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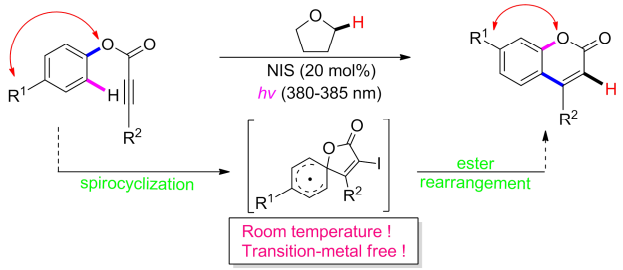

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Photoinduced Cyclization of Alkynoates to Coumarins with *N*-Iodosuccinimide as a Free-radical Initiator under Ambient and Metal-free Conditions

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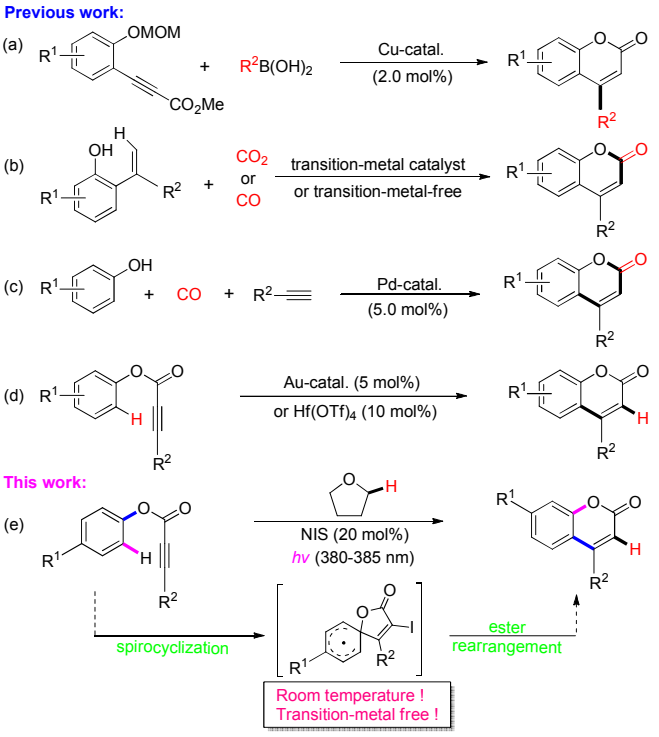
ABSTRACT

An efficient photoinduced strategy for the preparation of coumarins was developed. In the presence of *N*-iodosuccinimide (NIS) as a free-radical initiator and under LED (380–385 nm) irradiation and metal-free conditions, the reaction of alkynoates underwent smoothly to afford the corresponding coumarins in high yields at room temperature with broad substrate scope via free radical intramolecular cyclization and ester rearrangement.

1. Introduction

Coumarin and its derivatives are privileged oxygen heterocycles, which are widely distributed throughout the animals, plants and microorganisms.[1] They display a broad variety of biological and pharmacological activities, such as anti-HIV,[2] anti-coagulant,[3] anti-bacterial,[4] anti-oxidant,[5] anti-diabetic[6] and so on. Furthermore, they are also used as additives in food and cosmetics,[7] and in the preparation of insecticides, optical brighteners,[8] dispersed fluorescence and laser dyes.[9] In general, coumarin core is prepared through a variety of organic transformations. There are several superior methods recommended by organic chemists. For example, Yamamoto established an efficient Cu-catalyzed hydroarylation from methyl phenylpropiolates with a MOM-protected hydroxy group at the *ortho*-position with arylboronic acids to 4-arylcoumarins (Scheme 1a).[10] Iwasawa reported a Pd-catalyzed direct carboxylation of alkenyl C−H bonds with CO_2, leading to a redox-neutral access to coumarins (Scheme 1b).[11] In 2017, Yu *et al.* disclosed a transition-metal free lactonization of heteroaryl and alkenyl C−H bonds with CO_2 to coumarin derivatives (Scheme 1b).[12] In addition, Alper, Gulías and Wang realized transition-metal-catalyzed oxidative cyclocarbonylation of 2-vinyphenols with CO in the presence of Pd-, Rh- or Co-catalyst (Scheme 1b).[13] Most recently, Wu discovered a Pd-catalyzed oxidative carbonylation procedure for the synthesis of coumarins from phenols, terminal alkynes and CO (Scheme 1c).[14] In 2004, Song and He developed the intramolecular Friedel–Crafts alkenylations of aryl phenyl propiolates catalyzed by $Hf(OTf)_4$ or Au(III), independently



Scheme 1. Synthesis of coumarins

(Scheme 1d).[15] Although considerable progress has been made in this field, the existing methods suffer from drawbacks such as narrow substrate scope, harsh reaction

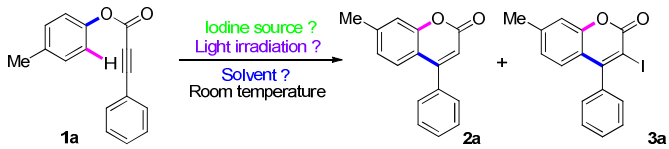
conditions, need of catalyst or high toxic CO as reagent in the most of cases. Thus, developing a facile, efficient and metal-free method to synthesize coumarins with broad functional group tolerance, mild and environmental-friendly conditions is highly desirable.

Visible light as a rich and green energy source has been shown to induce large amounts of organic transformations through electron transfer, energy transfer and hydrogen transfer processes. Photo-catalytic strategies can provide a better choice for organic synthesis because it avoids additional metals, ligands and high temperature. Visible-light promoted organic reactions have received the considerable attention, and emerged as a hot research topic in chemistry during the past few years.[16] Recently, Pan and She reported the visible-light induced synthesis of 3-halocoumarins from alkynoates, respectively.[17] In this manuscript, we wish to report an alternative and straightforward route to coumarins from the corresponding alkynoates via a photoinduced intramolecular cyclization and ester rearrangement. The reaction underwent smoothly with *N*-iodosuccinimide (NIS) as free-radical initiator under photo-irradiation, ambient and metal-free conditions, which generated the desired products in high yields with broad substrate scope (Scheme 1e).

2. Results and discussion

For the optimization of the reaction conditions, a model reaction of *p*-tolyl 3-phenylpropiolate (**1a**) was chosen and the reaction was carried out at a 0.20 mmol scale. When the model reaction was performed in the presence of C_6H_5I (1.0 equiv.) as the free radical initiator in toluene at room temperature under LED (365–370 nm) irradiation in air for 8 h, the desired product **2a** was isolated in 17% yield with a trace amount of product 3-iodocoumarin (**3a**) (Table 1, entry 1). The structure of **2a** was characterized by ^{1}H and ^{13}C NMR, and further confirmed by X-ray single crystal analysis.[18] To further evaluate the feasibility of the reaction, solvent effect was examined, and the results were listed in entries 2–6 of Table 1. None of **2a** was obtained when the reaction was conducted in DCE (1,2-dichloroethane) or CH_3CN, and only 10–12% yields of **3a** was generated (Table 1, entries 2 and 3). Neither **2a** nor **3a** was detected as the model reaction was performed in DMSO or DMF (Table 1, entries 4 and 5). To our delight, 28% yield of **2a** was acquired along with a neglectable amount of **3a** when THF was used as solvent (Table 1, entry 6). In order to increase the yield of the desired product, some iodine sources were screened. An improved yield (46%) of **2a** was obtained when *N*-iodosuccinimide (NIS, 1.0 equiv.) was used as free radical initiator, with 16% yield of product **3a** (Table 1, entry 7). Other iodine sources, such as tetrabuylammonium iodide (TBAI) and I_2 failed to improve the yield of desired product (Table 1, entries 8 and 9). To improve the yield of the target product **2a**, and reduce the yield of by-product **3a**, we tried to change the amount of NIS added in the reaction, and the results were summarized in Table 1 (entries 10–15). Surprisingly, when 20 mol% of NIS was used, the yield of **2a** was reached to 91% and almost no by-product **3a** was generated (Table 1, entry 10). More than 35 mol% of NIS or less than 20 mol% of NIS was added, inferior yields of product **2a** were found (Table 1, entries 11–15). Considering the influence of the light source on the reaction, a series of light sources were tested and the optical wavelength in the range of 380–385 nm is best, yielding **3a** in an almost quantitative yield (Table 1, entry 16). Other light sources, including 254, 395–405, 410–415, 420–425, 450–455, 515–520, 520–525, 530–535 nm and white light were no longer the effective ones, and almost no **2a** was observed (Table 1, entries 17–25). Further investigation explored that the optimal reaction time is 8 h (Table 1, entries 26–29).

Table 1. Optimization of the reaction conditions[a]



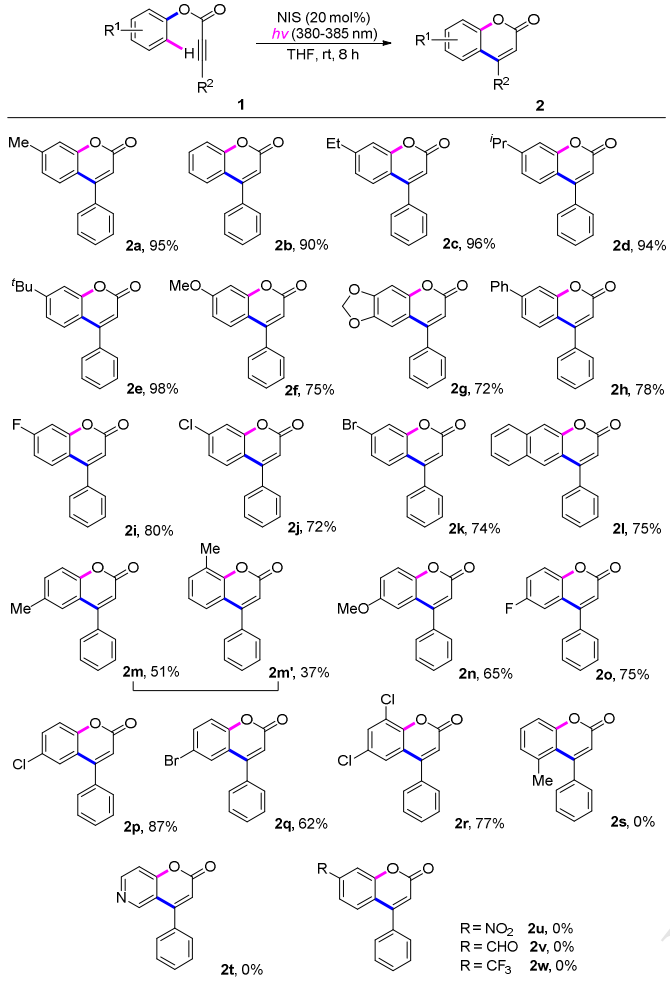
1a 2a 3a

Entry	Iodine source	Solvent	Light source	Yield (**2a**/**3a**, %)[b]
1	C_6H_5I (1 equiv.)	Toluene	365–370 nm	17/Trace
2	C_6H_5I (1 equiv.)	DCE	365–370 nm	0/10
3	C_6H_5I (1 equiv.)	CH_3CN	365–370 nm	0/12
4	C_6H_5I (1 equiv.)	DMSO	365–370 nm	0/0
5	C_6H_5I (1 equiv.)	DMF	365–370 nm	0/0
6	C_6H_5I (1 equiv.)	THF	365–370 nm	28/Trace
7	NIS (1 equiv.)	THF	365–370 nm	46/16
8	TBAI (1 equiv.)	THF	365–370 nm	0/0
9	I_2 (1 equiv.)	THF	365–370 nm	19/15
10	NIS (20 mol%)	THF	365–370 nm	91/Trace
11	NIS (50 mol%)	THF	365–370 nm	87/Trace
12	NIS (35 mol%)	THF	365–370 nm	90/Trace
13	NIS (15 mol%)	THF	365–370 nm	82/0
14	NIS (10 mol%)	THF	365–370 nm	57/0
15	NIS (5 mol%)	THF	365–370 nm	25/0
16	*NIS (20 mol%)*	*THF*	*380–385 nm*	*95/0*
17	NIS (20 mol%)	THF	254 nm	Trace/15
18	NIS (20 mol%)	THF	395–405 nm	Trace/23
19	NIS (20 mol%)	THF	410–415 nm	0/20
20	NIS (20 mol%)	THF	420–425 nm	0/23
21	NIS (20 mol%)	THF	450–455 nm	0/25
22	NIS (20 mol%)	THF	515–520 nm	0/25
23	NIS (20 mol%)	THF	520–525 nm	0/24
24	NIS (20 mol%)	THF	530–535 nm	0/22
25	NIS (20 mol%)	THF	White light (18 W)	Trace/23
26	NIS (20 mol%)	THF	380–385 nm	30/15[c]
27	NIS (20 mol%)	THF	380–385 nm	63/12[d]
28	NIS (20 mol%)	THF	380–385 nm	78/Trace[e]
29	NIS (20 mol%)	THF	380–385 nm	88/0[f]

[a]Reaction conditions: **1a** (0.20 mmol), solvent (2.0 mL) at room temperature in air under light irradiation for 8 h. [b]Isolated yield. [c]2 h. [d]4 h. [e]6 h. [f]10 h.

With the optimized reaction conditions in hand, we then probed into the generality of reaction. Firstly, some substituted groups including typical electron-withdrawing and electron-donating groups on the aromatic rings of the ester moieties in substrates **1** were surveyed, shown in Scheme 2. In general, these groups at the *para*-position of the benzene rings resulted in high yields of the desired products (**2a**–**2k**). However, when the *para*-position of the aromatic ring in the ester moiety is replaced by a strong electron-withdrawing group (NO_2, CHO or CF_3), no products (**2u**–**2w**) were observed. Naphthalen-2-yl 3-phenylpropiolate is also a suitable substrate, forming an anticipated product **2l** in 75%

Scheme 2. The scope of phenol moiety in the substrates[a]

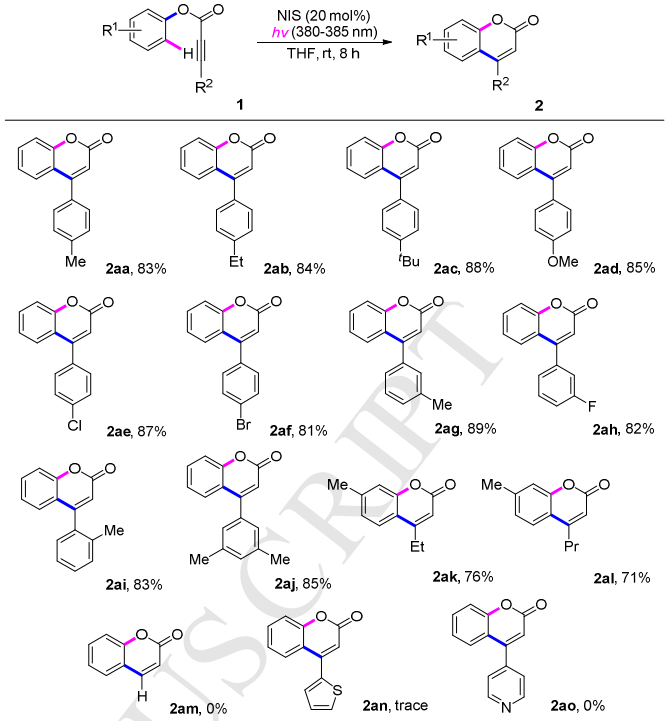


[a]Reaction conditions: **1** (0.20 mmol), NIS (20 mol%), THF (2.0 mL), room temperature, LED (380–385 nm, 1.5 W) irradiation for 8 h.

yield. In addition, when the meta-position of the aromatic ring in the ester moiety is substituted by a methyl group, two regio-isomers (2m and 2m') were generated in 51% and 37% yields. On the other hand, *meta*-substituted groups including MeO, F, Cl and Br on the substrates afforded the expected products (**2n**–**2q**) in good yields with excellent regio-selectivity. It is noteworthy that the reaction of 3,5-dichlorophenyl 3-phenylpropiolate underwent well to generate the corresponding product **2r** in 77% yield under optimal reaction conditions. Unfortunately, the use of *ortho*-substituted substrates and heterocyclic substrates failed in this reaction, no any desired products (**2s** and **2t**) were detected.

We continued our investigation on the scope of propiolic acid unit in the substrates under the optimized reaction conditions. As shown in Scheme 3, substrates derived from 3-arylpropiolic acids with the different electron-donating groups (Me, Et, ^{t}Bu and MeO) or electron-withdrawing groups (F, Cl and Br) on the aromatic rings underwent the reaction smoothly to afford the corresponding products (**2aa**–**2ai**) in good yields (81–89%). Furthermore, phenyl 3-(3,5-dimethylphenyl)propiolate was performed under the present reaction conditions to produce the target product **2aj** in 85% yield. For substrates from 3-alkylpropiolic acids, such as 3-ethylpropiolic acid and 3-propylpropiolic acid, the corresponding products 4-ethyl-7-methyl-2*H*-chromen-2-one (**2ak**) and 7-

Scheme 3. The scope of propiolic acid unit in the substrates[a]

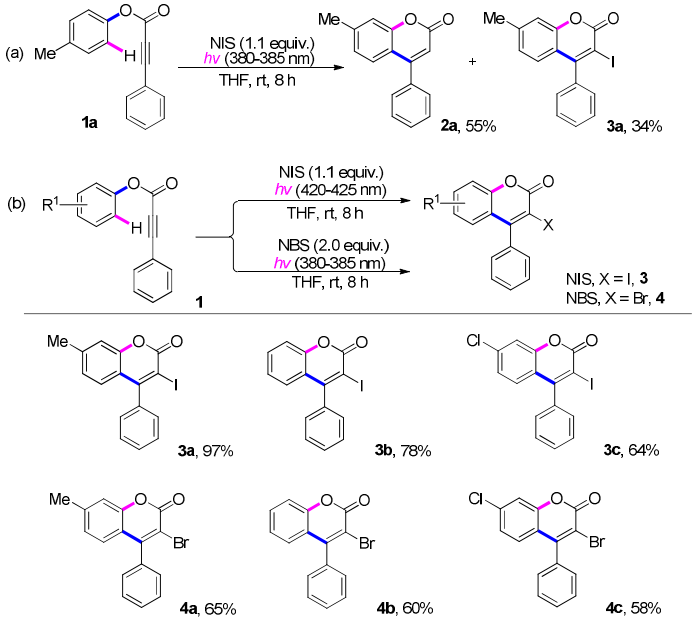


[a]Reaction conditions: **1** (0.20 mmol), NIS (20 mol%), THF (2.0 mL), room temperature, LED (380–385 nm, 1.5 W) irradiation for 8 h.

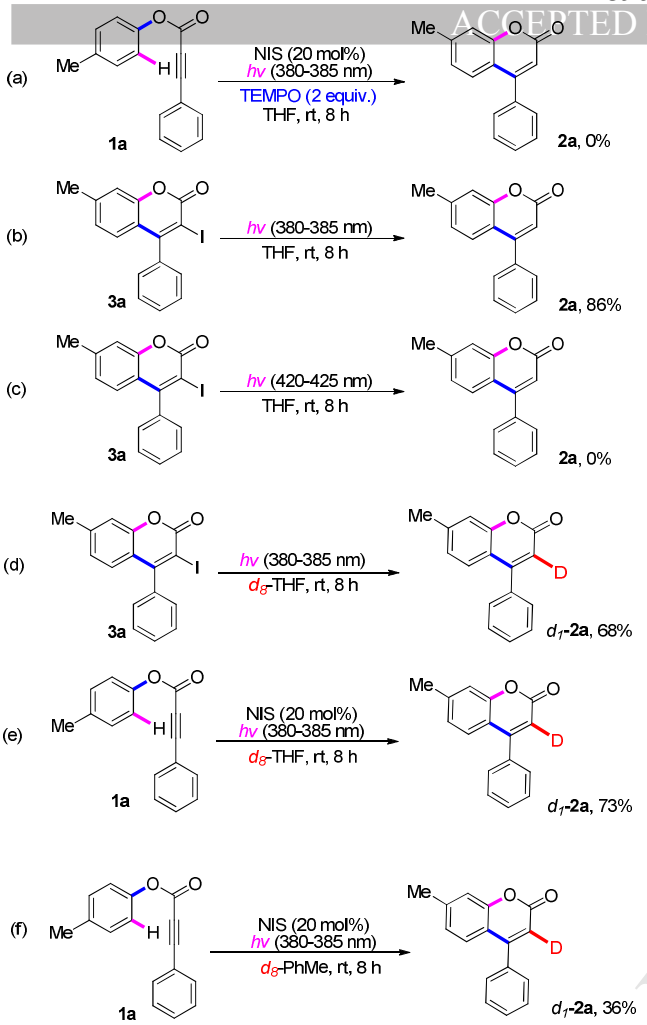
methyl-4-propyl-2H-chromen-2-one (**2al**) were generated in 76% and 71% isolated yields, respectively. When phenyl propiolate (**1m**) was used in the reaction, no desired product (**2am**) was detected. However, substrates prepared from 3-(2-thiphenyl) propiolic acid and 3-(3-pyridyl) propiolic acid showed the negative effect for the reaction, and no any products were observed (**2an** and **2ao**).

To gain insights into the reaction mechanism, the relationship of optical wavelength with the ratio of **2a**/**3a** was investigated, shown in Scheme 4, as well as in Table 1. When the model reaction of **1a** was carried out in the presence of NIS (1.1 equiv.) under the

Scheme 4. The formation of halogenation products[a]



[a]Reaction conditions: **1** (0.20 mmol), NIS or NBS, THF (2.0 mL), room temperature, LED irradiation for 8 h.

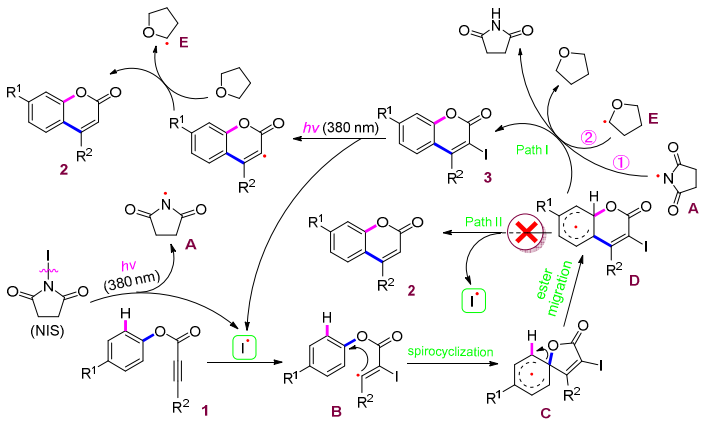


Scheme 5. The control experiments

irradiation of blue LED (420–425 nm) for 8 h, iodination product (**3a**) was achieved in 97% yield with a trace amount of deiodination product (**2a**) (Scheme 4b). When LED (380–385 nm) was used, iodination product (**3a**) and deiodination product (**2a**) were achieved in 34% and 55% yields, respectively (Scheme 4a). On the contrary, when **1a** was performed with NIS (20 mol%) under the irradiation of LED (380–385 nm) for 8 h, **2a** was got 95% yield, and no **3a** was detected (Table 1, entry 16). The preliminary results indicated that the wavelength of light and loading of NIS play important roles in the formation of deiodination product (**2a**) and iodination product (**3a**). The generality about the formation of iodination products (**3**) from the corresponding starting materials (**1**) in the presence of NIS (1.1 equiv.) under the irradiation of blue LED (420–425 nm) was examined, listed in Scheme 4, which is in accordance with Han and Pan's results.[17a] Further investigation was extended to competition of bromination and debromination processes using *N*-bromosuccinimide (NBS). The results shown in Scheme 4 also indicated that bromination products (**4**) could be obtained in good yields, and no any debromination products were found when the reaction started in the presence of NBS (2.0 equiv.) under the irradiation of LED (380–385 nm). In addition, the chlorination and dechlorination could not occur even the reaction of **1a** was carried out with NCS (2.0 equiv.) and LED (380–385 nm) irradiation for prolonged time. These facts demonstrated that the reactivity order of C–X bond is C–I > C–Br > C–Cl via free radical pathway, and dehalogenation process is from the corresponding halogenation products.

In order to understand the reaction process clearly, when 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), a radical scavenger, was added into the solution of **1a** in THF under standard conditions, the reaction was completely inhibited (Scheme 5a), indicating the conversion may be involved in a free radical process. According to possibility of **2a** from **3a**, when prepared **3a** was added to the solvent of THF and irradiated under LED (380–385 nm) for 8 h, providing **2a** in 86% yield (Scheme 5b). However, no **2a** was obtained when the reaction was irradiated with LED light of 420–425 nm. This phenomenon indicated that C–I bond of **3a** was cleavage by LED light (380–385 nm), but now with LED light (420-425 nm) failed (Scheme 5c). Subsequently, the hydrogen source for **3a** to **2a** was examined, and the solvent THF is confirmed to be the hydrogen transfer reservoir in the reaction from the control experiments of **3a** and **1a** in d_8-THF solution under the irradiation of LED (380–385 nm), providing d_1-**2a** in 68% and 73 % yield, respectively (Scheme 5d and 5e). We repeated the reaction again by using d_8-toluene as solvent, and d_1-**2a** was isolated in 36% yield under the standard reaction conditions, illustrating that the 3-hydrogen comes from solvent (Scheme 5f, see SI for details).

Based on the experimental results and related literature,[17a] a possible mechanism is illustrated in Scheme 6. Under light (380–385 nm) irradiation, the homolytic cleavage of *N*-iodosuccinimide generated succinimide free radical **A** and iodine radical, which underwent an addition to carbon-carbon triple bond of alkynoate to form an intermediate **B**, followed by an intramolecular radical addition, providing an intermediate **C**. Then, the obtained **C** proceeded an intramolecular ester rearrangement to afford intermediate **D**, which reacted with succinimide radical **A** (via ① in first priority) or alkoxyalkyl radical **E** (via ② in cycle-run) via a hydrogen atom abstraction, affording iodination product **3** (Path I). Under LED (380 nm) continuing irradiation, the iodination **3** could be converted into the deiodination product **2** through a homolytic cleavage C–I of vinyl iodide and protonation sequence reaction. It should be noted that the formation of **2** via Path II could be ruled out (^{1}H NMR of d_1-**2a** in SI).



Scheme 6. Proposed mechanism

3. Conclusions

In conclusion, we have developed a straightforward method for the synthesis of coumarins from the corresponding alkynoates via a photoinduced intramolecular cyclization. The reaction underwent smoothly with *N*-iodosuccinimide as free-radical initiator under irradiation of LED (380–385 nm) and metal-free conditions at room temperature, providing the desired products in good to excellent yields with broad substrate scope. A preliminary mechanism indicated that this transformation is involved in a free radical process. Further efforts are being carried out to investigate the potential application of this

methodology in our laboratory.

4. Experimental Section

General Considerations

All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (400 MHz or 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

Aryl alkynoates were prepared according to the reported method.[19] The chemicals and solvents were purchased from commercial suppliers either from Aldrich (USA) or Shanghai Chemical Company (China) without further purification. All the solvents were dried and freshly distilled prior to use. All the reactions were carried out under air atmosphere. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2.

Typical procedure for cyclization of alkynoates to coumarins with N-iodosuccinimide

A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with *p*-tolyl 3-phenylpropiolate (**1a**, 47.2 mg, 0.20 mmol), *N*-iodosuccinimide (NIS, 9.0 mg, 20 mol%) and THF (2.0 mL). The reaction vessel was exposed to LED (380–385 nm, 1.5 W) irradiation at room temperature in air with stirring for 8 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20/1) to give the desired product **2a** (44.8 mg, 95% yield).

5. Spectral Data

*5.1. 7-Methyl-4-phenyl-2H-chromen-2-one (**2a**):*[20]

Light yellow solid. m.p. 89.1–89.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52–7.50 (m, 3H), 7.44–7.42 (m, 2H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.19 (s, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.29 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.84, 155.51, 154.15, 143.06, 135.26, 129.48, 128.69, 128.27, 126.55, 125.23, 117.28, 116.40, 113,86, 21.45. HRMS (ESI) ($[M + H]^+$) calcd for $C_{16}H_{12}O_2$: 237.0910, found: 237.0916.

*5.2. 4-Phenyl-2H-chromen-2-one (**2b**):*[15b]

Light yellow solid. m.p. 89.1–90.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57–7.55 (m, 1H), 7.54–7.52 (m, 3H), 7.51–7.49 (m, 1H), 7.46–7.44 (m, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.25–7.21 (m, 1H), 6.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.59, 155.54, 154.06, 135.06, 131.82, 129.59, 128.76, 128.31, 126.90, 124.07, 118.85, 117.17, 115,04. HRMS (ESI) ($[M + H]^+$) calcd for $C_{15}H_{10}O_2$: 223.0754, found: 223.0757.

*5.3. 7-Ethyl-4-phenyl-2H-chromen-2-one (**2c**):*

Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52–7.50 (m, 3H), 7.44–7.42 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.22 (s, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.29 (s, 1H), 2.76–2.71 (m, 2H), 1.29–1.25 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.76, 155.44, 154.22, 149.23, 135.21, 129.42, 128.63, 128.20, 126.63, 124.02, 116.51, 116.00, 113,83, 28.62, 14.90. HRMS (ESI) ($[M + H]^+$) calcd for $C_{17}H_{14}O_2$: 251.1067, found: 251.1069.

*5.4. 7-(iso-Propyl)-4-phenyl-2H-chromen-2-one (**2d**):*

Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52–7.51 (m, 3H), 7.45–7.43 (m, 2H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.26 (s, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.31 (s, 1H), 3.05–2.95 (m, 1H), 1.29 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.91, 155.52, 154.33, 153.95, 135.30, 129.48, 128.70, 128.27, 126.74, 122.73, 116.72, 114.73, 113,95, 34.02, 23.49. HRMS (ESI) ($[M + H]^+$) calcd for $C_{18}H_{16}O_2$: 265.1223, found: 265.1222.

*5.5. 7-(tert-Butyl)-4-phenyl-2H-chromen-2-one (**2e**):*

Light yellow solid. m.p. 141.7–141.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51–7.50 (m, 3H), 7.44–7.40 (m, 4H), 7.28–7.25 (m, 1H), 6.29 (s, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.65, 156.09, 155.16, 153.98, 135.08, 129.36, 128.56, 128.11, 126.30, 121.42, 116.14, 113.90, 113,75, 34.86, 30.73. HRMS (ESI) ($[M + H]^+$) calcd for $C_{19}H_{18}O_2$: 279.1380, found: 279.1380.

*5.6. 7-Methoxy-4-phenyl-2H-chromen-2-one (**2f**):*[11]

Light yellow solid. m.p. 152.2–152.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52–7.50 (m, 3H), 7.45–7.42 (m, 2H), 7.38 (d, *J* = 8.9 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.81–6.78 (m, 1H), 6.21 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.90, 161.08, 155.91, 155.71, 135.46, 129.49, 128.72, 128.27, 127.88, 112.39, 111.73, 101.01, 55.70. HRMS (ESI) ($[M + H]^+$) calcd for $C_{16}H_{12}O_3$: 253.0859, found: 253.0854.

*5.7. 8-Phenyl-6H-[1,3]dioxolo[4,5-g]chromen-6-one (**2g**):*[22]

Light yellow solid. m.p. 142.2–144.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52–7.50 (m, 3H), 7.45–7.39 (m, 2H), 6.88 (s, 1H), 6.82 (s, 1H), 6.23 (s, 1H), 6.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.10, 155.82, 151.27, 151.09, 144.77, 135.60, 129.54, 128.83, 128.17, 112.76, 112.12, 104.28, 102.31, 98.47. HRMS (ESI) ($[M + H]^+$) calcd for $C_{16}H_{10}O_4$: 267.0652, found: 267.0655.

*5.8. 4,7-Diphenyl-2H-chromen-2-one (**2h**):*[23]

Light yellow solid. m.p. 144.4–144.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63–7.60 (m, 3H), 7.56–7.53 (m, 4H), 7.49–7.39 (m, 6H), 6.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.75, 155.35, 154.53, 144.94, 138.90, 135.15, 129.66, 129.03, 128.84, 128.51, 128.36, 127.27, 127.13, 122.90, 117.81, 115.28, 114.68. HRMS (ESI) ($[M + H]^+$) calcd for $C_{21}H_{14}O_2$: 299.1067, found: 299.1069.

*5.9. 7-Fluoro-4-phenyl-2H-chromen-2-one (**2i**):*

Light yellow solid. m.p. 119.4–120.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55–7.53 (m, 3H), 7.51–7.47 (m, 1H), 7.45–7.43 (m, 2H), 7.14–7.11 (m, 1H), 7.00–6.85 (m, 1H), 6.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.46 (d, *J* = 252.8 Hz), 160.31, 155.43, 155.27 (d, *J* = 6.2 Hz), 135.02, 129.84, 128.97, 128.73 (d, *J* = 10.0 Hz), 128.31, 115.74 (d, *J* = 2.7 Hz), 113.91 (d, *J* = 2.6 Hz), 112.17 (d, *J* = 22.3 Hz), 104.72 (d, *J* = 25.3 Hz). HRMS (ESI) ($[M + H]^+$) calcd for $C_{15}H_9FO_2$: 241.0659, found: 241.0662.

*5.10. 7-Chloro-4-phenyl-2H-chromen-2-one (**2j**):*[24]

Light yellow solid. m.p. 176.9–177.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55–7.53 (m, 3H), 7.44–7.41 (m, 4H), 7.22–7.19 (m, 1H), 6.36 (s, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ: 159.96, 155.00, 154.51, 137.82, 134.74, 129.88, 128.97, 128.28, 127.88, 124.67, 117.60, 117.47, 114.94. HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_9ClO_2$: 257.0364, found: 257.0369.

*5.11. 7-Bromo-4-phenyl-2H-chromen-2-one (**2k**):*[24]

Light yellow solid. m.p. 138.3–139.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57–7.53 (m, 4H), 7.44–7.43 (m, 2H), 7.35 (m, 2H), 6.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.84, 155.05, 154.33, 134.67, 129.88, 128.97, 128.28, 127.99, 127.51, 125.84, 120.42, 117.96, 115.16. HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_9BrO_2$: 300.9859, found: 300.9864.

*5.12. 4-Phenyl-2H-benzo[g]chromen-2-one (**2l**):*[25]

Light yellow solid. m.p. 134.4–135.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63–8.61 (m, 1H), 7.87–7.84 (m, 1H), 7.67–7.63 (m, 2H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.57–7.54 (m, 3H), 7.51–7.45 (m, 3H), 6.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.74, 156.57, 151.47, 135.64, 134.82, 129.59, 128.86, 128.83, 128.48, 127.63, 127.15, 123.90, 123.36, 122.72, 122.34, 114.52, 114.20. HRMS (ESI) ([M + H]$^+$) calcd for $C_{19}H_{12}O_2$: 273.0910, found: 273.0909.

*5.13. 6-Methyl-4-phenyl-2H-chromen-2-one (**2m**):*[11]

Light yellow solid. m.p. 127.7–127.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54–7.52 (m, 3H), 7.47–7.43 (m, 2H), 7.37–7.34 (m, 1H), 7.30–7.28 (m, 1H), 7.25 (s, 1H), 6.34 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.84, 155.53, 152.22, 135.27, 133.79, 132.83, 129.51, 128.77, 128.32, 126.61, 118.57, 116.94, 115.05, 20.84. HRMS (ESI) ([M + H]$^+$) calcd for $C_{16}H_{12}O_2$: 237.0910, found: 237.0907.

*5.14. 8-Methyl-4-phenyl-2H-chromen-2-one (**2m'**):*[20]

Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53–7.51 (m, 3H), 7.45–7.43 (m, 2H), 7.40 (d, *J* = 1.9 Hz, 1H), 7.32 (d, *J* = 2.0 Hz, 1H), 7.14–7.10 (m, 1H), 6.36 (s, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.86, 156.03, 152.45, 135.52, 133.19, 129.50, 128.74, 128.42, 126.63, 124.74, 123.57, 118.69, 114.85, 15.74. HRMS (ESI) ([M + H]$^+$) calcd for $C_{16}H_{12}O_2$: 237.0910, found: 237.0912.

*5.15. 6-Methoxy-4-phenyl-2H-chromen-2-one (**2n**):*[12]

Light yellow solid. m.p. 149.8–150.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54–7.52 (m, 3H), 7.47–7.45 (m, 2H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.15–7.12 (m, 1H), 6.93 (d, *J* = 2.9 Hz, 1H), 6.38 (s, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.90, 155.84, 155.31, 148.54, 135.24, 129.67, 128.89, 128.30, 119.40, 118.95, 118.19, 115.60, 109.96, 55.75. HRMS (ESI) ([M + H]$^+$) calcd for $C_{16}H_{12}O_3$: 253.0859, found: 253.0855.

*5.16. 6-Fluoro-4-phenyl-2H-chromen-2-one (**2o**):*[26]

Light yellow solid. m.p. 172.8–173.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56–7.54 (m, 3H), 7.46–7.44 (m, 2H), 7.40–7.37 (m, 1H), 7.29–7.24 (m, 1H), 7.19–7.16 (m, 1H), 6.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.16, 158.54 (d, *J* = 242.2 Hz), 154.65 (d, *J* = 2.7 Hz), 150.20 (d, *J* = 1.6 Hz), 134.56, 129.88, 128.97, 128.17, 119.80 (d, *J* = 8.4 Hz), 119.20 (d, *J* = 24.5 Hz), 118.69 (d, *J* = 8.2 Hz), 115.98, 112.46 (d, *J* = 25.0 Hz). HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_9FO_2$: 241.0659, found: 241.0663.

*5.17. 6-Chloro-4-phenyl-2H-chromen-2-one (**2p**):*[21]

Light yellow solid. m.p. 150.4–151.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56–7.54 (m, 3H), 7.51–7.48 (m, 1H), 7.46–7.43 (m, 3H), 7.35 (d, *J* = 8.8 Hz, 1H), 6.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.94, 154.57, 152.60, 134.54, 131.84, 129.96, 129.64, 129.08, 128.27, 126.19, 118.71, 116.13. HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_9ClO_2$: 257.0364, found: 257.0370.

*5.18. 6-Bromo-4-phenyl-2H-chromen-2-one (**2q**):*[15b]

Light yellow solid. m.p. 134.4–135.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65–7.63 (m, 1H), 7.60–7.55 (m, 4H), 7.44 (s, 2H), 7.31–7.29 (m, 1H), 6.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.94, 154.53, 153.06, 134.72, 134.49, 130.00, 129.34, 129.11, 128.29, 120.65, 119.05, 117.00, 116.12. HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_9BrO_2$: 300.9859, found: 300.9861.

*5.19. 5,7-Dichloro-4-phenyl-2H-chromen-2-one (**2r**):*[27]

Light yellow solid. m.p. 139.2–139.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 2.4 Hz, 1H), 7.57–7.55 (m, 3H), 7.43–7.41 (m, 2H), 7.35 (d, *J* = 2.4 Hz, 1H), 6.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.68, 154.43, 148.58, 134.20, 131.90, 130.16, 129.29, 129.16, 128.26, 125.04, 123.19, 121.16, 116.70. HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_8Cl_2O_2$: 290.9974, found: 290.9979.

*5.20. 4-(p-Tolyl)-2H-chromen-2-one (**2aa**):* [10]

Light yellow solid. m.p. 124.3–125.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54–7.53 (m, 2H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.37–7.32 (m, 4H), 7.25–7.21 (m, 1H), 6.37 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.82, 155.70, 154.19, 139.87, 132.29, 131.79, 129.52, 128.37, 127.02, 124.05, 119.07, 117.27, 114.88, 21.32. HRMS (ESI) ([M + H]$^+$) calcd for $C_{16}H_{12}O_2$: 237.0910, found: 237.0910.

*5.21. 4-(4-Ethylphenyl)-2H-chromen-2-one (**2ab**):*[28]

Light yellow solid. m.p. 125.4–126.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56–7.53 (m, 2H), 7.41–7.35 (m, 5H), 7.23 (t, *J* = 8.1 Hz, 1H), 6.37 (s, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.82, 155.71, 154.18, 146.12, 132.49, 131.77, 128.46, 128.33, 127.06, 124.04, 119.07, 117.26, 114.87, 28.67, 15.34. HRMS (ESI) ([M + H]$^+$) calcd for $C_{17}H_{14}O_2$: 251.1067, found: 251.1069.

*5.22. 4-(4-(tert-Butyl)phenyl)-2H-chromen-2-one (**2ac**):*[21]

Light yellow solid. m.p. 124.4–125.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58–7.52 (m, 4H), 7.41–7.39 (m, 3H), 7.23 (td, J_1 = 0.9 Hz, J_2 = 7.6 Hz, 1H), 6.37 (s, 1H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.77, 155.61, 154.17, 153.01, 132.22, 131.74, 128.21, 127.08, 125.75, 124.00, 119.03, 117.21, 114.85, 34.79, 31.20. HRMS (ESI) ([M + H]$^+$) calcd for $C_{19}H_{18}O_2$: 279.1380, found: 279.1381.

*5.23. 4-(4-Methoxyphenyl)-2H-chromen-2-one (**2ad**):*[10]

Light yellow solid. m.p. 129.5–129.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58–7.53 (m, 2H), 7.43–7.40 (m, 3H), 7.27–7.22 (m, 1H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.36 (s, 1H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.88, 160.83, 155.31, 154.24, 131.77, 129.93, 127.45, 127.00, 124.05, 119.14, 117.33, 114.63, 114.32, 55.43. HRMS (ESI) ([M + H]$^+$) calcd for $C_{16}H_{12}O_3$: 253.0859, found: 253.0861.

*5.24. 4-(4-Chlorophenyl)-2H-chromen-2-one (**2ae**):* [10]

Light yellow solid. m.p. 185.9–186.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59–7.55 (m, 1H), 7.53–7.51 (m, 2H), 7.45–7.40 (m, 4H), 7.27–7.23 (m, 1H), 6.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.40, 154.39, 154.17, 135.96, 133.55, 132.12, 129.77, 129.21, 126.65, 124.27, 118.66, 117.43, 115.37. HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_9ClO_2$: 257.0364, found: 257.0369.

*5.25. 4-(4-Bromophenyl)-2H-chromen-2-one (**2af**):*[11]

Light yellow solid. m.p. 201.1–202.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J = 8.4 Hz, 2H), 7.57 (td, J_1 = 1.4 Hz, J_2 = 7.7 Hz, 1H), 7.45–7.41 (m, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.27–7.23 (m, 1H), 6.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.37, 154.41, 154.19, 134.04, 132.17, 132.13, 130.00, 126.64, 124.27, 124.15, 118.61, 117.44, 115.35. HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_9BrO_2$: 300.9859, found: 300.9859.

*5.26. 4-(m-Tolyl)-2H-chromen-2-one (**2ag**):*[10]

Light yellow solid. m.p. 134.4–135.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56–7.49 (m, 2H), 7.43–7.39 (m, 2H), 7.33 (d, J = 7.6 Hz, 1H), 7.26–7.21 (m, 3H), 6.36 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.71, 155.79, 154.11, 138.65, 135.10, 131.79, 130.34, 128.93, 128.66, 127.02, 125.47, 124.06, 119.00, 117.20, 114.95, 21.38. HRMS (ESI) ([M + H]$^+$) calcd for $C_{16}H_{12}O_2$: 237.0910, found: 237.0912.

*5.27. 4-(3-Fluorophenyl)-2H-chromen-2-one (**2ah**):*[29]

Light yellow solid. m.p. 104.8–106.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59–7.55 (m, 1H), 7.54–7.49 (m, 1H), 7.46 (dd, J_1 = 1.1 Hz, J_2 = 8.0 Hz, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.27–7.21 (m, 3H), 7.19–7.17 (m, 1H), 6.38 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.72(d, J = 246.98 Hz), 160.35, 154.16, 137.18 (d, J = 7.5 Hz), 132.13, 130.69 (d, J = 8.2 Hz), 126.67, 124.30, 124.20 (d, J = 3.0 Hz), 118.59, 117.41, 116.76, 116.56, 115.73, 115.52. HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_9FO_2$: 241.0659, found: 241.0665.

*5.28. 4-(o-Tolyl)-2H-chromen-2-one (**2ai**):*[10]

Light yellow solid. m.p. 114.4–116.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (td, J_1 = 1.5 Hz, J_2 = 7.8 Hz, 1H), 7.42–7.39 (m, 2H), 7.35–7.30 (m, 2H), 7.20–7.16 (m, 2H), 7.07 (dd, J_1 = 1.4 Hz, J_2 = 7.9 Hz, 1H), 6.32 (s, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.71, 156.02, 153.77, 135.27, 134.64, 131.88, 130.46, 129.20, 128.36, 126.88, 126.06, 124.24, 119.39, 117.06, 115.65, 19.69. HRMS (ESI) ([M + H]$^+$) calcd for $C_{16}H_{12}O_2$: 237.0910, found: 237.0915.

*5.29. 4-(3,5-Dimethylphenyl)-2H-chromen-2-one (**2aj**):*[21]

Light yellow solid. m.p. 136.2–137.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56–7.51 (m, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.23 (td, J_1 = 0.8 Hz, J_2 = 7.6 Hz, 1H), 7.15 (s, 1H), 7.05 (s, 2H), 6.35 (s, 1H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.79, 156.00, 154.16, 138.52, 135.16, 131.74, 131.21, 127.13, 126.12, 124.04, 119.15, 117.21, 114.87, 21.28. HRMS (ESI) ([M + H]$^+$) calcd for $C_{17}H_{14}O_2$: 251.1067, found: 251.1067.

*5.30. 4-Ethyl-7-methyl-2H-chromen-2-one (**2ak**):*

Light yellow solid. m.p. 87.1–88.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, J = 8.1 Hz, 1H), 7.13–7.09 (m, 2H), 6.23 (s, 1H), 2.80 (q, J = 7.4 Hz, 2H), 2.44 (s, 3H), 1.32 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.39, 157.39, 153.62, 142.62, 125.25, 123.74, 117.28, 116.80, 111.84, 24.53, 21.46, 12.03. HRMS (ESI) ([M + H]$^+$) calcd for $C_{12}H_{12}O_2$: 189.0910, found: 189.0913.

*5.31. 7-Methyl-4-propyl-2H-chromen-2-one (**2al**):*

Light yellow solid. m.p. 86.2–86.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, J = 8.1 Hz, 1H), 7.13–7.09 (m, 2H), 6.21 (s, 1H), 2.72 (t, J = 7.6 Hz, 2H), 2.44 (s, 3H), 1.78–1.69 (m, 2H), 1.05 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.25, 156.04, 153.77, 142.64, 125.22, 123.96, 117.32, 116.85, 112.77, 33.59, 21.45, 21.32, 13.83. HRMS (ESI) ([M + H]$^+$) calcd for $C_{13}H_{14}O_2$: 203.1067, found: 203.1068.

*5.32. 3-Iodo-7-methyl-4-phenyl-2H-chromen-2-one (**3a**):*[17a]

Light yellow solid. m.p. 164.2–164.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58–7.50 (m, 3H), 7.23–7.21 (m, 2H), 7.18 (s, 1H), 6.94 (q, J = 8.3 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.54, 157.97, 153.08, 143.67, 138.98, 129.10, 128.73, 127.68, 127.45, 125.67, 117.66, 116.58, 90.51, 21.61. HRMS (ESI) ([M + H]$^+$) calcd for $C_{16}H_{11}IO_2$: 362.9876, found: 362.9877.

*5.33. 3-Iodo-4-phenyl-2H-chromen-2-one (**3b**):*[17a]

Light yellow solid. m.p. 129.9–130.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56–7.55 (m, 4H), 7.39–7.37 (m, 1H), 7.25–7.23 (m, 2H), 7.15 (td, J_1 = 1.0 Hz, J_2 = 7.6 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.65, 157.86, 153.12, 138.98, 132.27, 129.26, 128.88, 127.83, 127.76, 124.56, 120.03, 116.58, 92.25. HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_9IO_2$: 348.9720, found: 348.9722.

*5.34. 7-Chloro-3-iodo-4-phenyl-2H-chromen-2-one (**3c**):*[17a]

Light yellow solid. m.p. 176.6–177.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60–7.53 (m, 3H), 7.39 (s, 1H), 7.24–7.22 (m, 2H), 7.12 (dd, J_1 = 2.0 Hz, J_2 = 8.6 Hz, 1H), 6.99 (d, J = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.98, 157.30, 153.27, 138.58, 138.15, 129.48, 129.03, 128.71, 127.68, 125.15, 118.66, 116.82, 92.07. HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_8ClIO_2$: 382.9330, found: 382.9327.

*5.35. 3-Bromo-7-methyl-4-phenyl-2H-chromen-2-one (**4a**):*[17b]

Light yellow solid. m.p. 191.1–191.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58–7.52 (m, 3H), 7.30–7.27 (m, 2H), 7.20 (s, 1H), 7.01–6.94 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.49, 154.60, 152.52, 143.43, 135.41, 129.21, 128.74, 128.05, 127.26, 125.85, 117.96, 116.87, 111.22, 21.59. HRMS (ESI) ([M + H]$^+$) calcd for $C_{16}H_{11}BrO_2$: 315.0015, found: 315.0010.

*5.36. 3-Bromo-4-phenyl-2H-chromen-2-one (**4b**):*[17b]

Light yellow solid. m.p. 153.3–153.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59–7.51 (m, 4H), 7.41–7.38 (m, 1H), 7.31–7.27 (m, 2H), 7.21–7.12 (m, 1H), 7.09–7.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.19, 154.54, 152.39, 135.20, 131.96, 129.28, 128.78, 128.00, 127.54, 124.63, 120.24, 116.70, 112.52. HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_9BrO_2$: 300.9859, found: 300.9860.

*5.37. 3-Bromo-7-chloro-4-phenyl-2H-chromen-2-one (**4c**):*[17b]

Light yellow solid. m.p. 190.3–192.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60–7.54 (m, 3H), 7.41 (m, 1H), 7.30–7.26 (m, 2H), 7.17–7.14 (m, 1H), 7.01 (d, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.70, 153.97, 152.65, 137.99,

134.93, 129.57, 129.00, 128.47, 128.01, 125.29, 119.00, 117.07, 112.60. HRMS (ESI) ([M + H]$^+$) calcd for $C_{15}H_8BrClO_2$: 334.9469, found: 334.9465.

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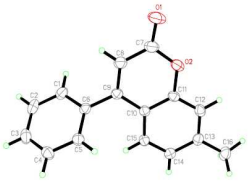
18. X-Ray single crystal structure of **2a** (CCDC: 1856166).



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Supplementary Material

Supplementary data associated with this article can be found in the online version at…