.2272 [M + H^+], found 525.2279.

*Diethyl 2-(8-chloro-2,3-dimethoxy-10-phenyl-11H-benzo[b]-fluoren-11-yl)-malonate (**3j**).* Colorless solid. Yield: 76% (103 mg). mp 135−137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H) 7.86 (d, J = 8.8 Hz, 1H), 7.63−7.57(m, 2H), 7.55−7.48 (m, 3H), 7.46−7.40 (m, 2H), 7.35 (s, 1H), 7.22 (s, 1H), 4.84 (d, J = 2.0 Hz, 1H), 4.20−4.12 (m, 2H), 4.02 (s, 3H), 3.90 (s, 3H), 3.60 (d, J = 2.4 Hz, 1H), 3.59−3.47 (m, 2H), 1.21 (t, J = 7.0 Hz, 3H), 0.62 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 166.7, 149.7, 149.6, 141.9, 140.5, 137.2, 136.7, 134.9, 133.3, 132.3, 132.2, 131.0, 130.6, 129.6, 129.5, 129.4, 128.8, 128.2, 126.6, 124.8, 115.7, 109.3, 102.8, 61.4, 60.5, 56.12, 56.06, 51.8, 45.6, 14.1, 13.4 ppm. HRMS (ESI) Calcd for $C_{32}H_{29}ClO_6$ 545.1725 [M + H^+], found 545.1718.

*Diethyl 2-(2,3,7-trimethoxy-10-phenyl-11H-benzo[b]fluoren-11-yl)-malonate (**3l**).* Colorless solid. Yield: 83% (112 mg). mp 170−172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H) 7.59−7.45 (m, 6H), 7.35 (s, 1H), 7.26 (s, 1H), 7.21 (s, 1H), 7.00 (dd, J = 9.0, 2.4 Hz, 1H), 4.83 (d, J = 2.4 Hz, 1H), 4.21−4.10 (m, 2H), 4.01 (s, 3H), 3.94 (s, 3H), 3.89 (s, 3H), 3.60 (d, J = 2.8 Hz, 1H), 3.59−3.47 (m, 2H), 1.21 (t, J = 7.2 Hz, 3H), 0.62 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 166.9, 157.6, 149.51, 149.46, 140.7, 138.4, 138.0, 136.9, 135.6, 135.4, 133.8, 130.7, 129.41, 129.37, 128.5, 127.8, 127.5, 126.9, 117.3, 115.0, 109.4, 106.5, 102.8, 61.3, 60.4, 56.10, 56.06, 55.3, 52.0, 45.4, 14.1, 13.4 ppm. HRMS (ESI) Calcd for $C_{33}H_{32}O_7$ 541.2221 [M + H^+], found 541.2236.

*Diethyl 2-(2,3-dimethoxy-8-methyl-10-p-tolyl-11H-benzo[b]-fluoren-11-yl)-malonate (**3m**).* Colorless solid. Yield: 84% (113 mg). mp 125−127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H) 7.82 (d, J = 8.4 Hz, 1H), 7.45 (s, 1H), 7.40 (s, 2H), 7.34−7.26 (m, 4H), 7.20 (s, 1H), 4.84 (s, 1H), 4.23−4.10 (m, 2H), 4.01 (s, 3H), 3.89 (s, 3H), 3.65 (d, J = 2.0 Hz, 1H), 3.61−3.45(m, 2H), 2.49 (s, 3H), 2.41 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H), 0.60 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 167.0, 149.5, 149.3, 140.9, 139.3, 137.4, 136.5, 134.9, 134.7, 134.0, 132.2, 131.8, 130.7, 130.1, 129.3, 129.2, 127.9, 127.8, 125.0, 115.6, 109.3, 102.7, 61.3, 60.4, 56.10, 56.06, 51.9, 45.6, 21.9, 21.4, 14.1, 13.4 ppm. MS (ESI) m/z 539 [M + H^+]. Anal. Calcd for $C_{34}H_{34}O_6$: C 75.82, H 6.36. Found: C 75.95, H 6.43.

*Diethyl 2-(2,3-methylenedioxy-10-phenyl-11H-benzo[b]fluoren-11-yl)-malonate (**3n**).* Colorless solid. Yield: 88% (109 mg). mp 145−147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H) 7.92 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.60−7.55 (m, 1H), 7.53−7.45 (m, 5H), 7.36−7.32 (m, 1H), 7.31 (s, 1H), 7.11(s, 1H), 6.00 (s, 2H), 4.84 (d, J = 2.4 Hz, 1H), 4.16 (q, J = 7.0 Hz, 2H), 3.65−3.51 (m, 3H), 1.20 (t, J = 7.2 Hz, 3H), 0.64 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 169.3, 166.8, 148.1, 148.0, 140.4, 139.8, 38.0, 137.8, 135.6, 135.1, 134.0, 131.5, 130.8, 129.44, 129.4, 128.5, 128.1, 127.9, 125.9, 125.7, 125.2, 116.1, 107.0, 101.3, 100.5 61.5, 60.5, 51.8, 45.5,

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14.1, 13.4 ppm. HRMS (ESI) Calcd for $C_{31}H_{26}O_6$ 495.1802 [M + H^+], found 495.1792.

*Diethyl 2-(2-methoxy-10-phenyl-11H-benzo[b]fluoren-11-yl)-malonate (**3o**).* Colorless solid. Yield: 78% (94 mg). mp 129−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.60−7.46 (m, 6H), 7.33 (t, J = 7.6 Hz, 1H), 7.18 (s, 1H), 6.95 (d, J = 8.0 Hz, 1H), 4.92 (s, 1H), 4.19−4.14 (m, 2H), 3.82 (s, 3H), 3.63−3.47 (m, 3H), 1.21 (t, J = 7.2 Hz, 3H), 0.59 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 169.4, 166.8, 160.0, 145.8, 140.3, 139.7, 137.9, 135.7, 134.1, 131.6, 130.8, 129.5, 129.4, 128.5, 128.1, 127.9, 125.9, 125.7, 125.1, 120.9, 116.3, 114.6, 111.2, 61.4, 60.5, 55.5, 52.2, 45.7, 14.1, 13.3 ppm. MS (ESI) m/z 481 [M + H^+]. Anal. Calcd for $C_{31}H_{28}O_5$: C 77.48, H 5.87. Found: C 77.61, H 5.77.

*Diethyl 2-(10-Phenyl-11H-benzo[b]fluoren-11-yl)-malonate (**3p**).* Brown oil. Yield: 65% (73 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 6.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.38−7.30 (m, 3H), 7.28−7.21(m, 3H), 7.20−7.10 (m, 4H), 5.44 (s, 1H), 4.27−4.16 (m, 5H), 1.22 (t, J = 7.2 Hz, 3H), 1.2 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 167.3, 151.1, 143.6, 141.7, 138.0, 136.5, 131.3, 130.7, 128.8, 127.9, 127.5, 127.4, 127.4, 127.3, 127.2, 126.1, 125.6, 125.3, 124.9, 124.0, 123.1, 122.7, 119.1, 118.6, 83.5, 61.07, 61.05, 53.6, 13.1, 13.0 ppm. MS (ESI) m/z 473 [M + Na^+]. Anal. Calcd for $C_{30}H_{26}O_4$: C 79.98, H 5.82. Found: C 79.90, H 5.90.

*2,3-Dimethoxy-10-phenyl-11H-benzo[b]fluorene (**3q**).* Brown oil. Yield: 64% (56 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.57−7.53 (m, 2H),7.50−7.43 (m, 5H), 7.37−7.33 (m, 1H), 7.00 (s, 1H), 4.04 (s, 3H), 3.92 (s, 3H), 3.75 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 149.6, 149.0, 140.3, 140.1, 139.1, 136.7, 135.6, 133.7, 133.6, 131.3, 129.9, 128.6, 128.1, 127.4, 125.9, 125.3, 125.0, 116.0, 108.1, 103.4, 56.2, 56.1, 36.4 ppm. HRMS (ESI) Calcd for $C_{25}H_{20}O_2$ 353.1536 [M + H^+], found 353.1562.

*Diethyl 2-(2,3-dimethoxy-10-methyl-11H-benzo[b]fluoren-11-yl)-malonate (**7a**).* Colorless solid. Yield: 70% (78 mg). mp 155−157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−8.01 (m, 1H), 7.88−7.86 (m, 2H), 7.48−7.46 (m, 2H), 7.31 (s, 1H), 7.30 (s, 1H), 4.87 (d, J = 2.4 Hz, 1H), 4.42−4.33 (m, 3H), 4.00 (s, 3H), 3.94 (s, 3H), 3.62−3.51 (m, 2H), 2.76 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H), 0.63 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 169.6, 166.8, 149.6, 149.3, 141.1, 140.0, 136.3, 134.1, 134.0, 132.0, 128.8, 128.5, 125.5, 125.0, 123.9, 114.8, 109.4, 102.7, 61.8, 60.8, 56.1, 54.2, 45.5, 15.6, 14.2, 13.4 ppm. HRMS (ESI) Calcd for $C_{27}H_{28}O_6$ 449.1959 [M + H^+], found 449.1959.

*Diethyl 2-(2,3-dimethoxy-8,10-dimethyl-11H-benzo[b]fluoren-11-yl)-malonate (**7b**).* Colorless solid. Yield: 70% (81 mg). mp 161−163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81(s, 1H), 7.78−7.75 (m, 2H), 7.31−7.28 (m, 2H), 7.26 (s, 1H), 4.86 (s, 1H), 4.41−4.33 (m, 3H), 3.99 (s, 3H), 3.93 (s, 3H), 3.61−3.51 (m, 2H), 2.72 (s, 3H), 2.55 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H), 0.63 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 169.6, 166.8, 149.6, 149.1, 141.2, 139.1, 136.2, 134.6, 134.3, 132.2, 132.1, 128.4, 128.1, 127.6, 123.1, 114.6, 109.5, 102.7, 61.8, 60.7, 56.1, 54.2, 45.5, 22.1, 15.5, 14.2, 13.4 ppm. MS (ESI) m/z 463 [M + H^+]. Anal. Calcd for $C_{28}H_{30}O_6$: C 72.71, H 6.54. Found: C 72.65, H 6.62.

*Diethyl 2-(2,3-methelenedioxy-10-methyl-11H-benzo[b]fluoren-11-yl)-malonate (**7c**).* Colorless solid. Yield: 88% (95 mg). mp 110−112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−8.00 (m, 1H), 7.86−7.84 (m, 1H), 7.80 (s, 1H), 7.48−7.45 (m, 2H), 7.23 (s, 1H), 7.20 (s, 1H), 6.01 (s, 2H), 4.85 (s, 1H), 4.43−4.32 (m, 3H), 3.69−3.55 (m, 2H), 2.74 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H), 0.64 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 169.3, 166.7, 148.1, 147.9, 140.9, 139.6, 137.7, 135.5, 133.9, 132.0, 128.8, 128.6, 125.5, 125.1, 123.8, 114.9, 107.1, 101.3, 100.4, 61.9, 60.8, 54.1, 45.5, 15.5, 14.1, 13.4 ppm. HRMS (ESI) Calcd for $C_{26}H_{24}O_6$ 433.1646 [M + H^+], found 433.1628.

*Diethyl 2-(2-methoxy-10-methyl-11H-benzo[b]fluoren-11-yl)-malonate (**7d**).* Colorless solid. Yield: 65% (68 mg). mp 145−147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 3.2 Hz, 1H), 8.02 (s, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.49−7.45 (m, 2H), 7.32−7.28 (m, 1H), 7.25−7.23 (m, 1H), 6.95 (dd, J = 8.4, 4.2 Hz, 1H), 4.94 (d, J = 2.4 Hz, 1H), 4.42−4.33 (m, 3H), 3.86 (s, 3H), 3.61−3.52 (m, 2H), 2.82 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H), 0.62 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 169.3, 166.8, 159.8, 145.5, 140.7, 139.6, 134.5, 134.0, 132.1, 129.0, 128.6, 125.5, 125.0, 123.8, 120.9, 115.0, 114.6, 111.4, 61.8, 60.8, 55.5, 54.4, 45.7, 15.6, 14.2, 13.3 ppm. MS (ESI) m/z 419 [M + H^+]. Anal. Calcd for $C_{26}H_{26}O_5$: C 74.62, H 6.26. Found: C 74.73, H 6.31.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02391.

Copies of ^{1}H and ^{13}C NMR spectra for all compounds. (PDF)

X-ray structural information for **7a**. (CIF)

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Notes

The authors declare no competing financial interest.

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