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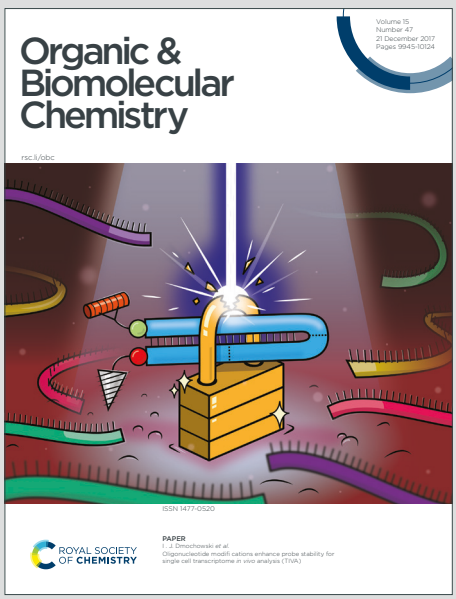

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ARTICLE

A visible-light-induced "on-off" one-pot synthesis of 3-arylacetylene coumarins with AIE properties

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A mild and simple one-pot stepwise method to synthesize 3-arylacetylene coumarins from alkynoates was demostrated. This catalytic system involves photosensitizer-free photocatalysis and thermocatalysis processes. A series of alkynoates and phenylacetylenes were well tolerated in the optimized multi-catalytic system. The corresponding 3-arylacetylene coumarins were obtained in moderate to excellent yields. The results of their optical properties studies showed that the aromatic ring at C4-position of coumarins is unfavorable for improving the molecular fluorescence quantum yield in solution. Based on the spectral studies and X-ray single crystal diffraction analysis, it was found that the AIE-activity may exist in some of the 3-arylvinyl-4-aryl-coumarins in their solid state. We expect that these molecules may have potential optical applications.

Introduction

Coumarins as one of important heteroaryls have potential applications in bioactive compounds,[1] natural products,[2] fluorescent probes/sensors[3] and non-fullerene acceptors.[4] To achieve better optical properties, the coumarin structures are often functionalized with alkyl, alkoxy, aryl, styryl, arylethynyl, amido or heterocyclic groups on their C3 or/and C4 positions.[5] Modifying these active positions, some of coumarin derivatives could also exhibit aggregation-induced emission (AIE) characteristics.[6] 3-Substituted coumarins containing D-π-A (D: Donor, A: Acceptor) structure not only accelerate the intramolecular charge transfer, but also adjust the absorption as well as emission wavelength range to red shift, to enhance the fluorescence properties.[7] Especially, the functionalization of coumarin C4 position can effectively enhance its fluorescence emission property. Their fluorescence quantum yields are significantly higher than that of coumarins without any substituent at the C4 position in the solid state.[8] The AIE phenomenon may be caused by weakened intermolecular π-π interactions.

Among of the coumarin compounds, the 3-arylacetylene have been found to have the excellent fluorescent properties in their solutions.[9] Up to now, there are several efficient ways to construct 3-arylacetylene (Fig.1): i) Pd-catalysed Sonogashira coupling reaction of aryl halides with terminal alkynes;[10] ii) C-H bond activation of aryl thiocarbamates;[11] iii) flash vacuum thermolysis (FVT) of furan ketones.[12] However, some drawbacks still exist in most of catalytic systems, such as severe reaction conditions, the pre-functionalization of the substrates and limited sources of the skeleton materials used in the preparation. Therefore, it is still a significant scientific challenge to develop mild and efficient synthetic approaches to obtain 3-arylacetylene coumarins.

One-pot synthesis method combined with multi-approaches (such as thermocatalysis, photocatalysis or/and electrocatalysis) is efficient in solving the environmental pollution and low availability of atoms problems while avoiding tedious separation steps and unnecessary side reactions.[13] In our previous works, the visible-light-induced on-off[14] and the electrochemical on-off[15] one pot reactions were separately realized to synthesize 3-styryl coumarins and pyrimidin-2(1*H*)-one. Herein, we developed a mild one-pot method to synthesize 3-arylvinyl-4-aryl-coumarins from alkynotes, which involves thermocatalysis and photocatalysis processes without any photocatalyst. The optical properties of the obtained 3-arylacetylene coumarins will be investigated.

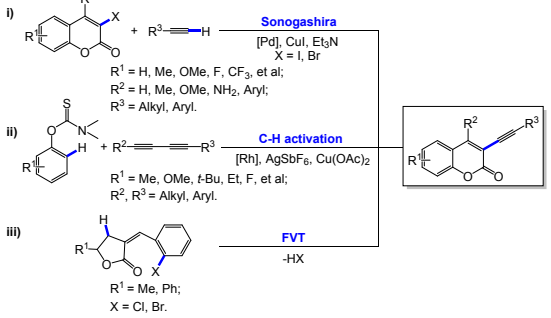

Figure 1. Methods to construct 3-arylacetylene coumarins.

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Electronic Supplementary Information (ESI) available: Electronic experimental procedures, characterization data, and copies of ^{1}H and ^{13}C NMR spectra. CCDC 1881743, 1966836, 1966837, 1966838 and 1966843. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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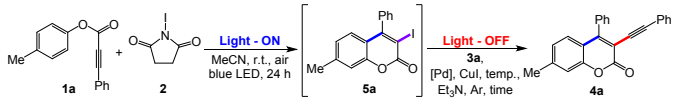
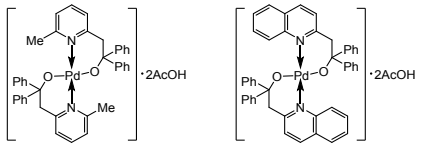
Results and discussion

Based on the literatures[16] and our previous work[13,14,15,17], a stepwise one-pot reaction involving light-driven radical cyclization and Pd-catalyzed Sonogashira cross-coupling processes was designed (Table 1). To realize the one-pot synthesis, the simple and efficient photocatalytic reaction of *p*-tolyl 3-phenylpropiolate (**1a**) with *N*-iodosuccinimide (NIS, **2**) was chosen to construct the main intermediate 3-iodocoumarin (**5a**). Our main focus was on optimization of Sonogashira reaction conditions for the multistep one-pot synthesis. After the photosynthetic step, the desired product **4a** could be isolated in excellent yield (80%) at 80 °C under Ar atmosphere by adding the following substances: phenylacetylene **3a** (3 equiv.), $Pd(PPh_3)_2Cl_2$ (10 mol %), CuI (10 mol %) and Et_3N (0.5 mL) (entry 1). No improvement of the one-pot transformation was observed when $Pd(PPh_3)_2Cl_2$ was changed into $Pd(PPh_3)_4$, $Pd(OAc)_2$, **Cat-Py1** or **Cat-Q1** (entries 2-5).[17] A more suitable reaction temperature was 60 °C (entries 6-8). The desired product **4a** was obtained in 74% yield, even if the Sonogashira reaction was carried out at room temperature. A lower yield of product **4a** was followed by shortening the reaction time to 8 hours (entry 9). To our delight, the one-pot reaction could proceed under air atmosphere with a satisfied yield (entry 10). In addition, there was no desired product without Et_3N (entry 11).

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



Entry	[Pd]	T/ °C	Time / h	Yield[b] (%)
1	$Pd(PPh_3)_2Cl_2$	80	12	80
2	$Pd(PPh_3)_4$	80	12	75
3	$Pd(OAc)_2$	80	12	70
4	Cat-Py1	80	12	54
5	Cat-Q1	80	12	64
6	**$Pd(PPh_3)_2Cl_2$**	**60**	**12**	**83**
7	$Pd(PPh_3)_2Cl_2$	40	12	76
8	$Pd(PPh_3)_2Cl_2$	r.t.	12	74
9	$Pd(PPh_3)_2Cl_2$	60	8	73
10[c]	$Pd(PPh_3)_2Cl_2$	60	12	65
11[d]	$Pd(PPh_3)_2Cl_2$	60	12	0

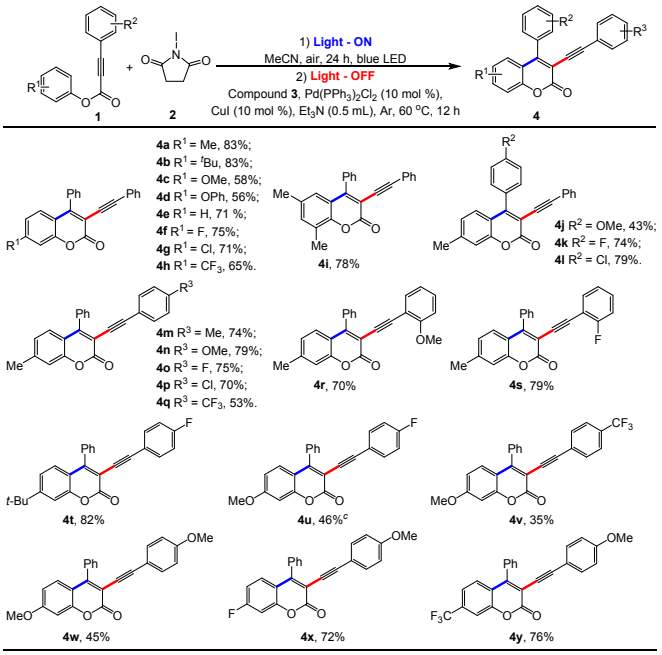


Cat-Py1 Cat-Q1

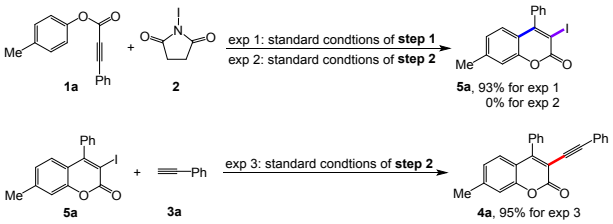
[a]Reaction conditions: 1) **1a** (0.2 mmol), **2** (2 equiv.), MeCN (1.5 mL), 3 W blue LED (λ_{max} = 450-465 nm), room temperature, under air atmosphere for 24 h; 2) **3a** (3 equiv.), [Pd] (10 mol %), CuI (10 mol %), Et_3N (0.5 mL) under Ar atmosphere. [b]Isolated yield. [c]Under air atmosphere. [d]Without Et_3N.

With the optimized conditions in hand, the scope of the substrates was examined (Scheme 1). Initially, various alkynoates could be transformed into the corresponding 3-arylacetylene coumarins (**4a-l**) in moderate to excellent yields. The electronic effect of the substituents (R^1 or R^2) is not obvious in this reaction. All the test phenylacetylenes with *para*-substituents (R^3) were well tolerated in this one-pot reaction to afford the corresponding products (**4m-q**) in moderate to good yields regardless of electron-donating (Me and OMe) or -withdrawing (F, Cl and CF_3) groups. The steric hindrance effect of the substitutes did not prevent the reaction (**4r-s**). In addition, several coumarins (**4t-y**) with D-π-A or D-π-D constructions were also successfully prepared in medium to excellent yields using this stepwise approach.

Scheme 1 Scope of the one-pot reaction[a,b]



[a]Reaction conditions: **1** (0.2 mmol), **2** (2 equiv.), MeCN (1.5 mL), 3 W blue LED (λ_{max} = 450-465 nm), room temperature, under air atmosphere for 24 h; then add **3** (3 equiv.), $Pd(PPh_3)_2Cl_2$ (10 mol %), CuI (10 mol %), Et_3N (0.5 mL) under Ar at 60 °C for 12 h. [b]Isolated yield. [c]Time 2: 24 h.



Scheme 2 Mechanistic studies.

To get insight into the reaction mechanism, several control experiments were carried out under the standard conditions (Scheme 2). 3-Iodocoumarin (**5a**) could be obtained in 93% yield under 3 W blue LED irradiation (exp 1), but it could not be afforded from the Pd-catalyzed reaction of *p*-tolyl 3-phenylpropiolate (**1a**) with NIS (exp 2). On the other hand, 3-iodocoumarin (**5a**) reacted well with phenylacetylene (**3a**) under Pd-catalyzed Sonogashira reaction to give 3-arylacetylene coumarin (**4a**) in 95% (exp 3). These experimental results indicate that 3-iodocoumarin (**5a**) is the crucial intermediate for this stepwise one-pot reaction.

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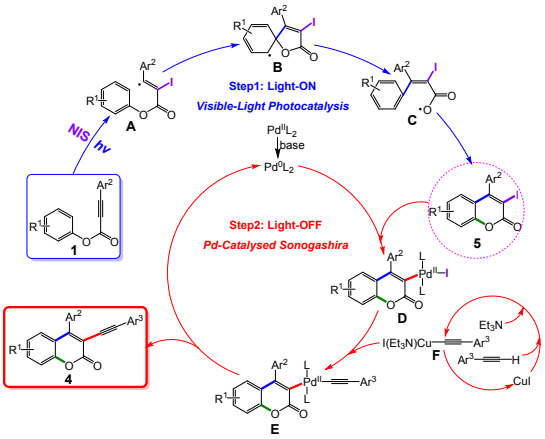
Based on the above experimental results and the previous reports,[16,18] a possible mechanism of the one-pot method was proposed involving the photocatalytic and thermocatalytic processes (Scheme 3). Initially, alkynoate **1** reacts with NIS *via* iodination/spirocyclization/ring expansion to afford the intermediate product **5**. Subsequently, the intermediate product **5** participates in a classical palladium-catalyzed Sonogashira coupling reaction to afford 3-arylacetylene coumarins **4**.



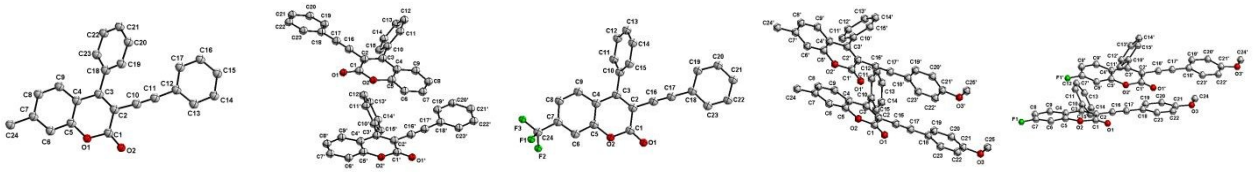
Scheme 3 Possible mechanism for this reaction.

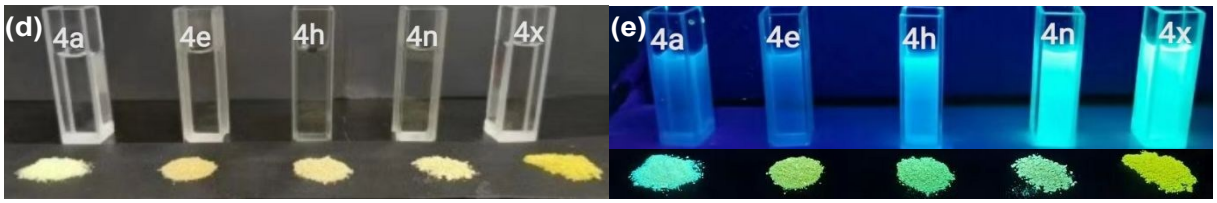
Considering the outstanding photoluminescence properties of 3-arylacetylene coumarins,[2-4] the spectral properties of all synthesized coumarins were investigated. The absorption and emission properties as well as fluorescence quantum yields (Φ_F) of all compounds (**4a-y**) were measured in MeCN (see ESI, Table S1). The shapes of absorption spectra of all compounds were similar, and the absorption maxima (λ_{abs}) were observed in the range from 352 to 375 nm (see ESI, Figures S1-S4). The emission maxima (λ_{em}) were mainly distributed in the spectral region between 445 and 506 nm (see ESI, Figures S5-S8). In comparison with other compounds, the absorption maxima of molecules (**4v-y**) with D-π-A configuration showed obvious red-shift, meanwhile, the trend observed in fluorescence emission maxima was the same for absorption maxima. Subsequently, the influence of various solvents (THF, MeCN, DMF, DMSO and EtOH) was analyzed on several synthesized compounds (**4a**, **4e**, **4h**, **4n** and **4x**) (see ESI, Figures S9-S13). The spectral properties of compounds **4a** (λ_{abs} = 357-363 nm, λ_{em} = 447-454 nm), **4e** (λ_{abs} = 352-359 nm, λ_{em} = 445-451 nm) and **4h** (λ_{abs} = 356-360 nm, λ_{em} = 446-455 nm) were almost independent of the polarity of solvent. The emission maxima of **4n** (λ_{abs} = 368-374 nm, λ_{em} = 466-489 nm) and **4x** (λ_{abs} = 365-370 nm, λ_{em} = 470-495 nm) have certain red-shift with the increase of the polarity of solvent (Table 2[a]). Comparing to other solvents, the high fluorescence quantum yields of compounds **4a**, **4e**, **4h**, **4n** and **4x** was detected in THF (Φ_F = 0.047-0.209) except compound **4n** (Φ_F = 0.160 in DMSO, Table 2[b]). More surprising, all studied compounds (**4a**, **4e**, **4h**, **4n** and **4x**) could emitted different intensities of yellow or yellow-green fluorescence under 365 nm UV light in solid-state (Table 2[d,e]). The fluorescence quantum yields of **4a** (0.486), **4e** (0.168) and **4x** (0.439) in solid state are higher than that in solution (Table 2[b]). These phenomenons suggested the following: 1) the electronic effect of substituents (R^1, R^2 or R^3) has obvious effect on the spectral properties; 2) the synthesized 3-arylacetylene coumarins might exist AIE-activity.[19]

Table 2 Absorption, emission and fluorescence quantum yields (Φ_F) of the compounds **4a**, **4e**, **4h**, **4n** and **4x** in different solvents[a,b]

Solvent	4a			4e			4h			4n			4x		
	λ_{abs} (nm)	λ_{em} (nm)	Φ_F	λ_{abs} (nm)	λ_{em} (nm)	Φ_F	λ_{abs} (nm)	λ_{em} (nm)	Φ_F	λ_{abs} (nm)	λ_{em} (nm)	Φ_F	λ_{abs} (nm)	λ_{em} (nm)	Φ_F
THF	361	447	0.047	357	446	0.061	359	446	0.136	372	466	0.143	370	470	0.209
MeCN	357	451	0.014	352	445	0.011	356	450	0.066	368	475	0.080	365	484	0.115
DMF	362	452	0.047	358	450	0.033	360	453	0.136	372	479	0.155	368	489	0.172
DMSO	363	454	0.034	359	451	0.106	360	454	0.055	374	488	0.160	370	494	0.137
EtOH	362	454	0.022	358	451	0.020	359	455	0.061	373	489	0.121	370	495	0.128
Solid	441	490	0.486	446	476	0.168	435	486	-	458	514	-	472	512	0.439

X-ray Analysis[c]





[a]UV and FL spectra were recorded at a concentration of 5 x 10^{-2} mM in different solvents. [b]Fluorescence quantum yield was calculated by using quinine sulfate as an external standard. [c]X-ray crystal structures of compounds **4a**, **4e**, **4h**, **4n** and **4x**. Photos of the THF solutions (10 mM) and solid powders of compounds **4a**, **4e**, **4h**, **4n** and **4x** under natural light[d] and 365 nm UV light[e].

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To further explore the AIE characteristic of the synthesized coumarin compounds, the single crystals of compounds **4a**, **4e**, **4h**, **4n** and **4x** have been obtained by the slow diffusion of their alcohol/dichloromethane (V/V = 1/1) solution for several days at room temperature (Table 2[c]). The X-ray single crystal diffraction analysis results of the five compounds showed that the coumarin fragment and phenylacetylene unit exhibit good coplanarity with small dihedral angles (**4a**: 10.44°, **4e**: 11.81°, **4h**: 4.25°, **4n**: 0.61° and **4x**: 2.31°), while the aromatic rings at 4-position lie out of the plane of the conjugated backbones with large dihedral angles (**4a**: 60.60°, **4e**: 63.26°, **4h**:60.45°, **4n**: 61.66° and **4x**: 60.85°), which indicate that their AIE characteristic is not caused by intramolecular planarization.[20a] It was found that though the crystal stacking models of the five compounds are different in their crystal packing diagrams. They all arrange in a loose accumulation due to the steric hindrance imposed by the 4-subsituted aromatic rings. There are multiple intermolecular forces (such as C-H···π and C-H···O or C-H···F short-range forces) between the adjacent molecules of each compounds (see ESI, Tables S3-S7). The experimental results confirm that the aromatic ring at 4-position of coumarins not only destroys the coplanarity of the whole molecule, but also hinders the strong π-π intermolecular interaction and the close π-π stacking between adjacent molecules. The collective force of these multiple electrostatic interactions can restrict intramolecular rotation (RIR) in the solid, thus resulting in the fluorescence enhancement in aggregation state.[20] The detailed AIE mechanism of the synthesized 3-arylvinyl-4-aryl-coumarins is under way in our laboratory.

Experimental section

General information

All reactions were performed using quartz tube. Solvents were dried by standard methods before they were used. Aryl alkynoates were synthesized according to the literature.[21] Commercial grade reagents were used without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. All reactions were carried out with photoreactor (Serial No: PEA12) which was purchased from LUOYANG JINFENG ELECTROMECHANICAL EQUIPMENT CO., LTD. The LCD Digital Hotplate Magnetic Stirrer MS-H-Pro+ and Digital Single Channel Adjustable Automatic Electronic Pipette Micropipette dPettee+ were 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 was recorded at 376.5 MHz on Bruker DPX-400, the chemical shifts δ are reported relative to $CFCl_3$ (δ = 0 ppm) as 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) was obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionisation (ESI). The UV/Vis absorption spectra was recorded on a Perkin Elmer Lambda 35 Spectrometer, and the fluorescence emission was recorded using a F-4500 FL spectrophotometer, the solid fluorescence quantum yield spectra was recorded on a C13534 UV-NIR absolute PL Quantum Yield Spectrometer.

General procedure for the synthesis of 3-arylacetylene coumarins 4

To a reaction tube equipped with a magnetic stirring bar were added phenyl 3-phenylpropiolate (0.2 mmol), NIS (2 equiv.), MeCN (1.5 mL) stirred under 3 W blue LED (λmax = 450-465 nm) under air atmosphere and at room temperature for 24 hours. Then $Pd(PPh_3)_2Cl_2$ (0.0144 g, 10 mol %), CuI (0.0039 g, 10 mol %), phenylacetylene (3 equiv.) and Et_3N (0.5 mL) were added. The obtained reaction mixture was heated at 60 °C for 12 hours under Ar atmosphere. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 6:1/1:1, V/V) to give the desired compound **4**.

Characterization data for intermediate 5a and products 4

3-iodo-7-methyl-4-phenyl-2*H*-chromen-2-one (5a). White solid (67.1 mg, 93%). mp. 157.6-159.0 °C. IR (KBr) 1716, 1614, 1582, 1531, 1340, 1250, 1132, 981, 958, 729, 692 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.58-7.54 (m, 3H), 7.24-7.20 (m, 3H), 6.97-6.91 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 158.4, 153.2, 143.9, 139.2, 129.3, 128.9, 127.8, 127.6, 125.9, 117.9, 116.8, 90.7, 21.8. HRMS (ESI) calcd. for $C_{16}H_{11}IO_2$ $[M+H]^+$: 362.9876, found: 362.9877.

7-methyl-4-phenyl-3-(phenylethynyl)-*2H*-chromen-2-one (4a). Light yellow solid (56.1 mg, 83%). mp. 171.7-172.9 °C. IR (KBr) 3053, 2918, 1719, 1615, 1533, 1485, 1436, 1064, 748, 687 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.55 (m, 3H), 7.50-7.48 (m, 2H), 7.26-7.23 (m, 5H), 7.21 (s, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 156.4, 153.0, 143.6, 134.6, 131.7, 129.3, 129.1, 128.7, 128.4, 128.2, 127.3, 125.8, 122.6, 117.3, 117.2, 110.0, 98.2, 83.9, 21.8. HRMS (ESI) calcd. for $C_{24}H_{17}O_2$ $[M+H]^+$: 337.1223, found: 337.1224.

7-(*tert*-butyl)-4-phenyl-3-(phenylethynyl)-*2H*-chromen-2-one (4b). Light yellow solid (62.8 mg, 83%). mp. 180.5-182.4 °C. IR (KBr) 3053, 2963, 1720, 1613, 1578, 1533, 1483, 1067, 710, 689 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.53 (m, 3H), 7.51-7.49 (m, 2H), 7.41 (d, *J* = 1.3 Hz, 1H), 7.23-7.20 (m, 7H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 156.8, 156.2, 153.0, 134.6, 131.7, 129.3, 129.1, 128.7, 128.4, 128.2, 127.2, 122.6, 122.1, 117.2, 113.9, 110.1, 98.2, 84.0, 35.3, 31.0. HRMS (ESI) calcd. for $C_{27}H_{23}O_2$ $[M+H]^+$: 379.1693, found: 379.1695.

7-methoxy-4-phenyl-3-(phenylethynyl)-*2H*-chromen-2-one (4c). Light yellow solid (40.5 mg, 58%). mp. 145.9-147.7 °C. IR (KBr) 3056, 2933, 2839, 1727, 1610, 1534, 1486, 1435, 1045, 751, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.53 (m, 3H), 7.49-7.47 (m, 2H), 7.26-7.17 (m, 6H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.72 (dd, *J* = 8.9 Hz, *J* = 2.5 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1, 160.0, 156.6, 154.8, 134.7, 131.6, 129.3, 129.1, 128.7, 128.5, 128.4, 128.2, 122.8, 113.3, 112.8, 107.8, 100.9, 97.6, 84.0, 55.9. HRMS (ESI) calcd. for $C_{24}H_{17}O_3$ $[M+H]^+$: 353.1172, found: 353.1174.

7-phenoxy-4-phenyl-3-(phenylethynyl)-*2H*-chromen-2-one (4d). Yellow solid (46.6 mg, 56%). mp. 185.3-186.9 °C. IR (KBr) 3054, 2921, 2853, 1727, 1614, 1585, 1484, 1367, 1047, 756, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.59-7.54 (m, 3H), 7.50-7.48 (m, 2H), 7.43-7.40 (m, 2H), 7.27-7.20 (m, 7H), 7.10 (dd, *J* = 8.7 Hz, *J* = 1.1 Hz, 2H), 6.90

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(d, *J* = 2.5 Hz, 1H), 6.85 (dd, *J* = 16.6Hz, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 159.7, 156.2, 154.9, 154.4, 134.6, 131.7, 130.2, 129.4, 129.1, 129.0, 128.7, 128.5, 128.2, 125.3, 122.6, 120.5, 114.7, 114.6, 108.7, 105.0, 98.0, 83.9. HRMS (ESI) calcd. for $C_{29}H_{19}O_3$ $[M+H]^+$: 415.1329, found: 415.1326.

4-phenyl-3-(phenylethynyl)-*2H*-chromen-2-one (4e).[10e] Light yellow solid (45.9 mg, 71%). mp. 169.3-170.4 °C. IR (KBr) 3054, 2922, 1719, 1601, 1538, 1484, 1445, 1059, 748, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.55 (m, 3H), 7.51-7.47 (m, 3H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.30-7.19 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 156.3, 152.9, 134.4, 132.1, 131.8, 129.4, 129.1, 128.8, 128.5, 128.2, 127.6, 124.5, 122.5, 119.7, 117.0, 111.2, 98.7, 83.8. HRMS (ESI) calcd. for $C_{23}H_{15}O_2$ $[M+H]^+$: 323.1067, found: 323.1068.

7-fluoro-4-phenyl-3-(phenylethynyl)-*2H*-chromen-2-one (4f). Light yellow solid (50.9 mg, 75%). mp. 204.1-205.2 °C. IR (KBr) 3059, 1737, 1603, 1546, 1495, 1431, 1050, 853, 748, 695 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.54 (m, 3H), 7.49-7.48 (m, 2H), 7.29-7.20 (m, 6H), 7.11 (dd, *J* = 8.8 Hz, *J* = 2.3 Hz, 1H), 6.95 (td, *J* = 8.3 Hz, *J* = 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5 (d, *J* = 256.0 Hz), 159.2, 155.7, 153.9 (d, *J* = 13.2 Hz), 134.2, 131.7, 130.0, 129.4 (d, *J* = 9.5 Hz), 129.0, 128.9, 128.6, 128.2, 122.4, 116.5, 112.6 (d, *J* = 22.7 Hz), 110.1, 104.5 (d, *J* = 25.7 Hz), 98.7, 83.5. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -104.5. HRMS (ESI) calcd. for $C_{23}H_{14}FO_2$ $[M+H]^+$: 341.0972, found: 341.0971.

7-chloro-4-phenyl-3-(phenylethynyl)-*2H*-chromen-2-one (4g). Light yellow solid (50.4 mg, 71%). mp. 177.8-178.4 °C. IR (KBr) 3058, 2923, 1735, 1596, 1518, 1484, 1413, 1054, 755, 693 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58-7.57 (m, 3H), 7.49-7.47 (m, 2H), 7.41 (d, *J* = 1.2 Hz, 1H), 7.30-7.16 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 155.4, 153.0, 138.0, 134.0, 131.8, 129.6, 129.0, 128.9, 128.6, 128.5, 128.3, 125.1, 122.3, 118.4, 117.3, 111.1, 99.2, 83.6. HRMS (ESI) calcd. for $C_{23}H_{14}ClO_2$ $[M+H]^+$: 357.0677, found: 357.0676.

4-phenyl-3-(phenylethynyl)-7-(trifluoromethyl)-*2H*-chromen-2-one (4h). Yellow solid (50.6 mg, 65%). mp. 169.3-170.8 °C. IR (KBr) 3056, 2924, 1739, 1613, 1546, 1497, 1425, 1058, 748, 682 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 1H), 7.62-7.58 (m, 3H), 7.51-7.49 (m, 2H), 7.46-7.40 (m, 2H), 7.32-7.22 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 153.5 (d, *J* = 230.4 Hz), 133.8, 133.3 (d, *J* = 33.0 Hz), 131.9, 129.8, 129.2, 129.0, 128.7, 128.3, 128.2, 124.5, 122.4, 122.1, 121.8, 120.9 (q, *J* = 7.3 Hz, *J* = 3.7 Hz), 114.4 (q, *J* = 8.1 Hz, *J* = 3.7 Hz), 113.3, 100.3, 83.4. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -62.9. HRMS (ESI) calcd. for $C_{24}H_{14}F_3O_2$ $[M+H]^+$: 391.0940, found: 391.0936.

6,8-dimethyl-4-phenyl-3-(phenylethynyl)-*2H*-chromen-2-one (4i). Yellow solid (54.9 mg, 78%). mp. 189.4-190.7 °C. IR (KBr) 3054, 3017, 2916, 1721, 1600, 1541, 1480, 1077, 1051, 752, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.55 (m, 3H), 7.48-7.46 (m, 2H), 7.25-7.21 (m, 6H), 6.85 (s, 1H), 2.47 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 156.8, 149.5, 135.0, 134.7, 133.6, 131.7, 129.2, 129.1, 128.7, 128.4, 128.2, 126.1, 125.0, 122.6, 119.2, 110.8, 98.4, 84.2, 20.9, 15.6. HRMS (ESI) calcd. for $C_{25}H_{19}O_2$ $[M+H]^+$: 351.1380, found: 351.1382.

4-(4-methoxyphenyl)-7-methyl-3-(phenylethynyl)-*2H*-chromen-2-one (4j). Yellow solid (31.7 mg, 43%). mp. 169.1-170.2 °C. IR (KBr) 3020, 1724, 1608, 1539, 1490, 1441, 1060, 1027, 757, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.7 Hz, 2H), 7.32-7.20 (m, 7H), 7.08 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 21.4 Hz, 1H), 3.92 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5, 160.0, 156.0, 153.0, 143.5, 131.7, 130.9, 128.6, 128.2, 127.4, 126.6, 125.7, 122.8, 117.5, 117.2, 113.8, 97.8, 84.2, 55.5, 21.7. HRMS (ESI) calcd. for $C_{25}H_{19}O_3$ $[M+H]^+$: 367.1329, found: 367.1330.

4-(4-fluorophenyl)-7-methyl-3-(phenylethynyl)-*2H*-chromen-2-one (4k). Yellow solid (52.6 mg, 74%). mp. 187.7-188.8 °C. IR (KBr) 3066, 1717, 1611, 1535, 1488, 1224, 1065, 751, 684 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.48 (m, 2H), 7.29-7.25 (m, 7H), 7.68-7.55 (m, 5H), 7.21 (s, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2 (d, *J* = 250.2 Hz), 159.7, 155.1, 152.9, 143.8, 131.7, 131.2 (d, *J* = 8.1 Hz), 130.5, 128.9, 128.3, 127.1, 125.9, 122.4, 117.3, 115.7, 115.5, 110.2, 98.4, 83.7, 21.7. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -111.1. HRMS (ESI) calcd. for $C_{24}H_{16}FO_2$ $[M+H]^+$: 355.1129, found: 355.1130.

4-(4-chlorophenyl)-7-methyl-3-(phenylethynyl)-*2H*-chromen-2-one (4l). Light yellow solid (58.4 mg, 79%). mp. 185.2-186.7 °C. IR (KBr) 2362, 2333, 1717, 1617, 1534, 1483, 1065, 752, 728, 686 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.54 (m, 2H), 7.46-7.44 (m, 2H), 7.29-7.26 (m, 5H), 7.21 (s, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.03 (dd, *J* = 33.4 Hz, *J* = 1.0 Hz, 1H), 2.46 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 154.8, 152.9, 143.8, 135.5, 133.0, 131.7, 130.6, 128.9, 128.8, 128.3, 127.0, 125.9, 122.4, 117.3, 117.0, 110.2, 98.7, 83.6, 21.7. HRMS (ESI) calcd. for $C_{24}H_{16}ClO_2$ $[M+H]^+$: 371.0833, found: 371.0834.

7-methyl-4-phenyl-3-(*p*-tolylethynyl)-*2H*-chromen-2-one (4m). Light yellow solid (52.1 mg, 74%). mp. 191.5-192.8 °C. IR (KBr) 2363, 2333, 1717, 1617, 1535, 1509, 1368, 1063, 811, 763, 712 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58-7.53 (m, 3H), 7.51-7.47 (m, 2H), 7.20 (s, 1H), 7.16-7.10 (m, 3H), 7.05-7.00 (m, 3H), 2.45 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 156.0, 152.9, 143.4, 139.0, 134.6, 131.6, 129.3, 129.2, 129.0, 128.4, 127.3, 125.7, 119.6, 117.4, 117.2, 110.2, 98.6, 83.4, 21.7, 21.6. HRMS (ESI) calcd. for $C_{25}H_{19}O_2$ $[M+H]^+$: 351.1380, found: 351.1384.

3-((4-methoxyphenyl)ethynyl)-7-methyl-4-phenyl-*2H*-chromen-2-one (4n). Light yellow solid (58.0 mg, 79%). mp. 180.9-182.4 °C. IR (KBr) 3056, 3018, 2970, 2926, 1732, 1612, 1503, 1449, 1058, 1023, 821, 756, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53-7.53 (m, 3H), 7.49-7.47 (m, 2H), 7.19 (s, 1H), 7.16-7.13 (m, 3H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 2H) 3.77 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0 159.9, 155.5, 152.8, 143.3, 134.7, 133.2, 129.2, 129.1, 128.4, 127.2, 125.7, 117.4, 117.1, 114.7, 113.9, 110.3, 98.5, 82.9, 55.3, 21.7. HRMS (ESI) calcd. for $C_{25}H_{19}O_3$ $[M+H]^+$: 367.1329, found: 367.1328.

3-((4-fluorophenyl)ethynyl)-7-methyl-4-phenyl-*2H*-chromen-2-one (4o). Yellow solid (52.9 mg, 75%). mp. 208.7-210.2 °C. IR (KBr) 3064, 3030, 2922, 2332, 1721, 1611, 1499, 1366, 1323, 1221, 1057, 761, 700, 643 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.55 (m, 3H), 7.49-7.47 (m, 2H), 7.21-7.14 (m, 4H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.93 (t, *J* = 8.7 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7 (d, *J* = 250.9 Hz), 159.8, 156.4, 153.0, 143.7, 134.6, 133.6 (d, *J* = 8.8 Hz), 129.4, 129.1, 128.4, 127.3, 125.8, 118.7 (d, *J* = 3.7 Hz), 117.3, 117.2, 115.5 (d, *J* = 22.0 Hz), 109.8, 97.1, 83.7, 21.7. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -109.9. HRMS (ESI) calcd. for $C_{24}H_{16}FO_2$ $[M+H]^+$: 355.1129, found: 355.1126.

3-((4-chlorophenyl)ethynyl)-7-methyl-4-phenyl-*2H*-chromen-2-one (4p). Yellow solid (51.7 mg, 70%). mp. 234.3-236.4 °C. IR (KBr) 3055, 3042, 2909, 1716, 1614, 1582, 1531, 729, 692, 630 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.54 (m, 3H), 7.49-7.47 (m, 2H),

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7.21-7.19 (m, 3H), 7.17-7.11 (m, 3H), 7.02 (dd, *J* = 8.2 Hz, *J* = 0.9 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 156.7, 153.0, 143.8, 134.7, 134.5, 132.8, 129.4, 129.1, 128.6, 128.4, 127.4, 125.8, 121.1, 117.2, 109.7, 96.9, 84.9, 21.8. HRMS (ESI) calcd. for $C_{24}H_{16}ClO_2$ $[M+H]^+$: 371.0833, found: 371.0837.

7-methyl-4-phenyl-3-((4-(trifluoromethyl)phenyl)ethynyl)-*2H*-chromen-2-one (4q). Light yellow solid (42.9 mg, 53%). mp. 221.9-223.8 °C. IR (KBr) 3060, 2924, 1739, 1613, 1540, 1486, 1322, 1256, 1166, 1125, 1048, 775, 730, 694, 655 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.56 (m, 3H), 7.50-7.48 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.04 (dd, *J* = 8.2 Hz, *J* = 1.1 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 157.6, 153.1, 144.2, 134.4, 131.8, 130.7, 130.2 (d, *J* = 32.3 Hz), 129.5, 128.7 (d, *J* = 55.8 Hz), 127.5, 126.4 (d, *J* = 1.5 Hz), 125.9, 125.1 (q, *J* = 8.1 Hz, *J* = 3.7 Hz), 122.5, 117.3, 117.2, 109.4, 96.3, 86.2, 21.8. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -62.9. HRMS (ESI) calcd. for $C_{25}H_{16}F_3O_2$ $[M+H]^+$: 405.1097, found: 405.1100.

3-((2-methoxyphenyl)ethynyl)-7-methyl-4-phenyl-*2H*-chromen-2-one (4r). Yellow solid (51.3 mg, 70%). mp. 162.1-163.4 °C. IR (KBr) 3057, 2984, 1726, 1615, 1582, 1487, 1454, 1246, 1054, 1017, 699, 647 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.49 (m, 5H), 7.26-7.14 (m, 4H), 7.01 (d, *J* = 8.2 Hz, 1H) 6.84-6.77 (m, 2H), 3.76 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 159.8, 155.5, 152.9, 143.3, 134.6, 133.7, 130.3, 129.2, 129.1, 128.3, 127.3, 125.7, 120.3, 117.4, 117.2, 112.0, 110.7, 110.3, 94.9, 87.7, 55.8, 21.7. HRMS (ESI) calcd. for $C_{25}H_{19}O_3$ $[M+H]^+$: 367.1329, found: 367.1327.

3-((2-fluorophenyl)ethynyl)-7-methyl-4-phenyl-*2H*-chromen-2-one (4s). Yellow solid (56.5 mg, 79%). mp. 179.6-181.3 °C. IR (KBr) 3057, 2984, 2940, 2840, 1726, 1615, 1582, 1487, 1455, 1246, 1054, 1017, 753, 699 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.48 (m, 5H), 7.31-7.17 (m, 4H), 7.04-6.96 (m, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7 (d, *J* = 253.8 Hz), 159.7, 156.8, 153.1, 143.9, 134.2, 133.5, 130.5 (d, *J* = 7.3 Hz), 129.4, 129.0, 128.5, 127.5, 125.8, 123.8 (d, *J* = 3.7 Hz), 117.2, 115.4 (d, *J* = 20.5 Hz), 111.4, 111.3, 109.6, 91.3, 88.5 (d, *J* = 3.7 Hz), 21.7. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -108.5. HRMS (ESI) calcd. for $C_{24}H_{16}FO_2$ $[M+H]^+$: 355.1129, found: 355.1126.

7-(*tert*-butyl)-3-((4-fluorophenyl)ethynyl)-4-phenyl-*2H*-chromen-2-one (4t). Light yellow solid (65.0 mg, 82%). mp. 185.9-186.7 °C. IR (KBr) 2961, 2905, 2869, 1738, 1614, 1500, 1415, 1367, 1330, 1218, 1049, 828, 763, 699 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.55 (m, 3H), 7.50-7.48 (m, 2H), 7.42 (d, *J* = 1.7 Hz, 1H), 7.27-7.19 (m, 4H), 6.93 (t, *J* = 8.7 Hz, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7 (d, *J* = 250.2 Hz), 159.9, 156.9, 156.3, 152.9, 134.5, 133.6 (d, *J* = 8.8 Hz), 129.4, 129.1, 128.4, 127.2, 122.2, 118.7 (d, *J* = 2.9 Hz), 117.2, 115.5 (d, *J* = 22.7 Hz), 113.9, 110.0, 97.1, 83.7, 35.3, 31.0. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -109.9. HRMS (ESI) calcd. for $C_{27}H_{22}FO_2$ $[M+H]^+$: 397.1598, found: 397.1596.

3-((4-fluorophenyl)ethynyl)-7-methoxy-4-phenyl-*2H*-chromen-2-one (4u). Yellow solid (33.8 mg, 46%). mp. 178.8-179.6 °C. IR (KBr) 3064, 2992, 2943, 2841, 1731, 1611, 1500, 1375, 1267, 1214, 1055, 829, 761, 700, 645 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.55 (m, 3H), 7.49-7.46 (m, 2H), 7.21-7.17 (m, 3H), 6.95-6.89 (m, 3H), 6.78 (dd, *J* = 8.9 Hz, *J* = 2.5 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1, 162.6 (d, *J* = 250.2 Hz), 160.1, 156.6, 154.8, 134.7, 133.5 (d, *J* = 8.8 Hz), 129.3, 129.0, 128.7, 128.4, 118.8 (d, *J* = 3.7 Hz), 115.5 (d, *J* = 22.0 Hz), 113.3, 112.9, 107.6, 100.9, 96.5, 83.7, 55.9. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -110.2. HRMS (ESI) calcd. for $C_{24}H_{16}FO_3$ $[M+H]^+$: 371.1078, found: 371.1081.

7-methoxy-4-phenyl-3-((4-(trifluoromethyl)phenyl)ethynyl)-*2H*-chromen-2-one (4v). Light yellow solid (29.4 mg, 35%). mp. 209.6-210.5 °C. IR (KBr) 3057, 2927, 2851, 1726, 1613, 1537, 1511, 1462, 1322, 1284, 1124, 837, 701, 630 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.56 (m, 3H), 7.50-7.47 (m, 4H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.9 Hz, 1H), 6.91 (d, *J* = 2.5 Hz, 1H), 6.80 (dd, *J* = 9.1 Hz, *J* = 2.6 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4, 159.9, 157.8, 155.0, 134.5, 131.7, 130.0 (d, *J* = 33.0 Hz), 129.5, 129.0, 128.9, 128.5, 126.5, 125.1 (q, *J* = 7.3 Hz, *J* = 3.7 Hz), 122.5, 113.2, 113.1, 107.1, 100.9, 95.8, 86.3, 55.9. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -62.9. HRMS (ESI) calcd. for $C_{25}H_{16}F_3O_3$ $[M+H]^+$: 421.1046, found: 421.1047.

7-methoxy-3-((4-methoxyphenyl)ethynyl)-4-phenyl-*2H*-chromen-2-one (4w). Yellow solid (34.0 mg, 45%). mp. 231.4-232.1 °C. IR (KBr) 3059, 3009, 2199, 1723, 1609, 1503, 1460, 1376, 1277, 1055, 1020, 828, 761, 706, 633 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.54 (m, 3H), 7.49-7.47 (m, 2H), 7.17 (t, *J* = 9.2 Hz, 3H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.79-6.75 (m, 3H), 3.89 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 160.2, 159.9, 155.7, 154.6, 134.8, 133.1, 129.2, 129.1, 128.6, 128.4, 114.9, 113.9, 113.4, 112.8, 108.1, 100.8, 97.9, 82.8, 55.9, 55.3. HRMS (ESI) calcd. for $C_{25}H_{19}O_4$ $[M+H]^+$: 383.1278, found: 383.1279.

7-fluoro-3-((4-methoxyphenyl)ethynyl)-4-phenyl-*2H*-chromen-2-one (4x). Light yellow solid (52.9 mg, 72%). mp. 197.3-198.1 °C. IR (KBr) 2378, 2313, 2203, 1728, 1606, 1547, 1511, 1427, 1247, 1050, 1025, 822, 762, 703 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.55 (m, 3H), 7.49-7.47 (m, 2H), 7.29-7.25 (m, 1H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.11 (dd, *J* = 8.9 Hz, *J* = 2.5 Hz, 1H), 6.94 (td, *J* = 8.4 Hz, *J* = 2.5 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3 (d, *J* = 255.3 Hz), 160.1, 159.3, 154.8, 153.8 (d, *J* = 13.2 Hz), 134.4, 133.3, 129.5, 129.2 (d, *J* = 9.5 Hz), 129.1, 128.5, 116.6 (d, *J* = 2.9 Hz), 114.5, 113.9, 112.6 (d, *J* = 22.7 Hz), 110.4 (d, *J* = 2.9 Hz), 104.5 (d, *J* = 25.7 Hz), 99.1, 82.5, 55.3. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -105.0. HRMS (ESI) calcd. for $C_{25}H_{16}FO_3$ $[M+H]^+$: 371.1078, found: 371.1076.

3-((4-methoxyphenyl)ethynyl)-4-phenyl-7-(trifluoromethyl)-*2H*-chromen-2-one (4y). Light yellow solid (63.7 mg, 76%). mp. 200.8-201.5 °C. IR (KBr) 3067, 3024, 2924, 2378, 2198, 1742, 1598, 1546, 1508, 1425, 1327, 1170, 1133, 1049, 1021, 830, 758, 699 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63-7.58 (m, 4H), 7.51-7.48 (m, 2H), 7.44-7.39 (m, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 152.3, 150.4, 142.3, 136.9, 136.6, 135.0, 133.3, 130.3, 128.9, 128.8, 127.8, 127.2, 126.0, 125.4, 125.1, 122.9, 120.7, 118.6, 116.6, 21.6, 19.9. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -62.9. HRMS (ESI) calcd. for $C_{25}H_{16}F_3O_3$ $[M+H]^+$: 421.1046, found: 421.1048.

Conclusions

In summary, we have developed a mild and efficient one-pot stepwise method to synthesize 3-arylacetylene coumarins from simple alkynoates *via* the thermocatalysis and photocatalysis processes. This catalytic system exhibits the excellent functional group tolerance and substrate suitability. Moreover, the optical properties of these synthesized coumarins were systematically studied. Based on the spectral studies and X-ray single crystal

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diffraction analysis, we found that some of the 3-arylvinyl-4-aryl-coumarins may have AIE-activity. The AIE- and other biological activity of 4-aryl substituted coumarins is under way in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 a) X. Yu, G. Shen, L. Neckers, H. Blake, J. Holzbeierlein, B. Cronk and B. Blagg, *J. Am. Chem. Soc.*, 2005, **127**, 12778-12779; b) E. B. B. Ong, N. Watanabe, A. Saito, Y. Futamura, K. H. A. E. Galil, A. Koito, N. Najimudin and H. Osada, *J. Biol. Chem.,* 2011, **286**, 14049-14056; c) K. V. Sashidhara, A. Kumar, M. Chatterjee, K. B. Rao, S. Singh, A. K. Verma and G. Palit, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 1937-1941; d) Y. Bansal, P. Sethi and G. Bansal, *Med. Chem. Res.*, 2013, **22**, 3049-3060; e) K. V. Sashidhara, R. K. Modukuri, S. Singh, K. B. Rao, G. A. Teja, S. Gupta and S. Shukla, *Bioorg. Med. Chem. Lett.,* 2015, **25**, 337-341; f) A. Thakur, R. Singla and V. Jaitak, *Eur. J. Med. Chem.*, 2015, **101**, 476-495; g) Z. Wang, L. Wang, Z. Wang and P. Li, *Asian J. Org. Chem.*, 2019, **8**, 1-11.

2 a) A. Lacy and R. O'Kennedy, *Curr. Pharm. Des.*, 2004, **10**, 3797-3811; b) B. E. Moulton, J. M. Lynam, A. D. Klair, W. Zheng, Z. Lin and I. J. S. Fairlamb, *Org. Biomol. Chem.*, 2010, **8**, 5398-5403; c) H. A. Stefani, K. Gueogjan, F. Manarin, S. H. P. Farsky, J. Z. Schpector, I. Caracelli, S. R. P. Rodrigues, M. N. Muscará, S. A. Teixeira, J. R. Santin, I. D. Machado, S. M. Bolonheis, R. Curi and M. A. Vinolo, *Eur. J. Med. Chem.,* 2012, **58**, 117-127; d) P. Mutai, G. Breuzard, A. Pagano, D. Allegro, V. Peyrot and K. Chibale, *Bioorg. Med. Chem.,* 2017, **25**, 1652-1665.

3 a) K. Fujimoto, M. Kajino and M. Inouye, *Res. Chem. Inter.*, 2013, **39**, 311-319; b) N. Myung, S. Connelly, B. Kim, S. J. Park, I. A. Wilson, J. W. Kelly and S. Choi, *Chem. Commun.*, 2013, **49**, 9188-9190; c) N. Prachumrak, S. Pojanasopa, R. Tarsang, S. Namuangruk, S. Jungsuttiwong, T. Keawin, T. Sudyoadsuk and V. Promarak, *New J. Chem.*, 2014, **38**, 3282-3294; d) Q. Hu, Y. Tan, M. Liu, J. Yu, Y. Cui and Y. Yang, *Dyes Pigments*, 2014, **107**, 45-50; e) Y. Liu, S. Zhang, X. Lv, Y. Sun, J. Liu and W. Guo, *Analyst*, 2014, **139**, 4081-4087; f) P. Wang, Y. Fang, J. Jiang, Y. Ji, Y. Li, J. Zheng, Q. Xu and J. Lu, *Chem. Asian J.*, 2017, **12**, 1790-1795.

4 P. S. Rao, A. Gupta, S. V. Bhosale, A. Bilic, W. Xiang, R. A. Evans and S. V. Bhosale, *Dyes Pigments*, 2017, **146**, 502-511.

5 a) A. Elangovan, J. Lin, S. Yang, H. Hsu and T. Ho, *J. Org. Chem.*, 2004, **69**, 8086-8092; b) J. P. Olson, H. B. Kwon, K. T. Takasaki, C. Q. Chiu, M. J. Higley, B. L. Sabatini and G. C. R. E. Davies, *J. Am. Chem. Soc.*, 2013, **135**, 5954-5957; c) K. Kawaai, T. Yamaguchi, E. Yamaguchi, S. Endo, N. Tada, A. Ikari and A. Itoh, *J. Org. Chem.*, 2018, **83**, 1988-1996; d) L. Chen, L. Wu, W. Duan, T. Wang, L. Li, K. Zhang, J. Zhu, Z. Peng and F. Xiong, *J. Org. Chem.*, 2018, **83**, 8607-8614; e) G. Bras, C. Radanyi, J. Peyrat, J. Brion, M. Alami, V. Marsaud, B. Stella and J. Renoir, *J. Med. Chem.,* 2007, **50**, 6189-6200; f) M. G. Woll, H. Qi, A. Turpoff, N. Zhang, X. Zhang, G. Chen, C. Li, S. Huang, T. Yang, Y. Moon, C. Lee, S. Choi, N. G. Almstead, N. A. Naryshkin, A. Dakka, J. Narasimhan, V. Gabbeta, E. Welch, X. Zhao, N. Risher, J. Sheedy, M. Weetall, and G. M. Karp, *J. Med. Chem.,* 2016, **59**, 6070-6085.

6 a) J. Chen, W. Liu, Y. Wang, H. Zhang, J. Wu, H. Xu, W. Jun and P. Wang, *Tetrahedron Lett.*, 2013, **54**, 6447-6449; b) F. Bu, R. Duan, Y. Xie, Y. Yi, Q. Peng, R. Hu, A. Qin, Z. Zhao and B. Z. Tang, *Angew. Chem. Int. Ed.*, 2015, **54**, 14492-14497; c) L. Q. Yan, Z. N. Kong, Y. Xia and Z. J. Qi, *New J. Chem.*, 2016, **40**, 7061-7068; d) R. Qian, H. Tong, C. Huang, J. Li, Y. Tang, R. Wang, K. Lou and W. Wang, *Org. Biomol. Chem.*, 2016, **14**, 5007-5011; e) S. K. Lanke and N. Sekar, *J. Fluoresc.*, 2016, **26**, 497-511; f) M. R. Shreykar and N. Sekar, *J. Fluoresc.*, 2017, **27**, 1687-1707; g) A. Kumar, S. Mondal, K. S. Kayshap, S. K. Hira, P. P. Manna, W. Dehaen and S. Dey, *New J. Chem.*, 2018, **42**, 10983-10988.

7 a) S. K. Padhan, N. Murmu, S. Mahapatra, M. K. Dalai and S. N. Sahu, *Mater. Chem. Front.*, 2019, **3**, 2437-2456; b) H. Wu, Y. Wang, W. Wu, Z. Xu, X. Zha and Y. Fan, *Spectrochim. Acta, Part A*, 2019, **222**, 117272-117278; c) P. P. Soufeena, T. A. Nibila and K. K. Aravindakshan, *Spectrochim. Acta, Part A*, 2019, **223**, 117201-117208; d) C. Huang and Y. Qian, *ChemistrySelect*, 2019, **4**, 2205-2210; e) X. Wang, H. Wang, Y. Niu, Y. Wang and L. Feng, *Spectrochim. Acta, Part A*, 2020, **226**, 117650-117656.

8 L. Yan, R. Li, W. Shen and Z. Qi, *J. Lumin.*, 2018, **194**, 151-155.

9 a) L. Wirtz and U. Kazmaier, *Eur. J. Org. Chem.*, 2011, **35**, 7062-7065; b) X. Yi, C. Zhang, S. Guo, J. Ma and J. Zhao, *Dalton Trans.*, 2014, **43**, 1672-1683; c) A. Depauw, E. Dossi, N. Kumar, C. F. Debuisschert, G. Huberfeld, N. Rouach and I. Leray, *Chem. Eur. J.*, 2016, **22**, 1-11.

10 a) M. Schiedel, C. A. Briehn and P. Bauerle, *J. Org. Chem.,*2002, **653**, 200-208; b) D. Huang, J. Sun, L. Ma, C. Zhang and J. Zhao, *Photochem. Photobiol. Sci.*, 2013, **12**, 872-882; c) G. Qiu, T. Liu and Q. Ding, *Org. Chem. Front.*,2016, **3**, 510-515; d) T. Sasaki, K. Miyagi, K. Moriyama and H. Togo, *Org. Lett.,* 2016, **18**, 944-947; e) T. Sasaki, K. Moriyama and H. Togo, *Beilstein J. Org. Chem.*, 2018, **14**, 345-353; f) G. Raffa, S. Belot, G. Balme and N. Monteiro, *Org. Biomol. Chem.*, 2011, **9**, 1474-1478; g) N. Panda, I. Mattan, S. Ojha and C. S. Purohit, *Org. Biomol. Chem.*, 2018, **16**, 7861-7870.

11 Y. Gao, F. Zeng, X. Sun, M. Zeng, Z. Yang, X. Huang, G. Shen, Y. Tan, R. Feng and C. Qi, *Adv. Synth. Catal.*, 2018, **360**, 1328-1333.

12 R. Koch, H. M. Berstermann and C. Wentrup, *J. Org. Chem.*, 2014, **79**, 65-71.

13 a) M. Zhang, L. Yang, H. Yang, G. An and G. Li, *Chemcatchem*, 2019, **11**, 1606-1609; b) C. Tian, L. M. Yang, H. T. Tian, G. H. An and G. M. Li, *J. Fluorine Chem.*, 2019, **219**, 23-28; c) M. Zhou, J. Li, C. Tian, X. Sun, X. Zhu, Y. Cheng, G. An and G. Li, *J. Org. Chem.*, 2019, **84**, 1015−1024; d) H. Yang, C. Tian, D. Qiu, H. Tian, G. An and G. Li, *Org. Chem. Front.*, 2019, **6**, 2365-2370; e) M. Gong, J. K. Kim, X. Zhao, Y. Li, J. Zhang, M. Huang and Y. Wu, *Green Chem.*, 2019, **21**, 3615-3620.

14 H. Kong, Q. Li, Y. Yin, M. Huang, J. K. Kim, Y. Zhu, Y. Li and Y. Wu, *Org. Biomol. Chem.*, 2019, **17**, 4621-4628.

15 Y. Kong, Y. Li, M. Huang, J. K. Kim and Y. Wu, *Green Chem.*, 2019, **21**, 4495-4498.

16 a) S. Ni, J. Cao, H. Mei, J. Han, S. Li and Y. Pan, *Green Chem.*, 2016, **18**, 3935-3939; b) Z. Wang, X. Li, L. Wang and P. Li, *Tetrahedron*, 2019, **75**, 1044-1051.

17 a) Q. Li, X. Zhao, Y. Li, M. Huang, J. K. Kim and Y. Wu, *Org. Biomol. Chem.*, 2017, **15**, 9775-9778; b) X. Zhao, M. Huang, Y. Li, J. Zhang, J. K. Kim and Y. Wu, *Org. Chem. Front.*, 2019, **6**, 1433-1437; c) Q. Li, Y. Yin, Y. Li, J. Zhang, M. Huang, J. K. Kim and Y. Wu, *Org. Chem. Front.*, 2019, **6**, 3238-3243; (d) G. Gu, M. Huang, J. K. Kim, J. Zhang, Y. Li and Y. Wu, *Green Chem.*, 2020, DOI: 10.1039/D0GC00292E.

View Article Online
DOI: 10.1039/D0OB00479K

18 a) U. Bunz, *Chem. Rev.*, 2000, **100**, 1605-1644; b) K. Sonogashira, *J. Organomet. Chem.*, 2002, **653**, 46-49; c) Y. Li, J. Wang, M. Huang, Z. Wang, Y. Wu and Y. Wu, *J. Org. Chem*., 2014, **79**, 2890-2897; d) Y. Li, J. Wang, B. Yan, M. Huang, Y. Zhu, Y. Wu and Y. Wu, *Tetrahedron*, 2015, **71**, 2729-2735.
19 a) F. Xu, H. Wang, X. Du, W. Wan, D. Wang, S. Chen, X. Han, N. Li, M. Yuan and J. Wang, *Dyes Pigments*, 2016, **129**, 121-128.
20 a) M. Yuan, X. Du, F. Xu, D. Wang, W. Wang, T. Li, Q. Tu, Y. Zhang, Z. Du and J. Wang, *Dyes Pigments*, 2015, **123**, 355-362; b) F. Bu, R. Duan, Y. Xie, Y. Yi, Q. Peng, R. Hu, A. Qin, Z. Zhao and B. Z. Tang, *Angew. Chem. Int. Ed.*, 2015, **54**, 14492-14497.
21 C. E. Song, D. Jung, S. Y. Choung, E. J. Roh and S. Lee, *Angew*. *Chem. Int. Ed.*, 2004, **43**, 6183-6185.