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Visible-light-driven, Photoredox-catalyzed Cascade of *Ortho*-hydroxycinnamic Esters to Access 3-Fluoroalkylated Coumarins

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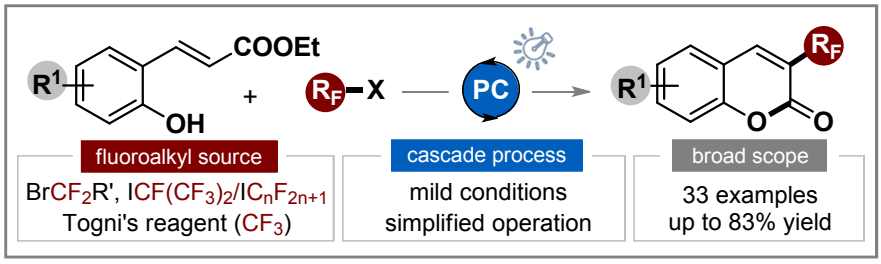


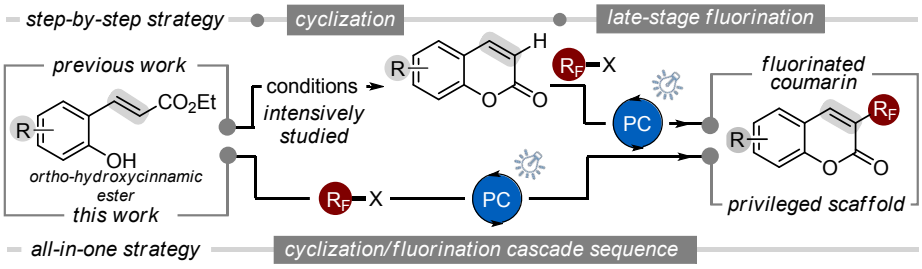
ABSTRACT: A general and straightforward protocol for *di*-/perfluoroalkylation of *ortho*-hydroxycinnamic esters *via* a photoredox-catalyzed cascade was developed to access a variety of 3-fluoroalkylated coumarins. This method was characterized by all-in-one synthetic design, simplified operation, mild reaction conditions, and broad substrate scope. Moreover, a sequential one-pot procedure starting from commercial available salicylaldehyde was also successfully realized to synthesize 3-fluoroalkylated coumarins.

As a privileged structural scaffold, coumarin, as well as its derivatives, frequently

exist in many biologically active pharmaceuticals,[1] natural products,[2] and fluorescent materials.[3] The preparation of functionalized coumarins, especially C3-functionalized analogues, has garnered extensive attention, aiming to enriching the library of coumarins with the upgraded properties.[4] It is commonly acknowledged that incorporating fluorine-containing substituents into the organic skeletons has a significantly beneficial impact on the physical properties including but not limited to solubility, lipophilicity, metabolic stability, and bioavailability.[5] Over the past few decades, substantial efforts have been made toward the introduction of fluorinated groups into coumarin framework.[6] However, most of the conventional methods involved multi-steps, excess oxidants, toxic or expensive fluoroalkylation reagents, and expensive transition metals. Hence, it is persistently necessary and fundamental to develop new straightforward protocols to prepare 3-fluoroalkylated coumarins under mild conditions.

Visible-light photoredox catalysis has witnessed rapid advancements in generating an array of fluorinated radicals and constructing structurally complex scaffolds, owing to its reaction condition mildness, operational simplicity, and environmental friendliness.[7] Following this line, several photocatalyzed syntheses of fluorinated coumarins have been established (Scheme 1).[8]

Scheme 1. Representative Synthetic Profiles of 3-Fluoroalkyl Coumarins *via* Photocatalysis



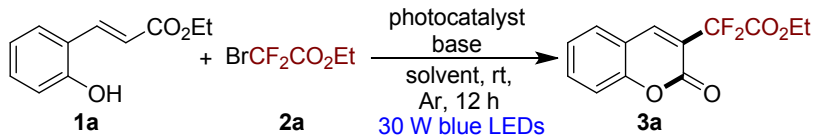
In general, the photocatalyzed strategies for accessing 3-fluoroalkylated coumarins heavily rely on the late-stage fluoroalkylation of the preformed coumarin core structure (Scheme 1).[9] In 2016, Yuan and co-authors described a photochemical difluoroalkylation of coumarins with $BrCF_2R$ under visible-light irradiation.[9a]

Thereafter, an efficient method using a transition-metal-free photochemical strategy for the direct Csp^2-H radical difluoromethylation of coumarins with HCF_2SO_2Na was established by Deng's group.[9b] Meanwhile, a few important studies of visible-light-induced *tri*/perfluoroalkylation of coumarins were also reported.[9c-9g] Despite all these advancements, trimming down the synthetic steps to access 3-functionalized coumarins in a more step-economic manner is still highly desirable.

As known, the cyclizations of readily available *ortho*-hydroxycinnamic esters has been intensively utilized to prepare various coumarins.[10] However, harsh conditions are usually requisite to overcome the inherent hurdle of the isomerization of *Z*-alkene in *ortho*-hydroxycinnamic esters, thus facilitating the following cyclization. Noticing this issue, we rationalized that photocatalytic radical addition of the double bond in *ortho*-hydroxycinnamic esters could offer an alternative facile pathway for the isomerization process. As a consequence, the incorporation of cyclization and fluorination would offer a step-economic route for the synthesis of fluorine-containing coumarins under mild conditions. As part of our continued interest in the photoredox catalysis[11] and fluorinated heterocycles[12], we herein disclose a general photoredox-catalyzed protocol for the construction of various fluoroalkylated coumarins from easy-to-prepare *ortho*-hydroxycinnamic esters (Scheme 1).

We began our studies with a model reaction of *ortho*-hydroxycinnamic ester **1a** and commercially available $BrCF_2COOEt$ (**2a**) under irradiation of 30 W blue LEDs (Table 1). Preliminary experiments were conducted in CH_3CN with 2 equimolar amount of **2a** under the atmosphere of Ar at room temperature. Gratifyingly, catalyst screening demonstrated that *fac*-$Ir(ppy)_3$ successfully gave the desired product **3a** in a moderate yield, whereas other commonly used photocatalysts gave inferior results in promoting this transformation (Table 1, entries 1-5). Subsequently, a series of bases were tested, which can effectively consume HBr produced in the process of this transformation (Table 1, entries 6-12). Satisfyingly, the yield for **3a** was improved upon using K_2CO_3, Et_3N or DIPEA as the base. Effects of solvent were also

Table 1. Optimization of Reaction Conditions[a]



1a **2a** **3a**

Entry	Photocatalyst	Solvent	Base	Yield[b] (%)
1	$Ru(bpy)_3(PF6)_2$	CH_3CN	NaOAc	trace
2	*fac*-Ir(ppy)$_3$	CH_3CN	NaOAc	41
3	$Ir(ppy)_2(dtbbpy)PF_6$	CH_3CN	NaOAc	18
4	$Ir[dF(CF_3)(ppy)_2](dtbbpy)PF_6$	CH_3CN	NaOAc	trace
5	Eosin Y	CH_3CN	NaOAc	NR
6	*fac*-Ir(ppy)$_3$	CH_3CN	K_2CO_3	65
7	*fac*-Ir(ppy)$_3$	CH_3CN	Cs_2CO_3	19
8	*fac*-Ir(ppy)$_3$	CH_3CN	K_2HPO_4	22
9	*fac*-Ir(ppy)$_3$	CH_3CN	K_3PO_4	49
10	*fac*-Ir(ppy)$_3$	CH_3CN	Et_3N	65
11	*fac*-Ir(ppy)$_3$	CH_3CN	DIPEA	62
12	*fac*-Ir(ppy)$_3$	CH_3CN	---	trace
13	*fac*-Ir(ppy)$_3$	CH_2Cl_2	K_2CO_3	22
14	*fac*-Ir(ppy)$_3$	DMF	K_2CO_3	62
15	*fac*-Ir(ppy)$_3$	DMSO	K_2CO_3	65
16	*fac*-Ir(ppy)$_3$	THF	K_2CO_3	62
17	*fac*-Ir(ppy)$_3$	MeOH	K_2CO_3	trace
18	*fac*-Ir(ppy)$_3$	dioxane	K_2CO_3	37
19[c]	*fac*-Ir(ppy)$_3$	CH_3CN	K_2CO_3	28
20[d]	*fac*-Ir(ppy)$_3$	CH_3CN	K_2CO_3	69
21[d, e]	*fac*-Ir(ppy)$_3$	CH_3CN	K_2CO_3	69
22[d, f]	*fac*-Ir(ppy)$_3$	CH_3CN	K_2CO_3	69

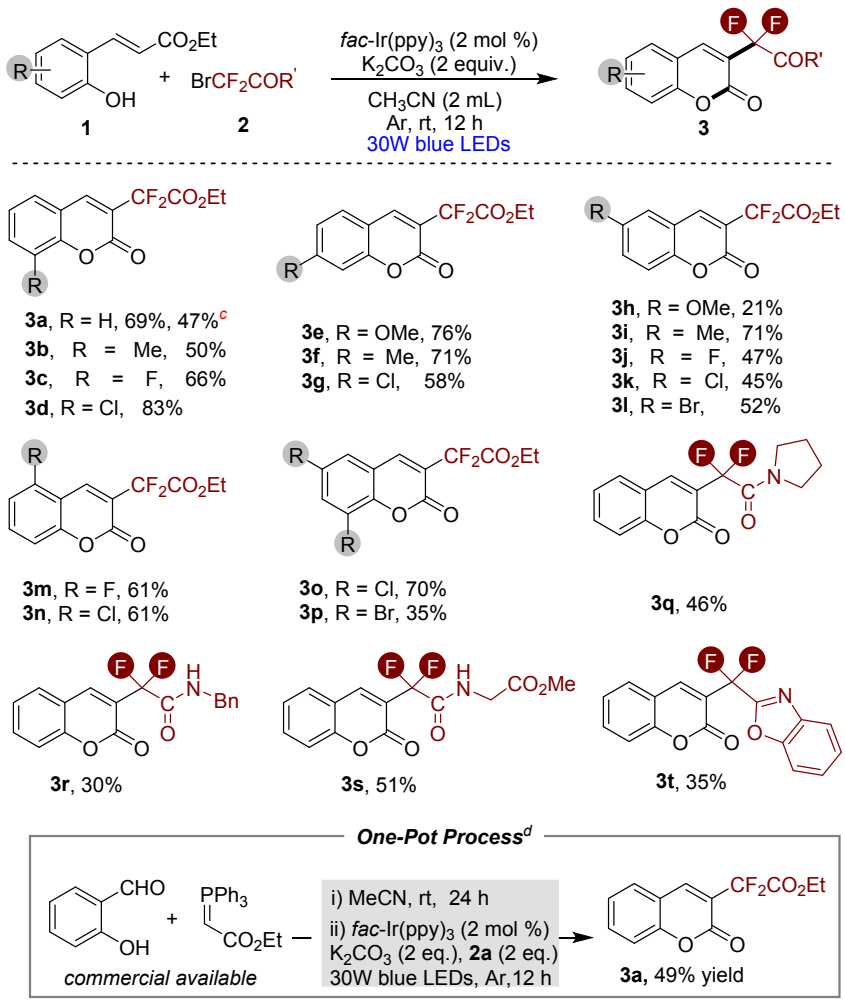
[a]Reaction conditions: **1a** (0.2 mmol) and **2a** (0.4 mmol), photocatalyst (2 mol %), and base (2.0 equiv.) in solvent (1 mL), Ar, irradiation with 30 W blue LEDs, rt, 12 h. [b]Isolated yields. [c]In air. [d]2 mL of solvent was used. [e]3 equiv. of **2a** was used. [f]30 W white LEDs.

investigated, but without any improvement in efficiency. The yield of **3a** was consistently reduced in dioxane, CH_2Cl_2, or MeOH. And comparable yields were obtained when DMF, DMSO or THF was used as the solvent (Table 1, entries 13-18). To further improve the yield, other reaction parameters were also tested. The reaction proceeded sluggishly and intricately in air (Table 1, entry 19). The yield of **3a** was

slightly increased when the reaction was performed at lower concentration (Table 1 entry 20), while increasing the amount of $BrCF_2CO_2Et$ was unable to further improve the yield (Table 1 entry 21). In addition, **3a** was formed in a comparably yield under white light irradiation (Table 1, entry 22).

Having established the optimal conditions, the versatility of this approach was subsequently explored and a range of *ortho*-hydroxycinnamic esters were prepared and subjected to the optimized reaction conditions. The electronic feature of substituents at *ortho*- or *meta*-position of the phenol moiety slightly affected the efficacy of this reaction, and thus comparable chemical yields were secured (Scheme 2, **3a-3g** and **3m-3n**). Specifically, with regard to the substituent at *para*-position of phenol group in the substrate, the presence of methoxy group evidently undermined the yield, while other substituents consistently provided moderate to good yields (Scheme 2, **3h-3l**). Disubstituted products **3o** and **3p** were also successfully prepared. To further demonstrate the generality of this protocol, a range of bromodifluoroamides and 2-(bromodifluoromethyl)benzoxazoles were also investigated, leading to the corresponding products **3q-3t** but with comparatively lower yields. The practicality and scalability of this protocol was successfully demonstrated by performing the reaction of **3a** on a gram scale under standard reaction conditions to give a slightly reduced yield (47%). Moreover, aiming to further simplifying the synthetic operation, a one-pot process by starting from salicylaldehyde and 2-(triphenylphosphoranylidene)acetic acid ethyl ester was developed, affording the desired product **3a** in 49% yield.

Scheme 2. Substrate Scope for the Synthesis of 3-CF_2-Containing Coumarins[a,b]

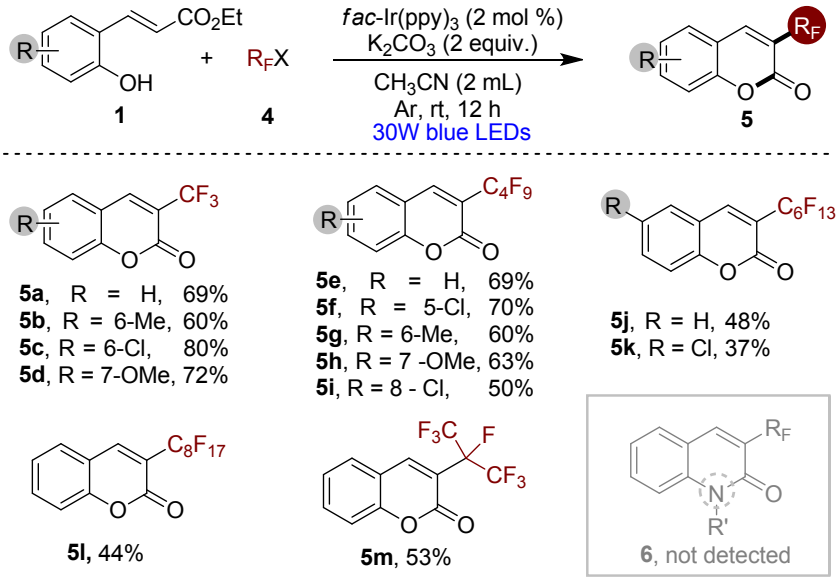


[a]Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), *fac*-Ir(ppy)$_3$ (2 mol %), and K_2CO_3 (0.4 mmol, 2.0 equiv.) in CH_3CN (2 mL); Ar, irradiation with 30 W blue LEDs, rt, 12 h. [b]Isolated yields. [c]Performed at 1.045 g scale for **1a,** coumarin was concurrently isolated in 17% yield. [d]Salicylaldehyde (0.2 mmol, 1.0 equiv.), 2-(triphenylphosphoranylidene)acetic acid ethyl ester (0.24 mmol, 1.2 equiv.), in CH_3CN (2 mL), rt, 12 h; then **2** (0.4 mmol, 2.0 equiv.), *fac*-Ir(ppy)$_3$ (2 mol %), and K_2CO_3 (0.4 mmol, 2.0 equiv.) were added and stirred at rt under Ar for an additional 12 h.

Encouraged by the above results, we extended this newly developed strategy to install 3-perfluoroalkylated coumarins by simply replacing $BrCF_2COR'$ with various commercially available perfluoroalkylated radical resources. As shown in Scheme 3, the substitution patterns and electronic characteristics of *ortho*-hydroxycinnamic esters have slight effects on their reaction efficiency, with the desired products **5a-5m** being obtained in moderate to good yields. However, *ortho*-aminocinnamic esters only

rendered a fairly complex reaction and the corresponding carbostyril derivatives **6** were undetected.

Scheme 3. Substrate Scope for the Synthesis of 3-Perfluoroalkyl Coumarins[a,b]



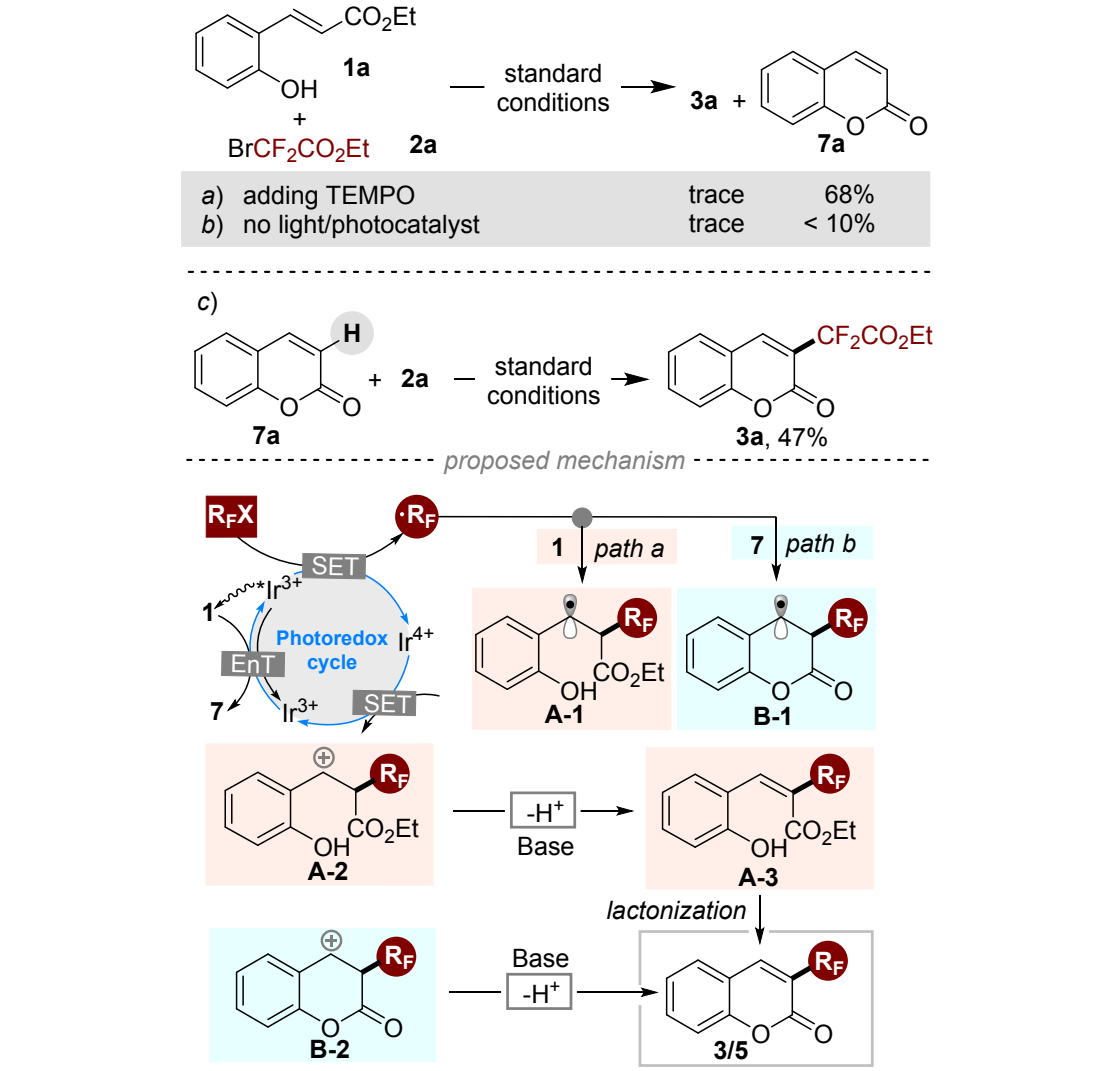
[a]Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), **4** (Togni's reagent II/IC_nF_{2n+1}/$ICF(CF_3)_2$, 1.0 mmol, 5.0 equiv.), *fac*-Ir(ppy)$_3$ (2 mol%), and K_2CO_3 (0.4 mmol, 2.0 equiv.) in CH_3CN (2 mL); Ar, irradiation with 30 W blue LEDs, rt, 12 h. [b]Isolated yields.

To gain mechanistic insights into the process, several control experiments were subsequently conducted (Scheme 4). Radical trapping experiments were firstly implemented by adding the radical scavenger 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, 5 equiv.) to the model reaction system. In this case, the formation of **3a** was almost completely suppressed along with the formation of coumarin **7a** with 68% yield (Scheme 4, eq a, see the Supporting Information for details). These results indicate that a free-radical pathway was probably involved in the process of fluoroalkylation reaction. As expected, the reaction was completely restrained in the absence of the catalyst or light irradiation, which suggests that a photoredox catalysis process was involved in the formation of **3a** and **7a** (Scheme 4, eq b). Importantly, the corresponding Stern–Volmer studies reveal that the photoexcited *fac*-Ir(ppy)$_3$ was quenched by *ortho*-hydroxycinnamic ethyl ester (**1a**) as well as $BrCF_2COOEt$ (**2a**) with similar efficiency

(see the Supporting Information for details). In addition, the reaction of coumarin with $BrCF_2COOEt$ under the standard conditions also gave the target product in 47% yield (Scheme 4, eq c).

Based on the above experimental results, two possible pathways for the photocatalytic transformation are exemplified in Scheme 4. In path a, photocatalyst *fac*-$Ir(ppy)_3$ facilely generated the highly reducing excited $*Ir(ppy)_3$ ($E_{1/2(IrIV/*IrIII)}$ = -1.73 V vs. SCE) under the irradiation of blue light. As shown in path b, the photoexcited *fac*-$Ir(ppy)_3$ was oxidatively quenched by R_FX ($E_{1/2}$ = -1.0 V to -1.6 V vs. SCE, see the Supporting Information for details)[13] with the generation of $\bullet R_F$ radical *via* a single-electron transfer (SET) process. Afterwards, the $\bullet R_F$ radical regioselectively attacked the most electron-rich position of the double bond in cinnamate **1** to give benzylic radical **A-1**. This intermediate was further oxidized to carbocation **A-2** by Ir(IV) species ($E_{1/2(IrIV/IrIII)}$ = +0.77 V vs. SCE) *via* the second SET process, thus completing the photocatalytic cycle and regenerating the ground state *fac*-$Ir(ppy)_3$. In the presence of base, the subsequent deprotonation of intermediate **A-2** gave (*Z*)-fluoroalkylated cinnamate **A-3** as the key intermediate.[6b] Finally, an intramolecular lactonization of intermediate **A-3** directly generated fluoroalkylated coumarins **3/5**. Alternatively, $*Ir(ppy)_3$ could be quenched through an energy transfer (EnT) pathway with the formation of coumarins **7** and simultaneous recycling of the ground state *fac*-$Ir(ppy)_3$ (path b). The subsequent radical addition and SET oxidation resulted in the formation of **B-1** and **B-2** respectively, which ultimately delivered the desired product **3** or **5** in the presence of base.[9a, c]

Scheme 4. Control Experiments and Plausible Reaction Mechanism



In summary, we first developed a general and facile assembly of 3-fluoroalkylated coumarins through a visible-light-induced cascade radical cyclization process starting from readily prepared *ortho*-hydroxycinnamic esters. By using various commercial fluoroalkylating reagents, a range of 3-*di*/*tri*/perfluoroalkylated coumarins were successfully prepared under mild conditions. The notable features of these reactions include mild reaction conditions, synthetic simplicity, and excellent functional group compatibility. Moreover, a sequential one-pot protocol starting from commercial available salicylaldehyde was also designed and successfully realized, efficiently generating 3-fluoroalkylated coumarins. Further synthetic applications and studies to unveil the biological activities of these privileged scaffolds are ongoing in

our laboratory.

EXPERIMENTAL SECTION

General Experimental Methods. Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. And the light source used for illuminating the reaction vessel (commercial supplier: Synthware) consisted of blue LEDs (λ_{max} = 460 nm) purchased from Taobao (https://gpiled.taobao.com). ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quint, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. ^{19}F NMR data were collected at 376 MHz with complete proton decoupling. UV–Vis spectra were recorded using a shimadzu UV-2600. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES+ mass spectrometer and acetonitrile was used to dissolve the sample. Cyclic Voltammetry (CV) experiments were recorded on a CHI650D Electrochemical workstation. Emission intensities were recorded using Perkin-Elemer LS 55 Fluorescence Spectrometer. Column chromatography was carried out on silica gel (200-300 mesh).

General procedures for synthesis of 1a-1p.

The starting materials **1** were prepared according to the previously described method.[14] The data of known compounds are consistent with the previously reports[6a, 10a, 15] and the copies of their ^{1}HNMR spectra were included in the Supporting Information. Characterization data of new compounds **1c**, **1d**, **1m** and **1p** were also provided herein.

Characterization data of compounds 1c, 1d, 1m and 1p

*(E)-Ethyl 3-(2-hydroxy-3-fluorophenyl)acrylate (**1c**)*. White solid (504 mg, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 16.0 Hz, 1H), 7.25 (d, J = 9.6 Hz, 1H), 7.06-7.11 (m, 1H), 6.81-6.86 (m, 2H), 6.65 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 6.4 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 168.0, 151.6 (d, J = 237.3 Hz), 143.6 (d, J = 15.4 Hz), 139.3 (d, J = 3.7 Hz), 124.2 (d, J = 3.3 Hz), 123.8 (d, J = 2.2 Hz), 119.84 (d, J = 7.2 Hz), 119.6, 116.6 (d, J = 18.5 Hz), 60.8,

14.3; HRMS (ESI): $C_{11}H_{11}FNaO_3^+$ $[M+Na]^+$ calcd 233.0584, found 233.0597.

*(E)-Ethyl 3-(2-hydroxy-3-chlorophenyl)acrylate (**1d**)*. White solid (576 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 16.0 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.34 (dd, J = 7.6, 1.2 Hz, 1H), 6.89 (t, J = 8.0 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 6.15 (s, 1H), 4.28 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 6.4 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.3, 150.4, 139.0, 130.2, 127.8, 123.0, 121.0, 120.9, 120.3, 60.6, 14.3; HRMS (ESI): $C_{11}H_{11}ClNaO_3^+$ $[M+Na]^+$ calcd 249.0289, found 249.0281.

*(E)-Ethyl 3-(2-hydroxy-6-chlorophenyl)acrylate (**1m**)*. White solid (560 mg, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (*br s*, 1H), 8.04 (d, J = 16.0 Hz, 1H), 7.16 (dd, J = 14.8, 8.0 Hz, 1H), 6.99 (d, J = 16.0 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.64 (t, J = 8.8 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 169.6, 162.7 (d, J = 252.5 Hz), 157.6 (d, J = 6.6 Hz), 134.6 (d, J = 3.2 Hz), 131.2 (d, J = 11.6 Hz), 121.3 (d, J = 8.9 Hz), 111.9 (d, J = 3.0 Hz), 110.9 (d, J = 13.7 Hz), 107.2 (d, J = 22.9 Hz), 61.0, 14.3; HRMS (ESI): $C_{11}H_{11}FNaO_3^+$ $[M+Na]+$ calcd 233.0584, found 233.0583.

*(E)-Ethyl 3-(2-hydroxy-3,5-dibromophenyl)acrylate (**1p**)*. White solid (871 mg, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 16.0 Hz, 1H), 7.55-7.60 (m, 2H), 6.54 (d, J = 16.0 Hz, 1H), 6.10 (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 166.7, 150.3, 137.7, 135.1, 130.9, 124.4, 121.5, 112.8, 112.0, 60.8, 14.3; HRMS (ESI): $C_{11}H_{10}Br_2NaO_3^+$ $[M+Na]+$ calcd 370.8889, found 370.8908.

General procedures for synthesis of 3a-3g and 5a-5m

To a mixture of ethyl 2-hydroxycinnamates **1** (0.20 mmol), K_2CO_3 (0.40 mmol, 2.0 equiv.), and F sources for 2.0 equiv. $BrCF_2X$ or 5 equiv. Togni reagent II/$C_nF_{2n+1}I$ in CH_3CN (2 mL) was added $Ir(ppy)_3$ (2.00 mmol %) under Ar atmosphere. The reaction mixture was stirred at room temperature under irradiation of 30 W blue LEDs (distance app. 3 cm) for 12 h. The solvent was removed *in vacuo* and the resulting residue was then purified by flash chromatography using silica gel (EtOAc/PE = 1/50).

Synthetic procedure for the preparation of 3a on gram scale

To a mixture of ethyl 2-hydroxycinnamates **1** (1.045 g, 5.5 mmol), K_2CO_3 (1.518 g, 11.0 mmol, 2.0 equiv.), and $BrCF_2CO_2Et$ (1.410 mL, 11.0 mmol, 2.0 equiv.) was added $Ir(ppy)_3$ (18 mg, 0.5 mmol %) under Ar atmosphere. The reaction mixture was stirred at room temperature under irradiation of 30 W blue LEDs (distance app. 3 cm) for 12 h. The solvent was removed *in vacuo* and the resulting

residue was then purified by flash chromatography using silica gel (EtOAc/PE = 1/50) to give **3a** (0.697 g, 47% yield).

Characterization data of compounds 3a-3t and 5a-5m

*Ethyl 2,2-Difluoro-2-(2-oxo-2H-chromen-3-yl)acetate (**3a**)*.[9a] White solid (37 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.61-7.66 (m, 2H), 7.35-7.39 (m, 2H), 4.38 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H); ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ -106.1 (s, 2F).

*Ethyl 2,2-Difluoro-2-(8-methyl-2-oxo-2H-chromen-3-yl)acetate (**3b**)*. White solid (28 mg, 50%): m.p. 64-65 ℃; IR (KBr) ν 2924, 1748, 1467, 1140, 970, 786, 460 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.47 (q, J = 7.6 Hz, 2H), 7.26 (t, J = 8.0 Hz, 1H), 4.39 (q, J = 7.2 Hz, 2H), 2.46 (s, 3H), 1.35 (t, J = 6.8 Hz, 3H); ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ -106.1 (s, 2F); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 162.4 (t, $J_{C\text{-}F}$ = 32.8 Hz), 158.1 (t, $J_{C\text{-}F}$ = 4.5 Hz), 152.6, 142.3 (t, $J_{C\text{-}F}$ = 6.9 Hz), 135.0, 126.9, 126.6, 124.7, 120.8 (t, $J_{C\text{-}F}$ = 25.6 Hz), 117.3, 110.6 (t, $J_{C\text{-}F}$ = 250.7 Hz), 63.5, 15.4, 13.8; HRMS (ESI): $C_{14}H_{12}F_2NaO_4^+$ $[M+Na]^+$ calcd 305.0596, found 305.0571.

*Ethyl 2,2-Difluoro-2-(8-fluoro-2-oxo-2H-chromen-3-yl)acetate (**3c**)*. White solid (38 mg, 66%), m.p. 116-118 ℃; IR (KBr) ν 2959, 1748, 1467, 1315, 1017, 744, 460 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.40-7.45 (m, 2H), 7.30-7.35 (m, 1H), 4.39 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H); ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ -106.3 (s, 2F), -132.2 (s, 1F); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 162.0 (t, $J_{C\text{-}F}$ = 32.6 Hz), 156.5 (t, $J_{C\text{-}F}$ = 4.4 Hz), 129.4 (d, $J_{C\text{-}F}$ = 253.8 Hz), 142.4 (d, $J_{C\text{-}F}$ = 11.8 Hz), 141.4 (td, $J_{C\text{-}F}$ = 7.1 Hz, 2.8 Hz), 125.2 (d, $J_{C\text{-}F}$ = 6.6 Hz), 124.4 (d, $J_{C\text{-}F}$ = 4.0 Hz), 122.2 (t, $J_{C\text{-}F}$ = 25.8 Hz), 120.0 (d, $J_{C\text{-}F}$ = 17.2 Hz), 119.3, 110.3 (t, $J_{C\text{-}F}$ = 251.5 Hz), 63.8, 13.8; HRMS (ESI): $C_{13}H_9F_3NaO_4^+$ $[M+Na]^+$ calcd 309.0345, found 309.0324.

*Ethyl 2,2-Difluoro-2-(8-chloro-2-oxo-2H-chromen-3-yl)acetate (**3d**)*. White solid (50 mg, 83%), m.p. 125-126 ℃; IR (KBr) ν 2959, 1728, 1447, 1201, 981, 780, 486 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.70 (dd, J = 8.0, 0.8 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 4.39 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H); ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ -106.2 (s, 2F); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 162.0 (t, $J_{C\text{-}F}$ = 32.6 Hz), 156.8 (t, $J_{C\text{-}F}$ = 4.4 Hz), 149.9, 141.5 (t, $J_{C\text{-}F}$ = 7.0 Hz),134.0, 127.7, 125.4, 122.1, 122.0 (t, $J_{C\text{-}F}$ = 25.7 Hz), 118.8, 110.3 (t, $J_{C\text{-}F}$ = 251.5 Hz), 63.7, 13.8; HRMS (ESI): $C_{13}H_9ClF_2NaO_4^+$ $[M+Na]^+$ calcd 325.0050, found 325.0054.

*Ethyl 2,2-Difluoro-2-(7-methoxy-2-oxo-2H-chromen-3-yl)acetate (**3e**)*.[9a] White solid (43 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.50 (d, J = 8.7 Hz, 1H), 6.92 (dd, J = 8.7, 2.3 Hz, 1H),

6.86 (d, J = 2.1 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H); ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ -105.5 (s, 2F).

Ethyl 2,2-Difluoro-2-(7-methyl-2-oxo-2H-chromen-3-yl)acetate ***(3f)***.[16] White solid (26 mg, 45%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.17-7.19 (m, 2H), 4.39 (q, J = 7.2 Hz, 2H), 2.49 (s, 3H), 1.34 (t, J = 6.8 Hz, 3H); ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ -105.9 (s, 2F).

Ethyl 2,2-Difluoro-2-(7-chloro-2-oxo-2H-chromen-3-yl)acetate ***(3g)***. White solid (35 mg, 58%), m.p. 93-95 ℃; IR (KBr) ν 2924, 1748, 1468, 1316, 1017, 744, 460 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.38 (s, 1H), 7.35 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 4.39 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 6.8 Hz, 3H); ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ -106.2 (s, 2F); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 162.1 (t, $J_{C\text{-}F}$ = 32.7 Hz), 157.3 (t, $J_{C\text{-}F}$ = 4.4 Hz), 154.4, 141.2 (t, $J_{C\text{-}F}$ = 7.0 Hz), 139.9, 130.0, 125.9, 121.2 (t, $J_{C\text{-}F}$ = 25.7 Hz), 117.4, 116.1, 110.3 (t, $J_{C\text{-}F}$ = 251.3 Hz), 63.7, 13.8; HRMS (ESI): $C_{13}H_9ClF_2NaO_4^+$ [M+Na]$^+$ calcd 325.0050, found 325.0027.

Ethyl 2,2-Difluoro-2-(6-methoxy-2-oxo-2H-chromen-3-yl)acetate ***(3h)***. White solid (13 mg, 21%), m.p. 166-167 ℃; IR (KBr) ν 2924, 1748, 1468, 1201, 1017, 744, 460 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.32 (d, J = 9.2 Hz, 1H), 7.21 (dd, J = 9.1, 2.6 Hz, 1H), 6.96 (d, J = 2.6 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H); ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ -106.2 (s, 2F); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 162.3 (t, $J_{C\text{-}F}$ = 32.7 Hz), 158.1 (t, $J_{C\text{-}F}$ = 4.5 Hz), 156.5, 148.7, 141.7 (t, $J_{C\text{-}F}$ = 7.0 Hz), 121.7, 121.5 (t, $J_{C\text{-}F}$ = 25.4 Hz), 118.1, 117.9, 110.8, 63.6, 56.0, 13.8; HRMS (ESI): $C_{14}H_{12}F_2NaO_5^+$ [M+Na]$^+$ calcd 321.0545, found 321.0526.

Ethyl 2,2-Difluoro-2-(6-methyl-2-oxo-2H-chromen-3-yl)acetate ***(3i)***.[9a] Colorless oil (40 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.41 (s, 1H), 7.28 (d, J = 3.2 Hz, 1H), 4.39 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H); ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ -106.1 (s, 2F).

Ethyl 2,2-Difluoro-2-(6-fluoro-2-oxo-2H-chromen-3-yl)acetate ***(3j)***. White solid (27 mg, 47%), m.p. 135-136 ℃; IR (KBr) ν 2959, 1729, 1448, 1291, 982, 781, 558 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.36-7.38 (m, 2H), 7.30-7.33 (m, 1H), 4.39 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H); ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ -106.4 (s, 2F), -115.9 (s, 1F); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 162.0 (t, $J_{C\text{-}F}$ = 32.6 Hz), 159.0 (d, $J_{C\text{-}F}$ = 246.1 Hz), 157.5 (t, $J_{C\text{-}F}$ = 4.4 Hz), 150.4, 140.9 (td, $J_{C\text{-}F}$ = 7.0, 2.8 Hz), 122.5 (t, $J_{C\text{-}F}$ = 25.6 Hz), 121.2 (d, $J_{C\text{-}F}$ = 24.5 Hz), 118.7 (d, $J_{C\text{-}F}$ = 8.3 Hz),

118.2 (d, $J_{C\text{-}F}$ = 9.1 Hz), 114.4 (d, $J_{C\text{-}F}$ = 24.1 Hz), 110.3 (t, $J_{C\text{-}F}$ = 251.5 Hz), 63.7, 13.8; HRMS (ESI): $C_{13}H_9F_3NaO_4^+$ $[M+Na]^+$ calcd 309.0345, found 309.0366.

*Ethyl 2,2-Difluoro-2-(6-chloro-2-oxo-2H-chromen-3-yl)acetate (**3k**)*. White solid (27 mg, 45%), m.p. 102-104 ℃; IR (KBr) *v* 2959, 1729, 1448, 1291, 982, 781, 487 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.57-7.61 (m, 2H), 7.34 (d, *J* = 8.6 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -106.4 (s, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0 (t, $J_{C\text{-}F}$ = 32.6 Hz), 157.3 (t, $J_{C\text{-}F}$ = 4.4 Hz), 152.6, 140.8 (t, $J_{C\text{-}F}$ = 7.0 Hz), 133.6, 130.6, 128.4, 122.4 (t, $J_{C\text{-}F}$ = 25.8 Hz), 118.5, 110.3 (t, $J_{C\text{-}F}$ = 251.6 Hz), 63.7, 13.8; HRMS (ESI): $C_{13}H_9ClF_2NaO_4^+$ $[M+Na]^+$ calcd 325.0050, found 325.0076.

*Ethyl 2,2-Difluoro-2-(6-bromo-2-oxo-2H-chromen-3-yl)acetate (**3l**)*. White solid (36 mg, 52%), m.p. 108-109 ℃; IR (KBr) *v* 2959, 1729, 1448, 1291, 982, 781, 487 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.76 (d, *J* = 2.1 Hz, 1H), 7.72 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -106.4 (s, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0 (t, $J_{C\text{-}F}$ = 32.7 Hz), 157.2, 153.1, 140.6 (t, $J_{C\text{-}F}$ = 7.0 Hz), 136.4, 131.4, 122.4 (t, $J_{C\text{-}F}$ = 25.8 Hz), 119.0, 118.7, 117.8, 110.4 (t, $J_{C\text{-}F}$ = 251.6 Hz), 63.7, 13.8; HRMS (ESI): $C_{13}H_9BrF_2NaO_4^+$ $[M+Na]^+$ calcd 368.9544, found 368.9564.

*Ethyl 2,2-Difluoro-2-(5-fluoro-2-oxo-2H-chromen-3-yl)acetate (**3m**)*. White solid (27 mg, 47%), m.p. 77-79 ℃; IR (KBr) *v* 2959, 1729, 1448, 1291, 982, 781, 558 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.61 (dd, *J* = 14.4, 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 8.4 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -106.2 (s, 2F), -117.1 (s, 1F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0 (t, $J_{C\text{-}F}$ = 32.6 Hz), 159.1 (d, $J_{C\text{-}F}$ = 258.0 Hz), 157.1 (t, $J_{C\text{-}F}$ = 4.4 Hz), 154.6 (d, $J_{C\text{-}F}$ = 4.4 Hz), 135.1 (td, $J_{C\text{-}F}$ = 7.3, 4.4 Hz), 134.2 (d, $J_{C\text{-}F}$ = 9.8 Hz), 121.4 (td, $J_{C\text{-}F}$ = 25.9, 1.6 Hz), 112.9 (d, $J_{C\text{-}F}$ = 3.9 Hz), 111.1 (d, $J_{C\text{-}F}$ = 19.6 Hz), 109.1 (t, $J_{C\text{-}F}$ = 251.6 Hz), 108.0 (d, $J_{C\text{-}F}$ = 19.1 Hz), 63.7, 13.8; HRMS (ESI): $C_{13}H_9F_3NaO_4^+$ $[M+Na]^+$ calcd 309.0345, found 309.0356.

*Ethyl 2,2-Difluoro-2-(5-chloro-2-oxo-2H-chromen-3-yl)acetate (**3n**)*. White solid (43 mg, 71%), m.p. 95-97 ℃; IR (KBr) *v* 2959, 1729, 1448, 1291, 982, 781, 558 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.42 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -106.1 (s, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.1 (t, $J_{C\text{-}F}$ = 32.6 Hz), 157.1 (t, $J_{C\text{-}F}$ = 4.4 Hz), 155.0, 138.3

(t, $J_{C\text{-}F}$ = 7.3 Hz), 133.8, 133.7, 125.8, 122.0 (t, $J_{C\text{-}F}$ = 25.6 Hz), 116.3, 115.8, 110.3 (t, $J_{C\text{-}F}$ = 251.7 Hz), 63.7, 13.8; HRMS (ESI): $C_{13}H_9ClF_2NaO_4^+$ $[M+Na]^+$ calcd 325.0050, found 325.0054.

*Ethyl 2,2-Difluoro-2-(6,8-dichloro-2-oxo-2H-chromen-3-yl)acetate (**3o**)*. Colorless oil (47 mg, 70%); IR (KBr) *v* 2959, 1729, 1448, 1080, 982, 781, 487 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.68 (d, *J* = 1.6 Hz, 1H), 7.53 (s, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -106.4 (s, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.8 (t, $J_{C\text{-}F}$ = 32.6 Hz), 156.2 (t, $J_{C\text{-}F}$ = 4.4 Hz), 148.6, 140.5 (t, $J_{C\text{-}F}$ = 7.1 Hz), 133.5, 130.4, 126.9, 123.2 (t, $J_{C\text{-}F}$ = 25.6 Hz), 123.1, 119.3, 110.1 (t, $J_{C\text{-}F}$ = 252.1 Hz), 63.8, 13.8; HRMS (ESI): $C_{13}H_8Cl_2F_2NaO_4^+$ $[M+Na]^+$ calcd 358.9660, found 358.9661.

*Ethyl 2,2-Difluoro-2-(6,8-dibromo-2-oxo-2H-chromen-3-yl)acetate (**3p**)*. Colorless oil (30 mg, 35%); IR (KBr) *v* 2959, 1729, 1448, 1081, 982, 781, 487 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.97 (d, *J* = 1.6 Hz, 1H), 7.71 (d, *J* = 1.6 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -106.3 (s, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.8 (t, $J_{C\text{-}F}$ = 32.4 Hz), 156.3 (t, $J_{C\text{-}F}$ = 4.2 Hz), 150.1, 140.4 (t, $J_{C\text{-}F}$ = 7.1 Hz), 139.1, 130.6, 123.1 (t, $J_{C\text{-}F}$ = 25.9 Hz), 119.8, 117.7, 111.6, 110.0 (t, $J_{C\text{-}F}$ = 250.6 Hz), 63.8, 13.8; HRMS (ESI): $C_{13}H_8Br_2F_2NaO_4^+$ $[M+Na]^+$ calcd 446.8650, found 446.8651.

*3-(1,1-Difluoro-2-oxo-2-(pyrrolidin-1-yl)ethyl)-2H-chromen-2-one (**3q**)*. White solid (27 mg, 46%), m.p. 170-171 ℃; IR (KBr) *v* 2959, 1729, 1448, 1291, 982, 781, 487 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.57-7.62 (m, 2H), 7.33-7.37 (m, 2H), 3.89 (t, *J* = 6.8 Hz, 2H), 3.59 (t, *J* = 6.8 Hz, 2H), 2.02 (p, *J* = 6.7 Hz, 2H), 1.89 (p, *J* = 6.7 Hz, 2H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ −103.5 (s, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.7 (t, $J_{C\text{-}F}$ = 29.4 Hz), 157.8 (t, $J_{C\text{-}F}$ = 3.8 Hz), 154.3, 141.3 (t, $J_{C\text{-}F}$ = 7.5 Hz), 133.2, 129.0, 124.9, 122.5 (t, $J_{C\text{-}F}$ = 25.7 Hz), 117.8, 116.8, 114.0 (t, $J_{C\text{-}F}$ = 256.1 Hz), 48.0, 46.8 (t, $J_{C\text{-}F}$ = 6.5 Hz), 26.6, 23.3; HRMS (ESI): $C_{15}H_{13}NF_2NaO_3^+$ $[M+Na]^+$ calcd 316.0756, found 316.0757.

*N-benzyl 2,2-Difluoro-2-(2-oxo-2H-chromen-3-yl)acetamide (**3r**)*. White solid (20 mg, 30%), m.p. 142-144 ℃; IR (KBr) *v* 2959, 1729, 1448, 1376, 1081, 781, 487 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.53-7.58 (m, 2H), 7.22-7.30 (m, 7H), 7.05 (s, 1H), 4.50 (d, *J* = 5.6 Hz, 2H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -107.2 (s, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.6 (t, $J_{C\text{-}F}$ = 28.9 Hz), 157.9 (t, $J_{C\text{-}F}$ = 4.0 Hz), 154.3, 143.2 (t, $J_{C\text{-}F}$ = 7.4 Hz), 136.7, 133.7, 129.3, 128.9, 127.87, 127.85, 125.2, 120.7 (t, $J_{C\text{-}F}$ = 25.9 Hz), 117.6, 116.9, 112.4 (t, $J_{C\text{-}F}$ = 254.4 Hz), 43.9; HRMS (ESI):

$C_{18}H_{13}NF_2NaO_3^+$ $[M+Na]^+$ calcd 352.0756, found 352.0739.

*Methyl (2,2-difluoro-2-(2-oxo-2H-chromen-3-yl)acetyl)glycinate (**3s**)*. White solid (30 mg, 51%), m.p. 146-147 ℃; IR (KBr) *v* 22924, 1748, 1468, 1201, 1017, 970, 460 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.60-7.65 (m, 2H), 7.36-7.38 (m, 2H), 5.30 (s, 1H), 4.17 (d, J = 5.2 Hz, 2H), 3.80 (s, 3H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -107.2 (s, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.0, 162.8 (t, $J_{C\text{-}F}$ = 29.6 Hz), 157.9 (t, $J_{C\text{-}F}$ = 3.9 Hz), 154.3, 143.3 (t, $J_{C\text{-}F}$ = 7.3 Hz), 133.8, 129.3, 125.2, 120.4 (t, $J_{C\text{-}F}$ = 25.8 Hz), 117.6, 116.9, 112.2 (t, $J_{C\text{-}F}$ =254.3 Hz), 52.7, 41.5; HRMS (ESI): $C_{14}H_{11}NF_2KO_5^+$ $[M+K]^+$ calcd 350.0237, found 350.0265.

*3-(Benzo[d]oxazol-2-yldifluoromethyl)-2H-chromen-2-one (**3t**)*. White solid (22 mg, 35%), m.p. 142-143 ℃; IR (KBr) *v* 2959, 1729, 1448, 1376, 1081, 725, 487 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.63-7.68 (m, 3H), 7.46 (t, J = 7.7 Hz, 1H), 7.37-7.42 (m, 3H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -98.8 (s, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$, ***C*-*C***F_2 lost in the background noise) δ 155.5–156.4 (m, 2C, ***C***=O, ***C***=N), 153.5, 149.6, 141.6 (t, $J_{C\text{-}F}$ = 6.8 Hz), 139.1, 132.9, 128.4, 125.9, 124.3, 124.1, 120.3, 116.5, 115.9, 110.5; HRMS (ESI): $C_{17}H_9NF_2NaO_3^+$ $[M+Na]^+$ calcd 336.0443, found 336.0450.

*3-Trifluoromethyl-2H-chromen-2-one (**5a**)*.[9c] White solid (30 mg, 69%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.66-7.01 (m, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.36-7.42 (m, 2H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -66.2 (s, 3F).

*6-Methyl-3-trifluoromethyl-2H-chromen-2-one (**5b**)*.[9c] White solid (27 mg, 50%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.40 (s, 1H), 7.30 (d, J = 8.4 Hz, 1H), 2.45 (s, 3H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -66.1 (s, 3F).

*6-Chloro-3-trifluoromethyl-2H-chromen-2-one (**5c**)*.[9d] White solid (44 mg, 88%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.62-7.64 (m, 2H), 7.36 (d, J = 8.4 Hz, 1H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -66.3 (s, 3F).

*7-Methoxy-3-trifluoromethyl-2H-chromen-2-one (**5d**)*.[6c] White solid (35 mg, 72%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.50 (d, J = 8.8 Hz, 1H), 6.92 (dd, J = 8.8, 1.6 Hz, 1H), 6.84 (d, J = 2.0 Hz, 1H), 3.91 (s, 3H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -65.7 (s, 3F).

*3-(Perfluorobutyl)-2H-chromen-2-one (**5e**)*.[17] White solid (50 mg, 69%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.70 (t, J = 7.9 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.37-7.41 (m, 2H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -80.9 (t, J = 9.3 Hz, 3F), -111.2 (t, J = 13.7 Hz, 2F), -121.4 – -121.7 (m,

2F), -125.5 – -126.0 (m, 2F).

*5-Chloro-3-(perfluorobutyl)-2H-chromen-2-one (**5f**)*. White solid (33 mg, 53%), m.p. 65-67 ℃; IR (KBr) *v* 3325, 3066, 1731, 1350, 1063, 973, 695, 458 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.62 (t, J = 8.0 Hz,1H), 7.43 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -80.8 – -80.9 (m, 3F), -111.2 (t, J = 12.7 Hz, 2F), -121.4 – -121.5 (m, 2F), -125.8 – -125.9 (m, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$, $\underline{\boldsymbol{C}}_4F_9$-carbons lost in the background noise) δ 155.7, 154.6, 142.8 (t, $J_{C\text{-}F}$ = 8.6 Hz), 134.7, 134.1, 125.8, 117.4 (t, $J_{C\text{-}F}$ = 24.4 Hz), 115.8, 115.7, 114.1 (t, $J_{C\text{-}F}$ = 33.7 Hz); HRMS (ESI): $C_{13}H_4ClF_9NaO_2^+$ $[M+Na]^+$ calcd 420.9648, found 420.9616.

*6-Methyl-3-(perfluorobutyl)-2H-chromen-2-one (**5g**)*. White solid (33 mg, 53%), m.p. 80-82 ℃; IR (KBr) *v* 3325, 3025, 1732, 1447, 1194, 973, 730, 421 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.33 (s, 1H), 7.21 (d, J = 8.4 Hz, 1H), 2.36 (s, 3H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -80.9 (t, J = 9.8 Hz, 3F), -111.2 (t, J = 13.6 Hz, 2F), -121.6 – -121.7 (m, 2F), -125.8 – -126.0 (m, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$, $\underline{\boldsymbol{C}_4}F_9$-carbons lost in the background noise) δ 155.6, 153.1, 146.4 (t, $J_{C\text{-}F}$ = 8.1 Hz), 135.8, 135.1, 129.2, 116.8, 116.6, 116.3, 20.6; HRMS (ESI): $C_{14}H_7F_9KO_2^+$ $[M+K]^+$ calcd 416.9934, found 416.9975.

*7-Methoxy-3-(perfluorobutyl)-2H-chromen-2-one (**5h**)*.[18] White solid (50 mg, 69%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.51 (d, J = 8.4 Hz, 1H), 6.92 (dd, J = 8.8 Hz, 1.6 Hz, 1H), 6.84 (s, 1H), 3.91 (s, 3H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -80.9 − -81.0 (m, 3F), -111.0 (t, J = 13.7 Hz, 2F), -121.7 − -121.8 (m, 2F), -125.8 − -125.9 (m, 2F).

*8-Chloro-3-(perfluorobutyl)-2H-chromen-2-one (**5i**)*. White solid (33 mg, 53%), m.p. 68−69 ℃; IR (KBr) *v* 3325, 2921, 1731, 1350, 1194, 973, 695, 458 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.30-7.35 (m, 1H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -80.9 − -80.8 (m, 3F), -111.2 (t, J = 13.2 Hz, 2F), -121.6 − -121.4 (m, 2F), -125.9 − -125.6 (m, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$, one of Ar-$\underline{\boldsymbol{C}}$ and $\underline{\boldsymbol{C}}$-$\underline{\boldsymbol{C}_4}F_9$-carbons lost in the background noise) δ 155.7, 154.7, 142.9 (t, $J_{C\text{-}F}$ = 8.2 Hz), 134.8, 134.1, 125.8, 115.8; HRMS (ESI): $C_{13}H_4ClF_9NaO_2^+$ $[M+Na]^+$ calcd 420.9648, found 420.9644.

*3-(Perfluorohexyl)-2H-chromen-2-one (**5j**)*.[19] White solid (45 mg, 48%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.63-7.71 (m, 2H), 7.37-7.40 (m, 2H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -80.7 – -80.9 (s, 3F), -111.0 – -111.1 (m, 2F), -120.8 (s, 2F), -121.7 (s, 2F), -122.7 (s, 2F), -126.1 (s, 2F).

*6-Chloro-3-(perfluorohexyl)-2H-chromen-2-one (**5k**)*. White solid (33 mg, 53%), m.p. 97-98 ℃; IR (KBr) *v* 2924, 1748, 1468, 1282, 1017, 744, 460 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.63-7.65 (m, 2H), 7.36 (d, J = 9.2 Hz, 1H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -80.8 (t, J = 9.9 Hz, 3F), -111.2 (t, J = 14.2 Hz, 2F), -119.9 – -121.1 (m, 2F), -121.7 (s, 2F), -122.7 (s, 2F) , -126.2 (td, J = 14.4, 6.5 Hz, 2F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$, ***C*-*C*$_6$**F_{13}-carbons lost in the background noise) δ 154.8, 153.3, 145.3 (t, J_{C-F} = 8.2 Hz), 134.7, 130.6, 128.6, 118.4, 117.9; HRMS (ESI): $C_{15}H_4ClF_{13}NaO_2^+$ $[M+Na]^+$ calcd 520.9584, found 520.9589.

*3-(Perfluorooctyl)-2H-chromen-2-one (**5l**)*.[17] White solid (50 mg, 44%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.63 (d, J = 6.8 Hz, 1H), 7.36-7.41 (m, 2H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -80.9 (t, J = 9.8 Hz, 3F), -111.0 (t, J = 14.1 Hz, 2F), -120.6 (s, 2F), -121.7 (s, 2F), -121.9 (s, 2F), -121.4 (s, 2F), -122.7 (s, 2F), -126.0 – -126.2 (m, 2F).

*3-(iso-Perfluoropropyl)-2H-chromen-2-one (**5m**)*. White solid (33 mg, 53%), m.p. 68-70 ℃; IR (KBr) *v* 2924, 1748, 1468, 1201, 1017, 970, 460 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.63-7.71 (m, 2H), 7.37-7.42 (m, 2H); $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ -73.9 (d, J_{C-F} = 5.0 Hz 6F), -175.2 (*br* s, 1F); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$, ***C***-$F(CF_3)_2$ lost in the background noise) δ 155.8 (d, J_{C-F} = 6.2 Hz), 154.4, 145.5 (d, J_{C-F} = 16.9 Hz), 134.4, 129.3, 125.2, 120.1 (qd, J_{C-F} = 288.0, 27.3 Hz, ***C***F_3), 117.2 (d, J_{C-F} = 2.5 Hz), 116.8, 115.9 (d, J_{C-F} = 22.7 Hz); HRMS (ESI): $C_{12}H_5F_7NaO_2^+$ $[M+Na]^+$ calcd 337.0070, found 337.0079.

ASSOCIATED CONTENT

Supporting Information

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

The setup for this blue LEDs-driven reaction.

^{1}H NMR spectra for compounds **1a-1p**.

^{1}H NMR and ^{19}F NMR spectra for compounds **3a-3t and 5a-5m.**

^{13}C NMR spectra for the new compounds of **1**, **3** and **5.**

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Notes

The authors declare no competing financial interest.

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