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PII: S0040-4020(20)30890-5

DOI: https://doi.org/10.1016/j.tet.2020.131677

Reference: TET 131677

To appear in: *Tetrahedron*

Received Date: 1 September 2020

Revised Date: 8 October 2020

Accepted Date: 12 October 2020

Please cite this article as: Zhang H, Li Q, Yin Y, Kim JK, Huang M, Li Y, Wu Y, The light “on-off” stepwise one-pot method for 3,4-diaryl coumarins with potential AIE properties, *Tetrahedron*, https://doi.org/10.1016/j.tet.2020.131677.

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Graphical Abstract

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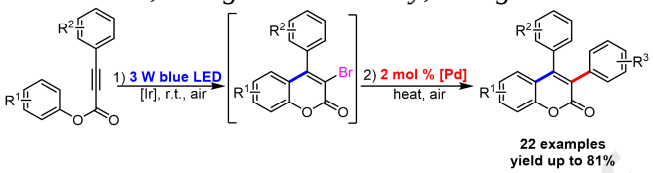

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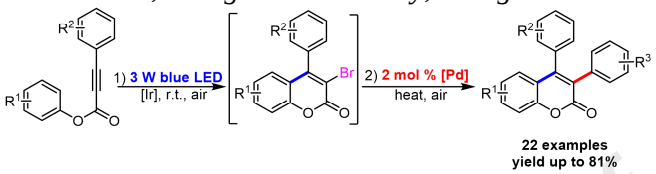

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
one-pot synthesis
light on-off
3,4-diaryl coumarin
aryl alkynoate
AIE activity

ABSTRACT

An efficient one-pot method involving visible-light-induced cyclization and Pd-catalyzed Suzuki cross-coupling processes to construct 3,4-diaryl coumarins is developed. Under the light on-off optimized conditions, a series of alkynoates and aryl boronic acids were well suitable for this catalytic system, and were successfully transformed into the corresponding products in moderate to high yields. Meanwhile, this synthetic system has good applicability for other Pd-catalyzed coupling reactions, such as Heck and Sonogashira reactions. 3,4,7-Triphenyl coumarin could be produced not only *via* the Suzuki reaction of 3-bromo-4,7-diphenyl with $PhB(OH)_2$, but also *via* the Pd-catalyzed C-H activation. Based on the spectral studies, we found that some of the 3,4-diaryl coumarins may have AIE activities. This work provides a straight forward way to create valuable multi-substituted coumarins with potential AIE properties.

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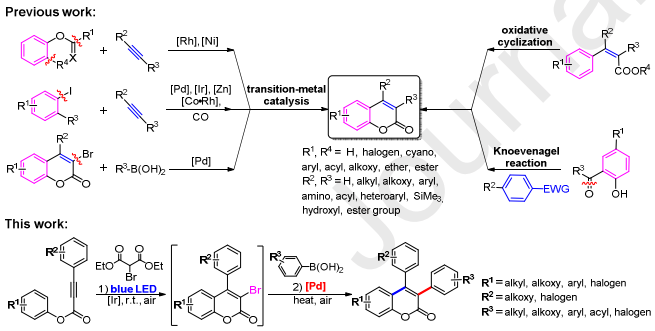
1. Introduction

Coumarins as one of the typical heterocyclic compounds are present in many natural products, [1] pharmaceuticals [2] and organic synthetic intermediates. [3] Coumarin derivatives not only have various potential biological activities, [4] but also have been applied in the field of luminescent materials. [5] Recently, we found that 3-arylvinyl-4-aryl-coumarins and 3-arylacetylene-4-aryl-coumarins have fascinating optical properties. [6,7] Especially, the excellent aggregation-induced emission (AIE) optical properties of 3-arylacetylene coumarins allows us to study the optical activity of 3,4-diaryl coumarins. [8] Up to now, 3,4-diaryl coumarins are synthesized by oxidative cyclization reaction, [8] Knoevenagel reaction [9] and transition metal-catalyzed coupling reactions (Scheme 1). [10] On the basis of the above literature investigations, we found that the existing synthetic methods need either expensive precursors or multi-step synthesis. In order to solve these shortcomings, the stepwise one-pot synthetic strategy is considered as the effective pathway.

Comparing to the multi-step synthesis, economic and environment-friendly one-pot synthetic strategy has been regarded as a promising way in organic chemistry, which increases product yield without the separation and purification of intermediate compounds. Recently, the stepwise one-pot synthetic method with the combination of various approaches have been developed to expand the application of this strategy in organic synthesis. [6,7,11,12] Inspired by the previous work, the one-pot synthesis with multi-step procedures involving photocatalysis [13] and thermocatalysis processes will be a good way to synthesize 3,4-diaryl coumarins. Herein, we demonstrate a mild stepwise one-pot method involving visible-light-induced cyclization and Pd-catalyzed Suzuki reaction to synthesize 3,4-diaryl coumarins from alkynoates, and their AIE activity have been preliminary studied.

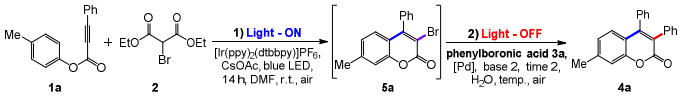


Scheme 1. Synthetic methods of 3,4-diaryl coumarins.

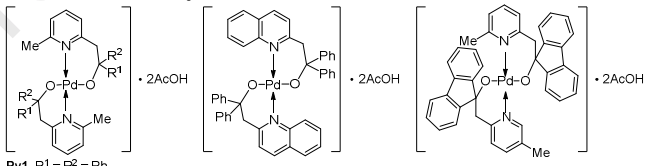
2. Results and discussion

Based on the previous work, [14] the visible-light-induced reaction of *p*-tolyl 3-phenylpropiolate (**1a**) and diethyl bromomalonate (**2**) was chosen to construct the important intermediate 3-bromocoumarin (**5a**). The optimization of Suzuki reaction conditions between phenylboronic acid (**3a**) and 3-bromocoumarin (**5a**) to produce the target product **4a** was our main investigation (Table 1). The cyclopalladium(II) complex with N,O-ligand **Py1** [15] was better choice for the one-pot synthesis (Table 1, entries 1-6). The amount of K_2CO_3 which was used in the Suzuki process could be reduced to 2 equivalents (Table 1, entries 7-8). Other tested bases such as Na_2CO_3, K_3PO_4 and CsOAc, gave the comparatively poor results (Table 1, entries 9-11). The better result was obtained when the Suzuki reaction temperature was reduced to 80 °C (Table 1, entries 12 and 13). Changing the amount of water, the product yield was not improved (Table 1, entries 14 and 15). The efficiency did not decrease due to the shortened reaction time or reducing the ture of product **4a** was determined by single crystal X-ray diffraction (Table S1 in ESI).

Table 1. Optimization of the one-pot reaction conditions.[a]



Entry	[Pd]	Base 2	T/°C	Yield/%
1	$PdCl_2$	K_2CO_3	100	59
2	$Pd(OAc)_2$	K_2CO_3	100	68
3	**Py1**	K_2CO_3	100	70
4	**Q1**	K_2CO_3	100	62
5	**Py4**	K_2CO_3	100	53
6	**Py6**	K_2CO_3	100	66
7[b]	**Py1**	K_2CO_3	100	67
8[c]	**Py1**	K_2CO_3	100	78
9[c]	**Py1**	Na_2CO_3	100	53
10[c]	**Py1**	K_3PO_4	100	63
11[c]	**Py1**	CsOAc	100	57
12[c]	**Py1**	K_2CO_3	80	81
13[c]	**Py1**	K_2CO_3	60	21
14[c, d]	**Py1**	K_2CO_3	80	77
15[c, e]	**Py1**	K_2CO_3	80	65
16[c, f]	**Py1**	K_2CO_3	80	76
17[c, g]	**Py1**	K_2CO_3	80	80
18[c, g, h]	**Py1**	**K_2CO_3**	**80**	**80**



Py1, R1 = R2 = Ph
Py6, R1 = Me, R2 = C6H13
Q1
Py4

[a]Reaction conditions: 1) **1a** (0.2 mmol), **2** (3 equiv.), $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mol %), CsOAc (2 equiv.), DMF (2 mL), 3 W blue LED (λ = 450-465 nm), room temperature, under air atmosphere for 14 h; 2) **3a** (2 equiv.), [Pd] (5 mol %), base 2 (4 equiv.), H_2O (0.2 mL), under air atmosphere for 12 h at 100 °C, isolated yield.
[b]Base 2 (1 equiv.).
[c]Base 2 (2 equiv.).
[d]H_2O (0.4 mL).
[e]H_2O (0.1 mL).
[f]Time 2: 6 h.
[g]Time 2: 8 h.
[h]**Py1** (2 mol %).

On the basis of the optimal conditions, the scope of the substrates was investigated (Scheme 2). Generally, various aryl alkynates and aryl boronic acids were well tolerated in the stepwise one-pot transformation (**4a-v**). The activity of aryl alkynoates possessing the electron-donating group on the *para*-position of the phenoxy ring were higher than that with the electron-withdrawing group (**4a-i**). 3,5-Dimethylphenyl 3-phenylpropiolate (**1j**) and naphthalen-2-yl 3-phenylpropiolate (**1k**) could be also transformed into their corresponding products in good yield. It was worth to note that 4,7-diphenyl-2*H*-chromen-2-one (**4h$_1$**) were selectively produced in good yield under the optimal conditions. It might be afforded by the debromination of 3-bromocoumarin. In the presence of excess phenylboronic acid (**3a**), the yield of 3,4,7-triphenyl coumarin (**4h$_2$**) was up to 68%, meanwhile, a small amount of 4,7-diphenyl coumarin (**4h$_1$**) was isolated. Both electron-donating and electron-withdrawing phenylboronic acids could participate in this one-pot reaction to give products (**4n-s**) in moderate to good yields. The poor yields were obtained with the steric hindrance of

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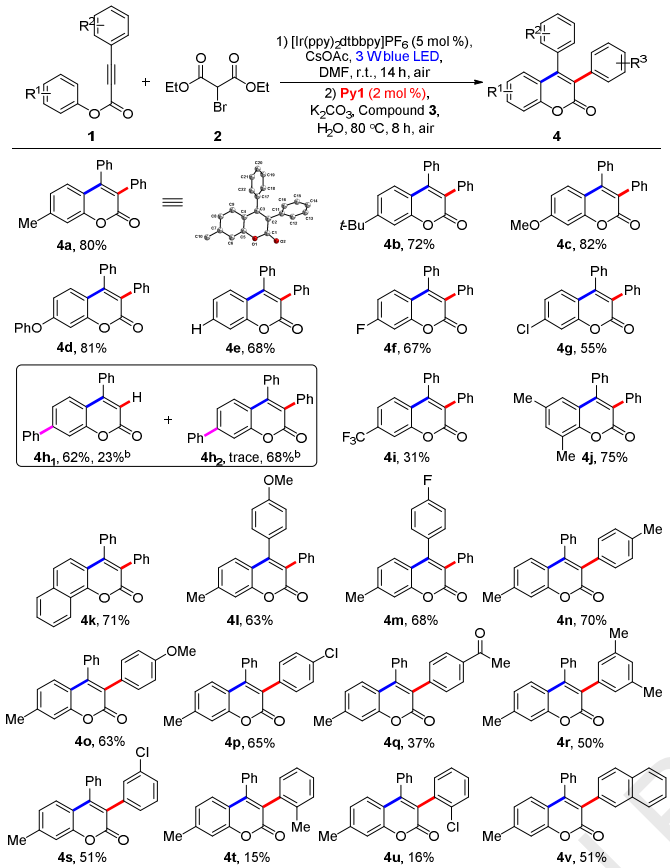
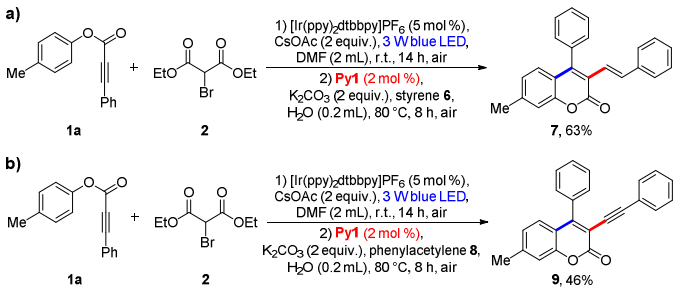
orth ...as boronic acid was well tolerated in this one-pot reaction to afford the corresponding product (**4v**) in 51% yield.



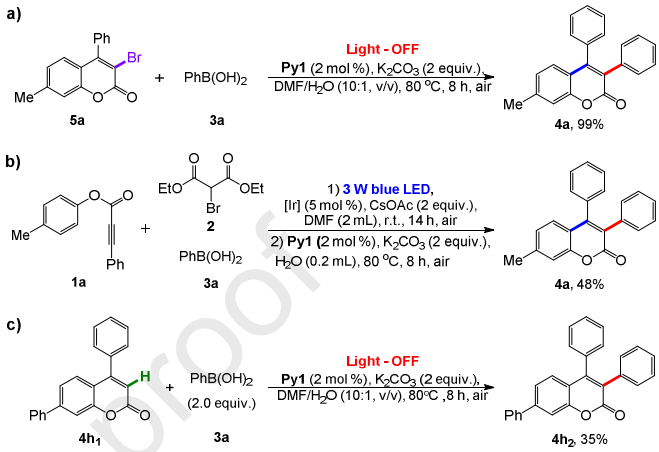
Scheme 2. Scope of the one-pot reaction.[a]
[a]Reaction conditions: **1a** (0.2 mmol), **2** (3 equiv.), $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mol %), CsOAc (2 equiv.), DMF (2 mL), 3 W blue LED (λ = 450-465 nm), room temperature, under air atmosphere for 14 h; then **3** (2 equiv.), **Py1** (2 mol %), K_2CO_3 (2 equiv.) and H_2O (0.2 mL) were added under air at 80 °C for 8 h. Isolated yield.
[b]$PhB(OH)_2$ (6 equiv.).

Furthermore, the two-step one-pot catalytic system could be also applied to construct 3-styryl coumarin (**7**) and 3-phenylacetylene coumarin (**9**) in moderate yields without any other optimization (Scheme 3). We believe that the one-pot synthetic method may have a significantly broader application in the synthesis of valuable multi-substituted coumarins.



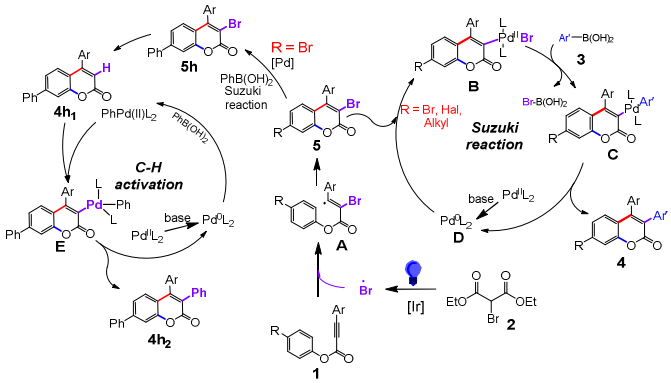
Scheme 3. The extended experiments of the one-pot reaction.

To get insight into the reaction mechanism, several control experiments were studied (Scheme 4). The result of the reaction between 3-bromocoumarin (**5a**) and phenyl boronic acid (**3a**) indicated that the compound **5a** might be the main intermediate for the two-step one-pot transformation (Scheme 4, a). When the three starting materials were added in the first step, the yield of the target compound was obviously reduced, which proves the two-step one-pot reaction should be carried out step by step not detected during our previous works under the standard conditions for the model reaction, [6] the debromination product $\mathbf{4h_1}$ was observed for the synthesis of compound $\mathbf{4h_2}$ (Scheme 2). It might be related to more active intermediate **5h**. Based on our investigation, it was found that the debromination product $\mathbf{4h_1}$ could be transformed into $\mathbf{4h_2}$ *via* the Pd-catalyzed C-H activation (Scheme 4, c). The results obtained will further broaden the research on N,O-ligand palladacycle catalysts. [15,16]



Scheme 4. Control experiments for the one-pot reaction.

Based on the above results and the previous studies, [10,14] a possible mechanism was proposed (Scheme 5). The investigated light on-off synthetic method proceeds *via* the photocatalytic and thermocatalytic processes. After the photocatalytic cycle studied by our previous work, [6,14c] the main intermediate 3-bromicoumarins **5** undergoes sequential Pd-mediated oxidative addition and reduction elimination reactions to give 3,4-diaryl coumarins **4**. In addition, more active intermediate **5h** could proceed debromination to afford compound $\mathbf{4h_1}$. The product $\mathbf{4h_2}$ might be isolated *via* two pathways: 1) the Pd-catalyzed C-H activation between compound $\mathbf{4h_1}$ and $PhB(OH)_2$; 2) the Suzuki reaction of intermediate **5h** with $PhB(OH)_2$.



Scheme 5. Possible pathway for the light on-off one-pot transformation.

Considering the outstanding photoluminescence property of coumarin derivatives, AIE activity of three synthesized coumarins **4a**, $\mathbf{4h_1}$ and $\mathbf{4h_2}$ have been preliminary studied (Figure 1 and figure S1 in ESI). To our delight, all the three compounds could emit different intensities of blue to blue-green fluorescence under 365 nm UV light in solid-state (Figure 1, a and b). This phenomenon indicates that these coumarin derivatives may have AIE-active. Then, the absorption and emission properties of the three compounds in pure THF and THF/H_2O mixtures were measured (Figure 1, c-h and Figures S1 in ESI). All compounds exhibit weak fluorescence with different intensities in pure THF

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so ...were

With the increase of water fraction in the mixed system, the fluorescence intensity of compounds **4a** and **4h$_2$** increased slowly, and gradually showed bright blue emission; when the water fraction increased to 90%, they exhibited 12 and 18-fold enhancement in fluorescence intensity compared to that in pure THF, respectively. However, different from compounds **4a** and **4h$_2$**, the fluorescence intensity of **4h$_1$** increased very slowly with the increase of water fraction, almost no fluorescence was emitted. These results preliminary indicates that some of the synthesized 3,4-diaryl coumarins have AIE-active. The investigation of the detailed AIE mechanism of the synthesized 3,4-diarylcoumarins is under way in our laboratory.

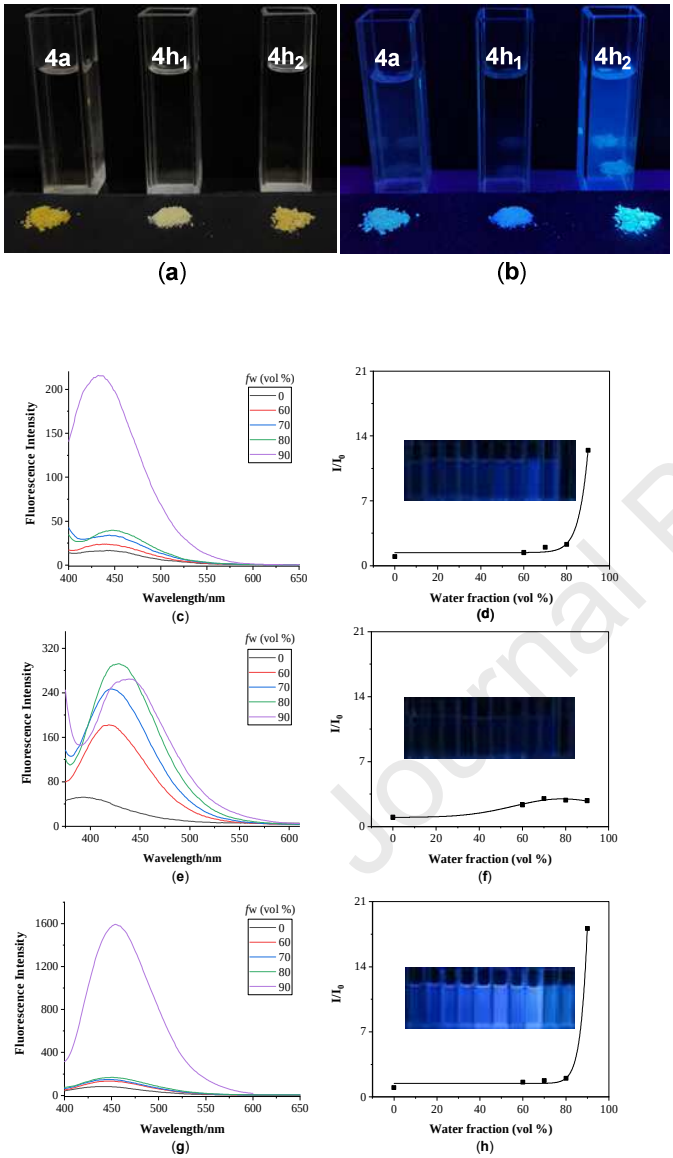

Figure 1. (a) Photos of solid powders and on the water fractions in THF solutions of compounds **4a**, **4h$_1$** and **4h$_2$** under natural light and (b) 365 nm UV light. (c) FL spectra changes of **4a**, (e) **4h$_1$** and (g) **4h$_2$** depending on the water fractions (0% and 60%-90%) in THF solutions. (d) Plot of relative PL intensity (I/I_0) versus the composition of THF/H_2O mixture of **4a**, (f) **4h$_1$** and (h) **4h$_2$**, where I_0 = PL intensity in pure THF solution. Inset: photographs of **4a**, **4h$_1$** and **4h$_2$** in THF/H_2O mixtures with different water fractions taken under irradiation of 365 nm UV light.

3. Conclusions

In summary, an efficient stepwise one-pot method to construct 3,4-diaryl coumarins using aryl alkynoates as the starting materials was developed. The high substrate tolerance was found ...were obtained in moderate to high yields under the stepwise conditions. The studied light "on-off" catalytic approach proceeds *via* the photocatalysis and thermocatalytic processes. 3-Bromocoumarins might be the main intermediates for this transformation. In addition, this reaction system has good applicability for other Pd-catalyzed coupling reactions, such as Heck and Sonogashira reactions. It was found that more active intermediate 3-bromo-4,7-diphenyl coumarin could proceed both of the Suzuki coupling reaction and Pd-catalyzed C-H activation. Based on the spectral studies, we found that some of the 3,4-diaryl coumarins may have AIE activities. The investigation of the detailed AIE mechanism of these multi-substituted coumarins is under way in our laboratory.

4. Experimental section

4.1. General information

All reactions were performed under air atmosphere using a quartz tube. Solvents were dried by standard methods before they were used. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co., Ltd. All reactions were carried out with a photoreactor (Serial No: PEA12) which was purchased from LUOYANG JINFENG ELECTROMECHANICAL EQUIPMENT Co., Ltd. The LCD digital hotplate magnetic stirrer MS-H-Pro$^+$ was purchased from Dragon Laboratory Instruments Limited. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 and 100 MHz NMR instruments using $CDCl_3$ as the solvent and TMS as the internal standard. ^{19}F NMR spectra were recorded at 376.5 MHz on Bruker DPX-400, the chemical shifts δ are reported relative to $CFCl_3$ (δ = 0 ppm) as the internal standard. The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd = doublet of doublet. High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionization (ESI). UV/vis absorption spectra were measured by SP-1900 ultraviolet-visible spectrophotometer. The fluorescence emission spectra were recorded using a F-4500 FL spectrophotometer. The melting point data of synthesized product is derived from XT4A type melting point. The measurement of the detector is unrevised. The X-ray single crystal structure is determined by the Oxford Diffraction Xcalibur CCD single crystal diffractometer.

4.2. General procedure for the synthesis of compounds **4a-v**

To a reaction tube equipped with a magnetic stir bar was added phenyl 3-phenylpropiolate (0.2 mmol), $[Ir(ppy)_2(dtbbpy)PF_6]$ (0.0092 g, 5 mol %, 0.05 equiv.) and cesium acetate (0.0768 g, 0.4 mmol, 2 equiv.). Under air atmosphere, diethyl bromomalonate (108 µL, 0.6 mmol, 3 equiv.) and DMF (2 mL) were added. The resulting mixture was stirred under 3 W blue LED (λ = 450-465 nm) at room temperature for 14 hours. Then **Py1** (0.0033 g, 2 mol %, 0.02 equiv.), phenylboronic acid (0.4 mmol, 2 equiv.) and potassium carbonate (0.0558 g, 0.4 mmol, 2 equiv.) were added. The resulting mixture was heated at 80 °C for 8 hours. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel (eluent: dichloromethane or petroleum ether/ethyl acetate = 9/1) to give the desired product **4**.

4.2.1. 7-methyl-3,4-diphenyl-2*H*-chromen-2-one (**4a**). [17]

Yellow solid (50.1 mg, 80%). m. p. 244.1-244.7 °C (lit. 243 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28-7.27 (m, 3H), 7.22 (s, 1H), 7.16-7.08 (m, 8H), 6.99-6.97 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4, 153.2, 151.5, 142.6, 134.5,

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133 ^{13}C 125.2, 118.0, 116.8, 21.5. HRMS (ESI) calcd. for $C_{22}H_{17}O_2$ $(M+H)^+$: 313.1223; found: 313.1220.

4.2.2. 7-(*tert*-butyl)-3,4-diphenyl-2*H*-chromen-2-one (**4b**).

Light yellow solid (51.0 mg, 72%). m. p. 137.9-138.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.44 (d, J = 1.76 Hz, 1H), 7.30-7.29 (m, 3H), 7.24-7.21 (m, 1H), 7.18-7.16 (m, 3H), 7.14-7.10 (m, 5H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 156.0, 153.2, 151.5, 134.7, 134.0, 130.6, 129.3, 128.2, 128.1, 127.7, 127.5, 127.3, 126.0, 121.6, 118.0, 113.5, 35.1, 31.0. HRMS (ESI) calcd. for $C_{25}H_{23}O_2$ $(M+H)^+$: 355.1693; found: 355.1696.

4.2.3. 7-methoxy-3,4-diphenyl-2*H*-chromen-2-one (**4c**). [10a]

Light yellow solid (53.6 mg, 82%). m. p. 168.4-168.9 °C (lit. 180-182 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.28 (m, 3H), 7.18-7.11 (m, 8H), 6.93-6.92 (d, J = 2.20 Hz, 1H), 6.77-6.74 (dd, J = 8.93 Hz, 2.45 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5, 161.6, 154.9, 151.8, 134.8, 134.1, 130.7, 129.3, 128.8, 128.3, 128.2, 127.7, 127.4, 123.7, 114.0, 112.2, 100.6, 55.8. HRMS (ESI) calcd. for $C_{25}H_{17}O_3$ $(M+H)^+$: 329.1172; found: 329.1173.

4.2.4. 7-phenoxy-3,4-diphenyl-2*H*-chromen-2-one (**4d**).

Light yellow solid (63.1 mg, 81%). m. p. 188.7-189.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.39 (m, 2H), 7.30-7.28 (m, 3H), 7.24-7.19 (m, 1H), 7.18-7.08 (m, 10H), 6.95 (d, J = 2.26 Hz, 1H), 6.84-6.81 (dd, J = 8.78 Hz, 2.51 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 160.9, 155.2, 154.5, 151.5, 134.6, 133.9, 130.6, 130.1, 129.3, 129.1, 128.3, 128.2, 127.7, 127.5, 125.0, 124.7, 120.2, 115.6, 114.2, 105.0. HRMS (ESI) calcd. for $C_{27}H_{19}O_3$ $(M+H)^+$: 391.1329; found: 391.1326.

4.2.5. 3,4-diphenyl-2*H*-chromen-2-one (**4e**). [10f]

Light yellow solid (40.5 mg, 68%). m. p. 237.3-238.2 °C (lit. 232-234 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.51 (m, 1H), 7.44-7.42 (m, 1H), 7.33-7.27 (m, 3H), 7.24-7.11 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 153.2, 151.5, 134.4, 133.8, 131.4, 130.5, 129.3, 128.3, 128.2, 127.8, 127.7, 127.6, 126.9, 124.1, 120.4, 116.7. HRMS (ESI) calcd. for $C_{21}H_{15}O_2$ $(M+H)^+$: 299.1067; found: 299.1069.

4.2.6. 7-fluoro-3,4-diphenyl-2*H*-chromen-2-one (**4f**).

Light yellow solid (42.4 mg, 67%). m. p. 167.3-168.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 3H), 7.18-7.12 (m, 9H), 6.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.2 (d, J = 253.82 Hz), 161.0, 154.2 (d, J = 13.20 Hz), 151.1 (d, J = 1.47 Hz), 134.3, 133.6, 130.5, 129.5 (d, J = 10.27 Hz), 129.2, 128.5, 128.4, 127.8, 127.7, 125.8 (d, J = 2.93 Hz), 117.2 (d, J = 2.93 Hz), 112.1 (d, J = 22.01 Hz), 104.2 (d, J = 25.68 Hz). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -106.1. HRMS (ESI) calcd. for $C_{21}H_{14}FO_2$ $(M+H)^+$: 317.0972; found: 317.0974.

4.2.7. 7-chloro-3,4-diphenyl-2*H*-chromen-2-one (**4g**).

Light yellow solid (36.5 mg, 55%). m. p. 176.4-176.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (s, 1H), 7.33-7.32 (m, 3H), 7.20-7.12 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.7, 153.4, 150.9, 137.3, 134.0, 133.5, 130.4, 129.2, 128.7, 128.5, 128.4, 127.8, 127.7, 126.9, 124.7, 119.2, 116.9. HRMS (ESI) calcd. for $C_{21}H_{14}ClO_2$ $(M+H)^+$: 333.0677; found: 333.0679.

4.2.8. 4,7-diphenyl-2*H*-chromen-2-one (**4h$_1$**).

Light yellow solid (36.8 mg, 62%). m. p. 124.3-124.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65-7.63 (m, 3H), 7.57-7.53 (m, NMR (100 MHz, $CDCl_3$): δ = 160.9, 155.5, 154.6, 145.0, 139.0, 135.2, 129.7, 129.1, 128.9, 128.6, 128.4, 127.3, 127.2, 123.0, 117.9, 115.4, 114.8. HRMS (ESI) calcd. for $C_{21}H_{15}O_2$ $(M+H)^+$: 299.1067; found: 299.1070.

4.2.9. 3,4,7-triphenyl-2*H*-chromen-2-one (**4h$_2$**).

Yellow solid (51.3 mg, 68%). m. p. 187.3-187.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64-7.62 (m, 3H), 7.50-7.46 (m, 2H), 7.43-7.39 (m, 2H), 7.32-7.28 (m, 4H), 7.21-7.14 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 153.6, 151.3, 144.5, 139.1, 134.5, 133.9, 130.5, 129.3, 129.1, 128.5, 128.4, 128.3, 128.1, 127.7, 127.6, 127.1, 126.6, 122.9, 119.4, 114.8. HRMS (ESI) calcd. for $C_{27}H_{19}O_2$ $(M+H)^+$: 375.1380; found: 375.1377.

4.2.10. 3,4-diphenyl-7-(trifluoromethyl)-2*H*-chromen-2-one (**4i**).

Yellow solid (22.7 mg, 31%). m. p. 152.4-153.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (s, 1H), 7.41-7.34 (m, 5H), 7.20-7.13 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4, 152.8, 150.4, 133.7, 133.2, 133.0 (d, J = 33.01 Hz), 130.3, 129.2, 129.0, 128.7, 128.6, 128.5, 128.0, 127.8, 123.2, 123.1 (d, J = 272.90 Hz), 120.6 (d, J = 3.67 Hz), 114.1 (q, J = 4.40 Hz). ^{19}F NMR (376.5MHz, $CDCl_3$): δ = -62.9. HRMS (ESI) calcd. for $C_{22}H_{14}F_3O_2$ $(M+H)^+$: 367.0940; found: 367.0942.

4.2.11. 6,8-dimethyl-3,4-diphenyl-2*H*-chromen-2-one (**4j**). [10a]

Yellow solid (48.9 mg, 75%). m. p. 153.8-154.7 °C (lit. 156-157 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.28 (m, 3H), 7.21 (s, 1H), 7.18-7.15 (m, 3H), 7.12-7.09 (m, 4H), 6.80 (s, 1H), 2.51 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 152.0, 149.7, 134.9, 134.2, 133.9, 133.1, 130.5, 129.3, 128.1, 127.7, 127.5, 127.4, 126.6, 125.8, 125.2, 119.9, 20.9, 15.7. HRMS (ESI) calcd. for $C_{23}H_{19}O_2$ $(M+H)^+$: 327.1380; found: 327.1381.

4.2.12. 1,2-diphenyl-3*H*-benzo[*f*]chromen-3-one (**4k**). [10a]

Light yellow solid (49.3 mg, 71%). m. p. 243.2-243.9 °C (lit. 245-246 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66-8.64 (m, 1H), 7.83-7.81 (m, 1H), 7.66-7.60 (m, 2H), 7.55-7.53 (m, 1H), 7.34-7.31 (m, 3H), 7.22-7.13 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 152.4, 150.2, 134.8, 134.5, 134.0, 130.6, 129.3, 128.6, 128.2, 127.7, 127.6, 127.5, 127.1, 127.0, 126.3, 123.8, 123.2, 123.0, 122.6, 115.5. HRMS (ESI) calcd. for $C_{25}H_{17}O_2$ $(M+H)^+$: 349.1223; found: 349.1220.

4.2.13. 4-(4-methoxyphenyl)-7-methyl-3-phenyl-2*H*-chromen-2-one (**4l**). [14b]

Light yellow solid (42.8 mg, 63%). m. p. 229.9-230.4 °C (lit. 226-228 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22-7.11 (m, 7H), 7.04-6.99 (m, 3H), 6.83-6.81 (d, J = 8.68 Hz, 2H), 3.79 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 159.4, 153.3, 151.4, 142.6, 134.3, 130.8, 130.6, 127.8, 127.5, 127.4, 126.7, 125.8, 125.2, 118.3, 116.9, 113.7, 55.2, 21.6. HRMS (ESI) calcd. for $C_{23}H_{19}O_3$ $(M+H)^+$: 343.1329; found: 343.1330.

4.2.14. 4-(4-fluorophenyl)-7-methyl-3-phenyl-2*H*-chromen-2-one (**4m**).

Light yellow solid (44.6 mg, 68%). m. p. 194.8-195.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (s, 1H), 7.20-7.19 (m, 3H), 7.11-7.06 (m, 5H), 7.02-6.97 (m, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4 (d, J = 248.69 Hz), 161.3, 153.3, 150.6, 142.9, 133.9, 131.2 (d, J = 8.07 Hz), 130.6, 130.5, 127.9, 127.4 (d, J = 43.28 Hz), 126.3, 125.4, 117.9, 117.0, 115.6, 115.4, 21.6. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -112.5. HRMS (ESI) calcd. for $C_{22}H_{16}FO_2$ $(M+H)^+$: 331.1129; found: 331.1130.

Journal Pre-proof

4. [14b]

Yellow solid (43.3 mg, 70%). m. p. 237.3-238.1 °C (lit. 232-234 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.29 (m, 3H), 7.22 (s, 1H), 7.13-7.10 (m, 2H), 7.08-7.06 (m, 1H), 7.02-6.97 (m, 5H), 2.45 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 153.2, 151.2, 142.5, 137.2, 134.8, 130.9, 130.4, 129.3, 128.4, 128.2, 128.1, 127.4, 125.8, 125.2, 118.1, 116.8, 21.6, 21.2. HRMS (ESI) calcd. for $C_{23}H_{19}O_2$ $(M+H)^+$: 327.1380; found: 327.1381.

4.2.16. 3-(4-methoxyphenyl)-7-methyl-4-phenyl-2*H*-chromen-2-one (**4o**).

White solid (43.1 mg, 63%). m. p. 199.7-200.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.30 (m, 3H), 7.22 (s, 1H), 7.13-7.10 (m, 2H), 7.07-7.03 (m, 3H), 6.99-6.97 (m, 1H), 6.72-6.70 (m, 2H), 3.73 (s, 3H), 2.45(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8, 158.8, 153.2, 151.1, 142.4, 134.9, 131.9, 129.4, 128.3, 128.2, 127.4, 126.2, 125.4, 125.3, 118.2, 116.8, 113.2, 55.1, 21.6. HRMS (ESI) calcd. for $C_{23}H_{19}O_3$ $(M+H)^+$: 343.1329; found: 343.1331.

4.2.17. 3-(4-chlorophenyl)-7-methyl-4-phenyl-2*H*-chromen-2-one (**4p**).

White solid (44.9 mg, 65%). m. p. 220.9-221.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.32 (t, J = 3.18 Hz, 3H), 7.23 (s, 1H), 7.16-7.14 (m, 2H), 7.11-7.05 (m, 5H), 7.01-6.99 (m, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 153.3, 152.0, 143.0, 134.4, 133.5, 132.5, 132.0, 129.3, 128.5, 128.4, 128.0, 127.6, 125.5, 124.6, 117.9, 117.0, 21.6. HRMS (ESI) calcd. for $C_{22}H_{16}ClO_2$ $(M+H)^+$: 347.0833; found: 347.0834.

4.2.18. 3-(4-acetylphenyl)-7-methyl-4-phenyl-2*H*-chromen-2-one (**4q**).

Light yellow solid (26.3 mg, 37%). m. p. 204.6-205.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78-7.76 (m, 2H), 7.32-7.30 (m, 3H), 7.25-7.23 (m, 3H), 7.12-7.10 (m, 3H), 7.03-7.01 (m, 1H), 2.53 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.8, 161.1, 153.4, 152.4, 143.3, 139.2, 135.9, 134.2, 131.0, 129.2, 128.7, 128.4, 127.7, 127.6, 125.5, 124.7, 117.8, 117.0, 26.6, 21.7. HRMS (ESI) calcd. for $C_{24}H_{19}O_3$ $(M+H)^+$: 355.1329; found: 355.1330.

4.2.19. 3-(3,5-dimethylphenyl)-7-methyl-4-phenyl-2*H*-chromen-2-one (**4r**).

Yellow solid (34.1 mg, 50%). m. p. 180.1-180.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.28 (m, 3H), 7.22 (s, 1H), 7.11-7.06 (m, 3H), 6.98-6.96 (m, 1H), 6.77-6.72 (m, 3H), 2.44 (s, 3H), 2.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 153.2, 151.3, 142.4, 136.9, 134.7, 133.7, 129.2, 128.7, 128.2, 128.0, 127.4, 127.2, 126.1, 125.2, 118.1, 116.8, 21.5, 21.1. HRMS (ESI) calcd. for $C_{24}H_{21}O_2$ $(M+H)^+$: 341.1536; found: 341.1537.

4.2.20. 3-(3-chlorophenyl)-7-methyl-4-phenyl-2*H*-chromen-2-one (**4s**).

Light yellow solid (35.7 mg, 51%). m. p. 179.0-180.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.52 (m, 1H), 7.33-7.28 (m, 3H), 7.23-7.20 (m, 1H), 7.14-7.07 (m, 5H), 7.01-6.93 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 153.3, 152.3, 143.1, 135.8, 134.1, 133.5, 130.7, 129.2, 128.9, 128.8, 128.5, 128.3, 127.7, 127.6, 125.4, 124.4, 117.8, 116.9, 21.6. HRMS (ESI) calcd. for $C_{22}H_{16}ClO_2$ $(M+H)^+$: 347.0833; found: 347.0835.

4.2.21. 7-methyl-4-phenyl-3-(*o*-tolyl)-2*H*-chromen-2-one (**4t**).

. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.19 (m, 5H), 7.10-7.05 (m, 3H), 7.00-6.95 (m, 3H), 6.92-6.90 (m, 1H), 2.45 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9, 153.5, 152.2, 142.7, 136.8, 134.5, 133.8, 130.6, 129.8, 129.3, 128.3, 128.2, 128.0, 127.9, 127.4, 125.3, 126.0, 117.9, 117.0, 21.6, 19.9. HRMS (ESI) calcd. for $C_{23}H_{19}O_2$ $(M+H)^+$: 327.1380; found: 327.1383.

4.2.22. 3-(2-chlorophenyl)-7-methyl-4-phenyl-2*H*-chromen-2-one (**4u**).

Yellow solid (10.8 mg, 16%). m. p. 155.8-156.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.30 (m, 2H), 7.28-7.25 (m, 3H), 7.23-7.20 (m, 1H), 7.17-7.12 (m, 2H), 7.11-7.06 (m, 2H), 7.05-7.03 (m, 1H), 7.00-6.98 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 153.6, 153.0, 143.1, 134.4, 134.1, 133.7, 131.9, 129.2, 128.7, 128.5, 128.1, 127.8, 127.5, 126.4, 125.4, 124.2, 117.6, 117.0, 21.6. HRMS (ESI) calcd. for $C_{22}H_{16}ClO_2$ $(M+H)^+$: 347.0833; found: 347.0834.

4.2.23. 7-methyl-3-(naphthalen-2-yl)-4-phenyl-2*H*-chromen-2-one (**4v**).

Light brown solid (34.9 mg, 48%). m. p. 205.7-206.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75-7.66 (m, 3H), 7.41 (s, 2H), 7.29-7.24 (m, 4H), 7.12-7.10 (m, 3H), 7.02-7.00 (m, 1H), 6.95-6.92 (m, 1H), 6.84-6.82 (m, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 153.7, 153.6, 142.9, 134.4, 133.2, 132.2, 132.0, 128.8, 128.5, 128.4, 128.2, 128.1, 127.7, 127.5, 126.2, 125.7, 125.4, 125.1, 125.0, 124.8, 117.9, 117.0, 21.6. HRMS (ESI) calcd. for $C_{26}H_{19}O_2$ $(M+H)^+$: 363.1380; found: 363.1382.

4.3. Applications and transformations

4.3.1. (*E*)-7-methyl-4-phenyl-3-styryl-2*H*-chromen-2-one (**7**). [6]

Yellow solid (42.6 mg, 63%). m. p. 171.0.-171.7 °C (lit. 169.8-171.6 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93-7.89 (d, J = 16.26 Hz, 1H), 7.57-7.55 (m, 3H), 7.31-7.19 (m, 8H), 6.97-6.92 (m, 2H), 6.70-6.66 (d, J = 16.26 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 152.3, 150.5, 142.4, 137.8, 135.1, 134.8, 129.0, 128.8, 128.5, 127.9, 127.2, 126.8, 125.4, 121.8, 120.3, 118.5, 116.6, 21.6.

4.3.2. 7-methyl-4-phenyl-3-(phenylethynyl)-2*H*-chromen-2-one (**9**). [7]

Light yellow solid (30.9 mg, 46%). m. p. 171.9.-172.6 °C (lit. 171.7-172.9 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.47 (m, 5H), 7.22-7.19 (m, 6H), 7.16-7.14 (m, 1H), 7.02-7.00 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 156.3, 152.8, 143.5, 134.4, 131.6, 129.2, 129.0, 128.6, 128.3, 128.1, 127.2, 125.7, 122.5, 117.2, 117.1, 109.8, 98.1, 83.7, 21.6.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We greatly acknowledge partial financial support from the National Natural Science Foundation (NSF) of China (21172200 and 21302172) and Basic Research Training Project of Zhengzhou University (JC2020053021).

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Journal Pre-proof

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Highlights

1) The one-pot method involves photocatalysis and thermocatalytic processes.
2) The light “on-off” stepwise one-pot method has excellent substrate tolerance.
3) A straight forward way to obtain various types of multi-substituted coumarins.
4) Some of the synthesized 3,4-diaryl coumarins have potential AIE activities.

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