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Palladium-Catalyzed Decarboxylative Cross-Coupling Reactions: A Route for Regioselective Functionalization of Coumarins

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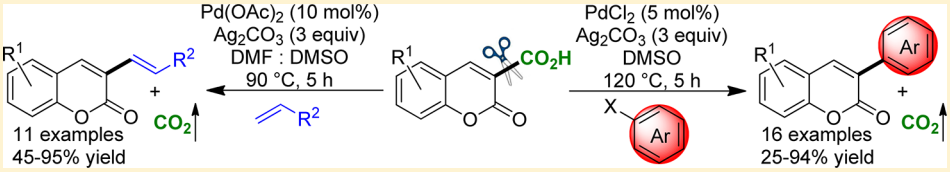
Supporting Information



ABSTRACT: A straightforward, regioselective, and step-economical ligand-free palladium-catalyzed decarboxylative functionalization of coumarin-3-carboxylic acids is devised. This protocol is compatible with a wide variety of electron-donating and -withdrawing substituents and allows for construction of various biologically important π-electron extended coumarins.

INTRODUCTION

Transition-metal-catalyzed biaryl formation traditionally involves the coupling of two activated aryl halide or sulfonate and the organometallic units.[1] Despite tremendous developments in this procedure, the requirement of prefunctionalization of coupling partners is wasteful since it requires the installation and then subsequent disposal of stoichiometric activating agents. On the other hand, the rapidly growing metal-promoted decarboxylative cross-coupling reaction, compared with previous transition-metal-catalyzed cross-coupling reactions, takes advantage of regioselective functionalizations and step-saving consequences.[2] Furthermore, it applies greener arenecarboxylic acid coupling partners with broad availability and low cost which produce nontoxic CO_2 byproduct. In 2002, Myers et al. introduced a novel Pd-catalyzed decarboxylative Heck reaction to form vinyl arenes.[3] Next, ground-breaking reports from two individual groups, Gooßen et al. and Forgione and Bilodeau et al., showed that arenecarboxylic acids acting as organometallic reagent equivalents can be used to couple with carbon electrophiles.[4] The represented milestone was further developed with several groups for expedient synthesis of a wide range of structurally diverse molecules.[5,6] Although some of the basic foundations of decarboxylation reaction of electron-poor arenecarboxylic acids have been arranged, decarboxylative functionalization of heteroarene carboxylic acids has received much less attention. Some focused efforts include decarboxylative arylation of pyrroles, indoles, (benzo)furans, (benzo)-thiophenes, and azoles.[7] Given the broad spectrum of interesting biological properties of functionalized heteroarenes, there remains much to be explored on the extension of reaction scope for heteroarenecarboxylic acid partners.

As part of our continuing efforts in Pd-catalyzed direct functionalization of heterocycles,[8] we reported a regioselective direct arylation of coumarins via oxidative boron Heck-type reaction.[8d] The regioselectivity was in bias of C-4 arylation, and 3-arylated coumarin was not detected. In our continuing investigations, we next turned our attention to construction of 3-arylcoumarins. These structural motifs have attracted considerable attention as they are widely found in natural products exhibiting notable biological and pharmaceutical properties. For example, isoprenoid-substituted 3-arylcoumarins, isolated from *Glycyrrhiza aspera*[9] and *G. Glabra*[10] natural sources, are known to exhibit significant PPAR-γ ligand-binding activity. Furthermore, fluorescent dyes of coumarins are of great interest in view of their possible applications as fluorescent labels in biological systems.[11]

The main synthetic strategy to construct these privileged scaffolds is based on the Suzuki reaction of coumarinyl halides and boronic acid/esters, which still requires prefunctionalization of the coumarin moiety and suffers from a lack of step economy.[12] An alternative method is zincation of coumarin at C-3 followed by a Negishi cross-coupling.[13] Outside of these contributions, there have been no focused efforts on direct functionalization of coumarins at C-3. Although a direct 3-arylation of coumarins via Pd-catalyzed coupling of coumarins and iodoarenes was recently disclosed, the process was limited by its low functional group tolerance and low yields of the adducts.[14]

On the other hand, the convenient ring-closure reaction of active methylenes and arylaldehydes for construction of coumarins[15] leaves behind a surplus carboxylate group at C-3 which should be removed before functionalization of coumarins. One might therefore expect that decarboxylative functionalization of these scaffolds would find significant utility in organic synthesis. In this context, decarboxylative allylation of coumarins has recently been achieved.[16]

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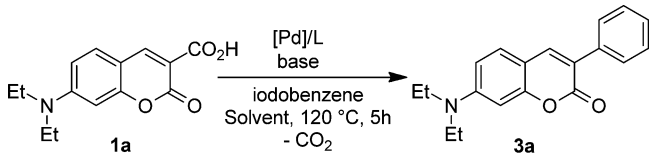
Table 1. Optimization of Decarboxylative Arylation of Coumarin-3-carboxylic Acid (1a)[a]



entry	[Pd]	L	base	solvent	T (°C)	time (h)	yield[b] (%)
1	$Pd(OAc)_2$		KOAc	DMSO	120	5	24
2	$Pd(OAc)_2$		Cs_2CO_3	DMSO	120	5	51
3	$Pd(OAc)_2$		Ag_2CO_3	DMSO	120	5	74
4	$Pd(dba)_2$		Ag_2CO_3	DMSO	120	5	48
5	$Pd(OH)_2/C$		Ag_2CO_3	DMSO	120	5	58
6	**$PdCl_2$**[c]		**Ag_2CO_3**	**DMSO**	120	5	**96 (92)**[d]
7	$PdCl_2$	PPh_3	Ag_2CO_3	DMSO	120	5	80
8	$PdCl_2$	PCy_3	Ag_2CO_3	DMSO	120	5	78
9	$PdCl_2$	dppe	Ag_2CO_3	DMSO	120	5	83
10	$PdCl_2$	phen	Ag_2CO_3	DMSO	120	5	84
11	$PdCl_2$		Ag_2CO_3	DMF	120	5	85
12	$PdCl_2$		Ag_2CO_3	DMA	120	5	74
13	$PdCl_2$		Ag_2CO_3	DME	120	5	58
14	$PdCl_2$			DMSO	120	5	0
15			Ag_2CO_3	DMSO	120	5	0
16[e]	$PdCl_2$		Ag_2CO_3	DMSO	120	5	50
17	$PdCl_2$		Ag_2CO_3	DMSO	100	5	80
18[f]	$Pd(acac)_2/CuI$	phen	K_2CO_3	NMP	160	24	trace
19[f]	$Pd(acac)_2/CuCl$	phen	K_2CO_3	NMP	160	24	trace
20[f]	$Pd(acac)_2/Cu(OAc)_2$	phen	K_2CO_3	NMP	160	24	trace

[a]Reaction conditions: coumarin-3-carboxylic acid (**1a**) (0.25 mmol, 1.0 equiv), iodobenzene (1.3 equiv), Pd catalyst (10 mol %), ligand (20 mol %), base (3.0 equiv), and solvent (3.0 mL). [b]GC yields. [c]Catalyst loading as low at 5 mol %. [d]Isolated yield in parentheses. [e]Ag_2CO_3 (1.0 equiv) was used. [f]Following reaction conditions was used: iodobenzene (0.2 mmol, 1.0 equiv), coumarin-3-carboxylic acid (**1a**) (3.0 equiv), Pd catalyst (1 mol %), cocatalyst (3 mol %), ligand (5 mol %), base (1.5 equiv), 3 Å MS (52 mg), and NMP (0.4 mL).

Furthermore, very recently, Messaoudi and Alami developed a $PdBr_2$/DPEphos catalytic system for decarboxylative arylation of quinolinone-3-carboxylic acids and disclosed two examples of arylated coumarins.[17] In spite of the importance of this contribution, the yields of arylated coumarins were moderate and the substrate scope was limited. Driven by the need for an efficient synthetic route to these privileged motifs, we hypothesized the development of an efficient, step-economical, and regioselective arylation as well as alkenylation of coumarins at C-3 via a palladium-catalyzed decarboxylative cross-coupling protocol.

RESULTS AND DISCUSSION

In this work, we disclose a convenient method for regioselective functionalization of coumarins at C-3. This protocol should give economically viable and environmentally attractive access to 3-aryl- and vinylcoumarins. To begin, coumarin **1a** and iodobenzene were chosen, and the reaction parameters (catalyst, solvent, base, etc.) were varied to achieve decarboxylative arylation (Table 1). While bases such as KOAc and Cs_2CO_3 resulted in only low to moderate yields, with Ag_2CO_3, 3-arylcoumarin **3a** was constructed in 74% yield (entries 1−3). Replacing $Pd(OAc)_2$ with other palladium sources such as $PdCl_2$, $Pd(dba)_2$, and $Pd(OH)_2/C$ proved $PdCl_2$ (catalyst loading as low at 5 mol %) as the most active catalyst, where **3a** was gratifyingly obtained in almost quantitative yield (entries 4−6). Screening reactions with respect to ligands including PPh_3, PCy_3, and bidendate ligands such as dppe and phenanthroline resulted in only comparable or lower yields of the product (entries 7−10). Therefore, ligand-free conditions were established for later investigations. Replacing DMSO with other solvents such as DMF, DMA, and DME also did not improve the yield (entries 11−13). Furthermore, it turned out that no arylated coumarin was observed in the absence of the base and palladium catalyst (entries 14 and 15). Next the effect of silver loading was investigated. In conventional bimetallic Pd/Ag systems, silver salt is employed to serve a dual purpose: as a base as well as a comediator to facilitate decarboxylation. It is also believed to prolong the lifetime of the active catalyst. However in the presence of haloarenes as the coupling partners of decarboxylative arylation reactions, silver salts form insoluble silver halides. Accordingly, a reduction in the amount of silver salts appears to be hardly feasible and stoichiometric amounts are necessary.[5a,d,19] Our result was in accord with the previous reports and showed that with lower amounts of the Ag salt, lower yields of the desired product were obtained (entry 16).

Attempts to lower the temperature to 100 °C afforded **3a** in a decreased yield of 80% (entry 17). Additionally, a Gooßen-type protocol applying Pd/Cu bimetallic catalytic systems was explored (entries 18−20).[5a] However, the results were not satisfactory, and only traces of the desired product were obtained.[18]

We were delighted to see that under the optimized reaction conditions, iodoarene (1.3 equiv), $PdCl_2$ (5 mol %), and Ag_2CO_3 (3.0 equiv) in DMSO at 120 °C for 5 h (similar to Becht's[19] and Tan's[20] conditions), the biaryl product **3a** was formed in 92% yield (Table 2, entry 1). It is noteworthy that the reaction proceeded with high selectivity relative to the protodecarboxylation side reaction. Protodecarboxylation, the

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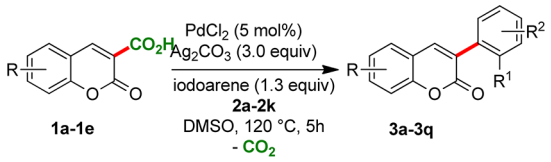
Table 2. Scope of the Arylation Reaction[a]



entry	product	yield (%)
1	**3a**: $R^1 = R^2 = H$	92
2	**3b**: $R^1 = H$, $R^2 = p$-OMe	94
3	**3c**: R^1 = OMe, $R^2 = H$	68
4	**3d**: R^1 = Me, $R^2 = H$	72
5	**3e**: R^1 = Me, $R^2 = p$-Me	55
6	**3f**: $R^1 = R^2$ = naph	67
7	**3g**: R^1 = Me, $R^2 = p$-NO_2	81
8	**3h**: $R^1 = NO_2$, $R^2 = p$-Me	88
9	**3i**: $R^1 = NO_2$, $R^2 = p$-NO_2	91
10	**3j**: R^1 = F, $R^2 = H$	68
11	**3k**: $R^1 = CF_3$, $R^2 = H$	58
12	**3l**: R^1 = Me, $R^2 = NO_2$	54
13	**3m**: $R^1 = R^2 = H$	0[b]
14	**3n**: $R^1 = R^2 = H$	93
15	**3o**: $R^1 = H$, R^2 = OMe	72
16	**3p**: $R^1 = R^2 = H$	88
17	**3q**: $R^1 = H$, R^2 = Me	25[c]

[a]All reactions were run under the optimized conditions. [b]Bromobenzene was used. [c]The following conditions were used: Pd$(CH_3CN)_2Cl_2$ (10 mol %), and Ag_2CO_3 (3.0 equiv) in DMSO (0.08 M) at 160 °C for 24 h.

simplest case of a catalytic activation of carboxylic acids, which usually requires the addition of a transition-metal mediator, generally a copper, silver, or mercury salt for CO_2 extrusion, is well established.[21]

Motivated by these results, we next sought to explore the scope of the ligand-free Pd-catalyzed decarboxylative cross-coupling reaction with iodoarenes possessing various steric and electronic properties (Table 2). The results indicated that the scope of the reaction was quite broad given that alkyl, alkoxy, halo, and nitro substituents were tolerated. The *p*-methoxy-substituted iodoarene afforded the corresponding cross-coupled product **3b** in excellent yield (entry 2). As expected, 2-iodoanisole showed inferior reactivity in this reaction, providing biaryl **3c** in only 68% yield (entry 3). In addition, the sterically demanding substitution patterns were tolerated toward the cross-coupling reaction of **1a**, leading to biaryls **3d–f** in good yields. Next, the scope of the reaction with electron-deficient iodoarenes was monitored. While comparable results were obtained with mononitro-substituted iodoarenes (81% and 88% of **3g** and **3h** respectively, entries 7 and 8), the dinitro-substituted iodoarene showed superior reactivity, resulting in the desired product in almost quantitative yield (91%, entry 9). Interestingly, less activated 2-fluoroiodobenzene, a good partner for further functionalizations, showed compatibility with this reaction (68% yield, entry 10). Notably, even the *o*-trifluoromethyl-substituted iodoarene, which due to its inferior reactivity is rarely used as a coupling partner in direct arylation reactions, was compatible with the reaction conditions (58% yield, entry 11).

To expand the scope further, unsubstituted as well as methoxy- and nitro- substituted coumarin-3-carboxylic acids were probed. While moderate yields were obtained with coumarin itself (entry 12), methoxy-substituted coumarins gratifyingly afforded 3-arylcoumarins **3n–p** in yields ranging from 72 to 93% (entries 14–16). Replacing iodobenzene with bromobenzene gave no biaryl product, and protodecarboxylation proceeded smoothly instead, leading to undesired coumarin formation (entry 13).[21] Thus, suppression of the competitive protonation reaction could not be effectively achieved using a bromoarene partner with lower reactivity.

Unfortunately, arylation of coumarin-3-carboxylic acid bearing a strongly electron-withdrawing NO_2 group was not successful. The substrate was readily subjected to proto-decarboxylation instead, resulting in unwanted 6-nitrocoumarin side product. We further focused on optimizing the decarboxylative arylation of 6-nitrocoumarin-3-carboxylic acid **1e** individually. A beneficial effect was observed for replacing $PdCl_2$ with Pd$(CH_3CN)_2Cl_2$ and increasing the reaction time to 24 h.[18] Under the altered reaction conditions, the nitro derivative of 3-arylcoumarin **3q** was obtained albeit in low yield (entry 17).

We also investigated the possibility of whether the proposed catalytic system could be effective toward the alkenylation of coumarin-3-carboxylic acids via a decarboxylative Heck-type coupling.[22] C-3 alkenyl groups on coumarins extend the delocalized π-electron system, which leads to longer wavelength absorption bands and more promising fluorescent behavior.[23]

For the alkenylation reaction, we started with coumarin-3-carboxylic acid **1b** (R = H) and methylacrylate **4a**. To our delight, the extension of the π-electron system of the coumarin was simply achieved using the Heck-type palladium-catalyzed decarboxylative cross-coupling reaction under slightly altered reaction conditions,[18] and adduct **5a** was obtained in almost quantitative yield (Table 3, entry 1). Motivated by this result, we next investigated the substrate scope of both coumarin and alkene substrates, as summarized in Table 3. Reactions involving alkenes conjugated with ethyl ester group **4b** led to good to excellent yields of the alkenylated coumarins **5b–d** (entries 2–4). Alkenes conjugated with an *n*-butyl group were also alkenylated on coumarins. While with 7-methoxycoumarin only a moderate yield of the desired product **5f** was obtained, coumarin- and 7-diethylaminocoumarin-3-carboxylic acid substrates resulted in good to excellent yields of the products **5e** and **5g**, respectively (entries 5–7). Notably, when 7-diethylaminocoumarin-3-carboxylic acid was reacted with methyl methacrylate, the β-elimination reaction was processed in bias of the formation of the less substituted alkene, and the allylated coumarin **5h** was obtained as the main product (entry 8).

Next, the scope of a nonactivated alkene such as styrene was explored. Although coumarin-3-carboxylic acid provided only a moderate yield of the product **5i**, coumarin **1a** was alkenylated in 91% yield (entries 9 and 10). Finally, we were pleased to find that acrylonitrile **4f** was also tolerated in this reaction and led to product **5k** as a potential fluorescent probe for cyanide ions[24] in 55% yield (entry 11).

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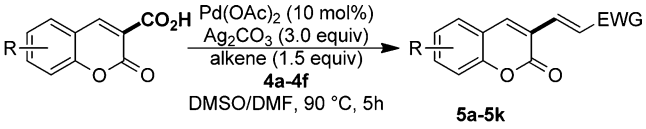
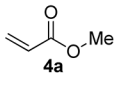
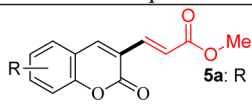
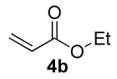
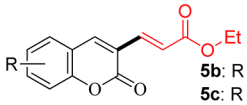
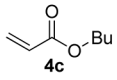
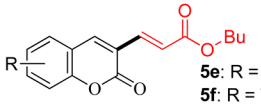
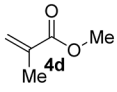
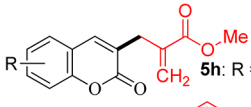
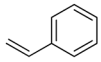
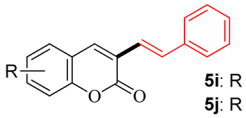
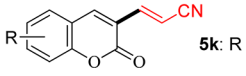
Table 3. Scope of the Alkenylation Reaction[a]



entry	alkene	product
1	 4a	 **5a**: R = H, 95%
2	 4b	 **5b**: R = H, 90%
3		**5c**: R = 7-OMe, 93%
4		**5d**: R = 7-NEt_2, 87%
5	 4c	 **5e**: R = H, 78%
6		**5f**: R = 7-OMe, 55%
7		**5g**: R = 7-NEt_2, 95%
8	 4d	 **5h**: R = 7-NEt_2, 55%
9	 4e	 **5i**: R = H, 45%
10		**5j**: R = 7-NEt_2, 91%
11	 4f	 **5k**: R = 7-NEt_2, 55%

[a]Reaction conditions: coumarin-3-carboxylic acid (0.2 mmol, 1.0 equiv), alkene (1.5 equiv), $Pd(OAc)_2$ (10 mol %), and Ag_2CO_3 (3.0 equiv) in DMSO/DMF (1/20) were heated in a sealed tube at 90 °C for 5 h.

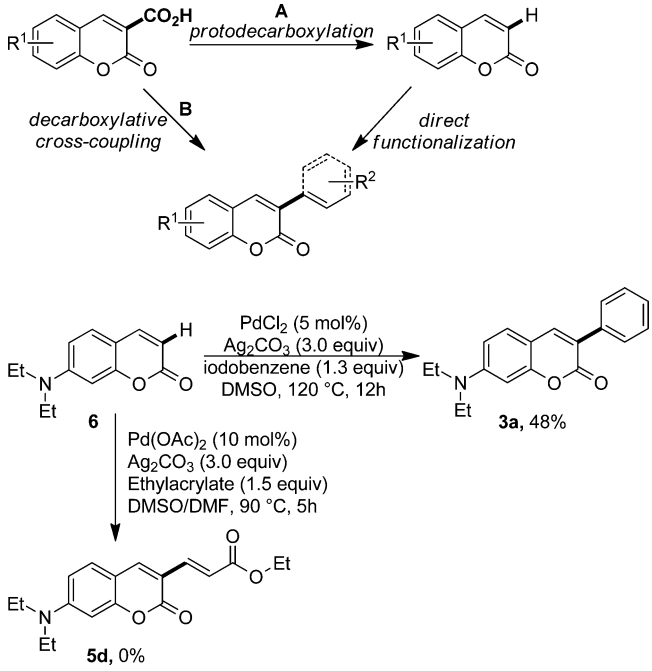
To clarify participation of competing pathway of protodecarboxylation/direct arylation or alkenylation of coumarins in this protocol (Scheme 1, path A), we explored direct functionalization of coumarin with iodoarene and electron-deficient alkene under the optimized reaction conditions (Scheme 1). Direct arylation reaction of coumarin **6** with iodobenzene resulted in only 48% of the desired product **3a**. Furthermore, oxidative Heck reaction of coumarin **6** with ethylacrylate was unsuccessful under the optimized reaction condition. These results indicate a preference for the decarboxylative cross-coupling pathway (Scheme 1, path **B**) in both arylation and alkenylation reactions.

In summary, we developed a versatile, regioselective, and step-economical decarboxylative arylation and alkenylation of coumarin-3-carboxylic acids via a palladium catalytic system. The protocol exhibited a broad substrate scope with respect to substrates used. Furthermore, ligand-free conditions were established in this approach, which was not feasible in most of the previously reported decarboxylative coupling reactions. This protocol may provide an appealing alternative to the existing approaches to construct functionalized coumarins as the key intermediates in the synthesis of drug candidates and fluorescent dyes.

EXPERIMENTAL SECTION

Typical Experimental Procedure for Decarboxylative Arylation of Coumarin-3-carboxylic Acids. A vial equipped with a stir bar was charged with coumarin-3-carboxylic acid (0.25 mmol, 1.0 equiv), aryl iodide (0.33 mmol, 1.3 equiv), $PdCl_2$ (5 mol %), and Ag_2CO_3 (0.75 mmol, 3.0 equiv). Dry degassed DMSO (3 mL) was then added, and the vial was capped. The resulting mixture was heated in an oil bath at 120 °C for 5 h, cooled, and then filtered through a short plug of silica. Removal of the solvent gave a crude mixture which was purified by flash column chromatography (hexanes/EtOAc gradient, 10%).

Scheme 1. Competition between Protodecarboxylation/Direct Functionalization and Decarboxylative Cross-Coupling Reactions



7-(Diethylamino)-3-phenyl-2H-chromen-2-one ***(3a):*** yellowish oil (67 mg, 92%); ^1H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, J = 7.1 Hz, 6H), 3.43 (q, J = 7.1 Hz, 4H), 6.54 (d, J = 2.2 Hz, 1H), 6.60 (dd, J = 8.7, 2.2 Hz, 1H), 7.31−7.34 (m, 2H), 7.39−7.42 (t, J= 7.6 Hz, 2H), 7.69−7.70 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 45.3, 97.7, 109.4, 128.2, 128.6, 128.7, 129.3, 136.3, 141.0, 156.6, 162.1; IR 1015, 1260, 1704, 2964 cm^{-1}; MS m/z 293 ($M^{\bullet+}$, 72), 278 (100), 250 (20), 221 (13.4). Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.95; H, 6.61; N, 4.86.

7-(Diethylamino)-3-(4-methoxyphenyl)-2H-chromen-2-one ***(3b):*** yellowish oil (76 mg, 94%); ^1H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, J = 7.1 Hz, 6H), 3.42 (q, J = 7.1 Hz, 4H), 3.84 (s, 3H), 6.53 (d, J = 2.5 Hz, 1H), 6.59 (dd, J = 8.8, 2.5 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 1H), 7.63−7.65 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 45.3, 55.8, 97.8, 109.3, 114.2, 129.3, 129.9, 139.8, 156.4, 159.7, 162.2; IR 1030, 1127, 1251, 1605, 1719, 2963 cm^{-1}; MS m/z 323 ($M^{\bullet+}$, 100), 308 (97), 279 (24), 149 (80), 55 (33), 41 (55). Anal. Calcd for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.45; H, 6.66; N, 4.21.

7-(Diethylamino)-3-(2-methoxyphenyl)-2H-chromen-2-one ***(3c):*** yellowish solid (55 mg, 68%); mp 90−92 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.21 (t, J = 7.1 Hz, 6H, $2CH_3$), 3.42 (q, J = 7.1 Hz, 4H), 3.82 (s, 3H), 6.54−6.59 (m, 2H), 6.96 (d, J = 8.2 Hz, 1H), 7.01 (t, J = 7.1 Hz, 1H), 7.28−7.30 (m, 1H), 7.30−7.38 (m, 2H), 7.60 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 45.3, 56.2, 97.8, 109.0, 109.1, 111.7, 120.9, 129.2, 129.8, 130.6, 131.5, 142.9, 145.1, 156.8, 157.8, 161.9; IR 1124, 1237, 1593, 1708, 2925 cm^{-1}; MS m/z 323 ($M^{\bullet+}$, 45), 308 (100), 217 (53), 202 (56), 174 (18), 149 (25). Anal. Calcd for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.41; H, 6.43; N, 4.24.

7-(Diethylamino)-3-o-tolyl-2H-chromen-2-one ***(3d):*** yellowish solid (55 mg, 72%); mp 105−107 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.26 (t, J = 6.8 Hz, 6H), 2.33 (s, 3H), 3.47 (q, J = 6.8 Hz,

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4H), 6.60 (s, 1H), 6.62 (d, J = 8.4 Hz, 1H), 7.27−7.32 (m, 5H), 7.53 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 20.5, 45.3, 97.8, 109.1, 109.3, 126.2, 128.6, 129.2, 130.5, 130.6, 136.2, 137.6, 142.7, 150.9, 156.9, 161.8; IR 1220, 1271, 1368, 1605, 1731, 2965 cm^{-1}; MS m/z 307 ($M^{\bullet+}$, 33), 292 (57), 149 (100), 57 (58), 41(80). Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.37; H, 6.80; N, 4.67.

7-(Diethylamino)-3-(2,4-dimethylphenyl)-2H-chromen-2-one ***(3e)****:* yellowish solid (44 mg, 55%); mp 105−106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (t, J = 7.0 Hz, 6H), 2.29 (s, 3H), 2.38 (s, 3H), 3.47 (q, J = 7.0 Hz, 4H), 6.59 (s, 1H), 6.63 (d, J = 8.6 Hz, 1H), 7.07 (d, J = 7.5 Hz, 1H), 7.12 (s, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 8.6 Hz, 1H), 7.51 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 20.4, 21.6, 45.3, 97.8, 109.2, 109.3, 126.9, 129.1, 130.4, 131.5, 133.3, 137.3, 138.3, 142.5, 150.9, 156.9, 161.9; IR 1073, 1127, 1269, 1606, 1719, 2964 cm^{-1}; MS m/z 321 ($M^{\bullet+}$, 59), 306 (79), 149 (100), 57 (33), 41 (39). Anal. Calcd for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.65; H, 7.31; N, 4.49.

7-(Diethylamino)-3-(naphthalen-1-yl)-2H-chromen-2-one ***(3f)****:* yellowish solid (57 mg, 67%); mp 140−141 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (t, J = 7.1 Hz, 6H), 3.48 (q, J = 7.1 Hz, 4H), 6.66−6.67 (m, 1H), 7.34 (d, J = 8.9 Hz, 1H), 7.48−7.57 (m, 4H), 7.69 (s, 1H), 7.88−7.93 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 45.4, 97.8, 109.2, 109.4, 121.1, 125.8, 126.0, 126.3, 126.6, 128.2, 128.9, 129.1, 129.4, 132.4, 134.2, 134.3, 143.9, 151.1, 157.1, 162.4; IR 1126, 1274, 1605, 1725, 2923 cm^{-1}; MS m/z 343 ($M^{\bullet+}$, 13), 329 (34), 314 (33), 279 (20), 167 (55), 149 (100), 71 (58), 57 (92), 43 (65). Anal. Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.69; H, 6.01; N, 3.95.

7-(Diethylamino)-3-(2-methyl-4-nitrophenyl)-2H-chromen-2-one ***(3g)****:* yellowish oil (71 mg, 81%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, J = 7.1 Hz, 6H), 2.39 (s, 3H), 3.44 (q, J = 7.1 Hz, 4H), 6.55 (s, 1H), 6.63 (d, J = 8.8 Hz, 1H), 7.31 (d, J = 8.2 Hz, 1H), 7.42 (d, J = 8.8 Hz, 1H), 7.53 (s, 1H), 8.06 (d, J = 8.2 Hz, 1H), 8.12 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 20.7, 45.4, 97.6, 108.6, 109.7, 119.9, 121.3, 125.4, 129.7, 131.6, 139.7, 143.2, 143.5, 147.8, 151.6, 157.3, 161.0; IR 1212, 1266, 1339, 1511, 1712, 2966 cm^{-1}; MS m/z 352 ($M^{\bullet+}$, 8), 307 (78), 292 (100), 149 (87), 89 (44), 75 (44), 55 (61), 41 (96). Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.31; H, 5.81; N, 7.88.

7-(Diethylamino)-3-(4-methyl-2-nitrophenyl)-2H-chromen-2-one ***(3h)****:* yellowish solid (77 mg, 88%); mp 187−189 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (t, J = 7.0 Hz, 6H), 2.46 (s, 3H), 3.42 (q, J = 7.0 Hz, 4H), 6.52 (s, 1H), 6.59 (d, J = 8.6 Hz, 1H), 7.29−7.33 (m, 2H), 7.43 (d, J = 7.6 Hz, 1H), 7.59 (s, 1H), 7.86 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.8, 21.4, 45.3, 97.8, 109.0, 109.4, 120.0, 125.5, 128.7, 129.4, 132.2, 134.2, 139.9, 140.7, 149.2, 151.2, 156.9, 161.3; IR 1120, 1209, 1350, 1519, 1590, 1711, 2926 cm^{-1}; MS m/z 352 ($M^{\bullet+}$, 35), 337 (62), 125 (43), 97 (90), 71 (88), 57 (100), 43 (87). Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.35; H, 5.86; N, 8.08.

7-(Diethylamino)-3-(2,4-dinitrophenyl)-2H-chromen-2-one ***(3i)****:* yellowish solid (87 mg, 91%); mp 193−195 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (t, J = 7.1 Hz, 6H), 3.46 (q, J = 7.1 Hz, 4H), 6.53 (d, J = 2.1 Hz, 1H), 6.65 (dd, J = 8.8, 2.2 Hz, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.4, 1H), 7.73 (s, 1H), 8.46 (dd, J = 8.4, 2.2 Hz, 1H), 8.86 (d, J = 2.2, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 45.5, 97.8, 110.0, 120.7, 127.4, 130.1, 133.4, 137.9, 142.3, 147.1, 149.2, 150.8, 157.8; IR 1015, 1345, 1513, 1590, 1718, 2962 cm^{-1}; MS m/z 383 ($M^{\bullet+}$, 73), 368 (100), 296 (42), 147 (87), 120 (39), 111 (27), 97 (39), 83 (35), 71 (39), 57 (65), 43 (48). Anal. Calcd for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N, 10.96. Found: C, 59.73; H, 4.59; N, 10.83.

7-(Diethylamino)-3-(2-fluorophenyl)-2H-chromen-2-one ***(3j)****:* yellowish solid (53 mg, 68%); mp 92−93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (t, J = 7.1 Hz, 6H), 3.47 (q, J = 7.1 Hz, 4H), 6.59 (s, 1H), 6.64 (d, J = 7.5 Hz, 1H), 7.15−7.23 (m, 2H), 7.33−7.34 (m, 2H), 7.6−7.62 (m, 1H), 7.73 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 45.4, 97.8, 109.1, 109.5, 116.3 (d, J = 22.0 Hz), 124.3 (d, J = 3.5 Hz), 129.5, 129.9 (d, J = 8.0 Hz), 131.9, 143.5, 143.6, 156.9, 158.7 (d, J = 251.2 Hz), 161.2; IR 1078, 1127, 1517, 1594, 1715, 2971 cm^{-1}; MS m/z 311 ($M^{\bullet+}$, 27), 296 (49), 149 (100), 84 (80), 57 (74), 41 (58). Anal. Calcd for $C_{19}H_{18}FNO_2$: C, 73.29; H, 5.83; N, 4.50. Found: C, 73.35; H, 5.74; N, 4.42.

3-(2-(Trifluoromethyl)phenyl)-2H-chromen-2-one ***(3k)****:* yellowish solid (52 mg, 58%); mp 138−139 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (t, J = 7.1 Hz, 6H), 3.43 (q, J = 7.1 Hz, 4H), 6.54 (d, J = 2.3 Hz, 1H), 6.59 (dd, J = 8.8, 2.3 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H) 7.46−7.49 (m, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 45.3, 97.7, 108.6, 109.4, 119.7, 126.6 (q, J = 272.2 Hz), 126.7 (q, J = 6.6 Hz), 128.6, 129.6, 129.9 (q, J = 29.6 Hz), 132.0, 132.9, 135.0, 142.9, 151.3, 157.1, 161.9; IR 1113, 1306, 1569, 1700, 2969 cm^{-1}; MS m/z 361 ($M^{\bullet+}$, 80), 346 (100), 318 (22), 149 (66), 41 (25). Anal. Calcd for $C_{20}H_{18}F_3NO_2$: C, 66.48; H, 5.02; N, 3.88. Found: C, 66.67; H, 5.13; N, 3.77.

3-(2-Methyl-4-nitrophenyl)-2H-chromen-2-one ***(3l)****:* white solid (38 mg, 54%); mp 155−157 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50 (s, 3H), 7.31−7.40 (m, 3H), 7.50−7.58 (m, 3H), 7.73 (s, 1H), 7.96 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 117.3, 119.6, 125.1, 125.8, 127.8, 128.1, 128.4, 132.1, 132.2, 134.6, 139.7, 141.2, 154.1; IR 1016, 1258, 1459, 2921 cm^{-1}; MS m/z 281 ($M^{\bullet+}$, 9), 85 (60), 71 (83), 57 (100), 43 (94). Anal. Calcd for $C_{16}H_{11}NO_4$: C, 68.32; H, 3.94; N, 4.98. Found: C, 68.53; H, 4.08; N, 5.12.

8-Methoxy-3-phenyl-2H-chromen-2-one ***(3n)****:* white solid (59 mg, 93%); mp 153−155 °C (lit.[25] mp 154−155 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.98 (s, 3H), 7.08−7.78 (m, 9H). Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 75.99; H, 4.69.

8-Methoxy-3-(4-methoxyphenyl)-2H-chromen-2-one ***(3o)****:* fawn solid (51 mg, 72%); mp 148−149 °C (lit.[26] mp 149−150 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.93 (s, 3H), 6.81−7.22 (m, 5H), 7.61 (d, J = 8.0 Hz, 2H), 7.62 (s, 1H). Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.55; H, 5.11.

5-Methoxy-3-phenyl-2H-chromen-2-one ***(3p)****:* white solid (55 mg, 88%); mp 123−124 °C (lit.[25] mp 124−125 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 3H), 7.10−7.88 (m, 9H). Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.37; H, 4.88.

6-Nitro-3-(p-tolyl)-2H-chromen-2-one ***(3q)****:* brown solid (18 mg, 25%); mp 209−210 °C (lit.[27] mp 210−211 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.43 (s, 3H), 7.27−7.29 (m, 2H), 7.51−7.54 (m, 1H), 7.64−7.67 (m, 2H), 8.08 (s, 1H), 8.39−8.41 (m, 1H), 8.57−8.59 (m, 1H). Anal. Calcd for $C_{16}H_{11}NO_4$: C, 68.32; H, 3.94; N, 4.98. Found: C, 68.61; H, 4.08; N, 5.18.

Typical Experimental Procedure for Decarboxylative Alkenylation of Coumarin-3-carboxylic Acids. A vial equipped with a stir bar was charged with coumarin-3-carboxylic acid (0.2 mmol, 1.0 equiv), aryl iodide (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (10 mol %), and Ag_2CO_3 (0.6 mmol, 3.0 equiv). Dry degassed DMSO (0.12 mL) and DMF (2.4 mL) were then added, and the vial was capped. The resulting mixture was heated in an oil bath at 90 °C for 5 h, cooled, and then filtered through a short plug of silica. Removal of the solvent gave a crude mixture which was purified by flash column chromatography (hexanes/EtOAc gradient).

(E)-Methyl 3-(2-oxo-2H-chromen-3-yl)acrylate ***(5a)****:* yellowish solid (44 mg, 95%); mp 175−178 °C (lit.[28] mp 176−178 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.85 (s, 3H, 3H), 7.15 (d, J = 15.9 Hz, 1H), 7.30−7.63 (m, 5H), 7.91 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.3, 117.1, 119.4, 122.8, 123.8, 125.3, 128.9, 133.3, 138.5, 144.0, 154.0, 160.7, 167.8; IR 1165, 1260, 1278, 1305, 1603, 1714, 2924 cm^{-1}; MS m/z 230 ($M^{\bullet+}$, 31), 199 (12), 171 (100), 115 (24), 85 (9), 71 (12), 57 (18). Anal. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38. Found: C, 68.10; H, 4.49.

(E)-Ethyl 3-(2-oxo-2H-chromen-3-yl)acrylate ***(5b)****:* yellowish solid (44 mg, 90%); mp 112−115 °C (lit.[29] mp 115−117 °C, lit.[27] mp 120−121 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (t, J = 7.1 Hz, 3H), 4.26 (q, J = 7.1 Hz, 2H), 7.09 (d, J = 15.9 Hz, 1H), 7.26−7.59 (m, 5H), 7.87 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 61.2, 117.1, 119.4, 122.9, 124.2, 125.2, 128.9, 133.3, 138.2, 143.8, 154.0, 159.5, 167.3; IR 1020, 1083, 1259, 1606, 1721, 2921 cm^{-1}; MS m/z 244 ($M^{\bullet+}$, 51), 221 (20), 171 (100), 147 (14), 115 (13), 97 (18), 69 (22), 57 (35), 43 (33). Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.54; H, 4.82.

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*(E)-Ethyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (**5c**):* yellowish solid (51 mg, 93%); mp 180−183 °C (lit.[30] mp 178−179 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (t, J = 7.0 Hz, 3H), 3.93 (s, 3H) 4.29 (q, J = 7.1 Hz, 2H), 6.86 (d, J = 1.9 Hz, 1H), 6.92 (dd, J = 8.7 Hz, 2.2 Hz, 1H), 7.07 (d, J = 15.9 Hz, 1H), 7.47 (d, J = 8.7 Hz, 1H), 7.57 (d, J = 15.8 Hz, 1H), 7.84 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 56.3, 61.0, 100.9, 113.1, 113.8, 119.3, 122.7, 130.0, 138.69, 144.2, 156.0, 159.8, 164.3, 167.6; IR 1023, 1158, 1261, 1604, 1706, 2923 cm^{-1}; MS m/z 274 ($M^{\bullet+}$, 73), 245 (10), 229 (35), 201 (100), 85 (13), 71 (16), 57 (18), 43 (11); Anal. Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.96; H, 5.29.

*(E)-Ethyl 3-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)acrylate (**5d**):* yellowish solid (55 mg, 87%); mp 135−137 °C (lit.[29] mp 109−112 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, J = 7.1 Hz, 6H), 1.31 (t, J = 7.1 Hz, 3H), 3.43 (q, J = 7.1 Hz, 4H), 4.23 (q, J = 7.1 Hz, 2H), 6.47 (d, J = 2.2 Hz, 1H), 6.59 (dd, J = 8.9 Hz, 2.3 Hz, 1H), 6.93 (d, J = 15.8 Hz, 1H), 7.26−7.29 (m, 1H), 7.52 (d, J = 15.8 Hz, 1H), 7.68 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 14.6, 45.4, 60.7, 97.4, 109.1, 109.8, 115.1, 119.9, 130.2, 139.8, 144.7, 152.1, 157.0, 160.7, 168.1; IR 1030, 1245, 1617, 1698, 2919, 2969; MS m/z 315 ($M^{\bullet+}$, 87), 300 (100), 270 (12), 198 (11), 149 (9), 59 (11). Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.86; H, 6.85; N, 4.60.

*(E)-Butyl 3-(2-oxo-2H-chromen-3-yl)acrylate (**5e**):* oil (42 mg, 78%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (t, J = 7.4 Hz, 3H), 1.42−1.46 (m, 2H), 1.67−1.70 (m, 2H), 4.22 (t, J = 6.6 Hz, 2H), 7.1 (d, J = 15.9 Hz, 1H), 7.26−7.60 (m, 5H), 7.87 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 19.6, 31.1, 65.1, 117.1, 119.4, 122.9, 124.3, 125.2, 128.9, 133.3, 138.2, 143.8, 154.0, 159.5, 167.3; IR 1258, 1605, 1708, 2961 cm^{-1}; MS m/z 272 ($M^{\bullet+}$, 25), 216 (13), 199 (27), 171 (100), 115 (19). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.29; H, 5.78.

*(E)-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (**5f**):* oil (33 mg, 55%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (t, J = 7.4 Hz, 3H), 1.46−1.48 (m, 2H), 1.70−1.73 (m, 2H), 3.93 (s, 3H), 4.24 (t, J = 6.7 Hz, 2H), 6.87 (d, J = 2.3 Hz, 1H), 6.92 (dd, J = 8.7 Hz, 2.4 Hz, 1H), 7.08 (d, J = 15.8 Hz, 1H), 7.48 (d, J = 8.7 Hz, 1H), 7.57 (d, J = 15.8 Hz, 1H), 7.85 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 19.6, 31.2, 56.3, 65.0, 100.9, 113.1, 113.8, 122.7, 130.0, 138.7, 144.2, 156.0, 164.3, 167.6; IR 1009, 1217, 1258, 1603, 1740, 2963 cm^{-1}; MS m/z 302 ($M^{\bullet+}$, 77), 246 (15), 229 (29), 201 (100), 147 (12), 73 (20), 57 (28). Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.79; H, 6.11.

*(E)-Butyl 3-(6-diethylamino-2-oxo-2H-3-chromenyl)-2-propenoate (**5g**):* yellowish solid (65 mg, 95%); mp 130−133 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, J = 7.4 Hz, 3H), 1.23 (t, J = 7.1 Hz, 6H), 1.40−1.45 (m, 2H), 1.65−1.68 (m, 2H), 3.43 (q, J = 7.1 Hz, 4H), 4.18 (t, J = 6.6 Hz, 2H), 6.47 (d, J = 2.3 Hz, 1H), 6.59 (dd, J = 8.89 Hz, 2.40 Hz, 1H), 6.94 (d, J = 15.8 Hz, 1H), 7.28−7.30 (m, 1H), 7.52 (d, J = 15.8 Hz, 1H), 7.69 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 14.2, 19.6, 31.2, 45.4, 64.7, 97.4, 109.0, 109.8, 115.1, 119.9, 130.2, 139.7, 144.7, 152.1, 156.9, 160.7, 168.3; IR 1003, 1162, 1577, 1707, 2930 cm^{-1}; MS m/z 343 ($M^{\bullet+}$, 71), 328 (100), 315 (22), 300 (45), 198 (69), 57 (32), 41 (91). Anal. Calcd for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.34; N, 4.08. Found: C, 70.22; H, 7.48; N, 4.24.

*Methyl 2-((7-(Diethylamino)-2-oxo-2H-chromen-3-yl)methyl)-acrylate (**5h**):* yellowish solid (35 mg, 55%); mp 107−110 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, J = 7.1 Hz, 6H), 3.43 (q, J = 7.1 Hz, 4H), 3.54 (s, 2H), 3.77 (s, 3H), 5.80 (d, J = 1.1 Hz, 1H), 6.33 (s, 1H), 6.52 (d, J = 2.4 Hz, 1H), 6.59 (dd, J = 8.8 Hz, 2.5 Hz, 1H), 7.25 (d, J = 8.8 Hz, 1H), 7.46 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 45.2, 52.3, 97.7, 109.1, 119.3, 128.0, 128.8, 137.6, 141.4, 151.1, 156.3, 162.9, 167.6; IR 1124, 1258, 1278, 1600, 1706, 2921 cm^{-1}; MS m/z 315 ($M^{\bullet+}$, 90), 300 (100), 255 (26), 111 (25), 97 (30), 71 (45), 57 (69), 43 (31). Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.24; H, 6.55; N, 4.20.

*(E)-3-Styryl-2H-chromen-2-one (**5i**):* yellowish solid (23 mg, 45%); mp 156−159 °C (lit.[23] mp 162−164 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, J = 16.4 Hz, 1H), 7.31−7.60 (m, 9H), 7.65 (d, J = 16.3 Hz, 1H), 7.85 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 116.9, 120.1, 122.5, 125.0, 125.4, 127.4, 128.1, 128.9, 129.2, 131.6, 132.9, 134.1, 137.2, 137.3, 153.3, 160.8; IR 1212, 1370, 1715, 2921 cm^{-1}; MS m/z 248 ($M^{\bullet+}$, 100), 219 (24), 191 (23), 173 (25), 105 (94), 77 (35). Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.51; H, 5.01.

*(E)-7-(Diethylamino)-3-styryl-2H-chromen-2-one (**5j**):* yellowish solid (58 mg, 91%); mp 193−196 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (t, J = 7.1 Hz, 6H), 3.46 (q, J = 7.1 Hz, 4H), 6.54 (d, J = 2.4 Hz, 1H), 6.62 (dd, J = 8.8 Hz, 2.5 Hz, 1H), 7.13 (d, J = 16.3 Hz, 1H), 7.28−7.39 (m, 5H), 7.49 (d, J = 16.3 Hz, 1H), 7.55 (d, J = 7.41 Hz, 2H), 7.71 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 45.3, 97.7, 109.6, 118.3, 123.5, 127.0, 128.0, 129.1, 129.2, 130.5, 138.1, 138.4, 156.0, 161.9; IR 1062, 1216, 1709, 2919 cm^{-1}; MS m/z 319 ($M^{\bullet+}$, 100), 304 (57), 275 (8). Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39. Found: C, 79.26; H, 6.75; N, 4.55.

*(E)-3-(7-(Diethylamino)-2-oxo-2H-chromen-3-yl)acrylonitrile (**5k**):* yellowish solid (29 mg, 54%); mp 239−241 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (t, J = 7.1 Hz, 6H), 3.49 (q, J = 7.1 Hz, 4H), 6.52 (d, J = 2.2 Hz, 1H), 6.64−6.68 (m, 2H), 7.14 (d, J = 16.2 Hz, 1H), 7.35− (m, 1H), 7.63 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 45.5, 97.3, 98.2, 108.8, 110.2, 115.0, 119.8, 130.6, 145.5, 152.2, 156.9, 160.3; IR 1012, 1260, 1584, 1711, 2853, 2920 cm^{-1}; MS m/z 268 ($M^{\bullet+}$, 75), 253 (100), 225 (34), 140 (9). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.89; H, 6.13; N, 10.59.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General remarks and NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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