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Synthesis of polycyclic heteroaromatic coumarins *via* photoinduced dehydrogenative annulation of 4-phenyl-3-heteroarylcoumarins

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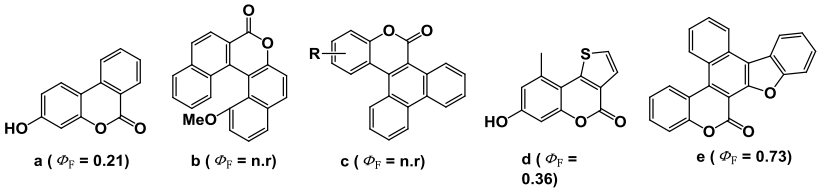
ABSTRACT: An efficient, oxidant and metal free synthesis of polycyclic heteroaromatic coumarins was developed. *H*-furo[2',3':3,4]naphtho[2,1-*c*]chromen-4-one (**2a**-**2f**), 1*H*-benzofuro[2',3':3,4]naphtho[2,1-*c*]chromen-1-one (**2g**-**2j**) and 4*H*-thieno[2',3':3,4]naphtho [2,1-*c*]chromen-4-one (**2k**-**2s**) derivatives were obtained by the irradiation of 4-phenyl-3-heteroarylcoumarin in EtOH–H_2O (9 : 1, v/v) using a high-pressure Hg lamp as the light source, at room temperature and under Ar atmosphere. Owing to the expansion of π-conjugation system, **2a**-**2s** showed strong fluorescence emissions in ethanol solution (Φ_F = 0.40-0.83).

INTRODUCTION:

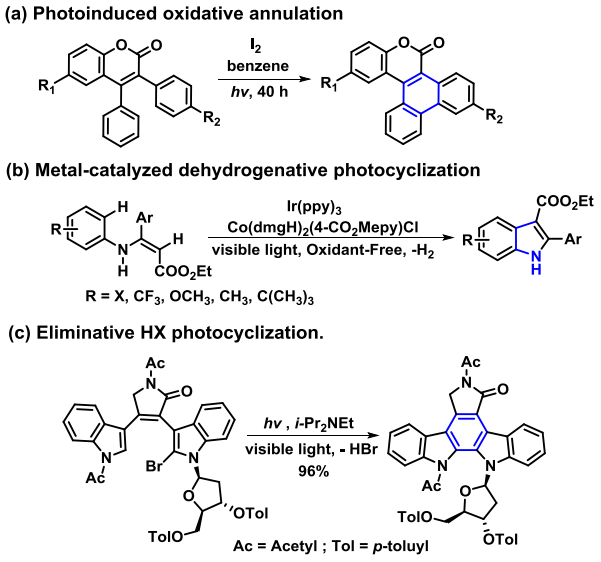
In recent years, π-expanded coumarins have attracted considerable attention due to their excellent pharmacological activities. Polycyclic conjugated coumarins, for examples, Isofraxidin isolated from *Acanthopanax Senticosus* and Calanolides isolated from *Calophyllum Lanigerum* trees, were found to be highly effective autumnariol and against HIV-1, respectively.[1] Besides, coumarin derivatives have been widely used in the field of fluorescent dyes, organic light-emitting materials, solar battery and liquid crystal materials due to their outstanding photophysical and photochemical properties.[2] The type of fused ring, the manner of fusion and the electronic effect from electron-donating or electron-withdrawing substituents all influenced the photophysical parameters. It has been showed that the introduction of fused rings constituted a powerful approach to control photophysical properties of π-expanded coumarins.[3] A variety of aromatic [*c*]coumarin derivatives along a few heterocoumarin analogues are shown in Scheme 1, which possess photophysical activity, especially compound **e** (Φ_F = 0.73).[4]

Scheme 1. Reported π-expanded coumarins with their corresponding Φ_F (n.r.: not reported)



The photoinduced intramolecular annulation of polycyclic compounds could be summarized mainly in three strategies: (a) photoinduced oxidative annulation with the presence of external oxidizer, e.g. O_2, I_2 or TCNE;[5] (b) transition metal-catalyzed dehydrogenative photocyclization, which might need additional ligand or other metals;[6] (c) dehydrohalogenation or dehydrated photocyclization.[7] For instances, irradiation of 3,4-diphenylcoumarin in benzene with the presence of iodine for 40 hours by a medium pressure mercury lamp gave photooxidation product benzo[*b*]phenanthro[9,10-*d*]pyran-9-one in decent yield (Scheme 2a).[5a] The synthesis of polycyclic indole derivatives was achieved *via* intramolecular direct double C-H activation in the presence of $Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$ and $Ir(ppy)_3$ under visible light irradiation along with the elimination of hydrogen (Scheme 2b).[6c] In Scheme 2c, a non-oxidative photocyclization was performed by exposing lactam to sunlight in the presence of diisopropylethylamine to provide the desired indolocarbazole. The photochemically induced conversion was promoted by the facile dehydrobromination of the incipient cyclization product.[7c]

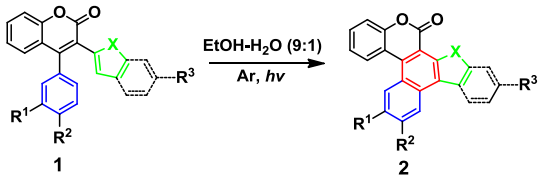
Scheme 2. Examples of photoinduced intramolecular annulation



We have successfully demonstrated the transition-metal and/or additive-free photoinduced

intramolecular cyclization.[8] Various heteroaromatics were synthesized from 1-aryl-2-(furan/thiophen-2-yl)butan-1,3-diones[9] and 2,3-di(hetero)-arylchromen-4-ones.[10] Encouraged by our previous work and the excellent photophysical properties of π-expanded coumarins, we would like to report the synthesis of polycyclic heteroaromatic coumarins **2** *via* photoinduced dehydrogenative annulation of 4-phenyl-3-heteroaryl-coumarins **1** (Scheme 3). Moreover, the fluorescence properties of **2** were further explored and high fluorescence quantum efficiencies (Φ_F = 0.40-0.83) were observed and discussed, which could be explained by the π-expanded conjugation system.

Scheme 3. Photoinduced syntheses of 2 *via* dehydrogenative annulation

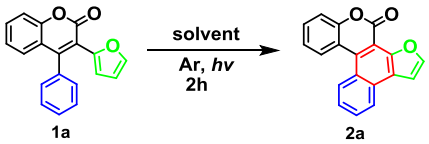


R^1 = H, OMe; R^2 = H, Me, OMe, OH, F, Cl, CF_3; R^3 = H, Me; X = O, S

RESULTS and DISCUSSION

Substrates **1a**-**1s** were synthesized according to the literature reports.[11] The full UV-absorption spectrum of **1a** is shown in SI. And the typical π→π* absorption is observed at 370 nm (ε = 104700 L mol^{-1} cm^{-1}), which is accordant with the excited light (365 nm) of a high-pressure mercury lamp.

Table 1. Optimization of Intramolecular cyclization of 1a[a]



Entry	Conc. (mM)	Solvent (v:v)	Time (h)	Conv[a] (%)	Yield[a] (%)
1	2.5	CH_2Cl_2	2	30	12
2	2.5	MeCN	2	50	40
3	2.5	MeOH	2	80	50
4	2.5	EtOH	2	84	57
5	2.5	EtOH-H_2O (9:1)	2	88	64
6	2.5	EtOH-H_2O (8:1)	2	81	61
7	2.5	EtOH-H_2O (6:1)	2	74	59

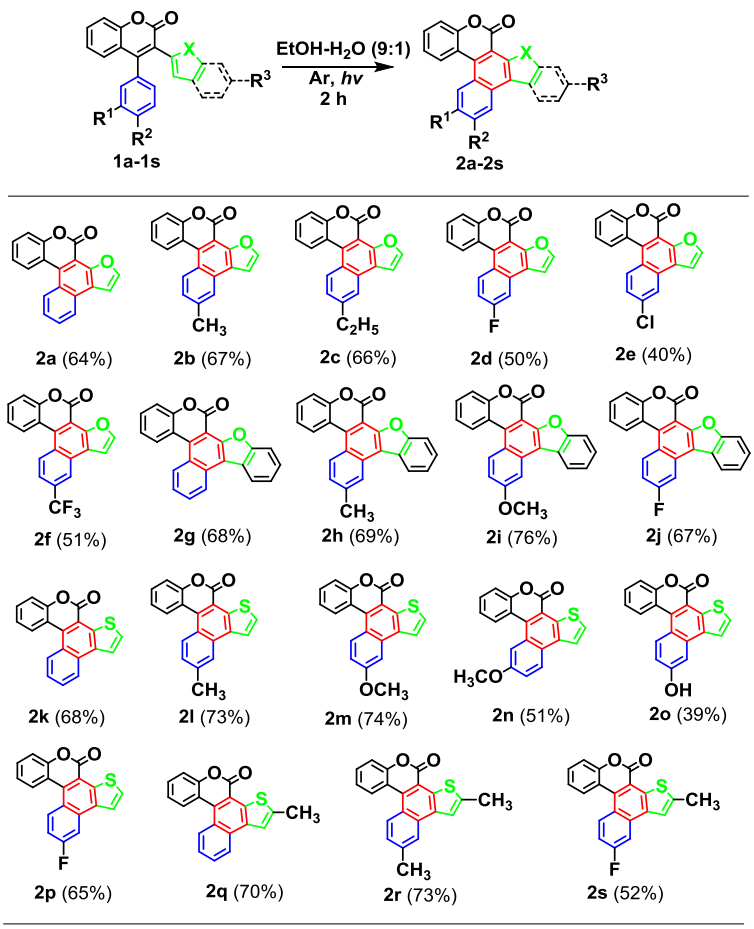
8	1	EtOH-H_2O (9:1)	2	82	54
9	5	EtOH-H_2O (9:1)	2	70	49
10	2.5	EtOH-H_2O (9:1)	1	69	49
11	2.5	EtOH-H_2O (9:1)	3	97	56
12	2.5	EtOH-H_2O (9:1)	4	100	52
13[b]	2.5	EtOH-H_2O (9:1)	2	99	39

[a] Irradiation of 1a (0.25 mmol) in various solvents (100 mL) with a 500 W high-pressure mercury lamp under Ar atmosphere at room temperature. [b] Performed in the open air atmosphere.

Initially, irradiation of **1a** (0.25 mmol) in CH_2Cl_2 (100 mL) with a high-pressure mercury lamp (500 W) at ambient temperature for 2 h gave annulation product **2a** in 12% (Table 1, entry 1). Replacement of DCM with acetonitrile, methanol or ethanol gave **2a** in better yields (40%, 50% and 57%, entries 2-4). Interestingly, the yields of **2a** were slightly elevated with addition water to the reaction mixture (59-64%, entries 5-7), while the conversion yields varies. The effects of substrate concentration and irradiation time were investigated. Thus, the annulation with either higher or lower substrate concentrations of **1a** was performed. Unfortunately, **2a** was obtained in reduced yields (entries 8-9). As it is expected, the conversion yields of **1a** were increased dramatically with extended irradiation time (entries 11-12), whereas, the yields for the formation of **2a** decreased slightly, especially in the presence of air (entry 13). As a result, the irradiation of **1a** (0.25 mM) in EtOH-H_2O (9:1, v/v, 100 mL) with mercury lamp under Ar atmosphere at room temperature for 2 h was determined to be the optimal condition.

With the optimized condition determined, a series of annulation products **2a**-**2s** were obtained and displayed in Table 2 along with yields in parenthesis. Generally, substrates **1** bearing benzofuran (**1g**-**1j**) and thiophene (**1k**-**1s**) gave the corresponding cyclization products in higher yields (52-76%) than that of the furan derivatives (**2a**-**2f**). And substrates with electron-donating groups (e.g. Me, OMe, and C_2H_5), produced better yields than the substrate bearing electron-withdrawing groups (F, CF_3). Notably, a free hydroxyl group could also be tolerated and **2o** was obtained in 39%. The presence of Cl group on **2e** makes it possible to perform further modification.

Table 2. Synthesis of polycyclic heteroaromatic coumarins (2a−2s) [a]



[a] All reactions were carried out on 0.25 mmol of **1** in EtOH-H_2O (100 mL, 9 : 1) and irradiated with a high-pressure mercury lamp (500 W) under an argon atmosphere at ambient temperature.

The structure of **2** was established *via* ^{1}H NMR, ^{13}C NMR, HRMS, UV and IR. Compound **2l** was also analyzed by X-ray. The fluorescence spectra of **2** were measured in EtOH (10^{-6} mol/L) and the corresponding excitation/emission maxima wavelength and quantum yields were listed in Table 3. Generally, irradiation of coumarin derivatives **2** with 303–370 nm light generated blue-purple fluorescence light (λem = 417−465 nm).

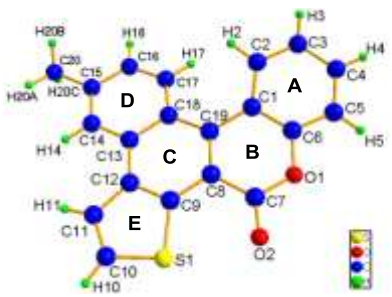
The quantum yields (Φ_F) of 4*H*-furo[2',3':3,4]naphtho[2,1-*c*]chromen-4-ones (**2a-2f**) are higher than those bearing thiophenyl moiety (**2k-2s**). Due to the presence of expanded π-conjugated system, **2g-2j** gave higher quantum yields than **2a-2f**. The presence of electron-donating substituent on heteroaromatic coumarins benefited the growth of quantum yields. For example, **2g-2j** have prominent fluorescence properties, and their fluorescence quantum yields are ranging from 0.76 to 0.83 with significant stokes shifts (140 to 149 nm). The quantum yield of **2g** is consistent with literature reported (0.73/benzene). [5a]

Table 3 Spectral properties of 2a-2s in ethanol solution(10^{-6} mol/L)

Compounds	λ_{ex}^{max}/nm	λ_{em}^{max}/nm	Stokes shift/nm	Φ_F
2a	347	449	102	0.64
2b	351	449	98	0.72
2c	303	449	146	0.76
2d	299	444	145	0.78
2e	304	447	143	0.53
2f	349	457	108	0.63
2g	313	462	149	0.78
2h	316	465	149	0.81
2i	319	462	143	0.83
2j	316	456	140	0.76
2k	316	439	123	0.51
2l	316	439	123	0.63
2m	318	439	121	0.67
2n	341	455	114	0.54
2o	319	443	124	0.40
2p	308	430	122	0.43
2q	319	417	98	0.65
2r	321	449	128	0.71
2s	319	444	125	0.62
1a	370	452	74	0.51

The crystal structure of **2l** was characterized by the single crystal X-ray diffraction, and the detail info is shown in Table S1(SI). As illustrated in Figure 1, the molecule of **2l** includes three benzene rings [A (C1-C6), C (C8, C9, C12, C13, C18, C19), and D (C13-C18)], one 2*H*-pyran-2-one ring B (C6, O1, C7, C8, C19, C1) and one thiophene ring E (C9, S1, C10, C11, C12). The atoms of ring B, ring C, ring D and ring E are almost coplanar with a mean deviation from the least-squares plane of 0.0853 A˚. It is important to note that the unexpected rotation (17.6˚) of ring A from the planar B-E was observed, which is believed to avoid steric conflicts between H2 and H17.

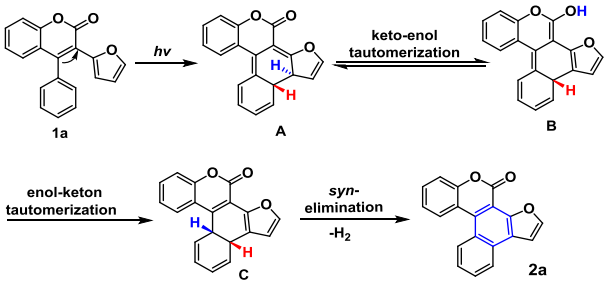
Figure 1. X-ray crystal structure of 2l



On the basis of literature reports and experimental evidence, a plausible mechanism for the formation of **2** is proposed and illustrated in Scheme 4. Irradiation of 3-(furan-2-yl)-4-phenylcoumarin (**1a**) with UV light (365 nm) at ambient temperature generates the intermediate **A** *via* an intramolecular 6π-electron-cyclization.[12] **A** undergoes [1,5]-H shift and gives the intermediate **B**.[13] The rearomatization of the furan ring is the force driving this [1,5]-sigmatropic shift.

The keto-enol tautomerization of **A** leads to the formation of intermediate **B**, which might be stabilized *via* the intramolecular hydrogen bond between the corresponding -OH and oxygen from furan ring and it is believed to be the driving force for this transformation. Then, syn-isomer intermediate **C** was obtained from another enol-keto tautomerization. Because polar protic solvent is beneficial to the process of keto-enol isomerization, account for the higher yield of **2a** in EtOH-H_2O (9:1) comparing to CH_2Cl_2 and MeCN. And the dose water is benefit to the keto-enol isomerization. Finally, syn-isomer **C** yields annulation product **2a** by the hydrogen evolution, which share similar concept with literature reports.[10] It is important to note that the cyclization product **2a** was obtained with the presence of oxygen (open air) in low yield. Thus we concluded the intramolecular photoinduced dehydrogenative cyclization proceeded through the S1 state. More importantly, by-product H_2 was also successfully detected *via* GC chromatography during the annulation, which powerfully proved the validity of the proposed mechanism (SI, Figure S4-5).

Scheme 4. Proposed mechanism for the formation of 2a

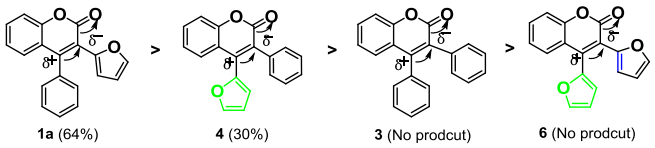


In order to further examine and validate the mechanism, 3,4-diphenyl-2*H*-chromen-2-one **3** was subjected to the optimal condition [*hv*, rt, 9 : 1 EtOH/H_2O (v/v)]. However, neither annulation product benzo[*b*]phenanthro-[9,10-*d*]pyran-9-one nor H_2 was detected. It is a strong indication that our reported photoinduced cyclization proceed *via* different

mechanism comparing to the literature report.[5a] Due to the presence of benzene ring at both **3** and **4** position of substrate **3**, there is no significant electron density difference between the phenyl substituents. Thus, no cyclization product was observed under the optimal condition.

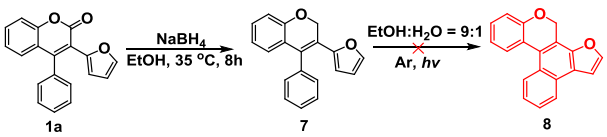
The presence of furyl or thiophenyl group at 3-position of coumarin is believe to be crucial for the cyclization of substrates **1**. With the presence of electron rich five-member heteroaromatic at the **3** position as well as the electron withdrawing property of the carbonyl group, the electron density difference between **3** and **4** facilitate the cyclization and yield the intramolecular dehydrogenative product **2**. Meanwhile, it is important to note that irradiation of 3-phenyl-4-(furan-2-yl)coumarin **4** in EtOH–H_2O (9 : 1, v/v) with a high-pressure mercury lamp at room temperature under Ar atmosphere also led to the formation of dehydrogenative cyclization product [5*H*-furo[2',3':3,4]naphtho[1,2-*c*] chromen-5-one] **5** but in lower yields (30%). As expected, irradiation of 3,4-di(furan-2-yl)coumarin **6** failed to give corresponding cyclization product due to the presence of same substituents at both **3** and **4** position. On the basis of experimental result, only substrates with different aryl substitutions gave cyclization product in decent to good yields and the 3-heteroarylcoumarin seems to be the best candidate due to the consistency with electron withdrawing property of carbonyl group. (Scheme 5)

Scheme 5. Effect of the substituents on dehydrogenative annulation reactivity



In addition, treatment of **1a** with $NaBH_4$ in EtOH at 35 ℃ for 8 h give reduced product **7** in 31% (Scheme 6).[14] As it is expected that subjection of **7** to the optimal condition [*hv*, rt, 9 : 1 EtOH/H_2O(v/v)] failed to provide dehydrogenative annulation product **8**, which could be easily explained by the lack of keto-enol tautomerization.

Scheme 6. Attempted annulation of 7 under the optimal reaction conditions



CONCLUSION

In summary, we have successfully demonstrated the synthesis of polycyclic heteroaromatic coumarins *via* photoinduced dehydrogenative annulation of 3-aryl-4-heteroarylcoumarins with a high-pressure mercury lamp in EtOH-H_2O (9:1, v/v) at room temperature. Compared with reported methods, the described method has the superiorities of a) no requirement of oxidant, additives and catalyst, b) green solvent (EtOH-H_2O), c) broad substrate scope, and d) moderate to very good atom efficiency. Owing to π-expanded conjugated system, heteroaromatics **2a**-**2s** possess excellent fluorescence in ethanol solution.

EXPERIMENTAL PROCEDURES AND ANALYTICAL DATA

General Information. All reagents were purchased from commercial suppliers and used without purification. Thin-layer chromatography (TLC) used silica gel 60 GF254 plate. The silica gel (size 200-300 mesh) used for the column chromatography was purchased from Qingdao Haiyang Chemistry Plant (China). Melting points were measured in a X-5 micro-melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded on 400 MHz spectrometer with TMS as internal reference and $CDCl_3$ or DMSO-d_6 as solvent. All chemical shift values were reported in parts per million (ppm) and referenced to the residual solvent peaks [$CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 ppm)] for ^{1}H NMR. ^{13}C NMR spectra were recorded on 400 or 600 MHz spectrometer and the $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm) for ^{13}C NMR spectra, with coupling constant (J) values reported in Hz. The infrared spectra were recorded on a Nicollet 170SX FTIR spectrophotometer with KBr pellets in the 4000–500 cm^{-1} region. High-resolution mass spectrometry (HRMS) was recorded using electron-spray ionization quadrupole-time of flight (ESI-Q-TOF) technique. The elemental analysis were carried out with a Perkin-Elmer 240C elemental analyzer. The crystal diffraction data was collected on a Bruker Smart-1000 CCD diffractometer. The fluorescence spectra were measured on a Hitachif-4600 fluorescence spectrometer equipped with a xenon discharge lamp.

General Procedures for Syntheses of Polycyclic Heteroaromatic Coumarins (2a−2s).

Substrate 3-(furan-2-yl)-4-phenyl-2*H*-chromen-2-one **1a** (72 mg, 0.25 mmol) was dissolved in a mixture of

EtOH-H_2O (100 mL, 9:1, v/v) at ambient temperature in a quartz tube (100 mL). The solution was deaerated by bubbling argon for 30 min and irradiated with a high pressure mercury lamp (500 W), which was cooled to about 25 ℃ with tap water by means of an internal cold finger. Then, the volatiles were removed under reduced pressure and residue was column chromatographied (ethyl acetate/petroleum ether, 1:20) to give **2a** (46 mg, 64%). Analogously, compounds **2b**-**2s** were synthesized using the same methodology described above, with yields 39~74%. (The reaction scheme is in SI-Scheme S1).

Procedures for Syntheses of 4-aryl-3-heteroaryl-2*H*-chromen-2-one derivatives (1a-1s, 3, 4, 6).

Synthesis of 3-bromo-4-hydroxy-2H-chromen-2-ones[16] The N-bromosuccinimide (2.9 g, 16.2 mmol) was added to a solution of 4-hydroxycoumarin (2.496 g, 15.4 mmol) in acetonitrile (50 mL), followed by ammonium acetate (0.116 g, 1.5 mmol). The reaulting mixture was stirred at ambient temperature for 3 h (Scheme 1). Then the volatiles were removed under the reduced pressure and the residue was taken in ethyl acetate and water mixture (50 mL, 1:1). The mixture was extracted with ethyl acetate (3×20 mL). Organic layer was collected, washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The oily residue was purified by column chromatography (ethyl acetate/petroleum ether, 1:40) to give 3-bromo-4-hydroxycoumarin as light yellow solid (3.266 g, 88%), which was used for the next step without characterization.

Synthesis of 3-bromo-2-oxo-2H-chromen-4-yltrifluoromethane-sulfonate[11] After the solution of 3-bromo-4-hydroxycoumarin (0.964 g, 4.0 mmol) in dry dichloromethane (100 mL) was cooled to 0 ^oC (ice bath) in a hot-oven dried Schlenk test tube, triethylamine (0.7 mL, 5.10 mmol) was added and stirred for another 5 min. Then triflic anhydride (2.6 mL, 15 mmol) was added slowly. After the reaction mixture was stirred at 0 ℃ for 6 h, it was poured into water and extracted with dichloromethane (3×20 mL). Organic layer was collected, washed (brine), dried (anhydrous Na_2SO_4) and concentrated under the reduced pressure. The oil residue was purified by column chromatography (ethyl acetate/petroleum ether, 1:30) to give white solid (0.925 g, 62%).

Syntheses of 4-aryl-3-heteroaryl-2H-chromen-2-one derivatives (1a-1s, 3, 4, 6)[17, 18] According a typical procedure, a hot-oven dried Schlenk tube was charged with 3-bromo-4-trifloxycoumarin (1.0 mmol, 0.373 g), phenylboronic acid (1.0 mmol, 0.122 g), $NaHCO_3$ (2.0 mmol, 0.168 g), $Pd(PhCN)_2Cl_2$(0.5 mol %) and CH_3OH (20 mL) under nitrogen atmosphere. The reaction mixture was stirred at 10 ℃ (water bath) for 4h. Then the reaction mixture was poured into water (20 mL) and extracted with ethyl acetate (3×20 mL). The organic layer was combined and volatiles were removed under reduced pressure. The crude product was purified on silica gel column chromatography (ethyl acetate/petroleum ether, 1:60) and was used directly in the next step.

A mixture of 3-bromo-4-phenyl-2*H*-chromen-2-one (0.5 mmol, 0.151 g), furan-2-ylboronic acid (1 mmol, 0.112 g), $Pd(PPh_3)_4$ (0.5 mol %) and $CsCO_3$ (1.5 mmol, 0.289 g) in 1,4-dioxane (20.0 mL) was stirred at 90 ℃ for a period of time. After completion of the reaction as indicated by TLC, the mixture was cooled to room temperature

and volatiles were removed under reduced pressure. The residue was purified by silica gel by column chromatography (EtOAc/petroleum ether, 1:30) to give **1a** in 50%. Analogously, **1b**-**1n**, **1p**-**1s, 3, 4** were prepared according to this methodology above described, with yields 50%~83%. (The reaction scheme is in SI-Scheme S2).

A cold diluted solution of BBr_3 (2.01 g, 8 mmol) in dry chloroform was added to a solution of 3-(furan-2-yl) -4-(4-methoxyphenyl)-2*H*-chromen-2-one (**1m**, 0.637 g, 2 mmol) in dry chloroform and stirred at 0 ℃ for 30 min. The reaction mixture was refluxed for 12 h, then, cooled to room temperature. The excess of BBr_3 was quenched by the addition of MeOH (20 mL). The volatiles were removed under the reduced pressure and the residue was column chromatographed (ethyl acetate/petroleum ether, 1:50 → 1:5) to give **1o** (48%).[19] (The reaction scheme is in SI-Scheme S3).

Synthesis of 3-(Furan-2-yl)-4-phenyl-2H-chromene (7).[20] The $NaBH_4$ (113 mg, 1.5 mmol) was added to a solution of 3-(furan-2-yl)-4-phenyl-2*H*-chromen-2-one **1a** (145 mg, 0.5 mmol) in EtOH (10 ml). The mixture was stirred at 35 ℃ for 8 h under Ar, poured into the saturated ammonium chloride to quench the reaction. The mixture was extracted with ethyl acetate (20 ml×3) and combined, the organic layer dried over (Mg_2SO_4), concentrated under reduced pressure. The oily residue was purified by column chromatography (petroleum ether) to give **7** (yield, 31 %).

4H-furo[2',3':3,4]naphtho[2,1-c]chromen-4-one ***(2a)***. Yield: 64%, 46 mg; Yellow solid; m.p. 179.3-180.1 ^{o}C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 7.28(d, *J* = 2.0 Hz, 1H), 7.36(dd, *J* = 6.7, 4.1 Hz, 1H), 7.42-7.55(m, 2H), 7.61(dd, *J* = 7.4, 4.1 Hz, 1H), 7.75(t, *J* = 7.5 Hz, 1H), 7.98(d, *J* =1.9 Hz, 1H), 8.20(t, *J* = 8.1 Hz, 1H), 8.38(d, *J* = 8.1 Hz, 1H), 8.80(d, *J* = 8.7 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 158.4, 151.5, 148.8, 146.9, 132.9, 131.5, 129.9, 129.7, 128.5, 128.4, 125.9, 125.5, 125.1, 124.5, 124.2, 118.8, 117.9, 108.9, 105.5. IR (KBr) *v* (cm^{-1}) 3366, 3160, 2925, 2845, 1745, 1599, 1465, 1107, 1071. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{19}H_{10}O_3Na$ 309.0522; Found 309.0533.

12-Methyl-4H-furo[2',3':3,4]naphtho[2,1-c]chromen-4-one ***(2b)***. Yield: 67%, 50 mg; Yellow solid; m.p. 212.7- 214.1 ^{o}C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.63(s, 3H), 7.28(d, *J* = 1.9 Hz, 1H), 7.37(s, 1H), 7.45(dd, *J* = 8.8, 1.0 Hz, 1H), 7.51 (t, *J* = 3.4 Hz, 2H), 7.98(d, *J* = 1.3 Hz, 2H), 8.42(d, *J* = 8.1 Hz, 1H), 8.73(d, *J* = 8.8 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 158.6, 151.6, 149.1, 146.7, 140.3, 133.0, 131.9, 129.9, 128.4, 128.4, 128.0, 124.7, 124.2, 123.9, 123.7, 118.9, 117.9, 108.4, 105.4, 21.9. IR (KBr) *v* (cm^{-1}) 2960, 2872, 1723, 1627, 1471, 1459, 1383, 1019, 759. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{12}O_3Na$ 323.0679; Found 323.0691.

12-Ethyl-4H-furo[2',3':3,4]naphtho[2,1-c]chromen-4-one ***(2c)***. Yield: 66%, 52 mg; Yellow solid; m.p. 236.1-237.1 ^{o}C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 1.41(t, *J* = 7.6 Hz, 3H), 2.93(s, *J* = 7.6 Hz, 2H), 7.30(d, *J* = 1.7 Hz, 1H), 7.37(s, 1H), 7.49 (t, *J* = 8.5 Hz, 3H), 7.99 (s, 2H), 8.43(d, *J* = 8.1 Hz, 1H), 8.75(d, *J* = 8.8 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 158.6, 151.5, 149.1, 146.7, 146.4, 132.9, 131.9, 129.9, 128.6, 128.4, 126.9, 124.8, 124.2, 123.9, 122.6, 118.9, 117.9, 108.3, 105.5, 29.2, 15.4. IR (KBr) *v* (cm^{-1}) 2943, 1723, 1625, 1470, 1075, 1354, 759. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{21}H_{14}O_3Na$ 337.0835; Found 337.0852.

12-Fluoro-4H-furo[2',3':3,4]naphtho[2,1-c]chromen-4-one ***(2d)***. Yield: 50%, 38 mg; Yellow solid; m.p. 222.4-223.8 oC. 1H NMR(400 MHz, CDCl3) δ(ppm) 7.28(s, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.55(dd, J = 12.7, 7.5 Hz, 2H), 7.79-7.96(m, 1H), 8.03(s, 1H), 8.38(d, J = 8.1 Hz, 1H), 8.91(dd, J = 9.4, 5.5 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, CDCl3) δ(ppm) 164.3(d,1J = 252.0 Hz), 158.3, 151.6, 149.4, 147.1, 133.6(d, 3J = 9.6 Hz), 133.3,

131.6(d, 3J = 9.5 Hz), 130.3, 128.3, 124.8, 124.7, 124.4, 122.5, 118.6, 118.1, 115.6(d, 2J = 23.9 Hz), 109.1(d, 2J = 21.4 Hz), 105.6. IR (KBr) ν (cm-1) 3065, 2912, 1723, 1625, 1470, 1075, 1354, 759. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{19}H_9FO_3Na$ 327.0428; Found 327.0425.

12-Chloro-4H-furo[2',3':3,4]naphtho[2,1-c]chromen-4-one ***(2e)***. Yield: 40%, 32 mg; Yellow solid; m.p. 215.9-216.8 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 7.60(d, *J* = 2.3 Hz, 1H), 7.77-7.70(m, 1H), 7.88(dt, *J* = 15.6, 4.6 Hz, 3H), 8.35(d, *J* = 1.9 Hz, 1H), 8.51 (d, *J* = 1.9 Hz, 1H), 8.67(d, *J* = 8.1 Hz, 1H), 9.12(d, *J* = 9.2 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 158.1, 151.6, 149.5, 147.3, 136.1, 133.0, 132.5, 130.4, 130.2, 128.2, 126.7, 124.5, 124.4, 123.9, 123.8, 118.5, 118.1, 109.1, 105.4. IR (KBr) *ν* (cm^{-1}) 2933, 1753, 1625, 1520, 1474, 1355, 739. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{19}H_9ClO_3Na$ 343.0132; Found 343.0132.

12-Trifluoromethyl-4H-furo[2',3':3,4]naphtho[2,1-c]chromen-4-one ***(2f)***. Yield: 51%, 45 mg; Yellow solid; m.p. 247.9-248.6 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 7.21-7.60(m, 3H), 7.71-8.09(m, 2H), 8.09(d, *J* = 4.8 Hz, 1H), 8.45(d, *J* = 8.0 Hz, 1H), 8.74(s, 1H), 9.03(d, *J* = 8.7 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 157.9, 151.6,149.4, 147.7, 132.7, 131.6, 130.9(d, *J* = 12.6 Hz), 130.8, 130.6, 129.7, 128.2, 127.2, 125.6, 124.6, 122.6, 122.0(d, *J* = 4.2 Hz), 121.6(d, *J* = 3.3 Hz), 118.3(d, *J* = 15.9 Hz), 110.4, 105.5. IR (KBr) *ν* (cm^{-1}) 3114, 2923, 2340, 1756, 1531, 1355, 1281, 759. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_9F_3O_3Na$ 377.0396; Found 377.0395.

1H-benzofuro[2',3':3,4]naphtho[2,1-c]chromen-1-one ***(2g)***. Yield: 68%, 57 mg; Yellow solid; m.p. 177.3-178.8 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 7.41(dd, *J* = 1.2, 6.8 Hz, 1H), 7.53(m, 4H), 7.66(dd, *J* = 0.8, 7.5 Hz, 1H), 7.86(dd, *J* = 7.8, 6.8 Hz, 2H), 8.34(d, *J* = 7.5 Hz, 1H), 8.42(d, *J* = 8.0 Hz, 1H), 8.66(d, *J* = 8.3 Hz, 1H), 8.87(d, *J* = 6.7Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 158.1, 156.9, 151.9, 151.2, 135.5, 132.7, 130.5, 130.3, 128.9, 128.9, 127.2, 125.7, 125.4, 124.3, 123.9, 123.4, 121.9, 119.5, 118.7, 118.0, 113.0, 108.8. IR (KBr) *ν* (cm^{-1}) 2939, 2840, 1745, 1599, 1464, 1106, 1071. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{23}H_{12}O_3Na$ 359.0679; Found 359.0680.[15]

9-Methyl-1H-benzofuro[2',3':3,4]naphtho[2,1-c]chromen-1-one ***(2h)***. Yield: 69%, 60 mg; Yellow solid; m.p. 249.2-250.1 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.63(s, 3H), 7.333-7.44(m, 2H), 7.50(dt, *J* = 19.9, 7.4 Hz, 4H), 7.82(d, *J* = 8.1 Hz, 1H), 8.25-8.31(m, 2H), 8.34(d, *J* = 8.1 Hz, 1H), 8.66(d, *J* = 8.8 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 158.1, 156.8, 151.9, 151.4, 140.9, 135.3, 132.9, 130.3, 128.8, 128.6, 127.7, 126.9, 124.2, 123.8, 123.6, 123.5, 123.4, 121.9, 118.8, 118.7, 117.9, 112.9, 107.9, 22.2. IR (KBr) *ν* (cm^{-1}) 2922, 2847, 1732, 1625, 1465, 1351, 1059. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{24}H_{14}O_3Na$ 373.0835; Found 373.0836.

9-Methoxy-1H-benzofuro[2',3':3,4]naphtho[2,1-c]chromen-1-one ***(2i)***. Yield: 76%, 69 mg; Yellow solid; m.p. 242.1-242.8 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 4.04(s, 3H), 7.17(dd, *J* = 9.5, 2.6 Hz, 1H), 7.37(d, *J* = 8.1 Hz, 1H), 7.38-7.65(m, 4H), 7.76(dd, *J* = 24.6, 5.2 Hz, 2H), 8.13(d, *J* = 7.5 Hz, 1H), 8.28(d, *J* = 8.1 Hz, 1H), 8.64(d, *J* = 9.4 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 160.9, 158.1, 156.7, 151.9, 151.8, 135.4, 134.7, 130.5, 130.3, 128.8, 126.8, 124.2, 123.8, 123.4, 121.4, 119.9, 118.6, 118.3, 117.9, 116.9, 112.9, 106.6, 103.9, 55.7. IR (KBr) *ν* (cm^{-1}) 2928, 2843, 1730, 1617, 1465, 1358, 1053. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{24}H_{14}O_4Na$ 389.0784; Found 389.0788.

9-Fluoro-1H-benzofuro[2',3':3,4]naphtho[2,1-c]chromen-1-one ***(2j)***. Yield: 67%, 59 mg; Yellow solid; m.p. 246.8-248.1 °C. ^{1}H NMR(400 MHz, $CDCl_3$ + d_6-DMSO) δ(ppm) 7.27-7.41(m, 2H), 7.45- 7.77(m, 4H), 7.87(d, *J* = 8.1, 1H), 8.10-8.33(m, 2H), 8.35(d, *J* = 8.0 Hz, 1H), 8.90(dd, *J* = 9.4, 5.7 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 157.1, 156.1, 151.2, 151.1, 135.1, 133.6(d, ^3J = 7.1 Hz), 131.4(d, ^3J = 6.1 Hz), 130.3, 128.1, 125.4(d, ^1J = 280.3 Hz), 123.7, 122.4, 121.7, 121.0, 118.3, 117.5(d, ^2J = 37 Hz), 114.9(d, ^2J = 26 Hz), 112.2, 108.2, 108.1, 107.5. IR (KBr) *ν* (cm^{-1}) 2919, 2853, 2341, 1741, 1624, 1451, 1058. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{23}H_{11}FO_3Na$ 377.0584; Found 377.0590.

*4H-thieno[2',3':3,4]naphtho[2,1-c]chromen-4-one (**2k**)*. Yield: 68%, 51 mg; Yellow solid; m.p. 204.4-205.7 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 7.30-7.41(m, 1H), 7.46-7.56(m, 2H), 7.62(d, *J* = 8.0 Hz, 1H), 7.67-7.91(m, 2H), 7.97(d, *J* = 5.5 Hz, 1H), 8.40(t, *J* = 7.3 Hz, 2H), 8.79(d, *J* = 8.6 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 160.9, 151.2, 137.4, 134.2, 132.9, 132.8, 131.2, 129.9, 129.7, 128.3, 128.2, 126.3, 126.2, 124.8, 124.3, 121.1, 118.8, 117.9, 115.7. IR (KBr) *v* (cm^{-1}) 3106, 2832, 1708, 1604, 1446, 1165, 767, 727. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{19}H_{10}O_2S$ Na 325.0294, Found 325.0300.

*12-Methyl-4H-thieno[2',3':3,4]naphtho[2,1-c]chromen-4-one (**2l**)*. Yield: 73% (55 mg); Yellow solid; m.p. 199.6-200.3 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.58(s, 3H), 7.26-7.38(m, 2H), 7.48(t, *J* = 5.0 Hz, 2H), 7.72(d, *J* = 5.5 Hz, 1H), 7.86(d, *J* = 5.5 Hz, 1H), 8.05(s, 1H), 8.29(d, *J* = 8.1 Hz, 1H), 8.53(d, *J* = 8.7 Hz, 1H). ^{13}C{^{1}H} NMR(101MHz, $CDCl_3$) δ(ppm) 160.9, 151.1, 140.1, 136.8, 134.2, 132.8, 132.7, 130.7, 129.8, 128.1, 128.1, 127.9, 124.2, 124.2, 121.0, 118.8, 117.8, 114.9, 22.0. IR (KBr) *v* (cm^{-1}) 2916, 2354, 1700, 1621, 1471, 1169, 769, 719. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{12}O_2SNa$ 339.0450; Found 339.0457.

*12-Methoxy-4H-thieno[2',3':3,4]naphtho[2,1-c]chromen-4-one (**2m**)*. Yield: 74%, 61 mg; Yellow solid; m.p. 143.1-144.5 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 4.03(s, 3H), 7.19(dd, *J* = 2.4, 2.6 Hz, 1H), 7.28-7.41(m, 1H), 7.38-7.59(m, 2H), 7.62(d, *J* = 2.5 Hz, 1H), 7.73(d, *J* = 5.4 Hz, 1H), 7.86(d, *J* = 5.5 Hz, 1H), 8.31(d, *J* = 8.1 Hz, 1H), 8.63(d, *J* = 9.4 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 160.9, 160.5, 151.2, 136.4, 134.9, 134.8, 132.9, 130.5, 129.9, 129.9, 128.2, 124.3, 121.0, 120.9, 118.8, 117.9, 117.1, 113.8, 104.7, 55.68. IR (KBr) *v* (cm^{-1}) 2932, 2836, 1699, 1614, 1483, 1166, 768, 722. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{12}O_3SNa$ 355.0399; Found 355.0405.

*11-Methoxy-4H-thieno[2',3':3,4]naphtho[2,1-c]chromen-4-one (**2n**)*. Yield: 51%, 42 mg; Yellow solid; m.p. 140.1-141.9 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.60(s, 3H), 7.41-7.49(m, 2H), 7.55(dd, *J* = 11.1, 8.7 Hz, 2H), 7.89(d, *J* = 5.5 Hz, 1H), 8.07(d, *J* = 5.5 Hz, 1H), 8.10(s, 1H), 8.74(d, *J* = 8.0 Hz, 1H), 9.72(d, *J* = 8.9 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 160.6, 159.9, 157.5, 154.6, 152.7, 152.6, 136.6, 132.2, 130.3, 127.8, 124.9, 120.4, 120.4, 117.2, 116.9, 114.9, 113.9, 112.7, 55.6. IR (KBr) *v* (cm^{-1}) 3082, 2837, 1719, 1589, 1451, 1169, 997, 754. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{12}O_3SNa$ 355.0399; Found 355.0407.

*12-Hydroxy-4H-thieno[2',3':3,4]naphtho[2,1-c]chromen-4-one (**2o**)*. Yield: 39%, 31 mg; Yellow solid; m.p. 146.3-147.1 °C. ^{1}H NMR(400 MHz, d_6-DMSO) δ(ppm) 7.26-7.30(m, 1H), 7.53(d, *J* = 5.1 Hz, 2H), 7.59(d, *J* = 1.7 Hz, 1H), 7.90(s, 2H), 8.20(d, *J* = 2.0 Hz, 1H), 8.25(d, *J* = 8.0 Hz, 1H), 8.62(d, *J* = 9.0 Hz, 1H), 10.73(s, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 172.9, 163.4, 156.7, 151.7, 146.8, 145.9, 130.3, 129.2, 127.4, 125.8, 124.0, 123.7, 120.9, 119.3, 115.2, 114.7, 108.1, 105.6, 102.4. IR (KBr) *v* (cm^{-1}) 3079, 2989, 2821, 1721, 1624, 1483, 1174, 748, 712. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{10}O_2SNa$ 341.0243; Found 341.0244.

*12-Fluoro-4H-thieno[2',3':3,4]naphtho[2,1-c]chromen-4-one (**2p**)*. Yield: 65%, 52 mg; Yellow solid; m.p. 182.1-183.4 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 7.33-7.42(m, 2H), 7.53(dt, *J* = 15.1, 7.5 Hz, 2H), 7.79(d, *J* = 5.5 Hz, 1H), 7.86(d, *J* = 5.4 Hz, 1H), 7.95(dd, *J* = 9.7, 2.5 Hz, 1H), 8.30(d, *J* = 8.1 Hz, 1H), 8.79(dd, *J* = 9.4, 5.6 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 162.9(d, ^1J = 254.5 Hz), 160.7, 151.2, 136.6, 135.2, 134.6(d, ^3J = 9.1 Hz), 132.8, 131.4, 131.1(d, ^3J = 9.1 Hz), 130.2, 128.0, 124.5, 123.1, 121.1, 118.5, 118.1, 115.7(d, ^2J = 24.2 Hz), 115.2, 109.4(d, ^2J = 21.2 Hz). IR (KBr) *v* (cm^{-1}) 3090, 2926, 2853, 1706, 1603, 1328, 1184, 755, 715. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for for $C_{19}H_9FO_2SNa$ 343.0199; Found 343.0208.

*2-Methyl-4H-thieno[2',3':3,4]naphtho[2,1-c]chromen-4-one (**2q**)*. Yield: 70%, 55 mg; Yellow solid; m.p. 195.1.4-196.5 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.67(s, 3H), 7.28-7.41(m, 1H), 7.34-7.62(m, 4H), 7.64(t, *J* = 7.5 Hz, 1H), 8.18(d, *J* = 8.2 Hz, 1H), 8.31(d, *J* = 8.1 Hz, 1H), 8.67(d, *J* = 8.6 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 160.9, 150.9, 145.8, 137.7, 133.4, 132.1, 131.5, 129.5, 129.2, 128.1, 126.2, 125.9, 124.7, 124.2, 119.1, 118.9, 117.8, 115.4, 16.1. IR (KBr) *v* (cm^{-1}) 2993, 2842, 2373, 1695, 1603, 1457, 1174, 1366.

HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{12}O_2SNa$ 339.0456; Found 339.0466.

2, 12-Dimethyl-4H-thieno[2',3':3,4]naphtho[2,1-c]chromen-4-one ***(2r)***. Yield: 73%, 60 mg; Yellow solid; m.p. 214.9-216.2 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.60(s, 3H), 2.70(s, 3H), 7.38(t, *J* = 8.7 Hz, 2H), 7.49(d, *J* = 2.6 Hz, 2H), 7.57(s, 1H), 8.04(s, 1H), 8.38(d, *J* = 8.1 Hz, 1H), 8.63(d, *J* = 8.7 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 161.1, 151.1, 145.6, 139.9, 137.6, 133.7, 132.6, 131.9, 129.5, 128.1, 128.1, 128.0, 124.5, 124.3, 124.2, 119.2, 119.2, 117.9, 114.9, 22.1, 16.2. IR (KBr) *v* (cm^{-1}) 2923, 2841, 1712, 1620, 1459, 1368, 1119. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{21}H_{14}O_2SNa$ 353.0607; Found 353.0619.

12-Fluoro-2-methyl-4H-thieno[2',3':3,4]naphtho[2,1-c]chromen-4-one ***(2s)***. Yield: 52%, 43 mg; Yellow solid; m.p. 214.0-215.3 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.72(s, 3H), 7.28-7.44(m, 2H), 7.41-7.60(m, 3H), 7.87(dd, *J* = 9.9, 2.6 Hz, 1H), 8.33(d, *J* = 8.1 Hz, 1H), 8.80(dd, *J* = 9.4, 5.6 Hz, 1H). ^{13}C{^{1}H} (101 MHz, $CDCl_3$) δ(ppm) 162.8(d, ^1J = 253.5 Hz), 160.8, 151.1, 146.3, 137.2(d, ^4J = 4.6 Hz), 134.4, 134.0(d, ^3J = 9.3 Hz), 131.6, 130.9(d, ^1J = 9.1 Hz), 129.9, 127.9, 124.4, 123.2, 119.2, 118.8, 118.1, 115.5(d, ^2J = 23.9 Hz), 115.1, 109.3(d, ^2J = 21.8 Hz), 16.2. IR (KBr) *v* (cm^{-1}) 2914, 2839, 1697, 1503, 1456, 1128. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{11}FO_2S$ Na 357.0356; Found 357.0369.

3-(Furan-2-yl)-4-phenyl-2H-chromen-2-one ***(1a)***. Yield: 50%, 144.2 mg; Yellow solid; m.p. 144.1.3-145.3.1 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 6.27(m, 1H), 6.79(d, *J* = 3.2 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 3H), 7.15-7.20(m, 2H), 7.34(d, *J* = 8.3 Hz, 1H), 7.40(d, *J* = 4.6 Hz, 3H), 7.43-7.47(m, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 159.4, 152.6, 149.6, 147.2, 142.9, 135.6, 131.6, 128.7, 128.5, 128.4, 127.9, 124.4, 120.8, 116.7, 116.4, 114.6, 111.2. IR (KBr) *v* (cm^{-1}) 3209, 2340, 1727, 1592, 1447, 992, 752, 697. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{19}H_{12}O_3Na$ 311.0679; Found 311.0686.

3-(Furan-2-yl)-4-(p-tolyl)-2H-chromen-2-one ***(1b)***. Yield: 67%, 202.6 mg; Yellow solid. m.p. 133.3-134.1 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.41(s, 3H), 6.30(dd, *J* = 3.3, 1.6 Hz, 1H), 6.77(d, *J* = 3.4 Hz, 1H), 7.10(t, *J* = 8.0 Hz, 3H), 7.14-7.20(m, 2H), 7.23(d, *J* = 7.9 Hz, 2H), 7.35(d, *J* = 8.2 Hz, 1H), 7.44-7.48(m, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 159.3, 152.5, 150.1, 147.2, 142.8, 138.2, 132.4, 131.4, 129.0, 128.5, 127.9, 124.2, 120.8, 116.5, 116.3, 114.3, 111.0, 21.4. IR (KBr) *v* (cm^{-1}) 3019, 2320, 1716, 1593, 1471, 1485, 989, 746. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{14}O_3Na$ 325.0835; Found 325.0842.

4-(4-Ethylphenyl)-3-(furan-2-yl)-2H-chromen-2-one ***(1c)***. Yield: 70%, 221.4 mg; Yellow solid; m.p. 110.6-111.5 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 1.18(t, *J* = 7.6 Hz, 3H), 2.61(q, *J* = 7.6 Hz, 2H), 6.18-6.23(m, 1H), 6.65(d, *J* = 3.4 Hz, 1H), 7.05 (dd, *J* = 11.6, 8.8 Hz, 5H), 7.15(d, *J* = 8.1 Hz, 2H), 7.26(d, *J* = 8.2 Hz, 1H), 7.35-7.40(m, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 159.5, 152.6, 150.2, 147.3, 144.7, 142.9, 132.7, 131.5, 128.7, 128.0, 127.9, 124.3, 120.9, 116.6, 116.5, 114.3, 111.1, 28.8, 15.5. IR (KBr) ν (cm^{-1}) 2977, 2367, 1703, 1590, 1480, 1375, 767, 725. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for Na 339.0992; Found 339.0996.

4-(4-Fluorophenyl)-3-(furan-2-yl)-2H-chromen-2-one ***(1d)***. Yield: 57% (174.6 mg); Yellow solid; m.p. 118.3-119.5 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 6.36(dd, *J* = 1.8, 1.9 Hz, 1H), 6.93(d, *J* = 3.4 Hz, 1H), 7.12-7.18(m, 5H), 7.20-7.24(m, 2H), 7.39(d, *J* = 8.1 Hz, 1H), 7.49-7.59(m, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 164.0, 161.4(d, ^1J = 243 Hz), 152.5, 148.3, 147.1, 143.1, 131.7, 131.6(d, ^3J = 3.0 Hz), 130.6(d, ^3J = 8.2 Hz), 127.6, 124.5, 120.8, 116.8, 115.7(d, ^2J = 22.2 Hz), 114.9, 111.3. IR (KBr) *v* (cm^{-1}) 3071, 2359, 1722, 1601, 1506, 1217, 1017, 739. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{19}H_{11}FO_3Na$ 329.0584; Found 329.0590.

4-(4-Chlorophenyl)-3-(furan-2-yl)-2H-chromen-2-one ***(1e)***. Yield: 50%, 161.4 mg; Yellow solid; m.p. 143.6-144.7 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 6.35(dd, *J* = 3.4, 1.5 Hz, 1H), 6.97(d, *J* = 3.4 Hz, 1H), 7.11(s, 1H), 7.13-7.19(m, 4H), 7.37(d, *J* = 8.0 Hz, 1H), 7.42-7.45(m, 2H), 7.48-7.52(m, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 158.9, 152.4, 147.8, 146.9, 143.2, 134.5, 134.1, 131.7, 130.2, 128.8, 127.5, 124.4, 120.5, 116.7, 116.5, 115.0, 111.3. IR (KBr) *v* (cm^{-1}) 2920, 2371, 1703, 1592, 1479, 924, 749, 731. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{19}H_{11}ClO_3Na$ 345.0289; Found 345.0286.

3-(Furan-2-yl)-4-(4-(trifluoromethyl)phenyl)-2H-chromen-2-one ***(1f)***. Yield: 53%, 188.8 mg; Yellow solid; m.p. 157.2-158.8 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 6.37 (dd, *J* = 3.2, 1.5 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 7.12-7.04 (m, 2H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.41(t, *J* = 7.3 Hz, 3H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 2H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 158.9, 152.4, 146.8, 143.4, 139.7, 131.8, 130.9, 130.6, 129.3, 127.4, 125.5(d, *J* = 3.5 Hz), 125.5(d, *J* = 3.0 Hz), 124.6, 122.8, 120.4, 116.9, 116.5, 115.5, 111.5. IR (KBr) *v* (cm^{-1}) 2936, 2367, 1705, 1598, 1493, 1322, 1109, 854, 766. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{11}F_3O_3Na$ 379.0552; Found 379.0553.

3-(Benzofuran-2-yl)-4-phenyl-2H-chromen-2-one ***(1g)***[6]. Yield: 72%, 243.6 mg. Yellow solid. m.p. 177.3- 178.8 ℃. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 6.00-7.02(m, 1H), 7.13-7.18(m, 2H), 7.21(t, *J* = 4.6 Hz, 2H), 7.29(dd, *J* = 6.5, 3.0 Hz, 2H), 7.35(s, 1H), 7.42-7.47(m, 4H), 7.51-7.57(m, 2H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 159.2, 154.5, 152.8, 151.6, 149.3, 135.6, 132.1, 128.7, 128.6, 128.4, 128.3, 128.2, 125.0, 124.5, 122.9, 121.6, 120.8, 116.8, 116.3, 111.1, 110.9. IR (KBr) *v* (cm^{-1}) 2929, 2370, 1722, 1603, 1522, 1443, 1112, 988, 794. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{23}H_{14}O_3Na$ 361.0835; Found 361.0833.

3-(Benzofuran-2-yl)-4-(p-tolyl)-2H-chromen-2-one ***(1h)***. Yield: 79%, 278.4 mg; Yellow solid; m.p. 174.4-176.5 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.43(s, 3H), 7.06(d, *J* = 7.8 Hz, 1H), 7.15(m, 4H), 7.20-7.28(m, 5H), 7.42(d, *J* = 8.2 Hz, 1H), 7.50-7.56(m, 2H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 159.4, 154.6, 152.9, 152.3, 149.4, 138.6, 132.4, 132.1, 129.1, 128.6, 128.4, 128.3, 124.9, 124.5, 122.9, 121.6, 120.9, 116.8, 116.4, 111.1, 110.8, 21.5. IR (KBr) *v* (cm^{-1}) 2920, 2360, 1716, 1593, 1504, 1115, 996, 813, 741. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{24}H_{16}O_3Na$ 375.0992; Found 375.0995.

3-(Benzofuran-2-yl)-4-(4-methoxyphenyl)-2H-chromen-2-one **(*1i*).** Yield: 80%, 294.7 mg; Yellow solid; m.p. 155.3-156.5 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 3.86(s, 3H), 6.97(d, *J* = 8.7 Hz, 2H), 7.08-7.12(m, 1H), 7.12-7.19(m, 2H), 7.18-7.21(m, 2H), 7.23(d, *J* = 5.2 Hz, 2H), 7.31(dd, *J* = 8.1, 1.3 Hz, 1H), 7.42(d, *J* = 8.2 Hz, 1H), 7.51-7.57(m, 2H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 159.6, 159.0, 154.2, 152.5, 151.7, 149.1, 131.7, 129.7, 127.9, 127.9, 127.1, 124.5, 124.1, 122.5, 121.2, 120.5, 116.4, 116.1, 113.6, 110.7, 110.4, 55.1. IR (KBr) *v* (cm^{-1}) 2850, 2354, 1718, 1607, 1503, 1246, 1028, 818, 744. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{24}H_{16}O_4Na$ 391.0941; Found 391.0936.

3-(Benzofuran-2-yl)-4-(4-fluorophenyl)-2H-chromen-2-one **(*1j*)**. Yield: 71%, 253.0 mg; Yellow solid; m.p. 151.5-153.4 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 6.99(d, *J* = 8.0 Hz, 1H), 7.11(dd, *J* = 6.8, 2.0 Hz, 2H), 7.14(dd, *J* = 5.4, 1.8 Hz, 2H), 7.17(dd, *J* = 5.5, 1.5 Hz, 2H), 7.23(dd, *J* = 6.0, 2.6 Hz, 2H), 7.36-7.40(m, 2H), 7.48-7.54(m, 2H); ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 162.9(d, ^1J = 250.5 Hz), 159.0, 154.5, 152.7, 150.3, 149.0, 132.2, 131.5(d, ^3J = 4.02 Hz), 130.6(d, ^3J = 8.1 Hz), 128.2, 127.9, 125.2, 124.6, 123.1, 121.7, 120.72, 116.7(d, ^2J = 29.2 Hz), 115.6(d, ^2J = 22.2 Hz), 111.4, 110.9. IR (KBr) *v* (cm^{-1}) 3168, 2357, 1727, 1600, 1498, 1296, 1219, 1110, 750. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{23}H_{13}FO_3Na$ 379.0741; Found 379.0741.

4-Phenyl-3-(thiophen-2-yl)-2H-chromen-2-one ***(1k)***. Yield: 78%, 240.4 mg; Yellow solid; m.p. 164.2-165.5 °C. ^{1}H NMR(400 MHz, $CDCl_3$) 6.84(dd, *J* = 4.9, 3.9 Hz, 1H), 6.95-6.97(m, 1H), 7.25-7.12(m, 5H), 7.41(d, *J* = 8.3 Hz, 1H), 7.47-7.44(m, 3H), 7.54-7.49(m, 1H). ^{13}C{^{1}H} NMR (101MHz, $CDCl_3$) δ(ppm) 160.6, 152.7, 150.6, 135.2, 134.6, 131.6, 130.9, 129.3, 129.0, 128.0, 127.9, 126.2, 124.4, 120.9, 120.3, 116.7. IR (KBr) *v* (cm^{-1}) 2926, 2349, 1707, 1600, 1450, 759, 704. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{19}H_{12}O_2SNa$ 327.0450; Found 327.0450.

3-(Thiophen-2-yl)-4-(p-tolyl)-2H-chromen-2-one ***(1l)***. Yield: 83%, 264.2 mg; Yellow solid; m.p. 166.0-167.9 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.35(s, 3H), 7.03(d, *J* = 3.0 Hz, 1H), 7.09-7.05 (m, 1H), 7.12 (q, *J* = 8.2 Hz, 4H), 7.29(d, *J* = 8.3 Hz, 1H), 7.41(d, *J* = 4.7 Hz, 1H), 7.45(d, *J* = 8.1 Hz, 1H), 7.62-7.54(m, 2H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 160.6, 152.7, 150.8, 139.0, 134.8, 132.2, 131.5, 130.8, 129.7, 129.2,

128.3, 128.1, 127.8, 126.2, 124.3, 121.0, 116.7, 21.6. IR (KBr) ν (cm^{-1}) 1707, 1560, 1504, 1241, 1025, 748, 703. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{14}O_2SNa$ 341.0607; Found 341.0606.

4-(4-Methoxyphenyl)-3-(thiophen-2-yl)-2H-chromen-2-one ***(1m)***. Yield: 80%, 267.5 mg; Yellow solid; m.p. 159.2-161.4 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 3.87(s, 3H), 6.87(dd, *J* = 5.0, 3.9 Hz, 1H), 6.98(d, *J* = 8.7 Hz, 2H), 7.02-7.06(m, 1H), 7.15(s, 1H), 7.17(s, 1H), 7.18-7.24(m, 2H), 7.26-7.27 (m, 1H), 7.41(d, *J* = 8.2 Hz, 1H), 7.52(m, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 160.6, 160.2, 152.7, 150.5, 134.9, 131.5, 130.8, 130.7, 128.0, 127.8, 127.2, 126.2, 124.3, 121.1, 120.4, 116.7, 114.5, 55.5. IR (KBr) ν (cm^{-1}) 2841, 2546, 1709, 1564, 1503, 1246, 758, 702. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{14}O_3SNa$ 357.0556; Found 357.0554.

4-(3-Methoxyphenyl)-3-(thiophen-2-yl)-2H-chromen-2-one ***(1n)***. Yield: 70%, 254.1 mg; Yellow solid; m.p. 129.8-131.9 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.31(s, 3H), 6.99(d, *J* = 3.1 Hz, 1H), 7.02(d, *J* = 4.9 Hz, 1H), 7.09(q, *J* = 8.2 Hz, 4H), 7.24(s, 1H), 7.36-7.39(m, 1H), 7.42(d, *J* = 8.1 Hz, 1H), 7.56(m, 2H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 160.6, 159.9, 157.5, 154.6, 152.7, 152.6, 136.6, 132.2, 130.3, 127.8, 124.9, 120.4, 120.4, 117.2, 116.9, 114.9, 113.9, 112.7, 55.6. IR (KBr) ν (cm^{-1}) 3079, 2829, 1716, 1588, 1451, 1031, 767, 710. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{14}O_3SNa$ 357.0556; Found 357.0555.

4-(4-Hydroxyphenyl)-3-(thiophen-2-yl)-2H-chromen-2-one ***(1o)***. Yield: 48%, 153.7 mg; Yellow solid; m.p. 180.0-181.4 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 6.83(d, *J* = 8.5 Hz, 2H), 6.89(t, *J* = 4.4 Hz, 1H), 6.94(d, *J* = 3.4 Hz, 1H), 7.05(d, *J* = 8.5 Hz, 2H), 7.14(d, *J* = 7.9 Hz, 1H), 7.27(t, *J* = 7.8, 7.5 Hz, 1H), 7.47(t, *J* = 4.6, 7.8 Hz, 2H), 7.61(t, *J* = 7.8, 7.5 Hz, 1H), 9.83(s, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 159.8, 158.0, 152.1, 150.9, 134.9, 131.9, 130.6, 130.5, 128.2, 127.9, 126.2, 125.1, 124.7, 120.8, 119.5, 116.4, 115.8. IR (KBr) ν (cm^{-1}) 3091, 2927, 2789, 1729, 1604, 1543, 1266, 768, 701. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{19}H_{12}O_3SNa$ 343.0399; Found 343.0397.

4-(4-Fluorophenyl)-3-(thiophen-2-yl)-2H-chromen-2-one ***(1p)***. Yield: 60%, 193.4 mg; Yellow solid; m.p. 169.5-171.0 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 6.36(dd, *J* = 3.3, 1.9 Hz, 1H), 6.94 (d, *J* = 3.4 Hz, 1H), 7.25-7.20(m, 2H), 7.19-7.11(m, 5H), 7.40(d, *J* = 8.1 Hz, 1H), 7.54-7.49(m, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ (ppm) 162.8(d, ^1J = 249.5 Hz), 159.2, 152.5, 148.3, 147.1, 143.1, 131.7, 131.6(d, ^4J = 3.6 Hz), 130.7(d, ^3J = 8.2 Hz), 127.6, 124.5, 120.8, 116.8, 115.7(d, ^2J = 21.9 Hz), 114.9, 111.3. IR (KBr) ν (cm^{-1}) 3071, 2922, 2369, 1705, 1594, 1454, 1322, 756. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{19}H_{11}FO_2SNa$ 345.0356; Found 345.0355.

3-(5-Methylthiophen-2-yl)-4-phenyl-2H-chromen-2-one ***(1q)***. Yield: 79%, 232.4 mg; Yellow solid; m.p. 159.5.4-161.5 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.37(s, 3H), 6.47(d, *J* = 3.1 Hz, 1H), 6.69 (d, *J* = 3.6 Hz, 1H), 7.12(dt, *J* = 8.0, 7.3 Hz, 2H), 7.23(dd, *J* = 6.6, 3.0 Hz, 2H), 7.38(d, *J* = 8.0 Hz, 1H), 7.50-7.44(m, 4H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 160.7, 152.5, 149.5, 142.7, 135.4, 132.2, 131.3, 131.2, 129.3, 129.1, 128.9, 127.8, 124.7, 124.3, 121.0, 120.5, 116.6, 15.2. IR (KBr) ν (cm^{-1}) 3061, 2911, 1709, 1596, 1452, 755, 700. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{14}O_2SNa$ 341.0607; Found 341.0607.

3-(5-Methylthiophen-2-yl)-4-(p-tolyl)-2H-chromen-2-one ***(1r)***. Yield: 74%, 245.9 mg; Yellow solid; m.p. 136.9-137.8 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.37(s, 3H), 2.43(s, 3H), 6.46-6.50(m, 1H), 6.71(d, *J* = 3.7 Hz, 1H), 7.09-7.15(m, 4H), 7.26(d, *J* = 7.9 Hz, 2H), 7.37(d, *J* = 8.2 Hz, 1H), 7.45-7.49(m, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 160.8, 152.5, 149.7, 142.5, 138.8, 132.4, 132.3, 131.2, 131.1, 129.7, 129.1, 127.9, 124.7, 124.2, 121.2, 120.4, 116.6, 21.6, 15.2. IR (KBr) ν (cm^{-1}) 2929, 2853, 1705, 1594, 1454, 1322, 756. HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{21}H_{16}O_2SNa$ 355.0763; Found 355.0764.

4-(4-Fluorophenyl)-3-(5-methylthiophen-2-yl)-2H-chromen-2-one ***(1s)***. Yield: 51%, 171.6 mg; Yellow solid; m.p. 150.2-151.6 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 2.38(s, 3H), 6.51(d, *J* = 3.1 Hz, 1H), 6.75(d, *J* = 3.6 Hz, 1H), 7.09(d, *J* = 8.0 Hz, 1H), 7.14-7.19(m, 3H), 7.23(dd, *J* = 8.4, 5.6 Hz, 2H), 7.39(d, *J* = 8.2 Hz, 1H), 7.48-7.52(m, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$) δ(ppm) 163.1(d, ^1J = 249.5 Hz), 160.5, 152.5, 148.5,

142.9, 132.1, 131.4, 131.3, 131.3, 131.2, 130.4(d, ^{3}J = 8.1 Hz), 127.6, 124.8, 124.4, 120.9(d, ^{3}J = 7.5 Hz), 116.7, 116.3(d, ^{2}J = 22.2 Hz), 15.2. IR (KBr) ν (cm^{-1}) 3074, 2909, 1703, 1598, 1503, 1211, 801, 755. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{13}FO_2SNa$ 359.0512; Found 359.0512.

*3,4-Diphenyl-2H-chromen-2-one (**3**)*. Yield: 72%, 214.8 mg; white solid; m.p. 132.2-133.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 9.07-9.13(m, 4H), 9.13-9.21(m, 5H), 9.28(dd, J = 4.9, 1.5 Hz, 3H), 9.41(d, J = 8.1 Hz, 1H), 9.49-9.53(m, 1H). $^{13}C\{^{1}H\}$ NMR(101 MHz, $CDCl_3$) δ(ppm) 161.4, 153.4, 151.7, 134.6, 134.0, 131.6, 130.7, 129.5, 128.5, 128.4, 127.9, 127.9, 127.8, 124.3, 120.7, 116.9. IR (KBr) ν (cm^{-1}) 3085, 2354, 1698, 1606, 1552, 1211, 996, 743. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{21}H_{14}O_2Na$ 321.0886; Found 321.0891.

*4-(Furan-2-yl)-3-phenyl-2H-chromen-2-one (**4**)*. Yield: 41%, 175.9 mg; Yellow solid. m.p. 214.5-215.7 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.16 (d, J = 3.4 Hz, 1H), 6.37 (dd, J = 3.3, 1.9 Hz, 1H), 7.18-7.23 (m, 2H), 7.25 (dd, J = 5.4, 4.2 Hz, 1H), 7.30 (t, 3H), 7.40 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 1.3 Hz, 1H), 7.52-7.57 (m, 1H), 7.71 (dd, J = 8.1, 1.0 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101MHz, $CDCl_3$) δ (ppm) 161.2, 153.4, 147.2, 143.8, 140.2, 134.7, 131.7, 129.9, 128.2, 128.2, 127.8, 127.5, 124.5, 117.1, 114.9, 111.5. IR (KBr), ν (cm^{-1}) 3081, 2362, 1691, 1595, 1446, 977, 762, 698. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{19}H_{12}O_3Na$ 311.0679; Found 311.0678.

*3,4-di(furan-2-yl)-2H-chromen-2-one (**6**)*. Yield: 56%, 155.8 mg; Yellow solid. m.p. 114.7-115.4 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.64 (dd, J = 7.8, 1.1 Hz, 1H), 7.58 (d, J = 1.4 Hz, 1H), 7.54 –7.49 (m, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 1.3 Hz, 1H), 7.25 (t, J = 7.3 Hz, 1H), 6.99 (d, J = 3.4 Hz, 1H), 6.57 (dd, J = 3.3, 1.6 Hz, 1H), 6.47–6.44 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101MHz, $CDCl_3$) δ (ppm) 159.2, 152.6, 147.0, 146.9, 143.9, 143.5, 137.9, 131.7, 127.3, 124.6, 119.4, 117.2, 116.8, 114.7, 113.3, 111.6, 111.6. IR (KBr), ν (cm^{-1}) 3054, 1678, 1591, 1428, 959, 769, 691. Anal. calcd. for $C_{17}H_{17}O_4$ (%): C, 73.31, H, 3.62, O, 23.00; found C, 73.22; H, 3.54, O, 23.09.

*3-(Furan-2-yl)-4-phenyl-2H-chromene (**7**)*. Yield: 36%, 85.6 mg; White solid; m.p. 89.1-89.9 ^{o}C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm) 5.24(d, J = 3.3 Hz, 1H), 6.04(m, 1H), 6.74 (d, J = 7.8 Hz, 1H), 6.85(m, 1H), 7.26(s, 2H), 7.03(d, J = 4.1 Hz, 2H), 7.23(d, J = 7.3 Hz, 2H), 7.42(m, 4H). $^{13}C\{^{1}H\}$ NMR(101 MHz, $CDCl_3$) δ(ppm) 150.6, 150.3, 141.4, 137.5, 132.1, 129.1, 128.6, 127.9, 126.7, 124.0, 121.8, 118.4, 117.2, 111.3, 110.2, 90.3, 77.4. IR (KBr) ν (cm^{-1}) 3048, 2903, 1656, 1585, 1446, 967, 742, 658. HRMS(ESI-TOF) m/z: [M + Na]+ Calcd for $C_{19}H_{14}O_2Na$ 297.0886; Found 297.0888.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

X-ray parameters and structures of **2l**.

Determination of fluorescence quantum yield for **2a**-**2s** and **1a**.

H_2 detection for the photochemical dehydrocyclization of **2l** by GC.

NMR spectra and MS spectra of compounds **1a**-**1s, 2a**-**2s, 3, 4, 6, 7**. Fluorescence spectra of **2a**-**2s** and **1a**.

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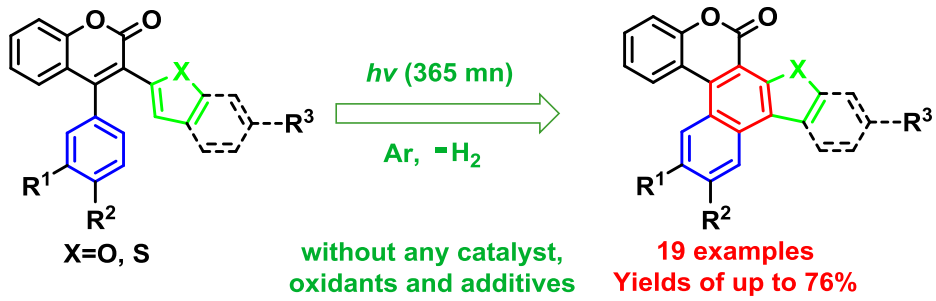
TOC graphic


O
O
X
R3
R1
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X=O, S
hv (365 mn)
Ar, -H2
without any catalyst,
oxidants and additives
19 examples
Yields of up to 76%