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Synthesis of coumarins *via* PIDA/I_2-mediated oxidative cyclization of substituted phenylacrylic acids†

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A variety of functionalized coumarins were synthesized from substituted phenylacrylic acids *via* PIDA/I_2-mediated and irradiation-promoted oxidative carbon–oxygen bond formation. Our studies show that the oxygen in the pendant carboxylic acid group cyclizes favorably to the aryl ring that is *cis* to it. The main advantages of this method include good functional group tolerance and the transition-metal-free characteristic.

Introduction

Coumarin and its derivatives are widely distributed in natural products.[1] Among the naturally occurring products, 4-aryl coumarin derivatives, also known as neoflavonoids, have received considerable attention after they were reported to show important biological properties[2] such as cytotoxic,[3a] anti-HIV,[3b] antibacterial,[3c] and antimalarial activities[3d] (for representative examples, see Fig. 1).

To date, many synthetic methods have been developed for the formation of 4-aryl coumarin compounds.[4–10] Most of the currently known strategies fall into one of the following categories, differing from each other in the starting materials: (1) condensation of phenols with esters of arylacetic acids (the Pechmann reaction) (Fig. 2, path **a**);[4] (2) reactions starting from substituted *o*-hydroxybenzophenones, utilizing the well-known Perkin reaction, Wittig reaction or Knoevenagel-type condensation reaction (Fig. 2, path **b**).[4,5] (3) Ester formation from propargylic acid derivatives, followed by intramolecular annulation, with the exception that aryl 3-phenylpropiolate was reported to also undergo direct cyclization mediated by catalysts to give 4-aryl coumarin compounds (Fig. 2, path **c**).[6] (4) Dehydrogenation of 3,4-dihydrocoumarin in the presence of iodine or Pd/C (Fig. 2, path **d**).[4,7] (5) Arylation of coumarins at 4-positions using organometallic reagents or arylboronic acids (Fig. 2, path **e**).[4,8] (6) A domino reaction between 3-(*o*-hydroxyaryl)acrylates and aryl iodides or bromides involving Pd-mediated allylic arylation and the subsequent lactonization (Fig. 2, path **f**).[9] (7) Cu-mediated hydroarylation of methyl phenylpropiolates containing a methoxy-methyl-ether (MOM)-protected hydroxy group at the *ortho*-position with various arylboronic acids (Fig. 2, path **g**).[10] In addition to the above strategies, some other methods[4,11] have also been developed to access this important scaffold. What's in common among the existing approaches is that the oxygen connected to the aryl ring comes from the phenol derivatives, which means this O-atom is installed to the aryl ring in the early stage of the synthetic route. In this paper, we report an alternative approach to access the 4-aryl coumarin skeletons, in which a pendant oxygen in the carboxylic acid moiety in phenylacrylic acid derivatives as the starting material is annulated to the benzene ring through oxidative carbon–oxygen bond formation (Fig. 2, path **h**). To our knowledge, the method described herein, differing from all existing approaches, represents the first synthesis of 4-aryl coumarins that does not use phenol derivatives as starting materials.

Owing to their superb oxidizing properties and low toxicity compared with classic heavy-metal oxidants, hypervalent iodine(III) reagents have recently been widely applied to form carbon–carbon bonds as well as construct heterocyclic compounds through carbon–heteroatom and heteroatom–heteroatom bond formation.[12] Several novel methods have been developed for the synthesis of lactones using hypervalent iodine reagents,[13] which realizes the oxidative bond formation

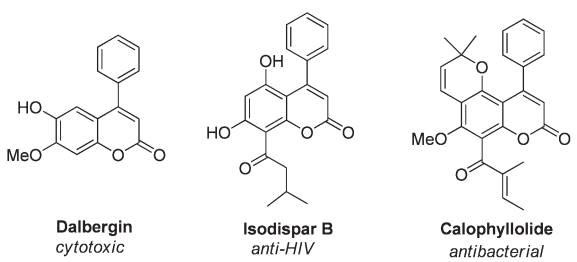

Fig. 1 Representative examples of some naturally occurring 4-arylcoumarin products.

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† Electronic supplementary information (ESI) available: NMR data. CCDC 911557. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ra23188g

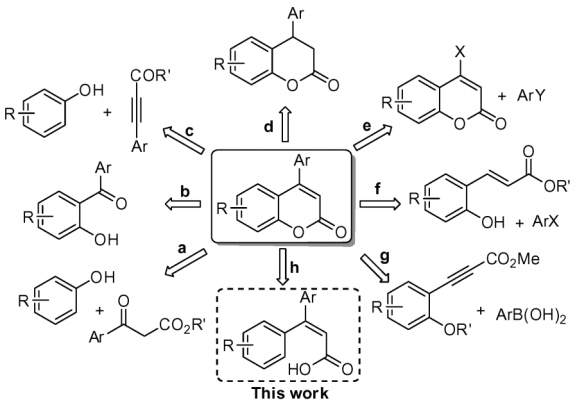


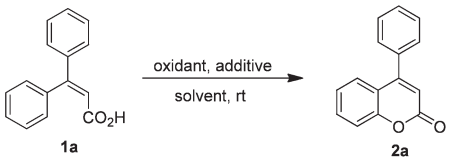
Fig. 2 Representative strategies for the construction of the 4-aryl coumarin skeleton.

between the oxygen of the carboxylic acid moiety and the aromatic sp^2-carbon or the benzylic sp^3-carbon. For example, Yokoyama and coworkers reported that oxidative cyclization of *o*-alkyl or *o*-arylaromatic acids with hypervalent iodine reagent or simply iodine gave the corresponding lactones under irradiation with a high-pressure mercury lamp.[14] Upon treatment with phenyliodine(III) bistrifluoroacetate (PIFA) or phenyliodine diacetate (PIDA), the *para*-substituted phenol or phenol ether derivatives bearing a side-chain containing a terminal carboxylic acid moiety underwent oxidative cyclization to give spiro dienone lactones.[15] Most recently, Gu and coworkers reported the synthesis of 3,4-dihydrocoumarins through oxidative cyclization of either electron-neutral or electron-deficient 3-arylpropionic acids with PIFA in the presence of $BF_3{\cdot}Et_2O$ in TFA.[16] Inspired by the above transformations, we envisioned a similar aromatic C–O bond formation which would eventually lead to coumarin compounds if phenylacrylic acid derivatives were subjected to certain oxidative conditions mediated by the hypervalent iodine reagent.

Result and discussion

We selected the readily available cinnamic acid and subjected it to the identical oxidative conditions (PIFA, $BF_3{\cdot}Et_2O$, TFA) described by Gu[16] as our initiative test of the feasibility of the reaction. However, no desired cyclized coumarin product was obtained, which indicated that the *trans*- configuration in the substrate, not to isomerize to the *cis* configuration during the reaction, prevented the cyclization from occurring. To get around the configuration problem, phenylacrylic acid **1a** was then chosen as the substrate for further study as cyclization between the oxygen in the pendant carboxylic acid group and the *cis*-phenyl ring can be naturally expected. However, the reaction gave a complex mixture and the expected 4-aryl coumarin **2a** was not formed under the mentioned conditions. No desired product was formed either after replacing PIFA with the less potent PIDA. Further explorations of more

Table 1 Optimization of the reaction conditions[a]



Entry	Oxidant	Additive (equiv.)	Solvent (conc.)	Time (h)	Yield[b] (%)
1	PIFA	$BF_3{\cdot}Et_2O$ (1.5)	TFA (0.2)	6	ND[c]
2	PIDA	$BF_3{\cdot}Et_2O$ (1.5)	TFA (0.2)	6	ND[c]
3	PIDA or PIFA	TFA (0.5)	DCM (0.2)	24	ND/ND[c]
4	PIDA or PIFA	LiBr (0.5)	DCM (0.2)	24	ND/ND[c]
5	PIFA	I_2 (0.2)	DCM (0.2)	6	20
6	PIDA	I_2 (0.2)	DCM (0.2)	6	46
7	—	I_2 (0.2)	DCM (0.2)	12	ND[c]
8	PIDA	I_2 (0.2)	DCM (0.1)	12	79
9	PIDA	I_2 (0.2)	DCM (0.05)	8	90
10	PIDA	I_2 (0.2)	DCM (0.05)	8	71[d]
11	PIDA	I_2 (0.2)	DCM (0.05)	2	92[e]
12	PIDA	I_2 (0.2)	toluene (0.05)	6	56
13	PIDA	I_2 (0.2)	DMF (0.05)	6	NR[f]
14	PIDA	I_2 (0.2)	CH_3CN (0.05)	6	NR[f]
15	PIDA	I_2 (0.2)	EtOH (0.05)	6	NR[f]

[a] Conditions: **1a** (0.2 mmol), I(III) oxidant (0.3 mmol) and additive in solvent (4 mL) stirred at rt. [b] Isolated yields. [c] No desired product was detected. [d] The reaction was carried out at 50 °C. [e] The reaction was irradiated with a tungsten lamp (200 W) at rt. [f] No reaction occurred.

favorable conditions including using TFA and LiBr as additives and DCM as solvent yielded no successful result. Inspired by Yokoyama's lactonization methods[14] in which molecular iodine was used as catalyst, we treated substrate **1a** with PIFA in the presence of 0.2 equivalent of iodine in DCM. To our delight, the reaction afforded the desired cyclized **2a** in 20% yield, with the formation of a decarboxylated and iodinated byproduct, *i.e.* (2-iodoethene-1,1-diyl)dibenzene ,in 15% yield and some other unidentified byproducts (Table 1, entry 5). When PIDA was used in place of PIFA, the reaction became much cleaner and the desired product was separated and amounted to an improved yield of 46%. A control experiment showed that no desired coumarin product was formed in the absence of PIDA or PIFA if solely iodine was used as the oxidant (Table 1, entry 7). Our further studies of condition-screening showed that the yield of product **2a** dramatically increased as the concentration of substrate **1a** in CH_2Cl_2 decreased (Table 1, entries 6, 8, 9). Particularly, when the reaction mixture was diluted to 0.05 M, the cyclized product **2a** was obtained in 90% yield, with the formation of only a trace amount of the decarboxylated and iodinated byproducts (Table 1, entry 9), even though the reaction needed relatively longer reaction time (8 h). On the other hand, an attempt to accelerate the reaction rate by raising the temperature to 50 °C turned out to be unsuccessful due to the formation of more byproducts under these conditions (Table 1, entry 10). However, much to our delight, when the reaction was irradiated with a tungsten lamp (200 W) at room temperature, the reaction went to completion within 2 h and

Table 2 Scope of substituted substrates in PIDA/I_2-mediated coumarin synthesis[a]

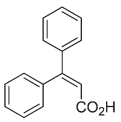
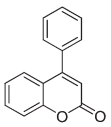
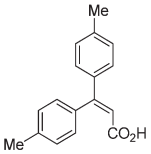
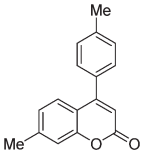
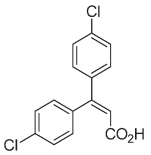
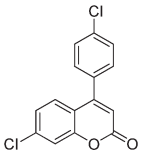
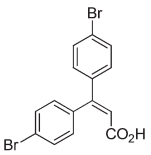
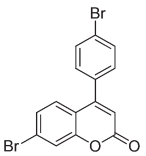
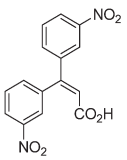
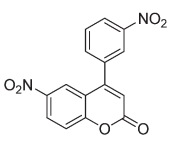
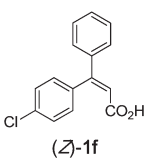
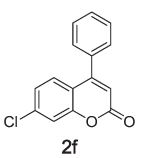
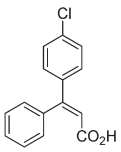
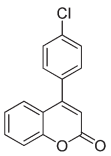
Entry	Substrate **1**	Product **2**	Time (h)	Yield[b](%)
1	 **1a**	 **2a**	2	92
2	 **1b**	 **2b**	2	81
3	 **1c**	 **2c**	4	82
4	 **1d**	 **2d**	6	68
5	 **1e**	 **2e**	24	46
6	 (*Z*)-**1f**	 **2f**	4	84
7	 (*E*)-**1g**	 **2g**	4	78

Table 2 (*Continued*)

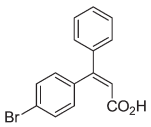
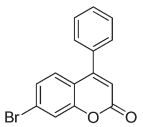
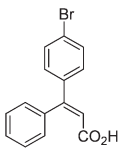
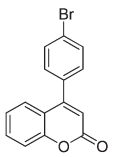
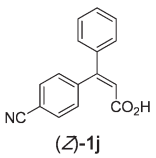
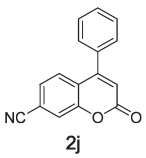
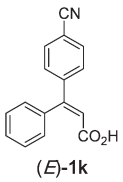
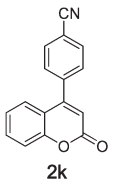
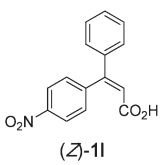
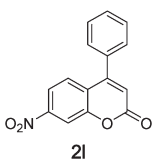
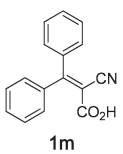
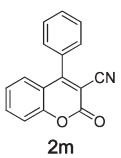
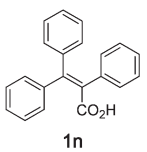
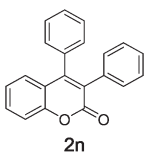
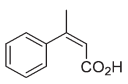
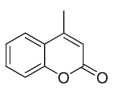
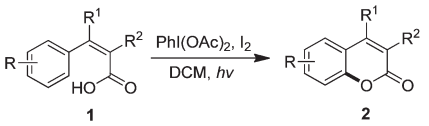
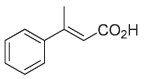
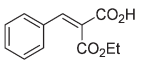
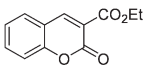
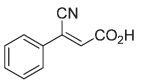
Entry	Substrate **1**	Product **2**	Time (h)	Yield[b](%)
8	 (*Z*)-**1h**	 **2h**	3	67
9[c]	 (*E*)-**1i**	 **2i**	3	75[c]
10	 (*Z*)-**1j**	 **2j**	8	61
11	 (*E*)-**1k**	 **2k**	7	65
12	 (*Z*)-**1l**	 **2l**	10	59
13	 **1m**	 **2m**	12	76
14[d]	 **1n**	 **2n**	3	43
15	 (*Z*)-**1o**	 **2o**	2	85

Table 2 (*Continued*)



1 2

Entry	Substrate **1**	Product **2**	Time (h)	Yield[b](%)
16[e]	 (*E*)-**1p**	ND	8	0
17[f,g]	 (*Z*)-**1q**	 **2q**	30	41
18[g]	 (*Z*)-**1r**	ND	12	0

[a] Optimal conditions: substrate **1** (0.2 mmol), PIDA (0.3 mmol), I_2 (0.04 mmol) in CH_2Cl_2, irradiation with a tungsten lamp (200 W) at rt, unless otherwise stated. [b] Isolated yields. [c] Trace of **2h** was detected. [d] 0.4 equiv. of I_2 was used for a complete reaction. [e] No reaction occurred at room temperature; when stirred at reflux in DCE, no desired product was detected. [f] The reaction was carried out using 3.0 equiv. of PIDA and 0.6 equiv. of I_2 under fluorescent light (40 W). [g] DCE was used as solvent, reflux.

yielded the product in an excellent 92% yield (Table 1, entry 11). Finally, our solvent study shows that toluene was inferior to CH_2Cl_2 while the other solvents including DMF, CH_3CN and EtOH prevented this conversion from taking place (Table 1, entries 12–15).

We initiated our investigation of the scope of substituents by firstly exploring the symmetrically substituted diaryl acrylic acids. It was found that the reaction could tolerate various substituents, such as methyl, chloro and bromo groups and afforded the corresponding 4-aryl coumarin in acceptable to good yields (Table 2, entries 2–4). Notably, even the substrate-bearing nitro groups underwent the same reaction and yielded the cyclized product **2e**, albeit in a lower yield (Table 2, entry 5), along with much longer time and an excess dosage of both PIDA and iodine.

When an unsymmetrically diphenyl substituted acrylic acid, *i.e.* (*Z*)-**1f**, was applied, the oxygen atom of the carboxylic acid cyclized to the adjacent chloro-substituted phenyl ring (Table 2, entry 6). This result is consistent with our earlier finding of the configuration requirement of this reaction. Similarly, the cyclization of the opposite isomer (*E*)-**1g** resulted in the formation of **2g** Table 2, entry 7). The reaction involving the bromo-substituted **1h** and **1i** displays similar cyclization selectivity, but with trace formation (5%) of the other isomer **2h** in the case of (*E*)-**1i** (Table 2, entry 9). We tentatively propose that the presence of bromo in (*E*)-**1i** facilitates the isomerization of the double bond *via* a conjugation effect

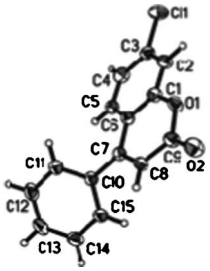


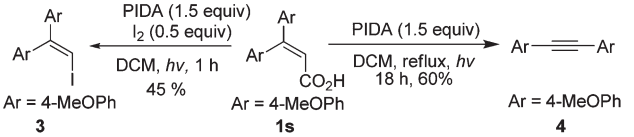
Fig. 3 X-ray crystal structure of **2f**.

during the reaction process, while the other substituents included in this study do not display this effect. For substrates bearing an electron-withdrawing cyano group on the phenyl ring, no isomerized byproduct was observed in either case (Table 2, entries 10–11). When a phenylacrylic acid bearing a nitro group was used, the reaction needs a much longer time and a lower yield of cyclized product was obtained (Table 2, entry 12). Further investigation revealed that the reaction was also applicable to the synthesis of highly substituted 4-aryl coumarins (Table 2, entry 14). Moreover, the method can be further extended to the preparation of 4-methyl coumarin compounds (Table 2, entry 15).

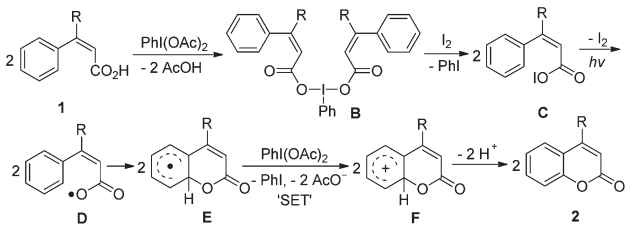
Some substituted cinnamic acids were explored to further study whether the isomerization of the double bond may occur and therefore allow the cyclization. Disappointingly, neither substrate (*E*)-**1p** or (*Z*)-**1r** was converted to the cyclized product under the same conditions (Table 2, entry 16). However, to our delight, a 41% yield of the cyclized **2q** was obtained[17] if the reaction was conducted using 3.0 equivalent of PIDA and 0.5 equivalent of iodine in DCE under reflux for 30 h (Table 2, entry 17).

In addition to the spectroscopic data, X-ray crystallography of the colorless crystal of **2f** (shown in Fig. 3) was obtained, which unambiguously confirmed the structure of the coumarin products.

Two unexpected reactions were observed associated with the symmetrically substituted diaryl acrylic acids **1s** in which a methoxy group is substituted on either of the two phenyl rings. When **1s** was subjected to the mentioned conditions (1.5 equiv. of PIDA, 0.5 equiv. of I_2, *hv*), no cyclization took place, but rather, a decarboxylated and iodinated product **3** was separated as the major product (see Scheme 1).[18] We postulate here that the electron-donating methoxy groups on the phenyl rings facilitate the electrophilic iodination of the double bond *via* conjugation, followed by decarboxylation and gave **3**.



Scheme 1 Formation of iodinated compound **3** and diphenylethylene **4** from **1s**.



Scheme 2 Proposed reaction pathway.

However, in the absence of I_2 and upon treatment of **1s** with PIDA in CH_2Cl_2 under reflux for 18 h, a completely different product of 1,2-diphenylethyne **4** was obtained in 60% yield.[19]

A plausible reaction mechanism is proposed based on previously reported results[14b] as well as this study, shown in Scheme 2. Initially, phenylacrylic acid **1** reacts with PIDA to form trivalent iodine **B** by losing two equivalents of AcOH. Then the reaction of intermediate **B** with molecular iodine forms hypoiodite **C**, with the concurrent release of PhI. Next, photolysis of **C** leads to homolytic cleavage of the I–O bond in **C** to generate the oxygen radical species **D**, which cyclizes to the adjacent phenyl ring to form radical **E**. Furthermore, mediated by PIDA, intermediate **E** is converted to cation intermediate **F** *via* a single-electron transfer (SET) process. Finally, the abstraction of a proton from **F** regenerates the aromatic system to afford the 4-aryl coumarin **2**. The mechanism suggests that any electron-withdrawing substituents on the phenyl ring would disfavor the reaction due to the formation of the cationic intermediate **F**, which is consistent with our results concerning the nitro-substituted substrate. Furthermore, a control experiment involving the adding of 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) as the additive was carried out. It was found that the reaction could be effectively retarded and no formation of the desired coumarin **2a** was observed, which might indicate that the reaction involves the formation of some radical species.

Conclusions

In conclusion, we have reported a new route to construct 4-aryl coumarin skeletons from phenylacrylic acid through PIDA/I_2-mediated intramolecular cyclization. In contrast to all the existing methods, this approach allows a direct, intramolecular C–O oxidative coupling between the sp^2-carbon of the phenyl ring and the oxygen atom of the pendant carboxylic acid moiety. Furthermore, this method features good functional-group tolerance as well as the environmentally friendly transition-metal-free characteristic.

Experimental

^1H and ^{13}C NMR spectra were recorded on 400 MHz or 600 MHz spectrometer at 25 °C. Chemical shifts values are given in ppm and referred to the internal standard of TMS set as 0.00 ppm. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; br, broad and dd, doublet of doublets. The coupling constants *J*, are reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained on a Q-TOF micro spectroMeter. Melting points were determined with a micro melting-point apparatus without correction. TLC plates were visualized by exposure to ultraviolet light. Dichloromethane and 1,2-dichloroethane were dried by CaH_2 before use, other reagents and solvents were purchased as reagent grade and were used without further purification. Flash column chromatography was performed over silica gel 200–300 m and a mixture of ethyl acetate (EtOAc) and petroleum ether (PE) was used as the eluent.

General procedure for the preparation of 1

According to the general procedure described in the literature,[20] 3,3-diarylacrylic acids were synthesized from the corresponding benzophenones *via* Horner–Wadsworth–Emmons reaction using $(EtO)_2P(=O)CH_2CO_2Et$ followed by saponification.

General procedure. To a suspension of sodium hydride (1.4 g, 35 mmol, 60% in mineral oil) in THF (20 mL) was added triethyl phosphonoacetate (5.4 g, 24.0 mmol) dropwise at 0 °C. The mixture was stirred at room temperature for 1 h and then a solution of benzophenone (10 mmol) in THF (10 mL) was added. The resulting mixture was stirred at room temperature and monitored by TLC analysis. After the completion of the reaction, the reaction mixture was treated with saturated aqueous NH_4Cl solution (50 mL). The aqueous phase was extracted with ethyl acetate (100 mL × 3) and the combined organic layer was washed with brine (100 mL × 2) and dried over Na_2SO_4. The organic solvent was removed under vacuum, and the residue was purified by silica gel column to give the 3,3-diarylacrylic acid ester. (In the preparation of unsymmetric products, two isomers were separated during this step, followed by saponification respectively.)

To a solution of 3,3-diarylacrylic acid ester in a mixture solvent EtOH/H_2O (12 mL/3 mL) was added KOH (0.8 g, 14.3 mmol). The mixture was stirred at room temperature for 5 h and then acidified with 3 M HCl. The resulting mixture was extracted with ethyl acetate (50 mL × 3) and the combined organic layer was washed with brine (50 mL × 2), H_2O (50 mL) and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography to give the desired phenylacrylic acid.

3,3-Diphenylacrylic acid (1a). Following the general procedure, **1a** was purified by silica gel chromatography (EtOAc/PE = 20/80). Yield: 60%, yellow solid, mp. 161-162 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.35–7.34 (m, 4H), 7.30 (t, J = 7.0 Hz, 2H), 7.26–7.25 (m, 2H), 7.20–7.18 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 159.0, 140.9, 138.5, 129.8, 129.3, 128.5, 128.4(6), 128.4(2), 127.9, 116.5. HRMS (ESI) m/z calcd for $C_{15}H_{13}O_2^+$ $[M + H^+]$ 225.0910, found 225.0913.

3,3-Di-*p*-tolylacrylic acid (1b). Following the general procedure, **1b** was purified by silica gel chromatography (EtOAc/PE = 40/60). Yield: 61%, white solid, mp. 168–169 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 7.12–7.18 (m, 6H), 7.02 (d, J = 8.0 Hz, 2H),

6.27 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.3, 154.4, 139.4, 138.5, 137.6, 136.5, 129.5, 129.5, 128.9, 128.4, 118.0, 21.3, 21.2. HRMS (ESI) *m/z* calcd for $C_{17}H_{17}O_2^+$ [M + H$^+$] 253.1223, found 253.1228.

3,3-Bis(4-chlorophenyl)acrylic acid (1c). Following the general procedure, **1c** was purified by silica gel chromatography (EtOAc/PE = 30/70). Yield: 65%, white solid, mp. 174–175 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.44 (t, *J* = 8.0 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.43 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.4, 151.2, 138.8, 137.3, 134.2, 132.8, 130.8, 129.6, 128.6, 128.0, 119.9. HRMS (ESI) *m/z* calcd for $C_{15}H_{11}{}^{35}Cl_2O_2^+$ [M + H$^+$] 293.0131, found 293.0135.

3,3-Bis(4-bromophenyl)acrylic acid (1d). Following the general procedure, **1d** was purified by silica gel chromatography (EtOAc/PE = 40/60). Yield: 73%, white solid, mp. 190–192 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.33 (br s, 1H), 7.60–7.56 (m, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.43 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.9, 151.8, 139.6, 138.1, 132.0, 131.6, 131.5, 130.4, 123.4, 121.9, 120.3. HRMS (ESI) *m/z* calcd for $C_{15}H_{11}{}^{79}Br_2O_2^+$ [M + H$^+$] 380.9120, found 380.9121.

3,3-Bis(3-nitrophenyl)acrylic acid (1e). Following the general procedure, **1e** was purified by silica gel chromatography (EtOAc/PE = 50/50). Yield: 80%, white solid, mp. 152–154 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.28 (t, *J* = 8.0 Hz, 2H), 8.09 (s, 1H), 8.06 (s, 1H), 7.68–7.80 (m, 4H), 6.70 (s, 1H). ^{13}C NMR (100 MHz, DMSO–d_6) δ 166.5, 149.6, 148.5, 148.1, 141.5, 140.0, 136.2, 134.7, 130.8, 130.3, 124.6, 124.3, 123.7, 123.3, 122.9. HRMS (ESI) *m/z* calcd for $C_{15}H_{11}N_2O_6^+$ [M + H$^+$] 315.0612, found 315.0612.

(*Z*)-3-(4-Chlorophenyl)-3-phenylacrylic acid (1f). Following the general procedure, **1f** was purified by silica gel chromatography (EtOAc/PE = 30/70). 34% yield over 2 steps from (4-chlorophenyl)(phenyl)methanone; white solid, mp. 167–169 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.28 (br s, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.40–7.35 (m, 3H), 7.27 (dd, *J* = 8.0, 2.0 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.0, 153.2, 140.5, 138.2, 133.1, 131.3, 129.9, 128.4, 128.3, 119.7. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}{}^{35}ClO_2^+$ [M + H$^+$] 259.0520, found 259.0523.

(*E*)-3-(4-Chlorophenyl)-3-phenylacrylic acid (1g). Following the general procedure, **1g** was purified by silica gel chromatography (EtOAc/PE = 30/70). 27% yield over 2 steps from (4-chlorophenyl)(phenyl)methanone; white solid, mp. 150–151 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.39–7.37 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.16–7.14 (m, 2H), 6.40 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1, 152.6, 139.8, 138.9, 134.4, 130.1, 129.4, 129.0, 128.5, 128.4, 120.0. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}{}^{35}ClO_2^+$ [M + H$^+$] 259.0520, found 259.0523.

(*Z*)-3-(4-Bromophenyl)-3-phenylacrylic acid (1h). Following the general procedure, **1h** was purified by silica gel chromatography (EtOAc/PE = 40/60). 24% yield over 2 steps from (4-bromophenyl)(phenyl)methanone; white solid, mp. 165–167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.36–7.34 (m, 3H), 7.18–7.15 (m, 2 H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 157.8, 139.8, 137.9, 131.7, 130.0, 129.2, 128.7, 128.1, 124.3, 116.8. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}{}^{79}BrO_2^+$ [M + H$^+$] 303.0015, found 303.0018.

(*E*)-3-(4-Bromophenyl)-3-phenylacrylic acid (1i). Following the general procedure, **1i** was purified by silica gel chromatography (EtOAc/PE = 40/60). 16% yield over 2 steps from (4-bromophenyl)(phenyl)methanone; white solid, mp. 168–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.40–7.30 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 158.0, 140.3, 137.3, 131.2, 131.0, 130.0, 128.6, 128.5, 122.8, 116.7. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}{}^{79}BrO_2^+$ [M + H$^+$] 303.0015, found 303.0018.

(*Z*)-3-(4-Cyanophenyl)-3-phenylacrylic acid (1j). Following the general procedure, **1j** was purified by silica gel chromatography (EtOAc/PE = 40/60). 26% yield over 2 steps from 4-benzoylbenzonitrile; white solid, mp. 174–176 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.39– 7.35 (m, 5H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.48 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.2, 152.4, 144.1, 139.2, 131.8, 129.9, 129.6, 128.7, 127.7, 119.7, 118.7, 110.5. HRMS (ESI) *m/z* calcd for $C_{16}H_{12}NO_2^+$ [M + H$^+$] 250.0863, found 250.0863.

(*E*)-3-(4-Cyanophenyl)-3-phenylacrylic acid (1k). Following the general procedure, **1k** was purified by silica gel chromatography (EtOAc/PE = 40/60). 18% yield over 2 steps from 4-benzoylbenzonitrile; white solid, mp. 180–182 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.41–7.39 (m, 3H), 7.17–7.15 (m, 2H), 6.51 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.0, 151.6, 145.4, 138.4, 132.9, 129.4, 129.1, 128.7, 128.6, 122.2, 119.0, 111.9. HRMS (ESI) *m/z* calcd for $C_{16}H_{12}NO_2^+$ [M + H$^+$] 250.0863, found 250.0863.

(*Z*)-3-(4-Nitrophenyl)-3-phenylacrylic acid (1l). Following the general procedure, **1l** was purified by silica gel chromatography (EtOAc/PE = 50/50). 40% yield over 2 steps from (4-nitrophenyl)(phenyl)methanone; white solid, mp. 181–183 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.39 (br s, 1H), 8.25 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H),7.42–7.37 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.52 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.7, 152.6, 147.4, 146.7, 139.5, 130.7, 130.2, 129.2, 128.3, 123.6, 120.4. MS (ESI) *m/z* calcd for $C_{15}H_{11}NO_4{}^+$ [M + H$^+$] 270.0766, found 270.0771.

2-Cyano-3,3-diphenylacrylic acid (1m)[21]. To a suspension of ethyl cyanoacetate (4.5 g, 40 mmol), benzophenone (5.4 g, 30 mmol) in heptane (13 mL) was added ammonium acetate (580 mg, 7.5 mmol) and glacial acetic acid (1.73 g, 1.65 mL). The mixture was stirred at reflux and a 0.15 mL solution of ammonium acetate-acetic acid was added (at a predetermined rate) every hour for 24 h. The reaction mixture was cooled to room temperature, treated with brine (100 mL) and then extracted with EtOAc (100 mL × 2). The combined organic layer was washed with brine (100 mL × 2) and dried over Na_2SO_4. The organic solvent was removed under vacuum and to the residue, EtOH (45 mL), H_2O (15 mL), and NaOH (2.0 g, 50 mmol) were added. The mixture was stirred at room temperature for 8 h. EtOH was removed under vacuum and the residue was acidified with 3 M HCl. The resulting mixture was extracted with EtOAc (100 mL × 2) and the combined organic layer was washed with brine (100 mL × 3) and dried over Na_2SO_4. The solvent was evaporated and the residue was

purified by silica gel column chromatography (EtOAc/PE = 60/40) to give 2-cyano-3,3-diphenylacrylic acid (3.2 g, 43%); white solid, mp. 209–211 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.55–7.36 (m, 5H), 7.18 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.7, 163.7, 139.2, 138.9, 131.4, 130.5, 130.0, 129.5, 129.0, 128.6, 117.7, 105.9.

2,3,3-Triphenylacrylic acid (1n)[22]. 1) To a suspension of NaH (2.2 g, 55 mmol, 60% in mineral oil) in THF (50 mL) was added phenylacetonitrile (5.8 mL, 50 mmol). The reaction mixture was stirred at 40 °C for 2 h and then cooled to room temperature whereupon a solution of benzophenone (1.8 g, 10 mmol) in THF (30 mL) was added dropwise *via* a dropping funnel. The resultant solution was heated to reflux for 6 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in a 2.5 : 2.5 : 1 solvent mixture of THF : MeOH : HCl (2 M, 60 mL) and stirred at room temperature for 3 h. The solvents were concentrated under reduced pressure and the aqueous layer was extracted with EtOAc (100 mL × 2). The combined organic phase was washed with saturated $NaHCO_3$ (100 mL), brine (100 mL × 2) and dried over Na_2SO_4. After the removal of the solvent *via* evaporation, the residue was purified by recrystallization with EtOAc/PE to give 2,3,3-triphenylacrylonitrile (1.7 g, 68%).

2) To a stirred solution of 2,3,3-triphenylacrylonitrile (1.1 g, 4 mmol), KOH (1.1 g, 20 mmol) in H_2O (0.27 mL, 5 mmol) and ethylene glycol (20 mL) were heated at 185 °C. Every hour of the reaction time period H_2O (0.3 mL) was added cautiously. The mixture was heated for 48 h and cooled to room temperature. The mixture was acidified with 3 M HCl to pH = 5–6 and extracted with EtOAc (50 mL × 2) and the combined organic phase was washed with brine (50 mL × 3). The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/PE = 30/70) to give 2,3,3-triphenylacrylic acid (0.85 g, 71%); white solid, mp. 211–212 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.27 (m, 5H), 7.20–7.09 (m, 8H), 6.96 (d, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 148.4, 142.0, 140.5, 137.4, 132.2, 130.9, 130.1, 129.1, 128.4, 128.2, 127.8, 127.8, 127.6.

(*Z*)-3-Phenylbut-2-enoic acid (1o)[23]. Following the general procedure, **1o** was purified by silica gel chromatography (EtOAc/PE = 30/70). Yield: 14%, white solid, mp. 131–133 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.90 (br s, 1H), 7.21–7.33 (m, 5H), 5.89 (s, 1H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 153.5, 141.1, 128.2, 128.0, 127.5, 118.9, 27.0.

(*E*)-3-Phenylbut-2-enoic acid (1p). Following the general procedure, **1p** was purified by silica gel chromatography (EtOAc/PE = 30/70). Yield: 42%, white solid, mp. 97–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.49 (m, 2H), 7.40–7.38 (m, 3H), 6.18 (s, 1H, C=CH), 2.61 (s, 3H, CH_3). Physical and spectral data were consistent with those reported in the literature.[23b]

(*Z*)-2-(Ethoxycarbonyl)-3-phenylacrylic acid (1q)[24]. To a mixture of diethyl malonate (6.4 mL), benzaldehyde (5.0 mL) in anhydrous toluene (15.0 mL) was added piperidine (0.5 mL). A 4 Å molecular sieve (0.2 g) was added and the reaction was stirred at reflux for 15 h. EtOAc (50 mL) was added and the mixture was washed with HCl 1 M (50 mL × 2), saturated $NaHCO_3$ (50 mL × 2) and water (50 mL). The organic phase was dried over Na_2SO_4 and solvent was evaporated under reduced pressure. Crude product was distilled under reduced pressure to obtain diethyl 2-benzylidenemalonate (8.9 g, 76%).

To a solution of LiOH·H_2O (0.42 g, 10 mmol) in a mixture solvent THF/H_2O (20 mL/20 mL) was added diethyl 2-benzylidenmalonate (2.5 g, 10 mmol). The reaction mixture was stirred for 5 h at room temperature. THF was evaporated under reduced pressure. The residue was then acidified to pH = 1 with HCl (3 M), and extracted with CH_2Cl_2 (50 mL × 2). The organic phase was combined, dried over Na_2SO_4, evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/PE = 30/70) to give (*Z*)-2-(ethoxycarbonyl)-3-phenylacrylic acid (**1q**) as white solid (1.8 g, 82%); mp. 91–92 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.35 (br s, 1H, COOH), 7.67 (s, 1H, CH=C), 7.49–7.44 (m, 5H, ArH), 4.26 (q, J = 7.0 Hz, 2H,CH_2), 1.20 (t, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.9, 165.4, 141.0, 133.0, 131.1, 129.7, 129.4, 127.5, 61.7, 14.1.

(*Z*)-3-Cyano-3-phenylacrylic acid (1r)[25]. To a mixture of benzonitriles (2.9 g, 25 mmol), glyoxylic acid (6.9 g, 37.5 mmol) in methanol (50.0 mL) was added potassium carbonate (8.8 g, 64 mmol). The reaction was stirred at reflux for 8 h. The resulting thick solid precipitate was filtered and washed with CH_2Cl_2. This solid was suspended in 250 mL of cold water, stirred for 3 h, and then filtered to provide the crude potassium (*Z*)-3-cyano-3-phenylacrylate. The crude solid was dissolved in 50 mL water and acidified by 3 M HCl. The resulting mixture was extracted with EtOAc (100 mL × 2) and the combined organic phase was washed with brine (100 mL × 2). The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/PE = 30/70) to give (*Z*)-3-cyano-3-phenylacrylic acid (3.8 g, 69%); white solid, mp. 140–142 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.54 (br s, 1H, COOH), 7.81–7.79 (m, 2H), 7.54–7.52 (m, 3H), 7.27 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.0, 132.8, 132.1, 131.8, 129.8, 127.4, 124.2, 115.8.

3,3-Bis(4-methoxyphenyl)acrylic acid (1s). Following the general procedure, **1s** was purified by silica gel chromatography (EtOAc/PE = 30/70). Yield: 77%, white solid, mp. 142–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.21 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.82– 6.88 (m, 4H), 6.17 (s, 1H), 3.83 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 161.0, 160.0, 158.8, 133.8, 131.1, 130.7, 130.3, 113.9, 113.8, 113.3, 55.4, 55.2. MS (ESI) m/z calcd for C17H17O4+ [M + H$^+$] 285.1121, found 285.1124.

General procedure for the preparation of coumarins 2

To a solution of phenylacrylic acid **1** (0.2 mmol) in dry CH_2Cl_2 (4 mL) in a 25 mL round-bottom flask was added PIDA (97 mg, 0.3 mmol). The mixture was stirred at rt for 5 min and then I_2 (10.2 mg, 0.04 mmol) was added. The reaction mixture was stirred at rt under irradiation with a tungsten lamp (200 W) and monitored by TLC analysis. After the completion of the reaction, the reaction mixture was concentrated *in vacuo* to remove the solvent. The residue was purified by silica gel

chromatography using a mixture of petroleum ether (PE) and ethyl acetate (EtOAc) as eluent, to give the desired product **2**.

4-Phenyl-2*H*-chromen-2-one (2a)

Following the general procedure, **2a** was purified by silica gel chromatography (EA/PE = 5/95). Yield: 92%, white solid, mp. 90–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.40 (m, 8H), 7.23 (t, J = 8.0 Hz, 1H), 6.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 155.7, 154.2, 135.2, 131.9, 129.7, 128.9, 128.4, 127.0, 124.2, 119.0, 117.3, 115.2. HRMS (ESI) m/z calcd for $C_{15}H_{10}NaO_2^+$ [M + Na^+] 245.0573, found 245.0577.

7-Methyl-4-(*p*-tolyl)-2*H*-chromen-2-one (2b)

Following the general procedure, **2b** was purified by silica gel chromatography (EA/PE = 10/90). Yield: 81%, white solid, mp. 153–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.36 (m, 4H), 7.20 (s, 1H), 7.03 (d, J = 8.0 Hz, 2H), 6.29 (s, 1H), 2.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 155.7, 154.3, 143.1, 139.8, 132.5, 129.5, 128.4, 126.7, 125.3, 117.4, 116.7, 113.8, 21.6, 21.4. HRMS (ESI) m/z calcd for $C_{17}H_{15}O_2^+$ [M + H^+] 251.1067, found 251.1068.

7-Chloro-4-(4-chlorophenyl)-2*H*-chromen-2-one (2c)

Following the general procedure, **2c** was purified by silica gel chromatography (EA/PE = 5/95). Yield: 82%, white solid, mp. 162–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 2.0 Hz, 1H) 7.36–7.39 (m, 3H), 7.22 (dd, J = 2.0 Hz, J = 8.0 Hz, 1H), 6.35 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 154.5, 153.8, 138.2, 136.3, 133.2, 129.7, 129.4, 127.6, 124.9, 117.7, 117.4, 115.2. HRMS (ESI) m/z calcd for $C_{15}H_9{}^{35}Cl_2O_2^+$ [M + H^+] 290.9974, found 290.9979.

7-Bromo-4-(4-bromophenyl)-2*H*-chromen-2-one (2d)

Following the general procedure, **2d** was purified by silica gel chromatography (EA/PE = 5/95). Yield: 68%, white solid, mp. 166–168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 2.0 Hz, 1H), 7.37 (dd, J = 8.0, 2.0 Hz, 1H), 7.32–7.28 (m, 3H), 6.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 154.4, 153.9, 133.6, 132.3, 129.9, 127.7, 127.6, 126.2, 124.5, 120.7, 117.7, 115.4. HRMS (ESI) m/z calcd for $C_{15}H_9{}^{79}Br_2O_2^+$ [M + H^+] 378.8964, found 378.8967.

6-Nitro-4-(3-nitrophenyl)-2*H*-chromen-2-one (2e)

Following the general procedure, **2e** was purified by silica gel chromatography (EA/PE = 10/90). Yield: 46%, white solid, mp. 176–178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50–8.46 (m, 2H), 8.37 (s, 1H), 8.25 (d, J = 2.0 Hz, 1H), 7.87– 7.81 (m, 2H), 7.59 (d, J = 9.0 Hz, 1H), 6.58 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 157.7, 152.2, 148.8, 144.2, 135.3, 134.0, 130.8, 127.3, 125.3, 123.4, 122.2, 118.9, 118.6, 118.1. HRMS (ESI) m/z calcd for $C_{15}H_9N_2O_6^+$ [M + H^+] 313.0455, found 313.0455.

7-Chloro-4-phenyl-2*H*-chromen-2-one (2f)[26]

Following the general procedure, **2f** was purified by silica gel chromatography (EA/PE = 10/90). Yield: 84%, yellow solid, mp. 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.53 (m, 3H), 7.44–7.42 (m, 4H), 7.20 (dd, J = 8.0, 2.0 Hz, 2 H), 6.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 155.1, 154.5, 137.9, 134.8, 130.0, 129.0, 128.4, 128.0, 124.7, 117.7, 117.5, 115.0. HRMS (ESI) m/z calcd for $C_{15}H_{10}{}^{35}ClO_2^+$ [M + H^+] 257.0364, found 257.2.

4-(4-Chlorophenyl)-2*H*-chromen-2-one (2g)

Following the general procedure, **2g** was purified by silica gel chromatography (EA/PE = 10/90). Yield: 78%, white solid, mp. 187–188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, J = 8.0 H, 1H), 7.52 (d, J = 8.0 H, 2H), 7.46–7.40 (m, 4H), 7.25 (t, J = 8.0 H, 1H), 6.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 154.4, 154.2, 136.0, 133.6, 132.2, 129.8, 129.2, 126.7, 124.3, 118.7, 117.5, 115.4. The spectral data are identical to those reported in the literature.[10]

7-Bromo-4-phenyl-2*H*-chromen-2-one (2h)

Following the general procedure, **2h** was purified by silica gel chromatography (EA/PE = 10/90). Yield: 67%, white solid, mp. 102–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H, 7.54–7.53 (m, 3H), 7.44–7.42 (m, 2H), 7.35 (m, 2H), 6.38 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 155.1, 154.4, 134.8, 130.0, 129.0, 128.3, 128.0, 127.6, 125.9, 120.5, 118.0, 115.3. HRMS (ESI) m/z calcd for $C_{15}H_9{}^{79}BrNaO_2^+$ [M + Na^+] 322.9678, found 322.9680.

4-(4-Bromophenyl)-2*H*-chromen-2-one (2i)

Following the general procedure, **2i** was purified by silica gel chromatography (EA/PE = 10/90). Yield: 75%, white solid, mp. 202–203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 8.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.25 (t, J = 8.0 Hz, 1H), 6.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 154.4, 154.2, 134.0, 132.2, 132.2, 130.0, 126.7, 124.3, 124.2, 118.6, 117.5, 115.4. HRMS (ESI) m/z calcd for $C_{15}H_9{}^{79}BrNaO_2^+$ [M + Na^+] 322.9678, found 322.9681.

2-Oxo-4-phenyl-2*H*-chromene-7-carbonitrile (2j)

Following the general procedure, **2j** was purified by silica gel chromatography (EA/PE = 10/90). Yield: 61%, white solid, mp. 134–135 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, J = 1.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.57–7.56 (m, 3H), 7.49 (dd, J = 1.0 Hz, J = 8.0 Hz, 1H), 7.44–7.22 (m, 2H), 6.51 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 154.3, 153.7, 134.0, 130.3, 129.2, 128.3, 128.0, 127.2, 122.7, 121.0, 117.8, 117.3, 115.0. HRMS (ESI) m/z calcd for $C_{16}H_{10}NO_2^+$ [M + H^+] 248.0706, found 248.0707.

4-(2-Oxo-2*H*-chromen-4-yl)benzonitrile (2k)

Following the general procedure, **2k** was purified by silica gel chromatography (EA/PE = 15/85). Yield: 65%, white solid, mp. 243–245 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.62–7.58 (m, 3H), 7.44 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.28–7.24 (m, 1H), 6.39 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 154.2, 153.6, 139.7, 132.7, 132.5, 129.3, 126.3, 124.5, 118.2, 118.0, 117.7, 116.0, 113.8. HRMS (ESI) m/z calcd for $C_{16}H_9NNaO_2^+$ [M + Na^+] 270.0525, found 270.0530.

7-Nitro-4-phenyl-2*H*-chromen-2-one (2l)

Following the general procedure, **2l** was purified by silica gel chromatography (EA/PE = 10/90). Yield: 59%, white solid, mp. 135–137 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, J = 2.0 Hz, 1H), 8.06 (dd, J = 9.0, 2.0 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.57–7.59 (m, 3H), 7.46–7.44 (m, 2H), 6.54 (s, 1H). ^{13}C NMR (125

MHz, $CDCl_3$) δ 159.1, 154.2, 153.9, 149.3, 134.1, 130.4, 129.3, 128.3, 128.2, 124.0, 118.6, 118.0, 112.9. HRMS (ESI) *m*/*z* calcd for $C_{15}H_{10}NO_4^+$ [M + H^+] 268.0604, found 268.0606.

2-Oxo-4-phenyl-2*H*-chromene-3-carbonitrile (2m)

Following the general procedure, **2m** was purified by silica gel chromatography (EA/PE = 20/80). Yield: 76%, yellow solid, mp. 217–218 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.69 (m,1H), 7.63–7.61 (m, 3H), 7.50–7.46 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 157.0, 154.0, 135.3, 131.7, 131.2, 129.2, 129.0, 128.5, 125.4, 118.1, 117.7, 113.6, 101.7. HRMS (ESI) *m*/*z* calcd for $C_{16}H_9NNaO_2^+$ [M + Na^+] 270.0531, found 270.0536.

3,4-Diphenyl-2*H*-chromen-2-one (2n)

Following the general procedure, **2n** was purified by silica gel chromatography (EA/PE = 10/90). Yield: 43%, white solid, mp. 228–229 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.52 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.30–7.31 (m, 3H), 7.24–7.12 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 153.3, 151.6, 134.5, 133.9, 131.5, 130.5, 129.4, 128.4, 128.3, 127.8, 127.7, 127.6, 127.0, 124.1, 120.5, 116.8. HRMS (ESI) *m*/*z* calcd for $C_{21}H_{15}O_2^+$ [M + H^+] 299.1067, found 299.1069.

4-Methyl-2*H*-chromen-2-one (2o)

Following the general procedure, **2o** was purified by silica gel chromatography (EA/PE = 10/90). Yield: 85%, white solid, mp. 82–83 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.34–7.29 (m, 2H), 6.30 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 153.6, 152.3, 131.8, 124.6, 124.2, 120.0, 117.1, 115.1, 18.6. HRMS (ESI) *m*/*z* calcd for $C_{21}H_{15}O_2^+$ [M + H^+] 161.0597, found 161.0582.

Ethyl 2-oxo-2*H*-chromene-3-carboxylate (2q)

Following the general procedure, **2q** was purified by silica gel chromatography (EA/PE = 10/90). Yield: 41%, white solid, mp. 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.67–7.61 (m, 2H), 7.38–7.32 (m, 2H), 4.42 (q, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 156.7, 155.1, 148.6, 134.3, 129.5, 124.9, 118.3, 117.9, 116.8, 62.0, 14.2. HRMS (ESI) *m*/*z* calcd for $C_{12}H_{11}O_4^+$ [M + H^+] 219.0652, found 219.0653.

4,4'-(2-Iodoethene-1,1-diyl)bis(methoxybenzene) (3)

Following the general procedure, **3** was purified by silica gel chromatography (EA/PE = 3/97). Yield: 82%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.71 (s, 1H), 3.84 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 159.2, 151.7, 134.4, 134.3, 130.9, 130.0, 113.7, 113.6, 76.0, 55.3, 55.2. HRMS(ESI) *m*/*z* calcd for $C_{16}H_{15}O_2^+$ [M + H^+] 239.1067, found 239.1069.

1,2-Bis(4-methoxyphenyl)ethyne (4)

Following the general procedure, without the addition of I_2, **4** was purified by silica gel chromatography (EA/PE = 5/95). Yield: 60%, white solid, mp. 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 4H), 6.86 (d, *J* = 8.0 Hz, 4H), 3.82 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 132.9, 115.7, 114.0, 88.0, 55.3. HRMS (ESI) *m*/*z* calcd for $C_{16}H_{15}O_2^+$ [M + H^+] 239.1067, found 239.1072.

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