JOC The Journal of Organic Chemistry

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Visible-Light-Induced C(sp^2)−C(sp^3) Coupling Reaction for the Regioselective Synthesis of 3-Functionalized Coumarins

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Cite This: *J. Org. Chem.* 2021, 86, 9552−9562 Read Online

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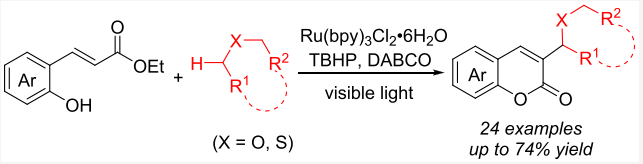
ABSTRACT: A photocatalysis strategy for the regioselective synthesis of 3-functionalized coumarins is reported. With visible light irradiation, a direct and regioselective C(sp^2)−C(sp^3) coupling reaction of 3-(2-hydroxyphenyl)acrylates with ethers or thioethers occurs by using $Ru(bpy)_3Cl_2·6H_2O$ as a photocatalyst and TBHP as an oxidant. The cascade process involves alkenylation of the C(sp^3)−H bond of ethers and lactonization, furnishing 3-alkylated coumarins as the final products. This approach is characterized by a broad substrate scope, mild reaction conditions, and simplified operation. The synthesis of 3-alkylated coumarins could be realized by a one-pot procedure, starting from commercially available salicylaldehyde.



INTRODUCTION

Coumarin and its derivatives are a huge class of compounds occurring in the structures of biologically active natural products and pharmaceuticals,[1] small-molecule fluorescent chemosensors,[2] as well as functional materials.[3] Consequently, the development of numerous strategies for the synthesis of these compounds has been stimulated in the past decade.[4] Among various coumarins, 3-substituted coumarins have attracted significant attention due to their important applications in medicine and chemical biology. Pertinent examples for the 3-substituted coumarins are illustrated in Figure 1.

The direct C−H functionalization through oxidative cross-coupling reactions is a powerful tool for the synthesis of 3-substituted coumarins. The published methods include palladium-catalyzed C−H olefination and arylation of coumarin[5] and C(sp^2)−C(sp^3) oxidative coupling reactions of coumarin with ethers or alkanes under metal catalysts[6] or metal-free conditions (Scheme 1a).[7] In 2019, Jin and co-workers reported a photocatalyzed C-3 alkylation of coumarins via decarboxylative coupling with *N*-hydroxyphthalimide esters (Scheme 1b).[8] However, the approaches require preparation of coumarins prior to functionalization, which often erodes step economy and sometimes suffers from the loss in regioselectivity. To complement existing methodology, efforts to devise a more efficient route were investigated. Herein, we reported a concise, regioselective synthesis of 3-alkyl coumarins from 3-(2-hydroxyphenyl)acrylates and ethers based on the visible-light-induced strategy combining direct C(sp^2)−C(sp^3) coupling and cyclization in one cascade process (Scheme 1c).

RESULTS AND DISCUSSION

To validate the conceptual framework outlined in Scheme 1c, the coupling of ethyl 3-(2-hydroxyphenyl)acrylate (**1a**) and THF (**2a**) was explored (Table 1). Primarily, $Ru(bpy)_3Cl_2·6H_2O$ (0.5 mol %) as a photocatalyst and *tert*-butyl hydroperoxide (TBHP, 5.5 M in decane, 3.0 equiv) as an oxidant were used for this model reaction. When the reaction mixture was irradiated with 10 W LED (450−455 nm) for 20 h, 3-(tetrahydrofuran-2-yl)coumarin **3a** was isolated in 45% yield (Table 1, entry 1). $Ru(bpy)_3Cl_2$ and $Ru(bpy)_3(PF_6)_2$ were also tested, but lower yields were obtained (Table 1, entries 2 and 3). We then fixed $Ru(bpy)_3Cl_2·6H_2O$ as a photocatalyst and screened several other oxidants, such as di-*tert*-butyl peroxide (DTBP), dicumyl peroxide (DCP), and dibenzoyl peroxide (BPO). In these cases, **3a** was obtained in very lower yields (Table 1, entries 4−7). Using 70% TBHP (in water) instead of 5.5 M TBHP (in decane) did not improve the reaction (Table 1, entry 8). To our surprise, the addition of an appropriate base remarkably increased the yield of **3a** (Table 1, entries 9−13). The best result was obtained in the case where 2 equiv of 1,4-diazabicyclo[2.2.2]octane (DABCO) was added to the reaction mixture (Table 1, entry 13). Subsequently, several solvents, such as EtOH, DMF, and dichloromethane (DCM), were screened. In these cases, a trace of or lower yield of **3a** was observed (Table 1, entries 14−16). In the case where MeOH was used as a solvent,

Received: April 12, 2021
Published: June 30, 2021

https://doi.org/10.1021/acs.joc.1c00848
J. Org. Chem. 2021, 86, 9552−9562

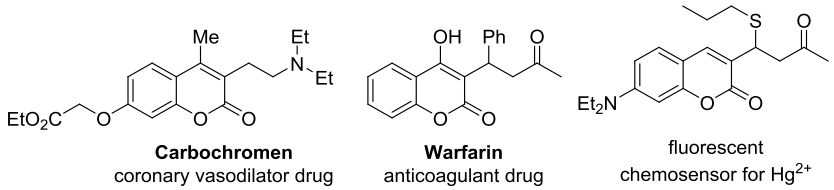
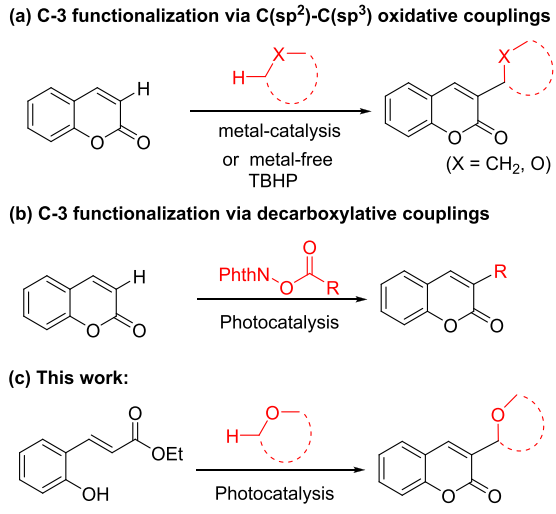


Figure 1. Pharmaceuticals and chemosensors containing a coumarin core.

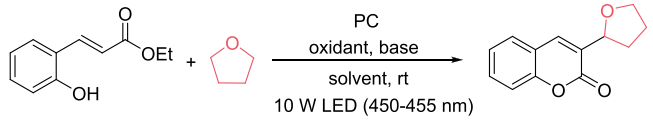
Scheme 1. Synthesis of 3-Substituted Coumarins via the C(sp^2)−C(sp^3) Coupling Strategies



coumarin (**4a**) was isolated (Table 1, entry 14). Decreasing or increasing the amount of oxidant TBHP led to a reduction in the yield (Table 1, entries 17 and 18). Finally, several control experiments were conducted. When the reaction was performed under an air atmosphere, without irradiation, or in the absence of photocatalyst, only coumarin, instead of the desired **3a**, was isolated (Table 1, entries 19−21).

Having identified optimized reaction conditions for the cascade C−C coupling/cyclization, the scope and limitations were investigated using a range of structurally modified 3-(2-hydroxyphenyl)acrylates (Scheme 2). Systematically altering the electron demand of substituent R^1 of the phenol moiety from methyl (**3b**) to methoxy (**3c**), fluoro (**3d**), chloro (**3e**), and bromo (**3f**) was well tolerated (51−71% yields). The structure of **3c** was unambiguously characterized by X-ray single-crystal analysis.[9] The addition of substituent R^2 was also well tolerated, enabling the formation of the desired products **3g−k**. In these cases, the electron-donating group (Me) substituted 3-(2-hydroxyphenyl)acrylate (product **3g**, 74% yield) gave a higher yield than the electron-withdrawing

Table 1. Reaction Optimization[a]



entry	PC	oxidant (equiv)	solvent	base	yield (%)[b]
1	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (3)	CH_3CN		45
2	$Ru(bpy)_3Cl_2$	TBHP (3)	CH_3CN		23
3	$Ru(bpy)_3(PF_6)_2$	TBHP (3)	CH_3CN		23
4	$Ru(bpy)_3Cl_2·6H_2O$	DTBP (3)	CH_3CN		24
5	$Ru(bpy)_3Cl_2·6H_2O$	TBPB (3)	CH_3CN		24
6	$Ru(bpy)_3Cl_2·6H_2O$	DCP (3)	CH_3CN		18
7	$Ru(bpy)_3Cl_2·6H_2O$	BPO (3)	CH_3CN		13
8	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (3)	CH_3CN		19[c]
9	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (3)	CH_3CN	K_2CO_3	0
10	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (3)	CH_3CN	LiO^tBu	21
11	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (3)	CH_3CN	DBU	52
12	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (3)	CH_3CN	quinuclidine	25
13	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (3)	CH_3CN	DABCO	67
14	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (3)	EtOH	DABCO	trace[d]
15	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (3)	DMF	DABCO	37
16	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (3)	DCM	DABCO	45
17	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (2)	CH_3CN	DABCO	43
18	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (4)	CH_3CN	DABCO	54
19	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (3)	CH_3CN	DABCO	trace[e]
20	$Ru(bpy)_3Cl_2·6H_2O$	TBHP (3)	CH_3CN	DABCO	0[f]
21[g]		TBHP (3)	CH_3CN	DABCO	0

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (1.0 mL), photocatalyst (5.0 mol %), oxidant (3.0 equiv), base (2.0 equiv), CH_3CN (0.6 mL), ambient temperature, Ar, 10 W LED (450−455 nm), 20 h. [b]Isolated yield. [c]70% TBHP in water. [d]Coumarin (**4a**) was isolated. [e]Air atmosphere. [f]Without visible light. [g]In the absence of a photocatalyst.

https://doi.org/10.1021/acs.joc.1c00848
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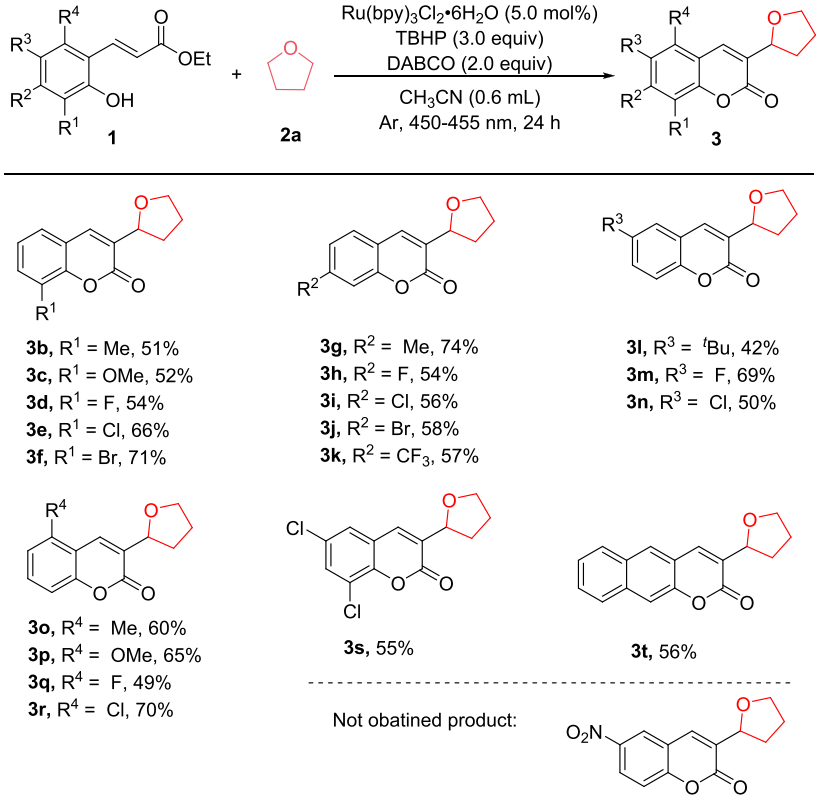
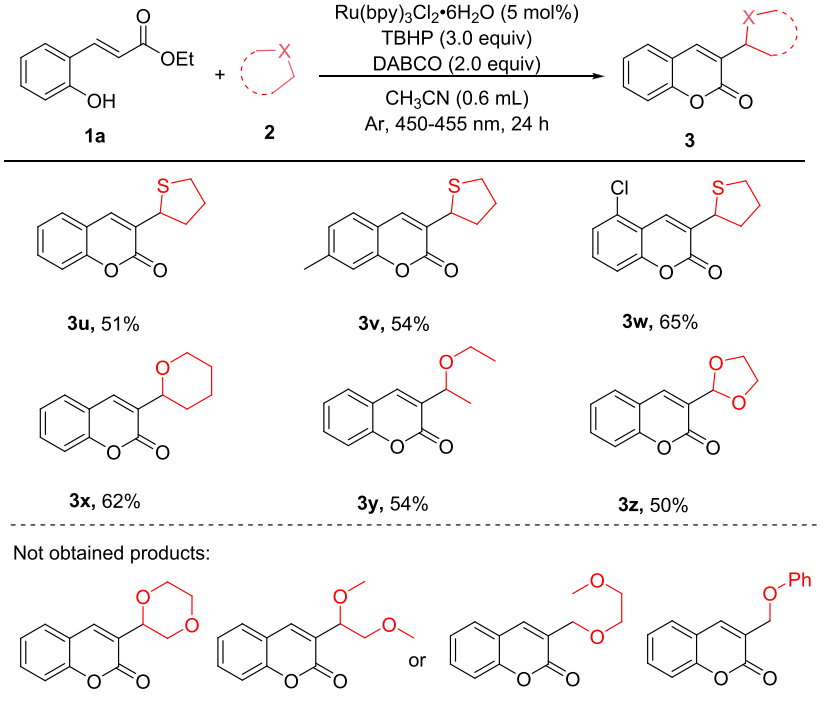
Scheme 2. Substrate Scope and Limitation of *O*-Hydroxycinnamates 1



Scheme 3. Scope and Limitation of Substrates 2



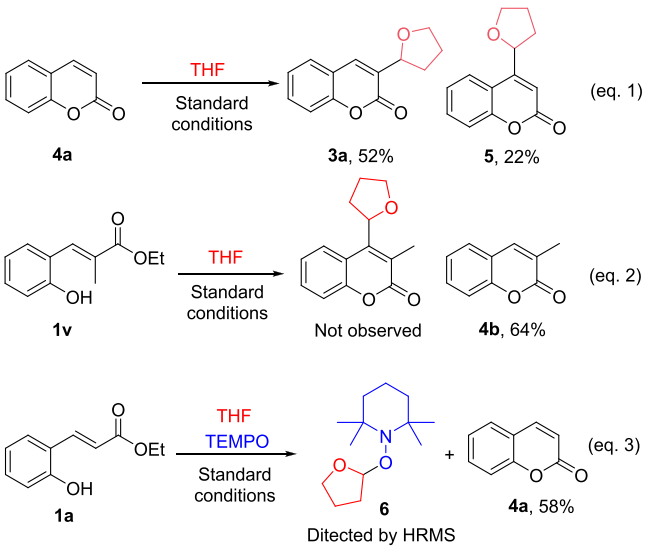
group (F, Cl, Br, CF_3) substituted substrates (products **3h**–**k**, 54–58% yields). The substituent R^3 of the phenol moiety could be electron-donating *t*-Bu (**3l**, 42% yield) or electron-withdrawing F (**3m**, 69% yield) or Cl (**3n**, 50% yield). The influence of substituent R^4 of the phenol moiety on the reaction was also examined. Thus, methyl- (**3o**), methoxy- (**3p**), and chloro- (**3r**) substituted substrates gave the corresponding products in higher yields (60–70%) compared with the fluoro-substituted substrate (**3q**, 49% yield). Ethyl 3-(3,5-dichloro-2-hydroxyphenyl)acrylate (**3s**) and ethyl 3-(3-hydroxyanthracen-2-yl)acrylate (**3t**) provided good yields (55% and 56%, respectively). When ethyl (*E*)-3-(2-hydroxy-5-nitrophenyl)acrylate (**1u**) was used as the substrate, however, we did not obtain any isolable products (Scheme 3).

https://doi.org/10.1021/acs.joc.1c00848
J. Org. Chem. 2021, 86, 9552–9562

Encouraged by these results, we extended our strategy to install 3-functionalized coumarins by simply replacing THF with tetrahydrothiophene or various commercially available ethers as alkyl radical sources. As shown in Scheme 3, tetrahydrothiophene could work to give the desired products **3u**−**3w** in satisfactory yields (51−65%). In the cases where tetrahydro-2*H*-pyran, ethyl ether, or 1,3-dioxolane was used, the reaction also proceeded smoothly to provide the corresponding products **3x**−**3z** in 50−62% yields with excellent site selectivity. However, 1,4-dioxane, 1,2-dimethoxyethane, and anisole only rendered a fairly complex reaction, and the desired products were undetected.

To gain mechanistic insights into this transformation, several control experiments were subsequently conducted (Scheme 4).

Scheme 4. Control Experiments

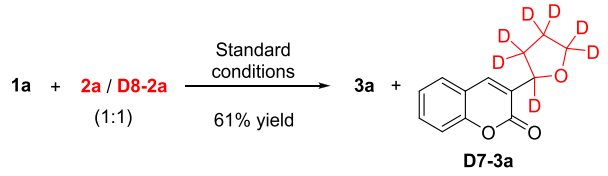


First, coumarin (**4a**) was submitted to the standard reaction conditions. The desired 3-alkylated coumarin **3a** and its 4-alkylated isomer **5** were isolated in 52% and 22% yields, respectively (Scheme 4, eq 1). When the 2-position of acrylate substrate was blocked by a group, e.g., ethyl (*E*)-3-(2-hydroxyphenyl)-2-methylacrylate (**1v**) was used as the substrate, we just isolated coumarin **4b** but did not obtain any cross-coupling products (Scheme 4, eq 2). When 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO, 2 equiv) was used as a radical trapping reagent into the model reaction system, the transformation was totally suppressed and no C-3 alkylated product **3a** was obtained. However, coumarin was isolated in 58% yield, while TEMPO-tetrahydrofuran-2-yl adduct **6** was detected by HRMS analysis of the reaction mixture (Scheme 4, eq 3). These results indicated that this reaction proceeded via a free radical pathway, and tetrahydrofuran-2-yl radical was a key intermediate.

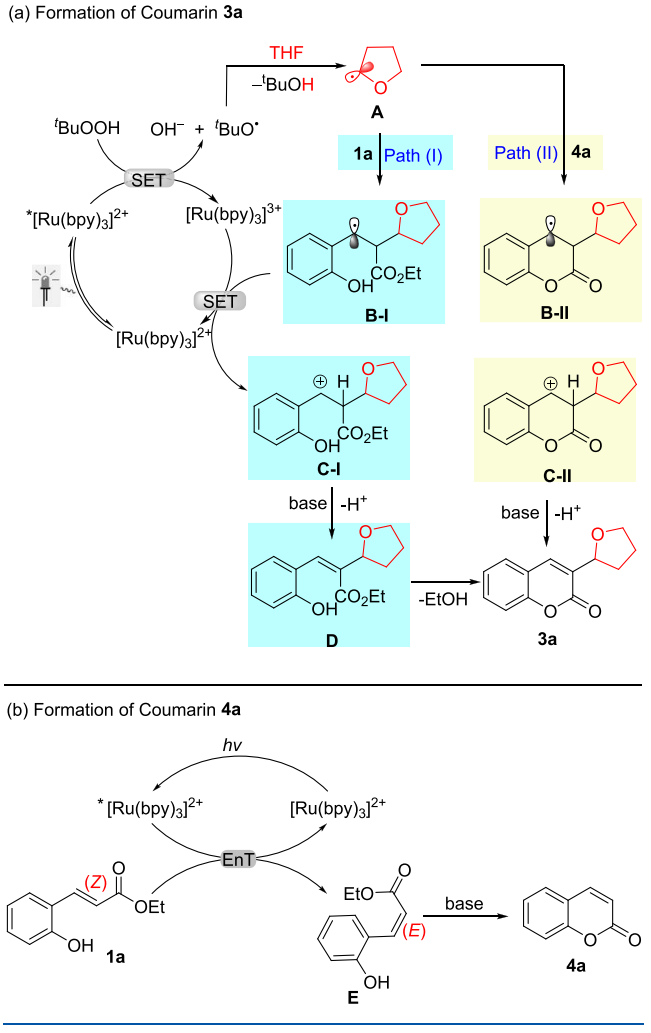
Subsequently, a kinetic isotope effect (KIE) experiment was conducted (Scheme 5). A kinetic isotope effect (k_H/k_D = 3.2) was observed when **1a** was treated with an equal mixture (1:1) of THF (**2a**) and THF-d_8 (**D8**−**2a**) under identical conditions. Thus, the C(sp^3)−H cleavage of THF is the rate-determining step in this process (see Supporting Information).

Based on our observations and previous literature reports,[10] a plausible mechanism for the formation of **3** is proposed in Scheme 6. Initially, photocatalyst $[Ru(ppy)_3]^{2+}$ generates the highly reducing excited $^*[Ru(ppy)_3]^{2+}$ ($E_{1/2[^*Ru(II)/Ru(III)]}$ = −0.81 V vs SCE) under the irradiation of blue light. Then, the single electron transfer (SET) from $^*[Ru(ppy)_3]^{2+}$ to oxidant *t*-BuOOH forms radical *t*-BuO•, accompanied by the oxidation of $^*[Ru(ppy)_3]^{2+}$ to $[Ru(ppy)_3]^{3+}$. The radical *t*-BuO• abstracts a hydrogen from THF to form a carbon radical **A**. Subsequently, the radical **A** regioselectively attacks the most electron-rich position of the double bond in cinnamate **1a** to form carbon radical **B**−**I** (Path I), which is further oxidized to carbocation **C**−**I** by $[Ru(ppy)_3]^{3+}$ ($E_{1/2[Ru(III)/Ru(II)]}$ = +1.29 V vs SCE) via SET process, completing the photocatalytic cycle and regenerating the ground state $[Ru(ppy)_3]^{2+}$. In the presence of a base, the carbocation **C**−**I** undergoes deprotonation to form intermediate **D**, which provides the final product **3a** through lactonization. Alternatively, an isomerization/cyclization/alkylation sequence may take place. Thus, the energy transfer (EnT) from $^*[Ru(ppy)_3]^{2+}$ to **1a** leads to the formation of coumarin **4a** as shown in Scheme 6b.

Scheme 5. Kinetic Isotope Effect Experiment



Scheme 6. Plausible Mechanism for the Formation of 3a and 4a



https://doi.org/10.1021/acs.joc.1c00848
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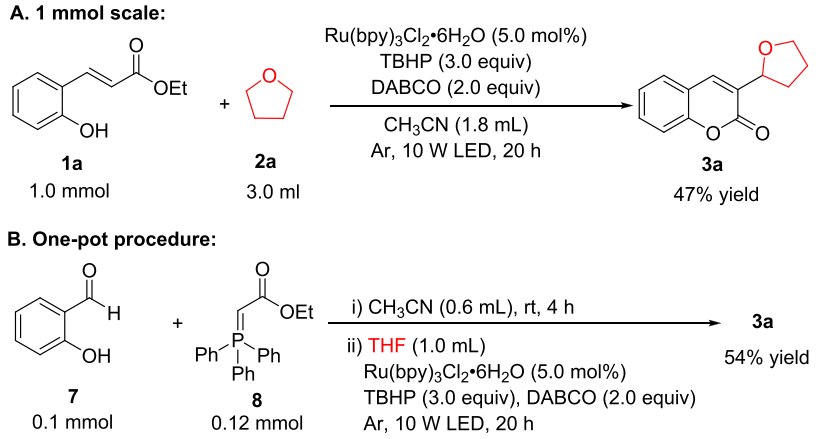
Scheme 7. Experiment in a mmol Scale and One-Pot Synthesis



The process might include an isomerization of (*E*)-cinnamate **1a** to its (*Z*)-isomer **E** and base-promoted lactonization.[4c,11] The Stern−Volmer experiment exhibited that the excited photocatalyst $^*[Ru(ppy)_3]^{2+}$ could be oxidatively quenched by cinnamate **1a** (see Figure S2), supporting the EnT mechanism. The addition of carbon radical **A** to **4a** generates carbon radical **B−II** (path II). The subsequent SET oxidation results in the carbocation intermediate **C−II**, which undergoes elimination to provide **3a**.

To demonstrate the practicality and scalability of this protocol, we performed the reaction of **1a** with THF on a 1 mmol scale under standard reaction conditions and obtained a 47% yield of **3a** (Scheme 7A). Furthermore, a one-pot synthesis of the desired product **3a** by starting from salicylaldehyde (**7**) and ethyl 2-(triphenylphosphoranylidene)-acetate (**8**) was developed, and 54% yield was obtained (Scheme 7B), indicating that the synthetic operation could be simplified.

CONCLUSION

In summary, we have demonstrated a regioselective synthesis of 3-functionalized coumarins by photocatalysis strategy using $Ru(bpy)_3Cl_2{\cdot}6H_2O$ as photocatalyst and TBHP as oxidant. With visible light irradiation, direct and regioselective C(sp^2)-C(sp^3) coupling reaction of 3-(2-hydroxyphenyl)acrylates with ethers or thioethers furnished 3-alkylated coumarins. The cascade process involves alkenylation of α-C(sp^3)-H bond of ethers/thioethers and lactonization. The features of this method include broad substrate scope, mild reaction conditions, and simplified operation. Additionally, the synthesis of 3-alkylated coumarins could be realized by a one-pot procedure starting from commercially available salicylaldehyde.

EXPERIMENTAL SECTION

General Information. Unless otherwise mentioned, solvents, compounds **2**, and reagents were purchased from commercial sources and used as received. The photochemical reactions were irradiated at room temperature using a 10 W blue LED lamp (450−455 nm) equipped with ten 20 mL quartz tubes (Figure S1). The distance from the light source to the irradiation container was about 2 cm. Flash column chromatography was performed using 300−400 mesh silica gel. Melting points were recorded on a SGW X-4. NMR spectra were obtained at 400 or 600 MHz for ^{1}H NMR, 100 or 150 MHz for $^{13}C\{^1H\}$ NMR, and 376 or 564 MHz for $^{19}F\{^1H\}$ NMR. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, m = multiplet. *J* values were reported in hertz (Hz). Chemical shifts (in ppm) were referenced to TMS (δ = 0 ppm) in $CDCl_3$ or the center line of a quintet at 3.30 ppm of MeOH-d_4 as an internal standard. $^{13}C\{^1H\}$ NMR spectra were obtained by using the same NMR spectrometers and chemical shifts were referenced to the center line of a triplet at 77.00 ppm of $CDCl_3$ or the center line of a heptet at 48.80 ppm of MeOH-d_4. High-resolution mass spectra (HRMS) were recorded on a Q-TOF-MS instrument (ESI). The fluorescence spectra were recorded on a fluorescence spectrophotometer with a xenon lamp excitation source.

General Procedures for the Synthesis of Compounds 1.[11] To an oven-dried 100 mL sealing tube equipped with a magnetic stirring bar were added sequentially salicylaldehyde (10.0 mmol), ethyl 2-(triphenylphosphoranylidene) acetate (12.0 mmol), and dry CH_2Cl_2 (40 mL). The reaction mixture was stirred at room temperature for 2−8 h. The conversion of the starting materials was monitored by TLC. Then, the reaction solution was concentrated in vacuo to remove the solvent. The crude product was purified by silica gel column chromatography [petroleum ether (PE)/ethyl acetate (EA) = 30:1−8:1, v/v].

*((E)-Ethyl 3-(2-Hydroxyphenyl)acrylate (**1a**).* Known compound.[12a] White solid; column chromatography (PE/EA = 5:1). Yield: 1.23 g, 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11−8.06 (m, 1H), 7.47−7.45 (m, 2H), 7.25−7.20 (m, 1H), 6.91−6.88 (m, 2H), 6.68 (d, *J* = 16.2 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.0 155.8, 141.1, 131.5, 129.2, 121.6, 120.5, 118.0, 116.4, 60.8, 14.3. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{11}H_{12}O_3H^+$ 193.0859, found: 193.0860.

*(E)-Ethyl 3-(2-Hydroxy-3-methylphenyl)acrylate (**1b**).* Known compound.[12b] White solid; column chromatography (PE/EA = 5:1). Yield: 1.45 g, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26−8.20 (m, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.3, 153.70, 140.8, 132.8, 126.1, 124.1, 121.6, 120.3, 117.8, 60.6, 16.0, 14.3. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{12}H_{14}O_3H^+$ 207.1016, found: 207.1016.

*((E)-Ethyl 3-(2-Hydroxy-3-methoxyphenyl)acrylate (**1c**).* Known compound.[12a] White solid; column chromatography (PE/EA = 5:1). Yield: 1.74 g, 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 16.2 Hz, 1H), 7.09−7.07(m, 1H), 6.87−6.81 (m, 2H), 6.60 (d, *J* = 16.2 Hz, 1H), 6.22 (s, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 167.55, 146.81, 145.3, 139.5, 120.9, 120.8, 119.6, 119.3, 111.7, 60.4, 56.2, 14.4. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{12}H_{14}O_4H^+$ 223.0965, found: 223.0966.

*((E)-Ethyl 3-(3-Fluoro-2-hydroxyphenyl)acrylate (**1d**).* Known compound.[12b] White solid; column chromatography (PE/EA = 5:1). Yield: 1.46 g, 69%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03−7.98 (m, 1H), 7.27−7.23 (m, 1H), 7.15−7.05 (m, 1H), 6.86−6.81

https://doi.org/10.1021/acs.joc.1c00848
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(m, 1H), 6.79−6.58 (m, 2H), 4.30 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 167.8, 151.4 (d, J = 235.0 Hz), 143.5 (d, J = 13.0 Hz), 139.1, 124.2 (d, J = 3.0 Hz), 123.67, 119.9 (d, J = 7.0 Hz), 119.8, 116.6 (d, J = 18.0 Hz), 60.7, 14.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}FO_3H^+$ 211.0765, found: 211.0765.

*((E)-Ethyl 3-(3-Chloro-2-hydroxyphenyl)acrylate (**1e**).* Known compound.[12b] White solid; column chromatography (PE/EA = 5:1). Yield: 1.45 g, 64%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 16.2 Hz, 1H), 7.41−7.41 (m, 1H), 7.39−7.39 (m, 1H), 6.91−6.87 (m, 1H), 6.60 (d, J = 16.2 Hz, 1H), 6.15 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 167.2, 150.4, 139.0, 130.2, 127.8, 122.9, 121.0, 120.9, 120.3, 60.6, 14.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}ClO_3H^+$ 227.0468, found: 227.0469.

*((E)-Ethyl 3-(3-Bromo-2-hydroxyphenyl)acrylate (**1f**).* Known compound.[12b] White solid; column chromatography (PE/EA = 5:1). Yield: 1.68 g, 62%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 16.2 Hz, 1H), 7.49−7.47 (m, 1H), 7.46−7.41 (m, 1H), 6.85−6.81 (m, 1H), 6.58 (d, J = 16.2 Hz, 1H), 6.03 (s, 1H), 4.27 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 167.2, 150.4, 139.0, 130.2, 127.8, 122.9, 121.0, 120.9, 120.3, 60.6, 14.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}ClO_3H^+$ 270.9964, found: 270.9964.

*((E)-Ethyl 3-(2-Hydroxy-4-methylphenyl)acrylate (**1g**).* Known compound.[12b] White solid; column chromatography (PE/EA = 5:1). Yield: 1.45 g, 70%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.02−7.98 (m, 1H), 7.35 (d, J = 7.9 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.67 (s, 1H), 6.63−6.58 (m, 1H), 4.29 (q, J = 7.2 Hz, 2H), 2.30 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.7, 155.3, 142.3, 140.5, 129.1, 121.8, 119.0, 117.4, 117.0, 60.6, 21.4, 14.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}O_3H^+$ 207.1016, found: 207.1015.

*((E)-Ethyl 3-(4-Fluoro-2-hydroxyphenyl)acrylate (**1h**).* Known compound.[12b] White solid; column chromatography (PE/EA = 5:1). Yield: 1.58 g, 75%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 16.2 Hz, 1H), 7.84 (s, 1H), 7.46−7.42 (m, 1H), 6.66−6.06 (m, 3H), 4.31 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.1, 164.5 (d, J = 250.0 Hz), 157.2 (d, J = 11.0 Hz), 140.2, 130.6 (d, J = 10.0 Hz), 118.2 (d, J = 3.0 Hz), 117.4 (d, J = 2.0 Hz), 107.9 (d, J = 22.0 Hz), 103.9 (d, J = 24.0 Hz), 60.9, 14.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}FO_3H^+$ 211.0765, found: 211.0764.

*((E)-Ethyl 3-(4-Chloro-2-hydroxyphenyl)acrylate (**1i**).* Known compound.[12b] White solid; column chromatography (PE/EA = 5:1). Yield: 1.66 g, 73%. ^1H NMR (400 MHz, $CDCl_3$) 8.01 (d, J = 16.2 Hz, 2H), 7.38 (d, J = 8.4 Hz, 1H), 6.93 (d, J = 2.0 Hz, 1H), 6.90−6.87 (m, 1H), 6.67 (d, J = 16.2 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.1, 156.4, 140.2, 136.7, 130.0, 120.9, 120.4, 118.2, 116.7, 61.1, 14.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}ClO_3H^+$ 227.0469, found: 227.0470.

*((E)-Ethyl 3-(4-Bromo-2-hydroxyphenyl)acrylate (**1j**).* Known compound.[12c] White solid; column chromatography (PE/EA = 5:1). Yield: 3.0 g, 74%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 16.2 Hz, 1H), 7.76 (s, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.08 (d, J = 1.8 Hz, 1H), 7.06−7.03 (m, 1H), 6.67 (d, J = 16.2 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.1, 156.4, 140.2, 136.7, 130.0, 120.9, 120.4, 118.2, 116.7, 61.1, 14.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}BrO_3H^+$ 270.9964, found: 270.9966.

*((E)-Ethyl 3-(2-Hydroxy-4-(trifluoromethyl)phenyl)acrylate (**1k**).* Known compound.[12b] White solid; column chromatography (PE/EA = 5:1). Yield: 1.65 g, 63%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 16.2 Hz, 1H), 7.67 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 7.13 (s, 1H), 6.75 (d, J = 16.2 Hz, 1H), 4.34 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.5, 155.4, 139.4, 132.8 (q, J = 33.0 Hz), 129.6, 125.0, 123.6 (q, J = 270.0 Hz), 120.45, 117.2 (q, J = 4.0 Hz), 113.4 (q, J = 4.0 Hz), 61.23, 14.23. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{11}F_3O_3H^+$ 261.0733, found: 261.0735.

*((E)-Ethyl 3-(5-(tert-Butyl)-2-hydroxyphenyl)acrylate (**1l**).* Known compound.[12d] White solid; column chromatography (PE/EA = 5:1). Yield: 1.50 g, 60%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.05−8.00 (m, 1H), 7.46 (d, J = 2.4 Hz, 1H), 7.28−7.25 (m, 1H), 6.81−6.78 (m, 1H), 6.69−6.64 (m, 1H), 6.55 (s, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H), 1.29 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.6, 153.2, 143.4, 141.3, 128.7, 126.0, 120.9, 118.1, 116.1, 60.7, 34.1, 31.4, 14.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{20}O_3H^+$ 249.1485, found: 249.1487.

*((E)-Ethyl 3-(5-Fluoro-2-hydroxyphenyl)acrylate (**1m**).* Known compound.[11] White solid; column chromatography (PE/EA = 5:1). Yield: 1.39 g, 66%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 16.2 Hz, 1H), 7.17−7.14 (m, 1H), 6.96−6.91 (m, 1H), 6.86−6.82 (m, 1H), 6.59 (d, J = 16.2 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.6, 156.7 (d, J = 237 Hz), 155.50, 151.9 (d, J = 2.0 Hz, 1H), 139.9 (d, J = 2.0 Hz), 122.5 (d, J = 8.0 Hz), 118.86 (d, J = 23.0 Hz), 117.4 (d, J = 8.0 Hz), 114.27 (d, J = 23.0 Hz), 61.04, 14.28. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}FO_3H^+$ 211.0765, found: 211.0766.

*((E)-Ethyl 3-(5-Chloro-2-hydroxyphenyl)acrylate (**1n**).* Known compound.[11] White solid; column chromatography (PE/EA = 5:1). Yield: 1.66 g, 73%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 16.2 Hz, 1H), 7.59 (s, 1H), 7.43 (d, J = 2.5 Hz, 1H), 7.19−7.17 (m, 1H), 6.83 (d, J = 8.6 Hz, 1H), 6.65 (d, J = 16.2 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.7, 154.2, 139.7, 131.0, 128.3, 125.4, 123.0, 119.1, 117.7, 61.1, 14.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}ClO_3H^+$ 227.0469, found: 227.0471.

*((E)-Ethyl 3-(2-Hydroxy-6-methylphenyl)acrylate (**1o**).* Known compound.[12e] White solid; column chromatography (PE/EA = 5:1). Yield: 1.47 g, 71%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 16.4 Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.76−6.69 (m, 2H), 5.98 (s, 1H), 4.29 (q, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.1, 155.2, 139.7, 139.1, 130.1, 122.9, 122.4, 120.6, 114.0, 60.6, 20.7, 14.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}O_3H^+$ 207.1016, found: 207.1016.

*((E)-Ethyl 3-(2-Hydroxy-6-methoxyphenyl)acrylate (**1p**).* Known compound.[12e] White solid; column chromatography (PE/EA = 5:1). Yield: 1.45 g, 65%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 16.4 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 7.05 (s, 1H), 6.98 (d, J = 16.4 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.5, 160.1, 157.0, 136.4, 131.2, 120.2, 111.1, 108.8, 102. 8, 60.5, 55.7, 14.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}O_4H^+$ 223.0965, found: 223.0963.

*((E)-Ethyl 3-(2-Fluoro-6-hydroxyphenyl)acrylate (**1q**).* Known compound.[10] White solid; column chromatography (PE/EA = 5:1). Yield: 1.39 g, 66%. ^1H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, J = 16.4 Hz, 1H), 7.87 (s, 1H), 7.16 (q, J = 8.0 Hz, 1H), 6.98 (d, J = 16.4 Hz, 1H), 6.69 (d, J = 8.2 Hz, 1H), 6.67−6.63 (m, 1H), 4.32 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 169.4, 162.7 (d, J = 252.0 Hz), 157.2 (d, J = 6.0 Hz), 134.3, 131.2 (d, J = 12.0 Hz), 121.6 (d, J = 9.0 Hz), 111.9 (d, J = 3.0 Hz), 111.0 (d, J = 13.5 Hz), 107.4 (d, J = 22.5 Hz), 63.63, 16.93. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}FO_3H^+$ 211.0765, found: 211.0765.

*((E)-Ethyl 3-(2-Chloro-6-hydroxyphenyl)acrylate (**1r**).* Known compound.[10] White solid; column chromatography (PE/EA = 5:1). Yield: 1.45 g, 64%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 16.0 Hz, 1H), 7.29 (s, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.07−6.98 (m, 2H), 6.82 (d, J = 8.2 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.4, 156.8, 137.9, 136.2, 130.6, 123.4, 122.0, 119.9, 115.0, 61.0, 14.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}ClO_3H^+$ 227.0469, found: 227.0470.

*((E)-Ethyl 3-(3,5-Dichloro-2-hydroxyphenyl)acrylate (**1s**).* Known compound.[10] White solid; column chromatography (PE/EA = 5:1). Yield: 1.25 g, 48%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 16.2

https://doi.org/10.1021/acs.joc.1c00848
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Hz, 1H), 7.39 (d, J = 2.4 Hz, 1H), 7.35 (d, J = 2.4 Hz, 1H), 6.57 (d, J = 16.2 Hz, 1H), 6.08 (s, 1H), 4.28 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.8, 149.0, 137.6, 129.5, 127.3, 125.6, 123.9, 121.5, 121.4, 60.7, 14.3. HRMS (ESI) m/z: $[M-H]^-$ calcd for $C_{11}H_9Cl_2O_3^-$ 258.9934, found: 258.9934.

*((E)-Ethyl 3-(3-Hydroxynaphthalen-2-yl)acrylate (**1t**).* Known compound.[12f] Yellow solid; column chromatography (PE/EA = 5:1). Yield: 1.46 g, 60%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 16.0 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.78−7.74 (m, 2H), 7.54−7.50 (m, 1H), 7.40−7.35 (m, 1H), 7.17 (d, J = 9.2 Hz, 1H), 6.84 (d, J = 16.4 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.1, 153.3, 138.5, 132.8, 131.6, 128.9, 128.7, 127.4, 123.8, 123.2, 123.0, 118.1, 113.8, 60.9, 14.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{14}O_3H^+$ 243.1016, found: 243.1017.

*((E)-Ethyl 3-(2-Hydroxy-5-nitrophenyl)acrylate (**1u**).* Known compound.[11] Yellow solid; column chromatography (PE/EA = 5:1). Yield: 1.02 g, 90%. ^1H NMR (400 MHz, CD_3OD): δ 7.96 (d, J = 16.2 Hz, 1H), 7.78−7.72 (m, 2H), 7.71 (d, J = 1.2 Hz, 1H), 6.77 (d, J = 16.2 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD): δ 168.3, 158.3, 150.4, 139.2, 130.6, 128.8, 122.5, 115.1, 111.2, 61.6, 14.4. HRMS (ESI) m/z: $[M-H]^-$ calcd for $C_{11}H_{10}NO_5^-$ 236.0564, found: 236.0566.

*((E)-ethyl 3-(2-Hydroxyphenyl)-2-methylacrylate (**1v**).* Known compound.[12g] White solid; column chromatography (PE/EA = 5:1). Yield: 1.43 g, 69%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.26−7.19 (m, 2H), 6.95−6.91 (m, 2H), 6.25 (s, 1H), 4.28 (q, J = 7.2 Hz, 2H), 2.03 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.1, 154.0, 134.4, 130.0, 130.0, 122.8, 120.3, 120.2, 115.8, 61.2, 14.3, 14.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}O_3H^+$ 207.1018, found: 207.1016.

General Procedure for the Preparation of Compounds 3. To an oven-dried test tube equipped with a magnetic stirring bar was added sequentially *ortho*-hydroxycinnamates **1** (0.10 mmol), DABCO (0.20 mmol, 2.0 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (5.0 mol %), TBHP (5.5 M in decane, 55 μL, 3.0 equiv), ether (**2**, 1.0 mL) and MeCN (0.6 mL). The reaction mixture was irradiated with 10 W LED (450−455 nm) under argon atmosphere at 25 °C for 20 h. The resulting mixture was evaporated under reduced pressure, the residue was purified by flash column chromatography on silica gel (PE/EA = 30:1−20:1, v/v) to give pure product **3**.

Preparation of 3a in a 1 mmol Scale. To an oven-dried 100 mL round-bottom flask equipped with a magnetic stirring bar were added sequentially **1a** (1.0 mmol), DABCO (2.0 mmol, 2.0 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (5.0 mol %), TBHP (5.5 M in decane, 550 μL, 3.0 equiv), THF (3.0 mL) and MeCN (1.8 mL). The reaction mixture was irradiated with 10 W LED (450−455 nm) under argon atmosphere at 25 °C for 20−24 h. The conversion of the starting materials was followed by TLC. Then, the reaction concentrated in vacuo to remove solvent. The crude product was purified by column chromatography on silica gel (PE/EA = 30:1- 20:1, v/v) to give 102 mg of pure **3a** (47% yield).

Preparation of 3a in One-Pot. To an oven-dried test tube equipped with a magnetic stirring bar was added sequentially salicylaldehyde (0.1 mmol, 1.0 equiv), (carbethoxymethylene)-triphenyl phosphorane (0.12 mmol, 1.2 equiv), dry CH_3CN (0.6 mL). The mixture was stirred at 25 °C for 4 h. Then, DABCO (0.20 mmol, 2.0 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (5.0 mol %), TBHP (5.5 M in decane, 55 μL, 3.0 equiv), THF (1.0 mL) and CH_3CN (0.6 mL) were add. The reaction mixture was irradiated with 10 W LED (450−455 nm) under argon atmosphere at 25 °C for 20 h. The conversion of the starting materials was followed by TLC. After removal of solvent in vacuo, the crude product was purified by column chromatography on silica gel (PE/EA = 30:1−20:1, v/v) to give 11.7 mg of pure **3a** (54% yield).

*3-(Tetrahydrofuran-2-yl)-2H-chromen-2-one (**3a**).* Colorless oil; column chromatography (PE/EA = 40:1−30:1). Yield: 14.5 mg, 67%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.50−4.7 (m, 2H), 7.33 (d, J = 5.6 Hz, 1H), 7.29−7.26 (m, 1H), 4.96 (t, J = 4.8 Hz, 1H), 4.13−4.10 (m, 1H), 3.98−3.94 (m, 1H), 2.55−2.50 (m, 1H), 2.04−2.00 (m, 1H), 1.97−1.92 (m, 1H), 1.79−1.75 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.5, 153.1, 136.4, 131.1, 130.9, 127.8, 124.4, 119.3, 116.4, 75.9, 68.9, 32.2, 25.7. IR (film): 3097, 2951, 2925, 2877, 1716, 1634, 1608, 1489, 1457, 1399, 1284, 1170, 1045 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{12}O_3Na^+$, 239.0679; found, 239.0680.

*8-Methyl-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3b**).* White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 11.7 mg, 51%. Mp: 71−72 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 1.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.19−7.15 (m, 1H), 4.98 (t, J = 6.8 Hz, 1H), 4.14−4.09 (m, 1H), 3.99−3.93 (m, 1H), 2.58−2.49 (m, 1H), 2.46 (s, 3H), 2.07−1.99 (m, 1H), 1.97−1.89 (m, 1H), 1.81−1.72 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.7, 151.5, 136.8, 132.3, 130.6, 125.9, 125.5, 124.0, 119.0, 75.9, 68.9, 32.3, 25.6, 15.5. IR (film): 3041, 2963, 2923, 2847, 1737, 1598, 1557, 1444, 1399, 1257, 1235, 1222, 1171, 1111, 1070, 952, 917, 832, 742, 649 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{14}O_3Na^+$, 253.0835; found, 253.0836.

*8-Methoxy-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3c**).* Known compound.[7] Colorless crystal; column chromatography (PE/EA = 40:1−30:1). Yield: 12.8 mg, 52%. Mp: 112−113 °C (lit. 109−111 °C).[7] ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 1.6 Hz, 1H), 7.22−7.19 (m, 1H), 7.09−7.04 (m, 2H), 5.00−4.96 (m, 1H), 4.14−4.09 (m, 1H), 3.98−3.93 (m, 1H), 3.97 (s, 3H), 2.56−2.51 (m, 1H), 2.03−1.98 (m, 1H), 1.96−1.91 (m, 1H), 1.79−1.75 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.9, 147.0, 142.8, 136.5, 131.3, 124.2, 119.9, 119.3, 112.8, 75.9, 68.9, 56.2, 32.2, 25.6. IR (film): 3085, 2955, 2924, 2851, 1722, 1621, 1568, 1461, 1378, 1276, 1181, 1144, 1089, 1051, 1025 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{14}O_4Na^+$, 269.0784; found, 269.0785.

*8-Fluoro-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3d**).* Colorless crystal; column chromatography (PE/EA = 40:1−30:1). Yield: 12.7 mg, 54%. Mp: 115−116 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 1.6 Hz, 1H), 7.35−7.29 (m, 1H), 7.25−7.19 (m, 2H), 4.96 (t, J = 7.0 Hz, 1H), 4.14−4.09 (m, 1H), 3.96 (q, J = 7.4 Hz, 1H), 2.57−2.50 (m, 1H), 2.05−2.00 (m, 1H), 1.98−1.91 (m, 1H), 1.81−1.74 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.1, 149.3 (d, J = 250.0 Hz), 142.9, 141.2(d, J = 12.0 Hz), 135.9 (d, J = 3.0 Hz), 132.1, 124.2 (d, J = 7.0 Hz), 122.9 (d, J = 4.0 Hz), 117.3 (d, J = 17.0 Hz), 75.8, 68.9, 32.2, 25.6. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −119.3 (s, 1F). IR (film): 3097, 2955, 2916, 2856, 1730, 1646, 1485, 1403, 1268, 1182, 1139, 1081, 1021 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{12}FO_3^+$, 235.0765; found, 235.0765.

*8-Chloro-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3e**).* Yellow solid; column chromatography (PE/EA = 40:1−30:1). Yield: 16.5 mg, 66%. Mp: 97−98 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.24−7.20 (m, 1H), 4.97 (t, J = 7.0 Hz, 1H), 4.14−4.09 (m, 1H), 3.96 (q, J = 7.4 Hz, 1H), 2.60−2.51 (m, 1H), 2.08−2.00 (m, 1H), 1.99−1.89 (m, 1H), 1.80−1.72 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.4, 148.8, 136.0, 132.0, 131.3, 126.2, 124.6, 121.3, 120.5, 75.8, 68.9, 32.2, 25.6. IR (film): 3054, 2925, 2954, 2865, 1722, 1606, 1466, 1384, 1270, 1177, 1160, 1089, 1077, 1057, 1019 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{11}ClO_3Na^+$, 273.0289; found, 273.0291.

*8-Bromo-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3f**).* White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 20.9 mg, 71%. Mp: 114−115 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 1.6 Hz, 1H), 7.73−7.70 (m, 1H), 7.46−7.44 (m, 1H), 7.18−7.14 (m, 1H), 4.97 (t, J = 7.0 Hz, 1H), 4.14−4.09 (m, 1H), 4.00−3.94 (m, 1H), 2.59−2.50 (m, 1H), 2.08−1.99 (m, 1H), 1.98−1.89 (m, 1H), 1.80−1.72 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.4, 149.8, 136.0, 134.4, 131.9, 127.0, 125.1, 120.5, 109.9, 75.8, 68.9, 32.2, 25.6. IR (film): 3092, 2967, 2925, 2873, 1725, 1637, 1597, 1447, 1384, 1266, 1168, 1066, 1044, 1021, 928 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{11}BrO_3Na^+$, 316.9784; found, 316.9786.

*7-Methyl-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3g**).* Known compound.[13] White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 17.0 mg, 74%. Mp: 61−62 °C (lit. 61.6−62.2

https://doi.org/10.1021/acs.joc.1c00848
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°C).[13] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.14 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 4.97−4.93 (m, 1H), 4.14−4.08 (m, 1H), 3.98−3.92 (m, 1H), 2.55−2.47 (m, 1H), 2.45 (s, 3H), 2.07−1.99 (m, 1H), 1.97−1.89 (m, 1H), 1.81−1.72 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.7, 153.2, 142.0, 136.4, 129.7, 127.4, 125.6, 116.8, 116.6, 75.9, 68.8, 32.2, 25.6, 21.7. IR (film): 3051, 2925, 2872, 1721, 1621, 1569, 1455, 1384, 1328, 1281, 1181, 1144, 1100, 1051, 1026 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{14}H_{14}O_3Na^+$, 253.0835; found, 253.0835.

7-Fluoro-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3h**). White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 12.7 mg, 54%. Mp: 73−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 1.2 Hz, 1H), 7.50−7.46 (m, 1H), 7.07−6.99 (m, 2H), 4.94 (t, *J* = 6.8 Hz, 1H), 4.13−4.08 (m, 1H), 3.98−3.93 (m, 1H), 2.56−2.48 (m, 1H), 2.08−1.99 (m, 1H), 1.97−1.89 (m, 1H), 1.80−1.72 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.9 (d, *J* = 251.0 Hz), 160.1, 154.1 (d, *J* = 13.0 Hz), 135.9, 129.8(d, *J* = 3.0 Hz), 129.2 (d, *J* = 10.0 Hz), 115.9, 112.5 (d, *J* = 23.0 Hz), 104.1 (d, *J* = 25.0 Hz), 75.8, 68.9, 32.2, 25.7. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −106.4 (s, 1F). IR (film): 3082, 2955, 2925, 2865, 1729, 1619, 1586, 1505, 1431, 1385, 1273, 1251, 1180, 1141, 1110, 1045, 1021 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{13}H_{11}FO_3Na^+$, 257.0584; found, 257.0585.

7-Chloro-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3i**). Yellow solid; column chromatography (PE/EA = 40:1−30:1). Yield: 14.0 mg, 56%. Mp: 65−67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 1.6 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.27−7.24 (m, 1H), 4.95−4.91 (m, 1H), 4.13−4.08 (m, 1H), 3.98−3.93 (m, 1H), 2.57−2.48 (m, 1H), 2.08−1.99 (m, 1H), 1.94−1.89 (m, 1H), 1.80−1.71 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.8, 153.3, 136.7, 135.6, 131.1, 128.5, 125.0, 117.8, 116.7, 75.8, 68.9, 32.2, 25.6. IR (film): 3085, 2925, 1724, 1633, 1062, 1567, 1488, 1461, 1411, 1180, 1076, 1047, 1021, 952 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{13}H_{11}ClO_3Na^+$, 273.0289; found, 273.0289.

7-Bromo-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3j**). White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 17.0 mg, 58%. Mp: 103−104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.42−7.39 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 4.94−4.90 (m, 1H), 4.13−4.08 (m, 1H), 3.98−3.93 (m, 1H), 2.55−2.50 (m, 1H), 2.05−1.99 (m, 1H), 1.97−1.94 (m, 1H), 1.78−1.75 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.7, 153.3, 135.8, 131.4, 128.7, 127.9, 124.7, 119.7, 118.2, 75.9, 68.9, 32.2, 25.6. IR (film): 3095, 2968, 2926, 2856, 1721, 1632, 1605, 1468, 1379, 1270, 1184, 1155, 1056, 1021, 784 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{13}H_{11}BrO_3Na^+$, 316.9784; found, 316.9783.

3-(Tetrahydrofuran-2-yl)-7-(trifluoromethyl)-2H-chromen-2-one (**3k**). White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 16.2 mg, 57%. Mp: 87−88 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 (d, *J* = 1.8 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 4.97−4.95 (m, 1H), 4.14−4.10 (m, 1H), 3.97 (q, *J* = 7.4 Hz, 1H), 2.59−2.53 (m, 1H), 2.07−2.01 (m, 1H), 1.99−1.93 (m, 1H), 1.79−1.74 (m, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 159.5, 152.6, 135.1, 133.7, 132.6 (q, *J* = 33.0 Hz), 128.4, 123.3 (q, *J* = 270.0 Hz), 121.9, 121.0 (q, *J* = 4.5 Hz), 113.9 (q, *J* = 4.5 Hz), 75.9, 69.0, 32.2, 25.7. $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$): δ −62.8 (s, 3F). IR (film): 2956, 3087, 2956, 2943, 2910, 1738, 1635, 1511, 1429, 1334, 1320, 1267, 1210, 1267, 1170, 1130, 1064, 1047, 1022 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{14}H_{11}F_3O_3H^+$, 285.0733, found: 285.0733.

6-(tert-Butyl)-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3l**). White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 11.4 mg, 42%. Mp: 91−92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 1.6 Hz, 1H), 7.55−7.52 (m, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.28 (s, 1H), 4.99−4.95 (m, 1H), 4.14−4.09 (m, 1H), 3.99−3.93 (m, 1H), 2.54−2.49 (m, 1H), 2.04−1.99 (m, 1H), 1.97−1.92 (m, 1H), 1.79−1.74 (m, 1H), 1.35 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.8, 151.1, 147.5, 136.9, 130.7, 128.6, 124.1, 118.6, 116.0,76.0, 68.9, 34.5, 32.3, 31.4, 25.6. IR (film): 3092, 2957, 2318, 1717, 1631, 1465, 1397, 1384, 1261, 1175, 1070 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{17}H_{20}O_3Na^+$, 295.1305; found, 295.1306.

5-Fluoro-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3m**). White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 16.2 mg, 69%. Mp: 81−82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 1.6 Hz, 1H), 7.33−7.29 (m, 1H), 7.23−7.17 (m, 2H), 4.97−4.94 (m, 1H), 4.14−4.08 (m, 1H), 3.99−3.94 (m, 1H), 2.56−2.51 (m, 1H), 2.05−2.00 (m, 1H), 1.97−1.94 (m, 1H) 1.79−1.75 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.1, 158.8 (d, *J* = 243.0 Hz), 149.2 (d, *J* = 2.0 Hz), 135.4 (d, *J* = 2.0 Hz), 132.4, 120.0 (d, *J* = 10.0 Hz), 118.3 (d, *J* = 24.0 Hz), 117.9 (d, *J* = 8.0 Hz), 113.0 (d, *J* = 24.0 Hz), 75.9, 68.9, 32.2, 25.7. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −117.6 (s, 1F). IR (film): 3071, 2951, 2925, 2865, 1731, 1582, 1490, 1439, 1403, 1266, 1181, 1049 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{13}H_{11}FO_3Na^+$, 257.0584; found, 257.0584.

6-Chloro-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3n**). Known compound.[6b] White crystal; column chromatography (PE/EA = 40:1−30:1). Yield: 12.5 mg, 50%. Mp: 124−125 °C (lit. 80−81 °C).[6b] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 1.6 Hz, 1H), 7.48−7.42 (m, 2H), 7.29 (s, 1H), 4.97−4.93 (m, 1H), 4.13−4.08 (m, 1H), 3.99−3.93 (m, 1H), 2.58−2.49 (m, 1H), 2.06−1.99 (m, 1H), 1.98−1.90 (m, 1H), 1.80−1.71 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.9, 151.5, 135.2, 132.4, 130.8, 129.6, 127.0, 120.3, 117.9, 75.9, 68.9, 32.2, 25.6. IR (film): 3092, 2955, 2920, 2847, 1715, 1564, 1480, 1403, 1381, 1268, 1244, 1180, 1080, 1048 cm^{-1}. HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{11}ClO_3Na^+$, 273.0289; found, 273.0290.

5-Methyl-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3o**). White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 13.8 mg, 60%. Mp: 124−125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 0.8 Hz, 1H), 7.39−7.35 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 4.98−4.95 (m, 1H), 4.14−4.11 (m, 1H), 4.00−3.96 (m, 1H), 2.57−2.53 (m, 3H), 2.55 (s, 1H), 2.04−2.02 (m, 1H), 2.00−1.96 (m, 1H), 1.82−1.71 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.5, 153.6, 136.0, 133.2, 130.6, 130.1, 125.6, 118.0, 114.4, 76.1, 68.8, 32.3, 25.7, 18.5. IR (film): 3075, 2952, 1722, 1629, 1481, 1401, 1282, 1262, 1180, 1155, 1086, 1047, 1022, 786 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{14}H_{14}O_3Na^+$, 253.0835; found, 253.0837.

5-Methoxy-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3p**). White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 16.0 mg, 65%. Mp: 60−61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 1.2 Hz, 1H), 7.42−7.38 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.98−4.95 (m, 1H), 4.17−4.11 (m, 1H), 3.98−3.93 (m, 1H), 3.94 (s, 3H), 2.52−2.47 (m, 1H), 2.01−1.94 (m, 2H), 1.79−1.74 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.6, 156.1, 154.1, 131.7, 131.4, 129.0, 109.9, 108.8, 105.1, 76.1, 68.8, 55.9, 32.3, 25.6. IR (film): 3131, 2897, 1732, 1608, 1471, 1398, 1285, 1256, 1181, 1109, 1090 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{14}O_4Na^+$ $[M + Na]^+$, 269.0784; found, 269.0785.

5-Fluoro-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3q**). White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 11.5 mg, 49%. Mp: 101−102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04−8.03 (m, 1H), 7.47−7.41 (m, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.02−6.93 (m, 1H), 4.99−4.95 (m, 1H), 4.16−4.11 (m, 1H), 3.99−3.94 (m, 1H), 2.55−2.51 (m, 1H), 2.08−2.00 (m, 1H), 1.99−1.90 (m, 1H), 1.80−1.77 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.8, 158.5 (d, *J* = 252.0 Hz), 153.7 (d, *J* = 6.0 Hz), 131.4 (d, *J* = 2.0 Hz), 131.1 (d, *J* = 10.0 Hz), 129.3 (d, *J* = 4.0 Hz), 112.2 (d, *J* = 4.0 Hz), 110.3 (d, *J* = 19.0 Hz), 109.4 (d, *J* = 19.0 Hz), 75.9, 68.9, 32.2, 25.6. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −119.3 (s, 1F). IR (film): 3084, 2955, 2923, 2856, 1716, 1619, 1467, 1247, 1181, 1143, 1066, 1053, 1036, 1019 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{13}H_{11}FO_3Na^+$, 257.0584; found, 257.0585.

5-Chloro-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3r**). Colorless solid; column chromatography (PE/EA = 40:1−30:1). Yield: 17.5 mg, 70%. Mp: 95−96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 1.6 Hz, 1H), 7.43−7.39 (m, 1H), 7.33−7.31 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 4.99−4.95 (m, 1H), 4.18−4.13 (m, 1H), 4.01−3.95 (m, 1H), 2.56−2.51 (m, 1H), 2.06−1.97 (m, 2H), 1.80−1.75 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.7, 153.8, 132.7, 132.3, 132.1, 130.9, 125.0, 117.8, 115.3, 76.0, 68.9, 32.2, 25.6. IR (film):

https://doi.org/10.1021/acs.joc.1c00848
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3071, 2946, 2921, 2852, 1731, 1646, 1599, 1569, 1452, 1399, 1205, 1161, 1048, 1021, 964 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{11}ClO_3Na^+$, 273.0289; found, 273.0291.

*6,8-Dichloro-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one (**3s**).* Yellow solid; column chromatography (PE/EA = 40:1−30:1). Yield: 15.6 mg, 55%. Mp: 133−134 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 1.6 Hz, 1H), 7.54 (d, J = 2.4 Hz, 1H), 7.39 (d, J = 2.4 Hz, 1H), 4.97−4.93 (m, 1H), 4.12−4.07 (m, 1H), 3.99−3.94 (m, 1H), 2.59−2.51 (m, 1H), 2.08−1.98 (m, 1H), 1.96−1.88 (m, 1H), 1.79−1.70 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.8, 147.5, 134.9, 133.3, 130.9, 129.5, 125.6, 122.3, 121.1, 75.8, 69.0, 32.2, 25.7. IR (film): 3071, 2955, 2918, 2850, 1723, 1564, 1455, 1402, 1376, 1250, 1190, 1072, 1099, 1042, 1021 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{10}Cl_2O_3Na^+$, 306.9899; found, 306.9901.

*3-(Tetrahydrofuran-2-yl)-2H-benzo[g]chromen-2-one (**3t**).* Known compound.[6b] Yellow solid; column chromatography (PE/EA = 40:1−30:1). Yield: 14.9 mg, 56%. Mp: 95−96 °C (lit. 89−91 °C).[6b] ^1H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 8.34 (d, J = 8.4 Hz, 1H), 7.97−7.87 (m, 2H), 7.71−7.67 (m, 1H), 7.59−7.56 (m, 1H), 7.47 (d, J = 8.8 Hz, 1H), 5.07−5.03 (m, 1H), 4.24−4.18 (m, 1H), 4.05−4.00 (m, 1H), 2.62−2.58 (m, 1H), 2.09−2.04 (m, 1H), 2.03−1.99 (m, 1H), 1.85−1.80 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.6, 152.5, 132.2, 132.1, 130.3, 130.1, 129.1, 128.9, 128.0, 125.9, 121.8, 116.7, 113.4, 76.2, 68.9, 32.3, 25.8. IR (film): 3049, 2952, 2869, 1716, 1635, 1575, 1516, 1438, 1384, 1209, 1182, 1092, 1050, 1019, 992 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{14}O_3Na^+$, 289.0835; found, 289.0836.

*3-(Tetrahydrothiophen-2-yl)-2H-chromen-2-one (**3u**).* Known compound.[14] Yellow solid; column chromatography (PE/EA = 40:1−30:1). Yield: 11.8 mg, 51%. Mp: 69−70 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.52−7.47 (m, 2H), 7.34−7.32 (m, 1H), 7.30−7.26 (m, 1H), 4.69 (t, J = 6.4 Hz, 1H), 3.09−3.08 (m, 1H), 2.99−2.96 (m, 1H), 2.45−2.41 (m, 1H), 2.10−2.07 (m, 1H), 2.06−2.00 (m, 1H), 1.99−1.93 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.2, 152.9, 139.0, 131.1, 130.8, 127.8, 124.4, 119.3, 116.4, 46.9, 37.1, 32.8, 30.0. IR (film): 2977, 2924, 2851, 1715, 1608, 1456, 1399, 1168 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{12}O_2SNa^+$, 255.0450; found, 255.0451.

*7-Methyl-3-(tetrahydrothiophen-2-yl)-2H-chromen-2-one (**3v**).* Yellow solid; column chromatography (PE/EA = 40:1−30:1). Yield: 13.3 mg, 54%. Mp: 75−76 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.13 (s, 1H), 7.09 (d, J = 7.6 Hz, 1H) 4.68 (t, J = 6.2 Hz, 1H), 3.11−3.06 (m, 1H), 3.00−2.94 (m, 1H), 2.45 (s, 3H), 2.42−2.37 (m, 1H), 2.11−2.01 (m, 2H), 2.00−1.92 (m, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 161.5, 153.1, 142.3, 138.9, 129.5, 127.4, 125.6, 116.8, 116.5, 46.9, 37.2, 32.8, 30.0, 21.7. IR (film): 2954, 2927, 2859, 2714, 1722, 1621, 1567, 1502, 1457, 1441, 1418, 1378, 1316, 1235, 1260, 1174, 1143, 1113, 1033, 967, 890, 860, 810, 781 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{14}O_2SNa^+$, 269.0606; found, 269.0607.

*5-Chloro-3-(tetrahydrothiophen-2-yl)-2H-chromen-2-one (**3w**).* White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 17.3 mg, 65%. Mp: 114−115 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.43−7.39 (m, 1H), 7.34−7.31 (m, 1H), 7.25 (d, J = 8.0 Hz, 1H), 4.69 (t, J = 6.4 Hz, 1H), 3.15−3.09 (m, 1H), 3.02−2.96 (m, 1H), 2.48−2.40 (m, 1H), 2.12−2.05 (m, 2H), 2.02−1.95 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.5, 153.6, 135.0, 132.2, 131.9, 131.1, 125.0, 117.7, 115.2, 47.0, 36.8, 32.9, 30.2. IR (film): 3080, 2956, 2924, 2869, 2847, 1753, 1726, 1569, 1483, 1463, 1443, 1380, 1339, 1260, 1189, 1155, 1122, 1100, 973, 914, 886, 816, 749, 680 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{11}ClO_2SH^+$, 267.0247; found, 267.0243.

*3-(Tetrahydro-2H-pyran-2-yl)-2H-chromen-2-one (**3x**).* Known compound.[6b] Colorless oil; column chromatography (PE/EA = 40:1−30:1). Yield: 14.3 mg, 62%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.51−7.47 (m, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.29−7.25 (m, 1H), 4.47 (d, J = 10.8 Hz, 1H), 4.19−4.16 (m, 1H), 3.69−3.62 (m, 1H), 2.22 (d, J = 13.4 Hz, 1H), 1.94−1.91 (m, 1H), 1.74−1.71 (m, 1H), 1.71−1.65 (m, 1H), 1.31−1.22 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.3, 153.0, 137.4, 130.9, 130.9, 127.9, 124.4, 119.4, 116.4, 74.5, 69.1, 32.2, 25.9, 23.5. IR (film): 3062, 2936, 2853, 1717, 1634, 1609, 1457, 1398, 1308, 1285, 1207, 1181, 1087, 1074, 1040, 987 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{14}O_3Na^+$, 253.0835; found, 253.0835.

*3-(1-Ethoxyethyl)-2H-chromen-2-one (**3y**).* Known compound.[6b] Colorless oil; column chromatography (PE/EA = 20:1−10:1). Yield: 11.8 mg, 54%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.53−7.49 (m, 2H), 7.35−7.29 (m, 2H), 4.62 (q, J = 6.4 Hz, 1H), 3.57−3.51 (m, 2H), 1.44 (d, J = 6.4 Hz, 3H), 1.27 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.8, 153.1, 137.2, 131.7, 131.1, 127.9, 124.4, 119.4, 116.5, 72.2, 64.7, 21.5, 15.5. IR (film): 3097, 2955, 2919, 2850, 1738, 1463, 1399, 1378 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{14}O_3Na^+$, 241.0835; found, 241.0836.

*3-(1,3-Dioxolan-2-yl)-2H-chromen-2-one (**3z**).* Known compound.[6b] White solid; column chromatography (PE/EA = 5:1−3:1). Yield: 10.9 mg, 50%. Mp: 78−79 °C (lit. 73−75 °C).[6b] ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.57−7.53 (m, 2H), 7.35 (d, J = 8.2 Hz, 1H), 7.32−7.28 (m, 1H), 5.95 (s, 1H), 4.17−4.12 (m, 2H), 4.11−4.07 (m, 2H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 160.0, 153.9, 139.8, 132.2, 128.5, 125.1, 124.6, 118.6, 116.7, 99.0, 65.5. IR (film): 3097, 2955, 2923, 2851, 1716, 1608, 1457, 1402, 1173, 1114, 1036, 753, 668 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_{10}O_4Na^+$, 241.0471; found, 241.0471.

*2H-Chromen-2-one (**4a**).* White solid; column chromatography (PE/EA = 40:1−30:1). Yield: 8.5 mg, 58%. Mp: 70−71 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 9.6 Hz, 1H), 7.56−7.49 (m, 2H), 7.35−7.27 (m, 2H), 6.43 (d, J = 9.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.8, 154.0, 143.4, 131.8, 127.8, 124.4, 118.8, 116.9, 116.7. IR (film): 1707, 1619, 1606, 1561, 1453, 1399, 1275, 1259, 1229, 1178, 1120, 1108 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_7O_2^+$, 147.0446; found, 147.0443.

*3-Methyl-2H-chromen-2-one (**4b**).* White solid; column chromatography (PE/EA = 50:1−40:1). Yield: 10.2 mg, 64%. Mp: 93−94 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.49−7.41 (m, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.27−7.23 (m, 1H), 2.22 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.2, 153.2, 139.2, 130.4, 126.9, 125.8, 124.2, 119.6, 116.5, 17.2. IR (film): 3041, 2981, 2952, 2925, 2843, 1705, 1635, 1610, 1489, 1463, 1449, 1295, 1192, 1125, 1004, 947, 919, 853, 767, 753, 723 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{10}H_9O_2^+$, 161.0597; found, 161.0597.

*4-(Tetrahydrofuran-2-yl)-2H-chromen-2-one (**5**).* Colorless oil; column chromatography (PE/EA = 50:1−40:1). Yield: 4.7 mg, 22%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 7.6 Hz, 1H), 7.30−7.26 (m, 1H), 6.60 (d, J = 1.2 Hz, 1H), 5.26−5.22 (m, 1H), 4.17−4.12 (m, 1H), 4.03−3.97 (m, 1H), 2.57−2.50 (m, 1H), 2.09−2.15 (m, 1H), 2.03−1.96 (m, 1H), 1.92−1.86 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.16, 156.82, 153.89, 131.52, 124.09, 124.01, 117.58, 117.45, 110.93, 75.77, 69.16, 32.89, 25.71. IR (film): 3086, 2956, 2930, 2867, 1717, 1639, 1483, 1455, 1275, 1171, 1043 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{12}O_3Na^+$, 239.0679; found, 239.0679.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00848.

Copies of ^1H NMR and ^{13}C NMR spectra for all new compounds; light reaction device; structures of substrates; mechanistic experiments; X-ray crystal structures and crystal data of compounds **3c** (PDF)

Accession Codes

CCDC 2054357 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cam-

https://doi.org/10.1021/acs.joc.1c00848
J. Org. Chem. 2021, 86, 9552−9562

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (21632003 and 21871229).

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