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Synthesis of 9,9-Disubstituted Fluorenes from 2-Iodobiphenyls and α-Diazoesters under Palladium Catalysis

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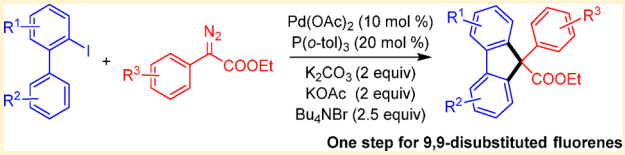
Supporting Information

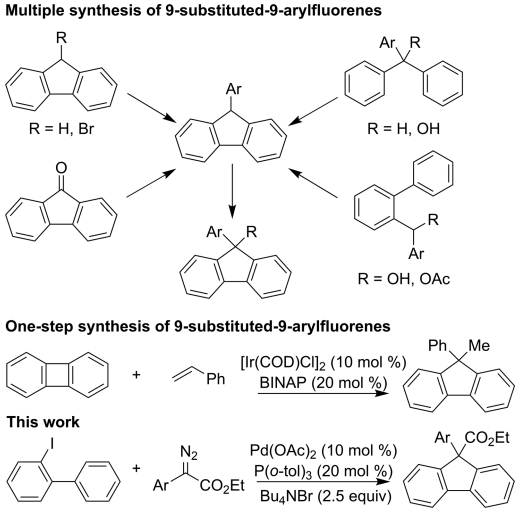
ABSTRACT: 9,9-Disubstituted fluorenes are widely employed in materials science. We have developed a straightforward approach for the synthesis of 9,9-disubstituted fluorenes from 2-iodobiphenyls and α-diazoesters. The reaction proceeds via a tandem palladium-catalyzed C(sp^2)−H activation/carbenoid insertion sequence.



Fluorenes have found extensive applications in various fields,[1] particularly in materials science.[2] They serve as essential building blocks for a range of organic materials, including optoelectronics,[3] semiconductors,[4] and solar cells,[5] by endowing materials with unique optical and electronic properties. The C−H bond of the methylene bridge in fluorene is relatively acidic and reactive.[6] Therefore, 9,9-disubstituted fluorene derivatives are usually employed in materials science. Currently, 9,9-dialkylfluorenes make up the most common group used,[7] primarily because the 9-alkylation of fluorenes is relatively easy. However, the alkyl groups can be photochemically or electrooxidatively cleaved.[8] By contrast, the introduction of aryl groups to C-9 of fluorene can give them an excellent morphological and thermal stability.[9] However, the 9-arylation of fluorenes is comparatively challenging. Although quite a few methods for the synthesis of 9-arylfluorene derivatives are available,[9c,10] they usually require more elaborate synthetic steps (Scheme 1).[11] Furthermore, only one aryl group is introduced for most of the reactions, and the methylene C−H bond in the 9-arylfluorenes should still be functionalized by additional reactions.[12] Therefore, it is highly desirable to develop straightforward synthetic methods for 9-substituted 9-arylfluorenes.[13] Recently, the Shibata group reported one-step synthesis of 9-methyl-9-phenylfluorenes via the cycloaddition of biphenylenes with alkenes. Although this excellent reaction represents a novel method, the use of biphenylenes as the starting material restricts the scope of accessible products and limits the substituents at the 9 position to methyl groups.[14]

Attracted by the synthetic utilities of palladacycles, our group has been interested in palladacycle chemistry,[15] especially C,C-palladacycles.[16] Recently, we developed several new organic reactions by taking advantage of the novel reactivities of dibenzopalladacyclopentadienes.[17] It should be noted that the dibenzopalladacyclopentadienes were obtained via C−H activation of 2-iodobiphenyls. For C,C-palladacycles, the two carbon−Pd bonds can be functionalized and therefore offer opportunities in the development of new synthetic reactions, in particular for the construction of cyclic structures. α-Diazoesters are superb synthons in organic synthesis and

Scheme 1. Synthetic Methods for 9-Substituted 9-Arylfluorenes



have been utilized to develop a myriad of organic transformations.[18] Notably, C,C-palladacycles can also react with α-diazoesters. An excellent example of this is the coupling of five-membered C(sp^2)−C(sp^3) palladacycles with α-aryl diazoesters as reported by the Martin group.[19] García-López and co-workers also described the reaction of α-aryl diazoesters and C(sp^2)−C(sp^3) palladacycles that were obtained via remote C−H activation.[20] Furthermore, the Li group found that rhodacycles could be captured by diazoesters.[21] Inspired by these excellent works and our dibenzopalladacyclopentadiene-based reactions, we envisioned that dibenzopalladacyclopentadienes could react with α-aryl diazoesters to form 9,9-disubstituted fluorenes as the products. Recently, Wang and co-workers reported the synthesis of fluorenes via the coupling

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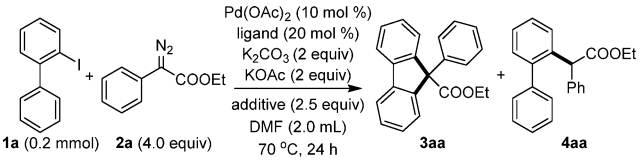
of 2-bromobiphenyl and (trimethylsilyl)diazomethane.[22] Furthermore, our group found that dibenzopalladacyclopentadienes could react with CH_2Br_2, affording fluorenes as the products.[23] In these two reactions, bare fluorenes, without substituents on the methylene bridges, were obtained. To be applied to the synthesis of materials, these fluorene products should still be further functionalized. Herein, we report a straightforward method for the synthesis of 9,9-disubstituted fluorenes via the coupling of α-aryl diazoesters and dibenzopalladacyclopentadienes.

We commenced our study by investigating the reaction of 2-iodo-1,1′-biphenyl (**1a**) with α-diazocarbonyl compound **2a**. As shown in Table 1, the desired product **3aa** was obtained in 15%

Table 1. Optimization of Reaction Conditions



1a (0.2 mmol) 2a (4.0 equiv) 3aa 4aa

entry	ligand	additive	solvent	3aa[a]	4aa[a]	1a[a]
1	–	–	DMF	15%	42%	39%
2	PPh_3	–	DMF	9%	73%	12%
3	PCy_3	–	DMF	3%	47%	23%
4	P(*p*-tol)$_3$	–	DMF	14%	60%	11%
5	P(*o*-tol)$_3$	–	DMF	25%	54%	15%
6	BINAP	–	DMF	5%	12%	42%
7	P(*o*-tol)$_3$	Bu_4NBr	DMF	74% (72%)[b]	18%	no
8	–	Bu_4NBr	DMF	20%	9%	2%
9	P(*o*-tol)$_3$	Bu_4NBr	DMA	59%	6%	30%
10	P(*o*-tol)$_3$	Bu_4NBr	CH_3CN	42%	37%	18%
11	P(*o*-tol)$_3$	Bu_4NBr	1,4-dioxane	23%	42%	21%
12	P(*o*-tol)$_3$	Bu_4NBr	acteone	28%	17%	52%
13	P(*o*-tol)$_3$	Bu_4NBr	THF	no	3%	92%
14	P(*o*-tol)$_3$	Bu_4NBr	CH_2Cl_2	trace	11%	83%
15[c]	P(*o*-tol)$_3$	Bu_4NBr	DMF	trace	trace	96%
16[d]	P(*o*-tol)$_3$	Bu_4NBr	DMF	trace	trace	94%
17[e]	P(*o*-tol)$_3$	Bu_4NBr	DMF	50%	15%	9%
18[f]	P(*o*-tol)$_3$	Bu_4NBr	DMF	33%	10%	54%

[a]The yields were determined by ^{1}H NMR analysis of the crude reaction mixture using $CHCl_2CHCl_2$ as the internal standard. [b]Isolated yield. [c]With 2 equiv of Na_2CO_3 and 2 equiv of NaOAc. [d]With 2 equiv of Cs_2CO_3 and 2 equiv of CsOAc. [e]10 mol % $Pd_2(dba)_3$ instead of $Pd(OAc)_2$. [f]5 mol % $Pd(OAc)_2$.

yield when the reaction was carried out in the presence of 10 mol % $Pd(OAc)_2$, 2 equiv of K_2CO_3, and 2 equiv of KOAc (entry 1). The direct coupling product **4aa** was formed in 39% yield, and 42% of **1a** was recovered. The addition of PPh_3 as the ligand failed to improve the yield of **3aa**, but it promoted the formation of **4aa** to a great extent (entry 2). Screening other phosphine ligands showed that P(*o*-tol)$_3$ could enhance the yield of **3aa** (entries 3−5).[24] Bidentate ligand BINAP suppressed the formation of **3aa** (entry 6). Thankfully, the yield was improved dramatically to 74% when 2.5 equiv of Bu_4NBr was added (entry 7).[25] The yield was much lower in the absence of P(*o*-tol)$_3$, which indicates that the combination of Bu_4NBr and the ligand was necessary for the optimal yield (entry 8). The yields were lower when the reaction was carried out in other polar solvents such as DMA, CH_3CN, 1,4-dioxane, and acetone (entries 9−12, respectively), and almost no desired products were formed in THF or CH_2Cl_2 (entry 13 or 14, respectively). As a comparison, the reactions did not occur when Na_2CO_3/NaOAc or Cs_2CO_3/CsOAc were used in place of K_2CO_3/KOAc (entry 15 or 16, respectively).[26] Product **1a** was also formed using $Pd_2(dba)_3$, albeit in a lower yield (entry 17). Lowering the catalyst loading also resulted in a much lower yield (entry 18).

With the optimal conditions for palladium-catalyzed coupling of 2-iodobiphenyl with ethyl diazophenylacetate in hand, we investigated the substrate scope of this transformation. We first examined the performance of different functional groups on the phenyl ring opposite to the iodo group. As shown in Table 2, substrates bearing an electron-donating substituent (methyl or methoxy group) at the 4′ positions underwent the coupling reaction with **2a** efficiently under the optimal conditions (entries 1 and 2, respectively). A range of electron-withdrawing groups were compatible, including trifluoromethyl, cyano, acetyl, alkoxycarbonyl, and aldehyde groups (entries 3−7, respectively). It should be noted that the aldehyde group survived under these reaction conditions. Fluoro, chloro, and even bromo groups were well-tolerated in the reaction, giving the desired fluorene derivatives in moderate yields (enrties 8−10, respectively). The substrate bearing a phenyl group was also suitable (entry 11). The compatibility of functional groups at 3′ positions was also examined. Substrates bearing electron-donating groups, including methyl and methoxy, were transformed into fluorene products in moderate yields (entries 12 and 13, respectively). As a comparison, the presence of an electron-withdrawing trifluoromethyl group resulted in a low yield (entry 14). For the substrates bearing a 3′-substituent, the reactions occurred selectively at the less hindered positions. 2-Iodobiphenyl bearing a 2′-methoxy group was also reactive, although the reaction was low-yielding (entry 15). Next, we investigated the reactivity of 2-iodobiphenyl derivatives with a substituent on the phenyl ring containing the iodo group. The substrates bearing an electron-donating or electron-withdrawing group underwent the coupling reaction (entry 16 or 17, respectively). Both fluoro and chloro groups were well-tolerated in relatively high yields (entries 18 and 19, respectively). Disubstituted 2-iodobiphenyls were also able to be transformed into multiple functionalized fluorenes (entries 20−22). Notably, 1-(2-iodophenyl)-1*H*-pyrrole **1x** could couple with **2a**, albeit in a low yield (entry 23). The low yield may result from the low reactivity of **1x**, as 45% of **1x** was recovered. 2-Bromobiphenyl was also reactive; however, the yield was low, and a large amount of **1y** remained intact (entry 24).

Next, we examined the performance of other α-diazocarbonyl compounds by using **1a** as the model coupling partner. The reactivity of a range of ethyl diazophenylacetates bearing different substituents on the benzene rings was investigated. As shown in Table 3, whereas the reaction of **2b** was high-yielding (entry 1), the yield of **3ac** was quite low (entry 2). Fluoro and chloro groups were tolerated (entries 3 and 4, respectively), and α-diazocarbonyl compounds **2f** and **2g** coupled with **1a** in moderate yields (entries 5 and 6, respectively). The benzyl-protected substrate **2h** and diethyl 2-diazomalonate **2i** were also suitable under the standard conditions (entries 7 and 8, respectively). Other diazo compounds, including 1-diazo-1-phenylpropan-2-one, 2-diazo-1,2-diphenylethan-1-one, and diazodiphenylmethane, failed to yield fluorene products. In these reactions, most of **1a** was recovered.

To prove that palladacycles were involved in the reaction, complex dibenzopalladacyclopentadiene **5a** was prepared

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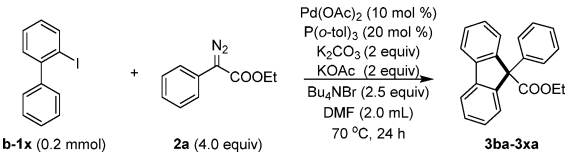
Table 2. 2-Iodobiphenyl Scope



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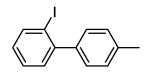
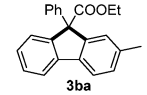
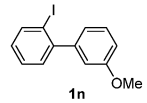
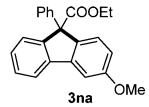
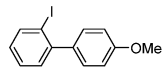
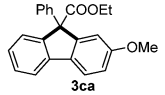
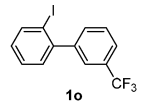
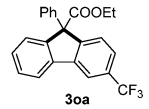
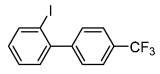
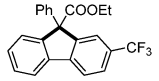
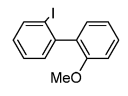
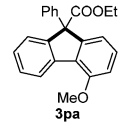
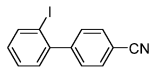
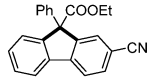
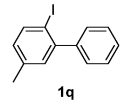
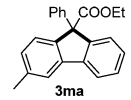
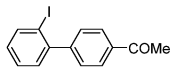
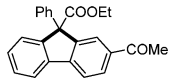
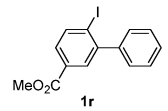
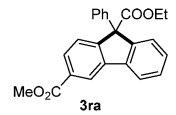
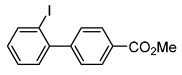
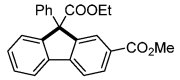
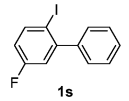
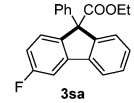
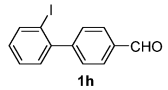
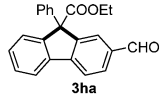
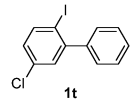
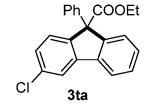
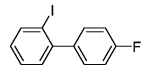
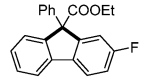
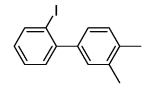
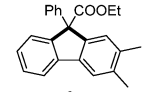
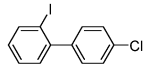
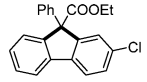
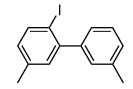
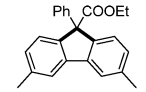
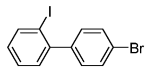
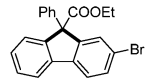
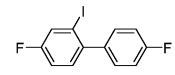
1	 1b	 3ba	82%	13	 1n	 3na	69%
2	 1c	 3ca	80%	14	 1o	 3oa	42%
3	 1d	 3da	56%	15	 1p	 3pa	31%
4	 1e	 3ea	47%	16	 1q	 3ma	69%
5	 1f	 3fa	87%	17	 1r	 3ra	46%
6	 1g	 3ga	76%	18	 1s	 3sa	87%
7	 1h	 3ha	63%	19	 1t	 3ta	70%
8	 1i	 3ia	74%	20	 1u	 3ua	62%
9	 1j	 3ja	63%	21	 1v	 3va	61%
10	 1k	 3ka	53%	22	 1w	3wa	52%
11	1l	3la	83%	23	1x	3xa	26%
12	1m	3ma	73%	24	1y	3aa	24%

[a]Isolated yields.

(Scheme 2).[27] When the palladacycle was subjected to the standard conditions, the fluorene product **3aa** was formed with a yield of 41% (**A**). The low yield could result from the negative impact of the bipyridine ligand on the reaction. To prove this assumption, we added 10 mol % 2,2′-bipyridine to the reaction mixture of **1a** and **2a**. The yield decreased dramatically to 24%, which implies that 2,2′-bipyridine should suppress the formation of the fluorene product (**B**). It should be mentioned that 2,2′-diiodobiphenyl could also be transformed into **3aa** with a 47% yield (**C**). The kinetic isotope effect in the reaction was also investigated. The intramolecular KIE was 4 to 1, and the intermolecular KIE was 2.3 to 1, which indicates that C−H activation is the rate-determining step (**D** and **E**).

On the basis of the above experimental results and previous reports,[19,20,23] the palladacycle should act as the key intermediate in the fluorene-forming reaction; thus, we

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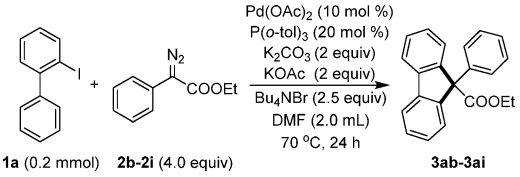
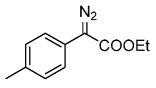
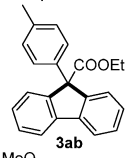
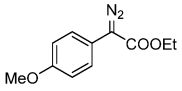
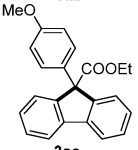
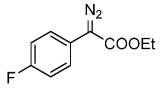
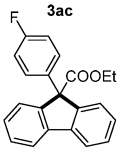
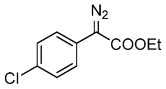
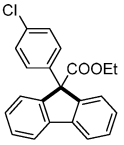
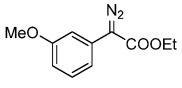
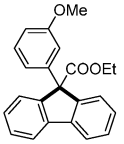
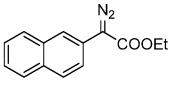
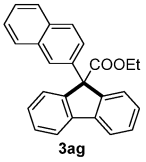
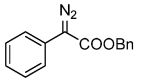
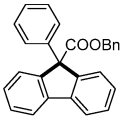
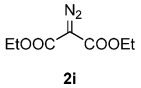
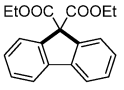
Table 3. α-Diazoester Scope



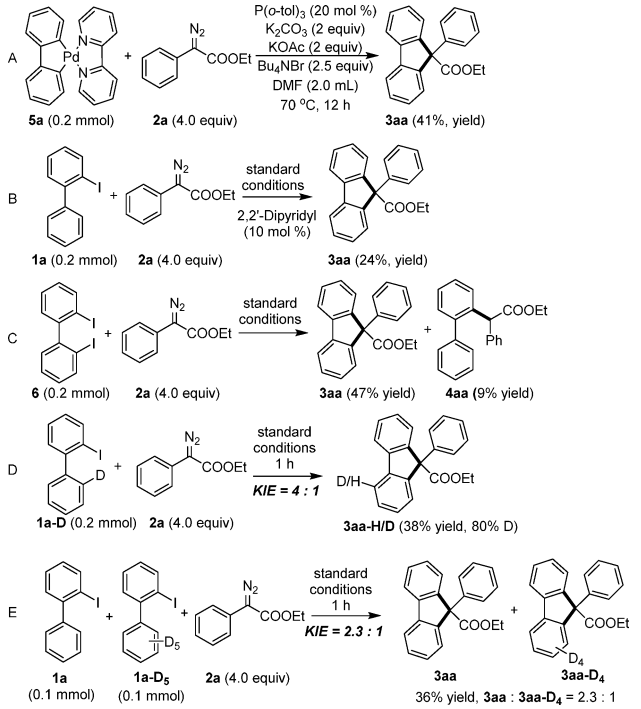
entry	substrate	product	yield[a]
1	 **2b**	 **3ab**	88%
2	 **2c**	 **3ac**	41%
3	 **2d**	 **3ad**	65%
4	 **2e**	 **3ae**	52%
5	 **2f**	 **3af**	64%
6	 **2g**	 **3ag**	51%
7	 **2h**	 **3ah**	53%
8	 **2i**	 **3ai**	43%

[a]Isolated yields.

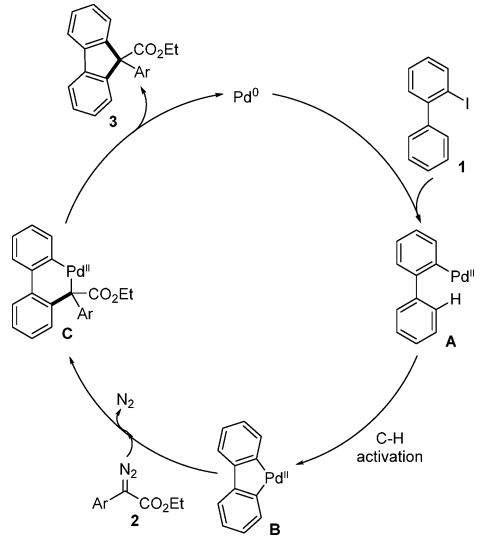
proposed a tentative mechanism (Scheme 3). Therefore, the palladacycle **B** is formed through the oxidative addition of 2-iodobiphenyls to Pd^0 and subsequent intramolecular C−H activation. Next, the insertion of diazo compound **2** gives the six-membered palladacycle **C**. Finally, reductive elimination generates the 9,9-disubstituted fluorene product and Pd^0 species.

The ester groups of the disubstituted fluorenes can be reduced to hydroxyl groups (Scheme 4).[28] The resulting hydroxyl groups allow the fluorenes to be further derivatized,

Scheme 2. Mechanistic Studies



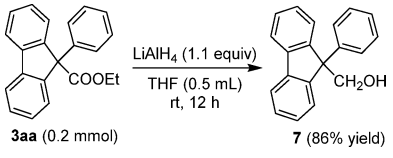
Scheme 3. Proposed Mechanism



which extends the synthetic applications of the fluorene products.

In conclusion, a tandem palladium-catalyzed C(sp^2)−H activation/carbenoid insertion sequence is described. This reaction provides a facile approach for the synthesis of 9,9-disubstituted fluorenes starting from 2-iodobiphenyls and α-diazoesters.

Scheme 4. Transformation of the Fluorene Product



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EXPERIMENTAL SECTION

General Information. High resolution mass spectra were measured on a Bruker MicroTOF II ESI-TOF mass spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX400 instrument (400 and 101 MHz, respectively); however, the ^{1}H NMR spectra and the ^{13}C NMR spectra of **3ab** and **7** were recorded on a Bruker ARX600 instrument (600 and 151 MHz, respectively). ^{1}H NMR spectra were recorded in $CDCl_3$ referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets. All reactions were carried out under a nitrogen (N_2) atmosphere using Schlenk techniques unless stated otherwise. All products were purified via preparative thin layer chromatography (PTLC) to give the corresponding compounds.

Palladium acetate was purchased from Strem Chemicals Inc. All of the solvents were purified by distillation prior to use. Unless otherwise noted, the other commercial materials were used without further purification. 2-Iodobiphenyls were synthesized by following the reported procedures.[29] Diazo compounds were synthesized by following the reported procedure.[30]

General Procedures for the Synthesis of 9,9-Disubstituted Fluorenes (3aa−3pa, 3ra−3xa, and 3ab−3ai). A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), P(*o*-tol)$_3$ (12.2 mg, 0.04 mmol), Bu_4NBr (161 mg, 0.5 mmol), K_2CO_3 (55.2 mg, 0.4 mmol), KOAc (39.2 mg, 0.4 mmol), the corresponding 2-iodobiphenyls (0.2 mmol), the corresponding diazo compounds (0.8 mmol), and DMF (2 mL). The reaction tube was evacuated and backfilled with nitrogen five times. The mixture was stirred at 70 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), washed with a saturated aqueous NaCl solution three times, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by preparative silica gel TLC with PE/EA (PE/EA = 20:1 unless otherwise noted) as the eluent to give the corresponding products.

Procedures for the Synthesis of (9-Phenyl-9*H*-fluoren-9-yl)methanol (7). To a 25 mL Schlenk-type tube with a PTFE stopcock and side arm were added a magnetic stir-bar and **3aa** (0.2 mmol, 62.8 mg). The reaction tube was equipped with a rubber septum and sealed. The reaction tube was evacuated and backfilled with nitrogen 10 times, followed by the addition of dry THF (0.5 mL) via a syringe. The reaction mixture was cooled to 0 °C, and $LiAlH_4$ (0.22 mL, 1 mol/L in THF, 1.1 equiv) was added dropwise via a syringe. The mixture was then warmed to room temperature and stirred for 12 h. The mixture was cooled to 0 °C and diluted with ethyl acetate, and the reaction was quenched by addition of water (0.2 mL), 10% aqueous NaOH (0.5 mL), and water (1 mL). Magnesium sulfate was added to the resulting slurry, which was then warmed to room temperature and stirred for 15 min. The mixture was then filtered, and the solvent was removed *in vacuo*. The residue was purified by preparative silica gel TLC with PE/EA (3:1) as the eluent to give the corresponding products (46.7 mg, 86% yield).[28]

Ethyl 9-Phenyl-9*H*-fluorene-9-carboxylate (3aa). Following the general procedure, the compound was isolated as a white solid (45.1 mg, 72% yield). Mp: 97.0−100.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, J = 7.5 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.32−7.27 (m, 3H), 7.20−7.14 (m, 2H), 4.29 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.9, 146.0, 141.9, 140.6, 128.6, 128.2, 127.6, 127.2, 127.0, 126.5, 119.9, 67.1, 61.8, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{22}H_{18}NaO_2^+$: 337.1199 (M + Na)$^+$, found 337.1203.

Ethyl 2-Methyl-9-phenyl-9*H*-fluorene-9-carboxylate (3ba). Following the general procedure, the compound was isolated as a white solid (53.8 mg, 82% yield). Mp: 93.0−95.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, J = 7.5 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.41−7.34 (m, 2H), 7.29−7.27 (m, 1H), 7.25−7.18 (m, 4H), 7.12−7.08 (m, 2H), 4.29−4.20 (m, 2H), 2.38 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.0, 146.2, 145.9, 142.1, 140.7, 137.9, 137.6, 129.1, 128.6, 128.2, 127.5, 127.14, 127.10, 126.9, 126.6, 119.59, 119.6, 67.0, 61.7, 21.8, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{23}H_{20}NaO_2^+$: 351.1356 (M + Na)$^+$, found 351.1356.

Ethyl 2-Methoxy-9-phenyl-9*H*-fluorene-9-carboxylate (3ca). Following the general procedure, the compound was isolated as a white solid (55.1 mg, 80% yield). Mp: 121.0−123.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.1 Hz, 1H), 7.29−7.27 (m, 1H), 7.25−7.20 (m, 3H), 7.15−7.08 (m, 3H), 6.95 (dd, J = 8.4, 2.4 Hz, 1H), 4.29−4.20 (m, 2H), 3.81 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.9, 159.6, 147.7, 145.6, 142.0, 140.5, 133.5, 128.6, 128.2, 127.2, 126.8, 126.53, 126.49, 120.6, 119.1, 114.5, 112.4, 67.1, 61.8, 55.5, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{23}H_{20}NaO_3^+$: 367.1305 (M + Na)$^+$, found 367.1309.

Ethyl 9-Phenyl-2-(trifluoromethyl)-9*H*-fluorene-9-carboxylate (3da). Following the general procedure, the compound was isolated as a white solid (42.8 mg, 56% yield). Mp: 116.0−118.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.65 (t, J = 8.5 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.30−7.27 (m, 2H), 7.25−7.24 (m, 1H), 7.13−7.06 (m, 2H), 4.26 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.1, 146.6, 146.5, 144.0, 140.9, 139.0, 129.5 (q, J = 31.5 Hz), 128.9, 128.6, 127.6, 127.3, 126.4, 125.6 (q, J = 3.7 Hz), 124.3 (q, J = 271.5 Hz), 124.2 (q, J = 3.9 Hz) 120.6, 120.0, 67.2, 62.1, 13.9. HRMS (ESI-TOF) m/z calculated for $C_{23}H_{17}F_3NaO_2^+$: 405.1073 (M + Na)$^+$, found 405.1079.

Ethyl 2-Cyano-9-phenyl-9*H*-fluorene-9-carboxylate (3ea). Following the general procedure, the compound was isolated as a white solid (31.9 mg, 47% yield). Mp: 123.0−125.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (s, 1H), 7.80 (t, J = 6.5 Hz, 2H), 7.67 (t, J = 6.5 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.30−7.27 (m, 3H), 7.08−7.05 (m, 2H), 4.27 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.7, 146.9, 146.4, 144.9, 140.5, 138.8, 132.4, 130.9, 129.5, 129.0, 128.8, 127.8, 127.4, 126.2, 120.9, 120.5, 119.2, 110.7, 67.1, 62.3, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{23}H_{17}NNaO_2^+$: 362.1151 (M + Na)$^+$, found 362.1160.

Ethyl 2-Acetyl-9-phenyl-9*H*-fluorene-9-carboxylate (3fa). Following the general procedure, the compound was isolated as a white solid (61.9 mg, 87% yield). Mp: 155.0−159.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (s, 1H), 8.04 (d, J = 7.9 Hz, 1H), 7.81 (d, J = 7.9 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.3 Hz, 1H), 7.38 (t, J = 7.3 Hz, 1H), 7.25−7.21 (m, 3H), 7.11 (m, 2H), 4.26 (q, J = 6.9 Hz, 2H), 2.60 (s, 3H), 1.25 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.5, 171.3, 147.1, 146.4, 145.2, 141.1, 139.3, 136.5, 129.0, 128.9, 128.8, 128.6, 127.5, 127.2, 127.1, 126.4, 120.8, 119.8, 67.1, 62.1, 26.8, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{24}H_{20}NaO_3^+$: 379.1305 (M + Na)$^+$, found 379.1305.

9-Ethyl 2-Methyl-9-phenyl-9*H*-fluorene-2,9-dicarboxylate (3ga). Following the general procedure, the compound was isolated as a white solid (56.5 mg, 76% yield). Mp: 177.0−180.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (s, 1H), 8.12 (d, J = 7.9 Hz, 1H), 7.81−7.77 (m, 2H), 7.63 (d, J = 7.5 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.25−7.23 (m, 3H), 7.14−7.09 (m, 2H), 4.26 (q, J = 6.9 Hz, 2H), 3.90 (s, 3H), 1.25 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.4, 167.0, 147.0, 146.2, 145.1, 141.2, 139.4, 130.1, 129.3, 128.8, 128.8, 128.5, 128.3, 127.4, 127.2, 126.5, 120.7, 119.7, 67.1, 62.0, 52.1, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{24}H_{20}NaO_4^+$: 395.1254 (M + Na)$^+$, found 395.1260.

Ethyl 2-Formyl-9-phenyl-9*H*-fluorene-9-carboxylate (3ha). Following the general procedure, the compound was isolated as a white solid (43.1 mg, 63% yield). Mp: 131.0−133.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.00 (s, 1H), 8.08 (s, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 7.4 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 7.0 Hz, 1H), 7.41 (t, J = 7.1 Hz, 1H), 7.30−7.27 (m, 2H), 7.25−7.24 (m, 1H), 7.14−7.09 (m, 2H), 4.27 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.8, 171.2, 147.2, 147.0, 146.6, 141.0, 139.3, 135.9, 130.4, 129.4, 128.9,

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128.7, 128.6, 127.6, 127.4, 126.5, 121.1, 120.4, 67.1, 62.2, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{23}H_{18}NaO_3^+$: 365.1148 $(M + Na)^+$, found 365.1155.

Ethyl 2-Fluoro-9-phenyl-9*H*-fluorene-9-carboxylate (3ia). Following the general procedure, the compound was isolated as a white solid (49.1 mg, 74% yield). Mp: 133.0−136.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70−7.64 (m, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.1 Hz, 1H), 7.32−7.27 (m, 3H), 7.25−7.23 (m, 2H), 7.12−7.06 (m, 3H), 4.26 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.4, 162.6 (d, J = 245.8 Hz), 148.2 (d, J = 8.4 Hz), 145.8 (d, J = 1.8 Hz), 141.4, 139.7, 136.5 (d, J = 2.3 Hz), 128.8, 128.4, 127.4, 127.3, 127.1, 126.4, 120.8 (d, J = 9.0 Hz), 119.6, 115.5 (d, J = 23.3 Hz), 114.5 (d, J = 23.7 Hz), 67.1, 62.01, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{22}H_{17}FNaO_2^+$: 355.1105 $(M + Na)^+$, found 355.1107.

Ethyl 2-Chloro-9-phenyl-9*H*-fluorene-9-carboxylate (3ja). Following the general procedure, the compound was isolated as a white solid (43.8 mg, 63% yield). Mp: 115.0−117.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, J = 7.5 Hz, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 1.7 Hz, 1H), 7.41 (t, J = 7.1 Hz, 1H), 7.36 (dd, J = 8.1, 1.8 Hz, 1H), 7.32 (td, J = 7.6, 0.9 Hz, 1H), 7.29−7.27 (m, 1H), 7.25−7.23 (m, 2H), 7.12−7.04 (m, 2H), 4.26 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.3, 147.7, 145.8, 141.2, 139.6, 139.0, 133.2, 128.8, 128.6, 128.5, 127.9, 127.45, 127.39, 127.1, 126.4, 120.8, 119.9, 67.1, 62.0, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{22}H_{17}ClNaO_2^+$: 371.0809 $(M + Na)^+$, found 371.0817.

Ethyl 2-Bromo-9-phenyl-9*H*-fluorene-9-carboxylate (3ka). Following the general procedure, the compound was isolated as a white solid (41.7 mg, 53% yield). Mp: 135.0−138.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73−7.70 (m, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.52 (dd, J = 8.1, 1.6 Hz, 1H), 7.42 (t, J = 7.1 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.30−7.27 (m, 1H), 7.25−7.21 (m, 2H), 7.11−7.07 (m, 2H), 4.26 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.3, 148.0, 145.7, 141.2, 139.6, 139.5, 131.4, 130.3, 128.8, 128.5, 128.1, 127.5, 127.1, 126.4, 121.3, 121.1, 119.9, 67.1, 62.0, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{22}H_{17}BrNaO_2^+$: 415.0304 $(M + Na)^+$, found 415.0311.

Ethyl 2,9-Diphenyl-9*H*-fluorene-9-carboxylate (3la). Following the general procedure, the compound was isolated as a white solid (64.7 mg, 83% yield). Mp: 139.0−141.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (s, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.66−7.56 (m, 4H), 7.44−7.36 (m, 3H), 7.33−7.28 (m, 2H), 7.22 (t, J = 7.9 Hz, 3H), 7.18−7.13 (m, 2H), 4.25 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.8, 146.6, 146.3, 141.8, 141.1, 140.7, 140.2, 139.8, 128.7, 128.6, 128.3, 127.6, 127.4, 127.2, 127.1, 127.0, 126.5, 125.8, 120.1, 119.9, 67.2, 61.8, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{28}H_{22}NaO_2^+$: 413.1512 $(M + Na)^+$, found 413.1514.

Ethyl 3-Methyl-9-phenyl-9*H*-fluorene-9-carboxylate (3ma). Following the general procedure, the compound was isolated as a white solid (47.8 mg, 73% yield). Mp: 109.0−111.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, J = 7.5 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.60 (s, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.43 (td, J = 7.5, 0.9 Hz, 1H), 7.33 (td, J = 7.6, 0.9 Hz, 1H), 7.30−7.27 (m, 2H), 7.25−7.22 (m, 1H), 7.19−7.13 (m, 3H), 4.27 (q, J = 7.1 Hz, 2H), 2.48 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.1, 146.4, 143.2, 142.1, 140.7, 140.6, 138.1, 128.6, 128.6, 128.1, 127.5, 127.1, 126.9, 126.6, 126.5, 120.5, 119.7, 66.8, 61.7, 21.5, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{23}H_{20}NaO_2^+$: 351.1356 $(M + Na)^+$, found 351.1355.

Methyl 3-Methoxy-9-phenyl-9*H*-fluorene-9-carboxylate (3na). Following the general procedure, the compound was isolated as a white solid (45.5 mg, 69% yield). Mp: 133.0−136.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, J = 7.5 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.40 (t, J = 7.1 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.28−7.27 (m, 1H), 7.25−7.19 (m, 3H), 7.13 (d, J = 8.0 Hz, 2H), 6.87 (dd, J = 8.5, 2.3 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.1, 160.2, 146.9, 142.1, 142.0, 140.3, 138.1, 128.8, 128.1, 127.74, 127.66, 127.1, 127.0, 126.4, 119.8, 113.9, 104.9, 66.4, 61.7, 55.5, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{23}H_{20}NaO_3^+$: 367.1305 $(M + Na)^+$, found 367.1304.

Ethyl 9-Phenyl-3-(trifluoromethyl)-9*H*-fluorene-9-carboxylate (3oa). Following the general procedure, the compound was isolated as a white solid (32.1 mg, 42% yield). Mp: 115.0−118.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.33−7.27 (m, 2H), 7.25−7.22 (m, 1H), 7.13−7.06 (m, 2H), 4.26 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.1, 149.6, 146.0, 141.2, 141.0, 139.3, 130.6 (q, J = 32.2 Hz), 128.8, 128.6, 127.6, 127.4, 127.2, 126.4, 124.4 (q, J = 3.6 Hz), 124.2 (q, J = 272.0 Hz), 120.3, 116.8 (q, J = 3.7 Hz), 67.2, 62.1, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{23}H_{17}F_3NaO_2^+$: 405.1073 $(M + Na)^+$, found 405.1082.

Ethyl 4-Methoxy-9-phenyl-9*H*-fluorene-9-carboxylate (3pa). Following the general procedure, the compound was isolated as a white solid (21.3 mg, 31% yield). Mp: 124.0−126.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.1 Hz, 1H), 7.29−7.27 (m, 2H), 7.25−7.17 (m, 4H), 7.14−7.07 (m, 2H), 6.91 (d, J = 8.0 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 4.01 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.0, 155.6, 147.8, 145.3, 142.03, 139.96, 128.5, 128.2, 127.1, 126.7, 126.6, 126.2, 123.9, 119.1, 110.1, 67.3, 61.7, 55.4, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{23}H_{20}NaO_3^+$: 367.1305 $(M + Na)^+$, found 367.1312.

9-Ethyl 3-Methyl-9-phenyl-9*H*-fluorene-3,9-dicarboxylate (3ra). Following the general procedure, the compound was isolated as a white solid (34.2 mg, 46% yield). Mp: 170.0−172.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.40 (s, 1H), 7.99 (dd, J = 8.0, 1.4 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.63 (t, J = 8.8 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.25−7.22 (m, 3H), 7.11−7.07 (m, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.96 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.3, 167.0, 150.9, 146.0, 141.2, 140.9, 139.7, 130.3, 129.7, 129.0, 128.8, 128.6, 128.3, 128.0, 127.5, 127.1, 127.0, 126.5, 121.1, 120.3, 67.3, 62.0, 52.2, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{24}H_{20}NaO_4^+$: 395.1254 $(M + Na)^+$, found 395.1258.

Ethyl 3-Fluoro-9-phenyl-9*H*-fluorene-9-carboxylate (3sa). Following the general procedure, the compound was isolated as a white solid (57.8 mg, 87% yield). Mp: 132.0−135.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, J = 7.5 Hz, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.53 (dd, J = 8.3, 5.1 Hz, 1H), 7.40 (t, J = 7.5 Hz, 2H), 7.33 (t, J = 7.5 Hz, 1H), 7.25−7.20 (m, 3H), 7.14−7.06 (m, 2H), 6.99 (td, J = 8.9, 2.3 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.6, 163.3 (d, J = 241.5 Hz), 146.7, 142.6 (d, J = 9.2 Hz), 141.6, 141.4 (d, J = 2.5 Hz), 139.6 (d, J = 3.0 Hz), 128.7, 128.4, 128.26, 128.25 (d, J = 9.0 Hz), 127.3, 127.1, 126.4, 120.1, 114.6 (d, J = 23.2 Hz), 106.8 (d, J = 23.7 Hz), 66.6, 61.9, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{22}H_{17}FNaO_2^+$: 355.1105 $(M + Na)^+$, found 355.1108.

Ethyl 3-Chloro-9-phenyl-9*H*-fluorene-9-carboxylate (3ta). Following the general procedure, the compound was isolated as a white solid (48.8 mg, 70% yield). Mp: 149.0−153.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73−7.68 (m, 2H), 7.60 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.42 (t, J = 7.1 Hz, 1H), 7.34 (t, J = 7.1 Hz, 1H), 7.28−7.27 (m, 1H), 7.25−7.22 (m, 3H), 7.10−7.07 (m, 2H), 4.24 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.4, 146.3, 144.4, 142.3, 141.4, 139.4, 134.4, 128.7, 128.4, 128.4, 128.1, 127.6, 127.4, 127.2, 126.4, 120.1, 66.8, 62.0, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{22}H_{17}ClNaO_2^+$: 371.0809 $(M + Na)^+$, found 371.0816.

Ethyl 2,3-Dimethyl-9-phenyl-9*H*-fluorene-9-carboxylate (3ua). Following the general procedure, the compound was isolated as a white solid (42.4 mg, 62% yield). Mp: 152.0−155.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.51 (s, 1H), 7.40−7.32 (m, 2H), 7.28−7.27 (m, 1H), 7.24−7.19 (m, 3H), 7.13−7.09 (m, 2H), 4.27−4.19 (m, 2H), 2.34 (s, 3H), 2.28 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ:

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172.2, 146.1, 143.8, 142.3, 140.9, 138.3, 136.7, 136.3, 128.6, 128.1, 127.8, 127.0, 127.0, 126.9, 126.5, 120.9, 119.4, 66.9, 61.7, 20.3, 20.1, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{24}H_{22}NaO_2^+$: 365.1512 $(M + Na)^+$, found 365.1515.

Ethyl 3,6-Dimethyl-9-phenyl-9*H*-fluorene-9-carboxylate (3va). Following the general procedure, the compound was isolated as a white solid (41.7 mg, 61% yield). Mp: 145.0−147.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (s, 2H), 7.45 (d, J = 7.8 Hz, 2H), 7.24−7.19 (m, 3H), 7.10 (d, J = 7.5 Hz, 4H), 4.22 (q, J = 7.1 Hz, 2H), 2.43 (s, 6H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.2, 143.6, 142.3, 140.7, 138.0, 128.5, 128.5, 127.0, 126.6, 126.4, 120.4, 66.5, 61.7, 21.5, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{24}H_{22}NaO_2^+$: 365.1512 $(M + Na)^+$, found 365.1515.

Ethyl 2,7-Difluoro-9-phenyl-9*H*-fluorene-9-carboxylate (3wa). Following the general procedure, the compound was isolated as a white solid (36.4 mg, 52% yield). Mp: 97.0−101.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (dd, J = 8.2, 4.9 Hz, 2H), 7.31−7.27 (m, 3H), 7.25−7.23 (m, 2H), 7.14−7.01 (m, 4H), 4.27 (q, J = 7.1 Hz, 2H), 1.26 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.8, 162.4, (d, J = 246.6 Hz), 148.0 (d, J = 8.8 Hz), 140.9, 135.7, 128.9, 127.7, 126.3, 120.5 (d, J = 9.1 Hz), 115.7, (d, J = 23.3 Hz), 114.6, (d, J = 23.9 Hz), 67.0, 62.2, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{22}H_{16}F_2NaO_2^+$: 373.1011 $(M + Na)^+$, found 373.1018.

Ethyl 9-Phenyl-9*H*-pyrrolo-[1,2-α]-indole-9-carboxylate (3xa). Following the general procedure, the compound was isolated as a yellow solid (15.8 mg, 26% yield). Mp: 79.0−81.0 °C. The eluent: PE/EA = 50:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, J = 7.6 Hz, 1H), 7.35−7.27 (m, 5H), 7.24−7.21 (m, 2H), 7.14−7.07 (m, 2H), 6.43 (t, J = 3.1 Hz, 1H), 6.34 (d, J = 2.5 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.7, 141.1, 139.6, 137.4, 137.1, 128.71, 128.67, 127.7, 127.5, 126.1, 123.7, 113.7, 110.7, 109.8, 105.6, 62.0, 60.8, 13.9. HRMS (ESI-TOF) m/z calculated for $C_{20}H_{17}NNaO_2^+$: 326.1151 $(M + Na)^+$, found 326.1154.

Ethyl 9-(*p*-Tolyl)-9*H*-fluorene-9-carboxylate (3ab). Following the general procedure, the compound was isolated as a white solid (57.7 mg, 88% yield). Mp: 92.0−95.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.77 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 7.4 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 2.31 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 172.0, 146.1, 140.5, 138.9, 136.8, 129.3, 128.1, 127.6, 126.9, 126.3, 119.8, 66.8, 61.7, 20.9, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{23}H_{20}NaO_2^+$: 351.1356 $(M + Na)^+$, found 351.1360.

Ethyl 9-(4-Methoxyphenyl)-9*H*-fluorene-9-carboxylate (3ac). Following the general procedure, the compound was isolated as a white solid (28.2 mg, 41% yield). Mp: 127.0−129.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.75 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.1, 158.6, 146.3, 140.5, 133.9, 128.1, 127.6, 126.9, 119.9, 114.0, 66.4, 61.8, 55.2, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{23}H_{20}NaO_3^+$: 367.1305 $(M + Na)^+$, found 367.1307.

Ethyl 9-(4-Fluorophenyl)-9*H*-fluorene-9-carboxylate (3ad). Following the general procedure, the compound was isolated as a white solid (43.2 mg, 65% yield). Mp: 124.0−126.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, J = 7.5 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H), 7.12−7.07 (m, 2H), 6.92 (t, J = 8.7 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.8, 161.9 (d, J = 245.0 Hz), 145.9, 140.5, 137.6 (d, J = 3.3 Hz), 128.4, 128.2 (d, J = 8.0 Hz), 127.7, 126.8, 120.0, 115.4 (d, J = 21.5 Hz), 66.4, 61.9, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{22}H_{17}FNaO_2^+$: 355.1105 $(M + Na)^+$, found 355.1104.

Ethyl 9-(4-Chlorophenyl)-9*H*-fluorene-9-carboxylate (3ae). Following the general procedure, the compound was isolated as a white solid (36.2 mg, 52% yield). Mp: 135.0−138.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.6, 145.6, 140.5, 140.4, 133.1, 128.7, 128.4, 128.0, 127.8, 126.7, 120.0, 66.5, 61.9, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{22}H_{17}ClNaO_2^+$: 371.0809 $(M + Na)^+$, found 371.0827.

Ethyl 9-(3-Methoxyphenyl)-9*H*-fluorene-9-carboxylate (3af). Following the general procedure, the compound was isolated as a white solid (44.0 mg, 64% yield). Mp: 132.0−134.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.18 (t, J = 8.0 Hz, 1H), 6.78−6.72 (m, 2H), 6.67−6.64 (m, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.70 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.8, 159.6, 145.7, 143.4, 140.6, 129.6, 128.2, 127.6, 127.0, 119.9, 119.0, 113.0, 111.9, 67.0, 61.8, 55.1, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{23}H_{20}NaO_3^+$: 367.1305 $(M + Na)^+$, found 367.1313.

Ethyl 9-(Naphthalen-2-yl)-9*H*-fluorene-9-carboxylate (3ag). Following the general procedure, the compound was isolated as a white solid (37.1 mg, 51% yield). Mp: 163.0−166.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80−7.74 (m, 3H), 7.73−7.68 (m, 2H), 7.64 (s, 1H), 7.62 (s, 2H), 7.45−7.39 (m, 4H), 7.31 (t, J = 7.5 Hz, 2H), 7.13 (dd, J = 8.6, 1.7 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.9, 146.0, 140.7, 139.3, 133.3, 132.5, 128.4, 128.3, 128.0, 127.7, 127.5, 127.1, 126.2, 126.0, 125.1, 125.0, 119.9, 67.2, 61.9, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{26}H_{20}NaO_2^+$: 387.1356 $(M + Na)^+$, found 387.1354.

Benzyl 9-Phenyl-9*H*-fluorene-9-carboxylate (3ah). Following the general procedure, the compound was isolated as a white solid (39.9 mg, 53% yield). Mp: 144.0−146.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.30−7.27 (m, 3H), 7.24−7.15 (m, 7H), 7.07−7.02 (m, 2H), 5.18 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.8, 145.8, 141.6, 140.6, 135.6, 128.6, 128.4, 128.3, 128.1, 127.9, 127.7, 127.2, 127.0, 126.6, 119.9, 67.4, 67.1. HRMS (ESI-TOF) m/z calculated for $C_{27}H_{20}NaO_2^+$: 399.1356 $(M + Na)^+$, found 399.1364.

Diethyl 9*H*-Fluorene-9,9-dicarboxylate (3ai). Following the general procedure, the compound was isolated as a white solid (26.7 mg, 43% yield). Mp: 90.0−93.0 °C. The eluent: PE/EA = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.5 Hz, 2H), 7.45 (td, J = 7.5, 1.0 Hz, 2H), 7.37 (td, J = 7.5, 1.0 Hz, 2H), 4.24 (q, J = 7.1 Hz, 4H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.4, 141.3, 140.1, 129.1, 127.7, 126.7, 120.0, 68.3, 62.2, 14.0. HRMS (ESI-TOF) m/z calculated for $C_{19}H_{18}NaO_4^+$: 333.1097 $(M + Na)^+$, found 333.1102.

(9-Phenyl-9*H*-fluoren-9-yl)methanol (7). Following the procedure, the compound was isolated as a white oil (46.7 mg, 86% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.77 (d, J = 7.5 Hz, 2H), 7.37 (t, J = 7.4 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 7.25−7.16 (m, 7H), 4.21 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 149.2, 141.6, 140.8, 128.8, 127.9, 127.7, 127.2, 127.0, 125.0, 120.3, 67.8, 61.0. HRMS (ESI-TOF) m/z calculated for $C_{20}H_{16}NaO$: 295.1093 $(M + Na)^+$, found 295.1088.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b02885.

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

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The authors declare no competing financial interest.

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