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Iodine-Catalyzed Cascade Annulation of 4-Hydroxycoumarins with Aurones: Access to Spirocyclic Benzofuran–Furocoumarins

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Abstract: An attractive approach for the preparation of spirocyclic benzofuran–furocoumarins has been developed through iodine-catalyzed cascade annulation of 4-hydroxycoumarins with aurones. The reaction involves Michael addition, iodination, and intramolecular nucleophilic substitution in a one-step process, and offers an efficient method for easy access to a series of valuable spirocyclic benzofuran–furocoumarins in good yields (up to 99%) with excellent stereoselectivity. Moreover, this unprecedented protocol provides several advantages, including readily available materials, an environmentally benign catalyst, a broad substrate scope, and a simple procedure.

Keywords: iodine-catalyzed cascade annulation; spiro-heterocycle; benzofuran; furocoumarin

Citation: Wang, X.; Yang, C.; Yue, D.; Xu, M.; Duan, S.; Shen, X. Iodine-Catalyzed Cascade Annulation of 4-Hydroxycoumarins with Aurones: Access to Spirocyclic Benzofuran–Furocoumarins. *Molecules* **2024**, *29*, 1701. https://doi.org/10.3390/molecules29081701

Academic Editor: Xinwei He

Received: 21 March 2024
Revised: 1 April 2024
Accepted: 4 April 2024
Published: 9 April 2024

1. Introduction

Spiro-heterocycles are very important structural motifs in various natural products and pharmaceutical molecules, with a broad range of biological and pharmacological activities [1–4]. Considering the biological importance of spiro-heterocycles, a sufficiently large number of methods for the preparation of spiro-heterocycles have been developed, including the multicomponent tandem reaction [5], ring-expansion method [6], N-heterocyclic carbene (NHC)-catalyzed tandem annulation [7,8], palladium-catalyzed [3+2] cycloaddition [9] or 1,3-dipolar cycloaddition [10]. Recently, more eco-friendly electrochemical strategies have been used for the preparation of spiro-heterocycles. For example, Zhu et al. [11] developed an electrochemical method for the highly diastereoselective synthesis of spirocyclic indolines with significant anti-tumor activity.

In recent years, combining two rings to generate novel spiro-heterocycles has become an important approach to drug design [12,13]. The design and synthesis of biologically active spiro-heterocycles have attracted the attention of many pharmacologists and chemists [14,15]. In particular, the spiro-heterocycles that contain benzofuran have become one of the most interesting classes of molecules due to their notable biological activities [16–18]. For example, griseofulvin **A** is one of the earliest spirocyclic drugs to exhibit antifungal activity [19], while spiro-benzofuran **B**, with isobenzofuranone and benzofuranone motifs, has been found to be a core chemical skeleton for antivirals against influenza viruses [20]. (−)-Spiro-ganodermaine **G**, which is isolated from the *Ganoderma* species, displayed suppressive activity on the expression of TGF-β1-induced fibronectin and α-SMA, with a potential role in treating renal fibrosis (Figure 1) [21]. Moreover, furocoumarins demonstrate a wide range of biological activities [22,23] as anticancer [24], antioxidant [25], antifungal [26] and antiproliferative [27]. Therefore, there is great interest in exploring novel spiro-heterocycles between spiro-benzofurans and furocoumarins. Recently, Cui et al. [28] reported a novel procedure for spirocyclic benzofuran–furocoumarin synthesis, by Lewis acid-catalyzed [3+2]-cyclization of iodonium ylides with azadienes, in moderate yields with excellent stereoselectivity (Scheme 1a). Meanwhile, Yavari et al. [29] developed an electrochemical approach for accessibility to spirocyclic benzofuran–furocoumarin (Scheme 1b).

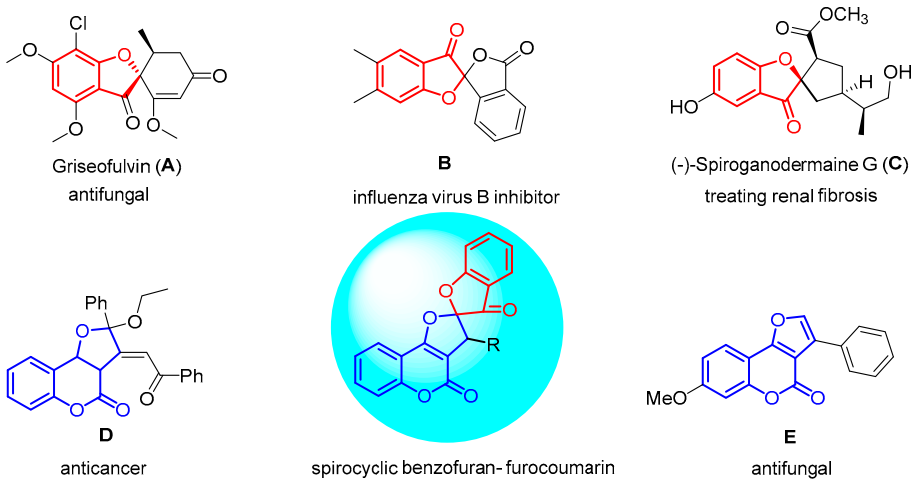
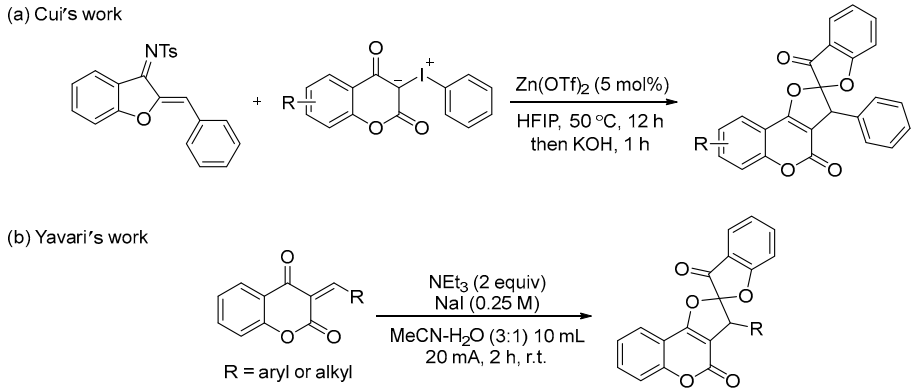


Figure 1. Example of biologically active spiro-benzofuran and furocoumarin derivatives.



Scheme 1. Strategies for the synthesis of spirocyclic benzofuran–furocoumarins.

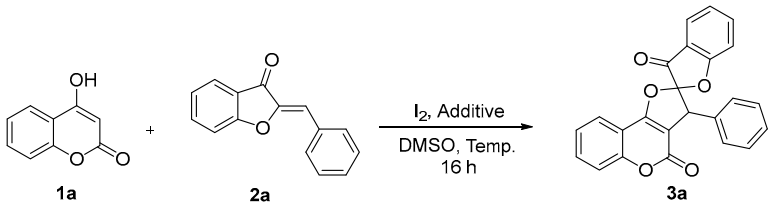
Molecular iodine, as a very simple and efficient reagent, has drawn considerable attention from synthetic chemists, and has been widely used in various organic transformations [30,31]. It is widely available, inexpensive, nontoxic, eco-friendly, and moisture resistant, and employed as a catalyst, resulting in the formation of new C–C [32,33], C–N [34,35], C–O [36], and C–S [37,38] bonds. In addition, molecular iodine has been recognized as a powerful tool for constructing the pharmacologically important heterocyclic rings [39–41]. Currently, several approaches have also been disclosed for the synthesis of spiro-heterocycles through iodine-mediated cascade reactions [42–44].

Based on the above discussion and our interest in exploring novel synthetic strategies for the construction of spiro-heterocycles, we developed an iodine-catalyzed cascade reaction of 4-hydroxycoumarins with aurones to afford spirocyclic benzofuran–furocoumarins with high stereoselectivity. This transformation displayed favorable compatibility for the preparation of various spirocyclic benzofuran–furocoumarins using I_2 as the efficient and green catalyst.

2. Result and Discussion

Initially, the reaction of 4-hydroxycoumarin **1a** and aurone **2a** was investigated to optimize the reaction conditions. The experimental results are summarized in Table 1. Fortunately, the desired spirocyclic benzofuran–furocoumarin **3a** obtained a 54% yield from the reaction with 20 mol % of I_2 at 80 °C (Table 1, entry 1). The structure of **3a** was determined based on their NMR spectroscopic similarities compared with the observed results [28,29]. In order to improve the efficacy of the reaction, different temperatures were evaluated for the reaction, and it was found that the yield of **3a** could be improved to 58% at 100 °C (Table 1, entry 2). Increasing the amount of I_2 did not yield better results (Table 1, entry 4). Subsequently, the effect of an additive was investigated, such as *L*-proline, TBAI, and TEBAC. It was found that TEBAC afforded the desired product **3a** in better yields (Table 1, entries 5–7). Furthermore, increasing the amount of TEBAC loading to 40 mol % gave a higher yield of **3a** at 68% (Table 1, entry 9). Notably, changing the ratio of **2a**/**1a** from 1:1.3 to 1:1.5 (Table 1, entries 10–12) improved the yield of **3a** to 82% within 16 h (Table 1, entry 12). Therefore, the optimized reaction conditions for **3a** were 20 mol % of iodine as the catalyst, and 40 mol % of TEBAC as the additive, in DMSO at 100 °C for 16 h (Table 1, entry 12).

Table 1. Optimization of the reaction conditions [a].



Entry	I_2 (mol %)	2a:1a	Additive (mol %)	Temp. (°C)	Yield (%) [b]	dr [c]
1	20%	1:1.2	-	80	54%	>20:1
2	20%	1:1.2	-	100	58%	>20:1
3	20%	1:1.2	-	120	52%	>20:1
4	30%	1:1.2	-	100	57%	>20:1
5	20%	1:1.2	*L*-proline (10%)	100	56%	>20:1
6	20%	1:1.2	TBAI (10%)	100	59%	>20:1
7	20%	1:1.2	TEBAC (10%)	100	63%	>20:1
8	20%	1:1.2	TEBAC (20%)	100	64%	>20:1
9	20%	1:1.2	TEBAC (40%)	100	68%	>20:1
10	20%	1:1.3	TEBAC (40%)	100	70%	>20:1
11	20%	1:1.4	TEBAC (40%)	100	71%	>20:1
12	20%	1:1.5	TEBAC (40%)	100	82%	>20:1

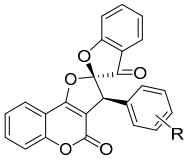
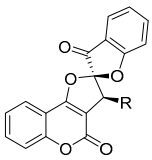
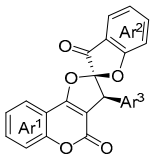
[a] Reaction conditions: aurone **2a** (0.25 mmol), 4-hydroxycoumarin **1a**, I_2 and additive in DMSO (0.5 mL) under air conditions for 16 h; [b] Isolated yields based on **2a**; [c] Based on final product ^{1}H NMR spectra; TEBAC = benzyltriethylammonium chloride; TBAI = tetrabutylammonium iodide.

With the optimal reaction conditions in hand, the substrate scope of 4-hydroxycoumarins and aurones were explored under standard reaction conditions. And the results are depicted in Scheme 2. The 4-hydroxycoumarins bearing electron withdrawing (F, Cl, Br, NO_2) or electron donating groups (OMe, Me) on Ar^1 reacted smoothly, providing good yields of the corresponding spirocyclic benzofuran–furocoumarins, **3ab**–**3ah** and **3bl**. The reaction of 4-hydroxy-2*H*-benzo[*h*]chromen-2-one also proceeded smoothly and afforded an 86% yield of the spiro products **3ae**. For the aurones, both the electron withdrawing (F, Cl, Br) and electron donating groups (OMe, OEt, Me) on Ar^2 of the benzofuranone moieties reacted with 4-hydroxycoumarin efficiently to afford 64−96% yields of the corresponding spiro products **3ai**–**3ao**. However, when the substrate bore a NO_2 group on Ar^2, the yield of the desired product **3bk** decreased to 62%. Subsequently, the effects of the substituents on the phenyl ring of Ar^3 were evaluated. As the results reveal, the electron donating and electron withdrawing substituents of the phenyl ring on Ar^3 have a substantial impact on

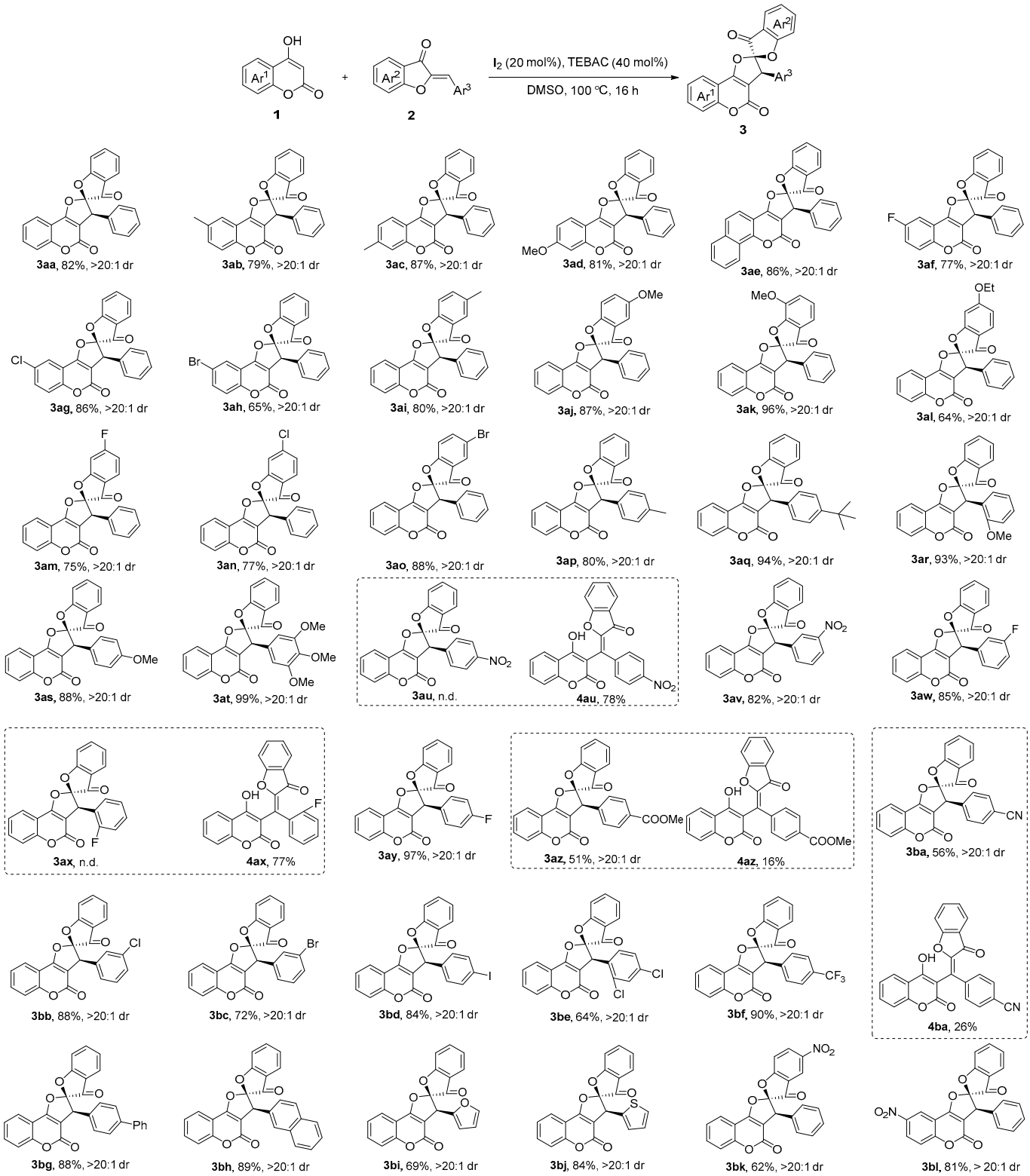
the efficacy of the reaction. Generally, an electron donating group displayed respectable suitability with good to excellent yields. The weak electron donating groups (CH_3) gave an 80% yield of **3ap**. Notably, substrates bearing a strong electron donating group (OMe, ^{t}Bu) on Ar^3 showed excellent reactivity. The -o-OCH_3, -p-OCH_3, and -p-^{t}Bu groups produced yields of 93%, 88%, and 94% for **3ar**, **3as** and **3aq**, respectively, while the substrates bearing three substituent groups of OCH_3 gave the best results **3at** with a 99% yield. Adversely, some electron withdrawing groups decreased in reaction efficiency to afford the desired spiro products. For the substrates bearing the strong electron withdrawing groups (-p-NO_2, -o-F), no desired spiro products were detected due to the competitive elimination pathway affording the coupled products **4au** and **4ax** with yields of 78% and 77%, respectively. While the COOMe and CN groups were tolerated, they only gave diminished yields of **3az** (51%) and **3ba** (56%), and a slight amount of the coupled products **4az** and **4ba** were observed. Interestingly, electron withdrawing groups, such as -m-NO_2, -m-F, -p-F, Cl, Br, I, -p-CF_3 and Ph, restored the activity and achieved good to excellent yields. Encouragingly, the heterocyclic furan and thiophene groups of Ar^3 are also compatible and effectively furnished **3bi** and **3bj** with yields of 69% and 84%. A naphthyl group of Ar^3 was also tolerated, and the desired spiro product **3bh** was isolated with an 89% yield.

Just as Table 2 has shown, this approach for the synthesis of spirocyclic benzofuran–furocoumarins offers two advantages in terms of broad substrate scope and higher yields compared to reported methods. However, it still suffers from two drawbacks, including long reaction time and high temperature.

Table 2. Comparison between reported methods and this method.

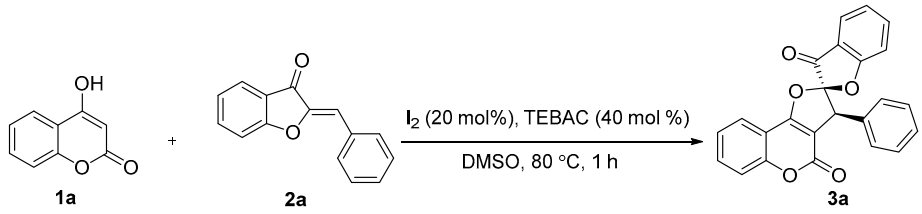
Entry	Products	Yields	Reaction Time	Temperature	dr
Cui's work	 5 examples R = Me, Cl, F	40–53%	13 h	r.t.	>20:1
Yavary's work	 16 examples R = Ar, Alkyl	60–78%	2 h	30 °C	>20:1
This work	 36 examples	51–99%	16 h	100 °C	>20:1

To improve the efficiency of this transformation, greener energy sources, including microwave and ultrasonic irradiation, were tested. As the results show, microwave irradiation displays obvious influence, which can improve the yield of **3a** from 7% to 30% compared with traditional protocol. However, when ultrasonic irradiation with a frequency of 35 KHz was used in the reaction, a 9% yield of **3a** was obtained, with a large amount of still unreacted substrate (Table 3).



Scheme 2. Substrate scope of 4-hydroxycoumarins and aurones for the synthesis of spirocyclic benzofuran–furocoumarins. Reaction conditions: 4-hydroxycoumarins **1** (0.375 mmol), aurones **2** (0.25 mmol), I_2 (20 mol %), and TEBAC (40 mol %) in DMSO (0.5 mL) at 100 °C for 16 h under air; isolated yield of the product based on **2**; dr based on final product ^{1}H NMR spectra.

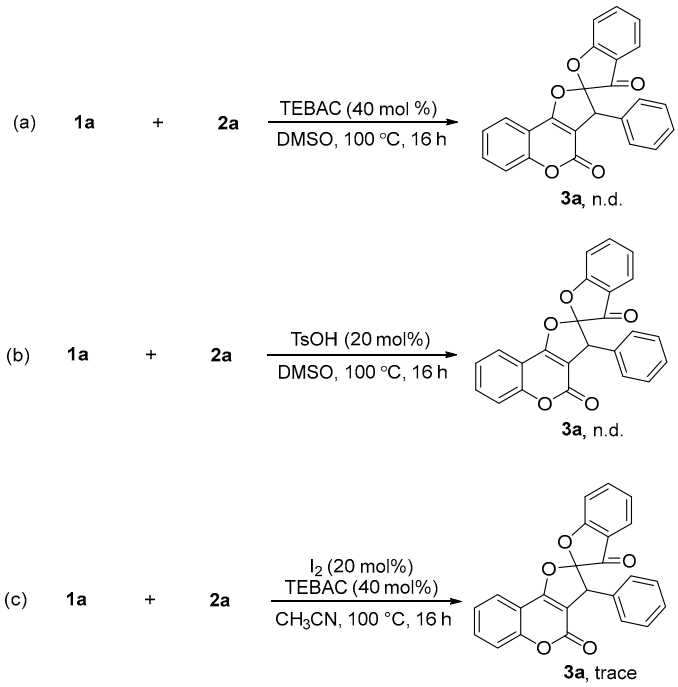
Table 3. Comparison between green energy sources and traditional protocol [a].



Entry	Energy Source	Condition	Yield (%)
1	Microwave irradiation	Power capacity: 200 W	30
2	Ultrasonic irradiation	Frequency rate: 35 KHz	9
3	Oil bath	-	7

[a] Reaction conditions: 4-hydroxycoumarins **1a** (0.375 mmol), aurones **2a** (0.25 mmol), I_2 (20 mol %), and TEBAC (40 mol %) in DMSO (2 mL) at 80 °C for 1 h; isolated yield of the product based on **2a**.

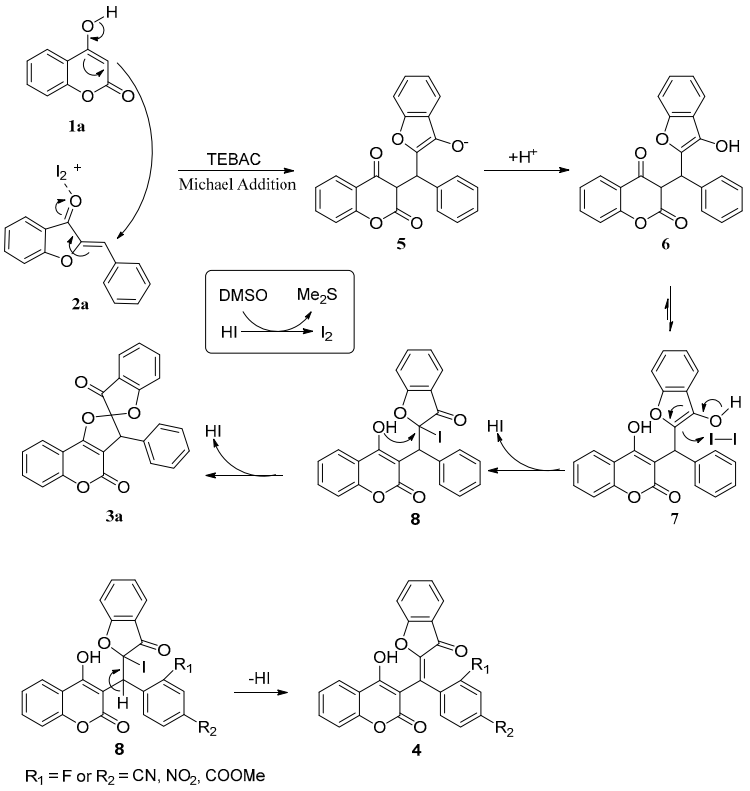
Afterward, control experiments were conducted to investigate the mechanism of the formation of spirocyclic benzofuran–furocoumarins. First, the reaction of **1a** and **2a** was carried out without I_2 under the optimum reaction conditions, and product **3a** was not detected (Scheme 3a). Subsequently, substrates **1a** and **2a** were subjected to TsOH in DMSO at 100 °C, and no desired product was detected (Scheme 3b). Finally, replacement of the solvent with MeCN allowed for trace amounts of the desired product **3a** (Scheme 3c). The above results indicate that the formation of **3** is based on the cooperative effect of I_2 and DMSO.



Scheme 3. Control experiments (**a**–**c**).

According to the experimental results above and the previous literature [45], a plausible pathway is proposed in Scheme 4. First, 4-hydroxycoumarin **1a** and aurone **2a** undergo Michael addition in the presence of I_2 to generate intermediate **5**, which captures the proton released from the 4-hydroxycoumarin, thus forming intermediate **6**. In this process, TEBAC, as an effective catalyst following the addition of 4-hydroxycoumarin, is used to improve the efficiency of the Michael addition reaction [46]. Subsequently, intermediate **6** automerizes into its enol-form—intermediate **7**. Further electrophilic substitution between intermediate **7** and I_2 is probably activated by DMSO and affords intermediate **8** immediately.

Thereafter, an intramolecular nucleophilic substitution of intermediate **8** gives the expected product—the spirocyclic benzofuran–furocoumarins **3a**. During the iodination of **7** to **8** and the cyclization of **8** into **3a**, HI is both generated and then oxidized back into I_2 by DMSO to accomplish the catalytic cycle. However, when intermediate **8** bears strong electron withdrawing groups, such as R_1 = F or R_2 = CN, NO_2, COOMe, the competitive elimination pathway will be promoted in order to generate product **4**.



Scheme 4. Proposed mechanism.

3. Materials and Methods

Unless otherwise specified, the starting materials and reagents used in the reactions were commercially available and used without further purification. Aurones **2** was prepared by the published procedures [47,48]. ^{1}H (400 MHz), ^{13}C (100 MHz), DEPT 135 (100 MHz) and DEPT 90 (100 MHz). NMR spectra were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$ or DMSO-d_6. HRMS were performed with an AB QSTAR Pulsar mass spectrometer. Melting points were tested on an XT-4A melting-point apparatus without correction. The reactions were monitored by thin-layer chromatography (TLC) using silica gel GF254. For column chromatography, silica gel (200–300 mesh) was also employed.

The ^{1}H NMR and ^{13}C NMR spectral of the products are given in Supplementary Materials.

General Procedure

A mixture of 4-hydroxycoumarins **1** (0.375 mmol), aurones **2** (0.25 mmol), TEBAC (40 mol %), and I_2 (20 mol %) was stirred in DMSO (0.5 mL) at 100 °C for 16 h; thereafter, saturated $Na_2S_2O_3$ solution (8 mL) was added to quench the reaction. The product was then extracted with CH_2Cl_2 (3 × 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was subjected to flash column chromatography on silica gel (petroleum ether/ethyl acetate/CH_2Cl_2 = 10:1:5) to give 51–99% yields of the pure products **3aa**–**3bl**.

3′-Phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3aa**). Yield 82%; White solid; Mp 243–244 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.85 (d, J = 7.6 Hz, 1H),

7.81–7.75 (m, 3H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.47–7.43 (m, 1H), 7.31–7.28 (m, 4H), 7.25–7.21 (m, 2H), 7.06 (m, 1H), 5.14 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 194.13 (C), 170.13 (C), 164.76 (C), 157.99 (C), 155.19 (C), 141.21 (CH), 134.30 (CH), 132.61 (C), 129.45 (CH), 128.73 (CH), 128.47 (CH), 125.95 (CH), 125.27 (CH), 124.85 (CH), 123.31 (CH), 118.10, 117.39 (CH), 113.55 (CH), 111.38 (C), 111.14 (C), 104.50 (C), 50.88 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{14}O_5Na$ [M+Na]$^+$: 405.0739, found: 405.0742.

8′-Methyl-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3ab**). Yield 79%; White solid; Mp 263–264 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 7.36 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.18–7.17 (m, 3H), 7.09–7.06 (m, 3H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.02 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.36 (C), 170.46 (C), 165.38 (C), 158.76 (C), 153.56 (C), 139.84 (CH), 134.36 (CH), 134.22 (C), 131.49 (C), 128.88 (CH), 128.44 (CH), 128.21 (CH), 125.34 (CH), 123.68 (CH), 122.62 (CH), 118.46 (C), 116.86 (CH), 113.10 (CH), 111.37 (C), 110.94 (C), 103.77 (C), 52.06 (CH), 20.86 (CH_3); HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{16}O_5Na$ [M+Na]$^+$: 419.0895, found: 419.0896.

7′-Methyl-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3ac**). Yield 87%; Yellow solid; Mp 277–278 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.53–7.48 (m, 2H), 7.20–7.17 (m, 4H), 7.10–7.06 (m, 4H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.01 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.42 (C), 170.45 (C), 165.61 (C), 158.79 (C), 155.54 (C), 144.79 (C), 139.83 (CH), 131.56 (C), 128.86 (CH), 128.43 (CH), 128.19 (CH), 125.58 (CH), 125.34 (CH), 123.65 (CH), 122.66 (CH), 118.51 (C), 117.25 (CH), 113.09 (CH), 110.96 (C), 109.18 (C), 102.79 (C), 52.06 (CH), 22.12 (CH_3); HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{16}O_5Na$ [M+Na]$^+$: 419.0895, found: 419.0897.

7′-Methoxy-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3ad**). Yield 81%; Yellow solid; Mp 285–286 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.4 Hz, 2H), 7.19–7.17 (m, 3H), 7.09–7.06 (m, 3H), 6.85 (d, *J* = 1.6 Hz, 1H), 6.84–6.81 (m, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.00 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.45 (C), 170.45 (C), 165.78 (C), 164.01 (C), 158.92 (C), 157.43 (C), 139.82 (CH), 131.68 (C), 128.86 (CH), 128.41 (CH), 128.15 (CH), 125.33 (CH), 124.02 (CH), 123.63 (CH), 118.53 (C), 113.08 (CH), 112.90 (CH), 110.97 (C), 104.90 (C), 100.90 (CH), 100.72 (C), 55.91 (CH), 51.96 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{16}O_6Na$ [M+Na]$^+$: 435.0845, found: 435.0846.

1′-Phenyl-1′*H*,3*H*,11′*H*-spiro[benzofuran-2,2′-benzo[*h*]furo[3,2-*c*]chromene]-3,11′-dione (**3ae**). Yield 86%; Yellow solid; Mp 268–269 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (dd, *J* = 6.4, 3.2 Hz, 1H), 7.84–7.82 (m, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.66–7.56 (m, 4H), 7.54–7.49 (m, 1H), 7.22–7.18 (m, 3H), 7.13–7.07 (m, 3H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.41 (C), 170.49 (C), 166.45 (C), 158.52 (C), 153.43 (C), 139.87 (CH), 135.51 (C), 131.48 (C), 129.35 (CH), 128.90 (CH), 128.48 (CH), 128.24 (CH), 128.10 (C), 127.52 (CH), 125.37 (CH), 124.55 (CH), 123.69 (CH), 123.10 (CH), 122.99 (C), 118.53 (C), 118.09 (CH), 113.11 (CH), 111.08 (C), 106.92 (C), 103.14 (C), 52.06 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{28}H_{16}O_5Na$ [M+Na]$^+$: 455.0895, found: 455.0893.

8′-Fluoro-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3af**). Yield 77%; White solid; Mp 245–246 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.65 (m, 1H), 7.53–7.49 (m, 1H), 7.37–7.34 (m, 1H), 7.31–7.25 (m, 2H), 7.20–7.17 (m, 3H), 7.10–7.06 (m, 3H), 6.75 (d, *J* = 8.4 Hz, 1H), 5.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.05 (C), 170.43 (C), 164.57 (d, *J* = 3.0 Hz, C), 158.54 (d, *J* = 244.0 Hz, C), 158.11 (C), 151.50 (d, *J* = 2.0 Hz, C), 139.96 (CH), 131.11 (C), 128.89 (CH), 128.52 (CH), 128.36 (CH), 125.42 (CH), 123.84 (CH), 120.92 (d, *J* = 25.0 Hz, CH), 118.91 (d, *J* = 9.0 Hz, CH), 118.33 (C), 113.12 (CH), 112.39 (d, *J* = 10.0 Hz, C), 110.90 (C), 108.71 (d, *J* = 26.0 Hz, CH), 104.91 (C), 52.01 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}FO_5Na$ [M+Na]$^+$: 423.0645, found: 423.0644.

8′-Chloro-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3ag**). Yield 86%; White solid; Mp 278–279 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.66 (m, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.54–7.49 (m, 2H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.21–7.18 (m, 3H), 7.11–7.06 (m, 3H), 6.76 (d, *J* = 8.4 Hz, 1H), 5.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

194.01 (C), 170.43 (C), 164.23 (C), 157.93 (C), 153.64 (C), 139.97 (CH), 133.28 (CH), 131.06 (C), 129.88 (C), 128.89 (CH), 128.53 (CH), 128.38 (CH), 125.44 (CH), 123.86 (CH), 122.53 (CH), 118.61 (CH), 118.30 (C), 113.13 (CH), 112.75 (C), 110.90 (C), 104.92 (C), 51.93 (CH); HRMS (ESI-TOF): m/z calcd for $C_{24}H_{13}ClO_5Na$ $[M+Na]^+$: 439.0349, found: 439.0352.

8′-Bromo-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3ah**). Yield 65%; Yellow solid; Mp 286–287 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 2.4 Hz, 1H), 7.68–7.63 (m, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 8.8 Hz, 1H), 7.21–7.19 (m, 3H), 7.11–7.06 (m, 3H), 6.77 (d, J = 8.4 Hz, 1H), 5.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.98 (C), 170.43 (C), 164.09 (C), 157.85 (C), 154.10 (C), 139.95 (CH), 136.06 (CH), 131.06 (C), 128.89 (CH), 128.53 (CH), 128.37 (CH), 125.55 (CH), 125.43 (CH), 123.85 (CH), 118.85 (CH), 118.31 (C), 117.08 (C), 113.22 (C), 113.12 (CH), 110.90 (C), 104.92 (C), 51.91 (CH); HRMS (ESI-TOF): m/z calcd for $C_{24}H_{13}BrO_5Na$ $[M+Na]^+$: 482.9844, found: 482.9848.

5-Methyl-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3ai**). Yield 80%; White solid; Mp 289–290 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, J = 7.6, 1.2 Hz, 1H), 7.58–7.54 (m, 1H), 7.44 (s, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.32 (dd, J = 8.4, 1.6 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.21–7.17 (m, 3H), 7.08–7.06 (m, 2H), 6.65 (d, J = 8.4 Hz, 1H), 5.01 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.40 (C), 168.94 (C), 165.43 (C), 158.58 (C), 155.33 (C), 141.05 (CH), 133.57 (C), 133.23 (CH), 131.50 (C), 128.87 (CH), 128.44 (CH), 128.19 (CH), 124.77 (CH), 124.30 (CH), 123.05 (CH), 118.33 (C), 117.12 (CH), 112.69 (CH), 111.73 (C), 111.24 (C), 103.91 (C), 52.01 (CH), 20.69 (CH_3); HRMS (ESI-TOF): m/z calcd for $C_{25}H_{16}O_5Na$ $[M+Na]^+$: 419.0895, found: 419.0900.

5-Methoxy-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3aj**). Yield 87%; White solid; Mp 269–270 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.0 Hz, 1H), 7.58–7.54 (m, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.20–7.18 (m, 3H), 7.13–7.04 (m, 4H), 6.67 (d, J = 9.2 Hz, 1H), 5.01 (s, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.64 (C), 165.79 (C), 165.43 (C), 158.56 (C), 156.04 (C), 155.32 (C), 133.25 (CH), 131.46 (C), 129.42 (CH), 128.85 (CH), 128.44 (CH), 128.23 (CH), 124.31 (CH), 123.04 (CH), 118.46 (C), 117.13 (CH), 114.03 (CH), 111.71 (C), 111.67 (C), 105.20 (CH), 103.93 (C), 56.01 (CH3), 52.13 (CH); HRMS (ESI-TOF): m/z calcd for $C_{25}H_{16}O_6Na$ $[M+Na]^+$: 435.0845, found: 435.0848.

7-Methoxy-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3ak**). Yield 96% White solid; Mp 257–258 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, J = 8.0, 1.6 Hz, 1H), 7.57–7.53 (m, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.26–7.23 (m, 2H), 7.19–7.17 (m, 3H), 7.12–7.10 (m, 2H), 7.04–6.97 (m, 2H), 5.04 (s, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.45 (C), 165.57 (C), 160.31 (C), 158.53 (C), 155.30 (C), 145.80 (C), 133.27 (CH), 131.23 (C), 128.93 (CH), 128.47 (CH), 128.24 (CH), 124.33 (CH), 124.17 (CH), 123.05 (CH), 122.70 (CH), 119.85 (C), 117.09 (CH), 116.60 (CH), 111.70 (C), 111.08 (C), 103.78 (C), 56.95 (CH3), 52.53 (CH); HRMS (ESI-TOF): m/z calcd for $C_{25}H_{16}O_6Na$ $[M+Na]^+$: 435.0845, found: 435.0847.

6-Ethoxy-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3al**). Yield 64%; White solid; Mp 246–247 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.72 (m, 1H), 7.69–7.63 (m, 2H), 7.50–7.45 (m, 1H), 7.39–7.28 (m, 4H), 7.21–7.17 (m, 2H), 6.72–6.67 (m, 1H), 6.24 (d, J = 9.6 Hz, 1H), 5.14 (d, J = 11.6 Hz, 1H), 4.07–4.00 (m, 2H), 1.45–1.39 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.43 (C), 173.07 (C), 169.19 (C), 165.49 (C), 158.62 (C), 155.35 (C), 133.21 (CH), 131.64 (C), 128.90 (CH), 128.45 (CH), 128.15 (CH), 126.57 (CH), 124.30 (CH), 123.07 (CH), 117.11 (CH), 113.32 (CH), 112.02 (C), 111.77 (C), 111.11 (C), 103.92 (C), 96.69 (CH), 64.78 (CH_2), 51.92 (CH), 14.40 (CH_3); HRMS (ESI-TOF): m/z calcd for $C_{26}H_{18}O_6Na$ $[M+Na]^+$: 449.1001, found: 449.1005.

6-Fluoro-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3am**). Yield 75%; White solid; Mp 224–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, J = 7.6, 1.2 Hz, 1H), 7.59–7.54 (m, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.32–7.30 (m, 1H), 7.28–7.26 (m, 1H), 7.25–7.23 (m, 1H), 7.21–7.17 (m, 3H), 7.08–7.05 (m, 2H), 6.73–6.70 (m, 1H), 5.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.99 (d, J = 2.0 Hz, C), 166.57 (C), 165.30 (C), 158.51 (d, J = 244.0 Hz, C), 158.42 (C), 155.34 (C), 133.37 (CH), 131.15 (C), 128.85 (CH), 128.52 (CH),

128.37 (CH), 127.37 (d, *J* = 26.0 Hz, CH), 124.39 (CH), 122.99 (CH), 119.05 (d, *J* = 8.0 Hz), 117.16 (CH), 114.39 (d, *J* = 8.0 Hz, CH), 111.67 (d, *J* = 14.0 Hz, C), 110.59 (d, *J* = 24.0 Hz, CH), 103.85 (C), 52.32 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}FO_5Na$ $[M+Na]^+$: 423.0645, found: 423.0646.

6-Chloro-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3an**). Yield 77%; White solid; Mp 265–266 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.62–7.55 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.22–7.19 (m, 3H), 7.08–7.05 (m, 3H), 6.78 (s, 1H), 5.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 192.75 (C), 170.55 (C), 165.25 (C), 158.40 (C), 155.36 (C), 146.25 (C), 133.37 (CH), 131.05 (C), 128.85 (CH), 128.58 (CH), 128.44 (CH), 126.08 (CH), 124.74 (CH), 124.39 (CH), 122.97 (CH), 117.17 (CH), 117.03 (C), 113.73 (CH), 111.58 (C), 111.43 (C), 103.85 (C), 52.22 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}ClO_5Na$ $[M+Na]^+$: 439.0349, found: 439.0350.

5-Bromo-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3ao**). Yield 88%; White solid; Mp 250–251 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.77 (d, *J* = 2.0 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59–7.55 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.20–7.18 (m, 3H), 7.07–7.05 (m, 2H), 6.66 (d, *J* = 8.4 Hz, 1H), 5.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.04 (C), 169.13 (C), 165.27 (C), 158.38 (C), 155.35 (C), 142.32 (CH), 133.39 (CH), 131.03 (C), 128.84 (CH), 128.56 (CH), 128.41 (CH), 127.79 (CH), 124.40 (CH), 122.98 (CH), 120.15 (C), 117.17 (CH), 116.28 (C), 114.86 (CH), 111.57 (C), 111.29 (C), 103.81 (C), 52.35 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}BrO_5Na$ $[M+Na]^+$: 482.9844, found: 482.9849.

3′-(*p*-Tolyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3ap**). Yield 80%; White solid; Mp 232-233 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.76 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.67–7.59 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.37–7.33 (m, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.11–7.06 (m, 4H), 6.88 (d, *J* = 8.4 Hz, 1H), 5.10 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 194.46 (C), 170.53 (C), 165.23 (C), 158.58 (C), 155.30 (C), 139.84 (CH), 137.92 (C), 133.21 (CH), 129.23 (CH), 128.77 (CH), 128.27 (C), 125.35 (CH), 124.30 (CH), 123.68 (CH), 123.01 (C), 118.44 (C), 117.12 (CH), 113.20 (CH), 111.73 (C), 110.93 (C), 104.15 (C), 51.69 (CH), 21.25 (CH_3); HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{16}O_5Na$ $[M+Na]^+$: 419.0895, found: 419.0899.

3′-(4-(tert-Butyl)phenyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3aq**). Yield 94%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.66 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.57–7.48 (m, 2H), 7.36 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.26–7.22 (m, 1H), 7.20–7.18 (m, 2H), 7.10–7.05 (m, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.75 (dd, *J* = 8.4, 3.2 Hz, 1H), 5.00 (s, 1H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 194.48 (C), 170.55 (C), 165.23 (C), 158.61 (C), 155.29 (C), 150.93 (C), 139.75 (CH), 133.20 (CH), 128.46 (CH), 128.27 (C), 125.39 (CH), 125.34 (C), 124.30 (CH), 123.66 (CH), 123.02 (CH), 118.48 (C), 117.10 (CH), 113.16 (CH), 111.73 (C), 111.05 (C), 104.15 (C), 51.56 (CH), 34.54 (C), 31.29 (CH_3); HRMS (ESI-TOF): *m*/*z* calcd for $C_{28}H_{22}O_5Na$ $[M+Na]^+$: 461.1365, found: 461.1367.

3′-(2-Methoxyphenyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3ar**). Yield 93%; Yellow solid; Mp 257–258 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.74 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.58–7.49 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.20–7.18 (m, 1H), 7.15 (d, *J* = 4.8 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 5.26 (s, 1H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 194.36 (C), 170.26 (C), 165.70 (C), 159.12 (C), 156.51 (C), 155.33 (C), 138.90 (CH), 133.21 (CH), 129.13 (CH), 128.63 (CH), 125.02 (CH), 124.29 (CH), 123.36 (CH), 123.03 (CH), 121.02 (C), 120.62 (CH), 118.67 (C), 117.06 (CH), 112.76 (CH), 111.75 (C), 111.27 (C), 109.25 (CH), 102.31 (C), 53.93 (CH_3), 46.66 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{16}O_6Na$ $[M+Na]^+$: 435.0845, found: 435.0848.

3′-(4-Methoxyphenyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3as**). Yield 88%; Yellow solid; Mp 220–221 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.65 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57–7.49 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.27–7.23 (m, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.03–6.99 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 4.98 (s, 1H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 194.50 (C),

170.47 (C), 165.19 (C), 159.38 (C), 158.59 (C), 155.29 (C), 139.87 (CH), 133.23 (CH), 130.05 (CH), 125.32 (CH), 124.32 (CH), 123.68 (CH), 123.32 (C), 123.01 (CH), 118.47 (C), 117.11 (CH), 113.90 (CH), 113.19 (CH), 111.72 (C), 110.89 (C), 104.15 (C), 55.21 (CH), 51.47 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{16}O_6Na$ $[M+Na]^+$: 435.0845, found: 435.0847.

3′-(3,4,5-Trimethoxyphenyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3at**). Yield 99%; White solid; Mp 279–280 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.61–7.53 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.30–7.26 (m, 1H), 7.13–7.09 (m, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.24 (s, 2H), 4.99 (s, 1H), 3.72 (s, 3H), 3.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.40 (C), 170.61 (C), 165.66 (C), 158.62 (C), 155.35 (C), 153.10 (C), 140.04 (CH), 137.69 (C), 133.42 (CH), 126.80 (C), 125.26 (CH), 124.42 (CH), 123.74 (CH), 123.10 (CH), 118.52 (C), 117.16 (CH), 113.24 (CH), 111.68 (C), 110.87 (C), 105.85 (CH), 103.39 (C), 60.78 (CH_3), 56.10 (CH_3), 52.55 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{27}H_{20}O_8Na$ $[M+Na]^+$: 495.1056, found: 495.1060.

3′-(3-Nitrophenyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3av**). Yield 82%; White solid; Mp 239–240 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.0 Hz, 1H), 8.09 (s, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.74–7.67 (m, 2H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 5.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.44 (C), 170.13 (C), 165.93 (C), 158.39 (C), 155.45 (C), 148.26 (C), 140.23 (CH), 135.28 (CH), 133.94 (C), 133.79 (CH), 129.53 (CH), 125.68 (CH), 124.61 (CH), 124.23 (CH), 124.09 (CH), 123.52 (CH), 123.20 (CH), 118.19 (C), 117.30 (CH), 113.14 (CH), 111.44 (C), 110.34 (C), 103.01 (C), 51.25 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}NO_7Na$ $[M+Na]^+$: 450.0590, found: 450.0588.

3′-(3-Fluorophenyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3aw**). Yield 85%; White solid; Mp 206–207 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.68–7.60 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.24–7.17 (m, 2H), 6.99–6.93 (m, 2H), 6.92–6.89 (m, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.98 (C), 170.41 (C), 165.61 (C), 162.71 (d, *J* = 244.0 Hz), 158.45 (C), 155.37 (C), 140.05 (CH), 133.97 (d, *J* = 7.0 Hz), 133.50 (CH), 129.99 (d, *J* = 8.0 Hz, CH), 125.49 (CH), 124.71 (d, *J* = 3.0 Hz, CH), 124.45 (CH), 123.93 (CH), 123.10 (CH), 118.30 (C), 117.19 (CH), 116.01 (d, *J* = 52.0 Hz, CH), 115.41 (d, *J* = 20.0 Hz, CH), 113.15 (CH), 111.55 (C), 110.64 (C), 103.45 (C), 51.51 (d, *J* = 2.0 Hz, CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}FO_5Na$ $[M+Na]^+$: 423.0645, found: 423.0644.

3′-(4-Fluorophenyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3ay**). Yield 97%; White solid; Mp 206–207 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.2 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.67–7.60 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.20–7.13 (m, 3H), 6.96 (t, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 5.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.13 (C), 170.34 (C), 165.46 (C), 162.57 (d, *J* = 246 Hz, C), 158.53 (C), 155.34 (C), 140.04 (CH), 133.43 (CH), 130.60 (d, *J* = 9.0 Hz, CH), 127.20 (d, *J* = 4.0 Hz, C), 125.42 (CH), 124.43 (CH), 123.86 (CH), 123.07 (CH), 118.40 (C), 117.17 (CH), 115.52 (d, *J* = 22.0 Hz, CH), 113.12 (CH), 111.61 (C), 110.68 (C), 103.69 (C), 51.36 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}FO_5Na$ $[M+Na]^+$: 423.0645, found: 423.0647.

Methyl 4-(3,4′-dioxo-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromen]-3′-yl)benzoate (**3az**). Yield 51%; White solid; Mp 228–229 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.68 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.63 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.60–7.56 (m, 1H), 7.54–7.50 (m, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.29–7.25 (m, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.08 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.87 (C), 170.29 (C), 166.74 (C), 165.69 (C), 158.45 (C), 155.39 (C), 140.08 (CH), 136.69 (C), 133.51 (CH), 130.06 (C), 129.76 (CH), 129.02 (CH), 125.46 (CH), 124.46 (CH), 123.93 (CH), 123.10 (CH), 118.30 (C), 117.20 (CH), 113.12 (CH), 111.56 (C), 110.67 (C), 103.37 (C), 52.20 (CH3), 51.80 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{16}O_7Na$ $[M+Na]^+$: 463.0794, found: 463.0792.

4-(3,4′-Dioxo-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromen]-3′-yl)benzonitrile (**3ba**). Yield 56%; Yellow solid; Mp 217-218 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.65–7.60 (m, 2H), 7.59–7.55 (m, 1H), 7.52–7.50 (m, 2H), 7.39 (d, *J* = 8.4 Hz,

1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.48 (C), 170.17 (C), 165.94 (C), 158.41 (C), 155.42 (C), 140.27 (CH), 137.09 (C), 133.76 (CH), 132.31 (CH), 129.79 (CH), 125.60 (CH), 124.60 (CH), 124.17 (CH), 123.16 (CH), 118.54 (C), 118.21 (C), 117.27 (CH), 113.11 (CH), 112.25 (C), 111.43 (C), 110.45 (C), 102.86 (C), 51.68 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{13}NO_5Na$ [M+Na]$^+$: 430.0691, found: 430.0689.

3′-(3-Chlorophenyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3bb**). Yield 88%; Yellow solid; Mp 241–242 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.70–7.67 (m, 1H), 7.64–7.61 (m, 1H), 7.60–7.53 (m, 2H), 7.38 (dd, *J* = 8.0, 3.6 Hz, 1H), 7.29–7.25 (m, 1H), 7.19–7.10 (m, 4H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.81 (dd, *J* = 8.0, 3.2 Hz, 1H), 4.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.92 (C), 170.37 (C), 165.57 (C), 158.40 (C), 155.37 (C), 140.04 (CH), 134.37 (C), 133.59 (C), 133.50 (CH), 129.71 (CH), 129.05 (CH), 128.60 (CH), 127.25 (CH), 125.52 (CH), 124.44 (CH), 123.95 (CH), 123.10 (CH), 118.29 (C), 117.21 (CH), 113.20 (CH), 111.55 (C), 110.62 (C), 103.47 (C), 51.42 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}ClO_5Na$ [M+Na]$^+$: 439.0349, found: 439.0350.

3′-(3-Bromophenyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3bc**). Yield 72%; Yellow solid; Mp 260–261 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.68 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.64–7.60 (m, 1H), 7.58–7.53 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.34–7.32 (m, 1H), 7.29–7.25 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.08-7.02 (m, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 4.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.91 (C), 170.36 (C), 165.56 (C), 158.39 (C), 155.37 (C), 140.05 (CH), 133.85 (C), 133.50 (CH), 131.91 (CH), 131.51 (CH), 129.99 (CH), 127.72 (CH), 125.52 (CH), 124.44 (CH), 123.96 (CH), 123.10 (CH), 122.56 (C), 118.29 (C), 117.21 (C), 113.21 (CH), 111.55 (C), 110.63 (C), 103.47 (C), 51.37 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}BrO_5Na$ [M+Na]$^+$: 482.9844, found: 482.9841.

3′-(4-Iodophenyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3bd**). Yield 84%; White solid; Mp 255–256 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.67 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.62 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.58 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.55–7.51 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 4.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.97 (C), 170.36 (C), 165.58 (C), 158.46 (C), 155.35 (C), 140.09 (CH), 137.61 (CH), 133.47 (CH), 131.24 (C), 130.83 (CH), 125.45 (CH), 124.44 (CH), 123.93 (CH), 123.08 (CH), 118.30 (C), 117.19 (CH), 113.25 (CH), 111.57 (C), 110.56 (C), 103.44 (C), 94.22 (C), 51.50 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}IO_5Na$ [M+Na]$^+$: 530.9705, found: 530.9706.

3′-(2,4-Dichlorophenyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3be**). Yield 64%; Yellow solid; Mp 253–254 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.80 (d, *J* = 7.6 Hz, 1H), 7.72–7.65 (m, 3H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.32–7.30 (m, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.25 (t, *J* = 5.6 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.70 (C), 170.39 (C), 165.90 (C), 158.47 (C), 155.40 (C), 139.69 (CH), 135.06 (C), 134.70 (C), 133.65 (CH), 130.88 (CH), 129.18 (CH), 129.08 (C), 127.35 (CH), 125.62 (CH), 124.52 (CH), 124.08 (CH), 123.15 (CH), 118.15 (C), 117.22 (CH), 113.08 (CH), 111.46 (C), 110.40 (C), 102.28 (C), 47.76 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{12}C_{l2}O_5Na$ [M+Na]$^+$: 472.9959, found: 472.9958.

3′-(4-(Trifluoromethyl)phenyl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3bf**). Yield 90%; Yellow solid; Mp 220–221 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.69 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.64 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.61–7.59 (m, 1H), 7.57–7.53 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.30–7.26 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.76 (C), 170.30 (C), 165.74 (C), 158.45 (C), 155.41 (C), 140.13 (CH), 135.65 (CH), 133.59 (C), 130.42 (q, *J* = 32.0 Hz, CF_3), 129.35 (CH), 125.50 (q, *J* = 4.0 Hz, CH), 124.50 (CH), 124.02 (CH), 123.12 (CH), 118.26 (C), 117.23 (CH), 113.17 (CH), 111.53 (CH), 110.60 (CH), 103.25 (C), 51.52 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{13}F_3O_5Na$ [M+Na]$^+$: 473.0613, found: 473.0616.

3′-([1,1′-Biphenyl]-4-yl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3bg**). Yield 88%; White solid; Mp 280–281 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.68 (dd,

J = 8.0, 0.8 Hz, 1H), 7.63 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.58–7.54 (m, 1H), 7.52–7.50 (m, 1H), 7.49–7.47 (m, 1H), 7.46 (s, 1H), 7.43–7.41 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.34–7.30 (m, 2H), 7.28–7.22 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.10–7.06 (m, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 5.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 194.32 (C), 170.50 (C), 165.44 (C), 158.61 (C), 155.36 (C), 140.97 (C), 140.55 (C), 139.92 (CH), 133.33 (CH), 130.47 (C), 129.31 (CH), 128.76 (CH), 127.40 (CH), 127.19 (CH), 127.06 (CH), 125.40 (CH), 124.38 (CH), 123.77 (CH), 123.07 (CH), 118.45 (C), 117.17 (CH), 113.23 (CH), 111.71 (C), 110.96 (C), 103.93 (C), 51.73 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{30}H_{18}O_5Na$ $[M+Na]^+$: 481.1052, found: 481.1053.

3′-(Naphthalen-2-yl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3bh**). Yield 89%; White solid; Mp 257–258 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.82–7.74 (m, 5H), 7.69 (s, 1H), 7.68–7.65 (m, 1H), 7.56–7.52 (m, 1H), 7.50–7.45 (m, 3H), 7.39–7.35 (m, 1H), 7.32 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 5.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 194.36 (C), 170.52 (C), 165.43 (C), 158.60 (C), 155.39 (C), 139.89 (CH), 133.35 (CH), 133.19 (C), 129.12 (C), 128.34 (CH), 128.21 (CH), 128.04 (CH), 127.67 (CH), 126.51 (CH), 126.21 (CH), 126.15 (CH), 125.40 (CH), 124.39 (CH), 123.77 (CH), 123.09 (CH), 118.31 (C), 117.18 (CH), 113.23 (CH), 111.73 (C), 111.03 (C), 104.07 (C), 52.05 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{28}H_{16}O_5Na$ $[M+Na]^+$: 455.0895, found: 455.0895.

3′-(Furan-2-yl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3bi**). Yield 69%; Yellow solid; Mp 194–195 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.70 (d, *J* = 7.6 Hz, 1H), 7.62–7.54 (m, 3H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.27–7.23 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.26–6.23 (m, 2H), 5.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.87 (C), 170.74 (C), 165.33 (C), 158.37 (C), 155.27 (C), 145.52 (C), 143.07 (CH), 139.94 (CH), 133.46 (CH), 125.55 (CH), 124.39 (CH), 123.92 (CH), 123.09 (CH), 118.12 (C), 117.14 (CH), 113.21 (CH), 111.56 (C), 110.61 (CH), 110.34 (C), 110.04 (CH), 101.82 (C), 45.50 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{22}H_{12}O_6Na$ $[M+Na]^+$: 395.0532, found: 395.0537.

3′-(Thiophen-2-yl)-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3bj**). Yield 84%; Yellow solid; Mp 194–195 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.68 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.60–7.55 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.28–7.24 (m, 1H), 7.20–7.18 (m, 1H), 7.14–7.10 (m, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.86–6.84 (m, 2H), 5.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.98 (C), 170.67 (C), 165.10 (C), 158.29 (C), 155.31 (C), 139.99 (CH), 133.68 (C), 133.47 (CH), 128.09 (CH), 126.72 (CH), 126.40 (CH), 125.46 (CH), 124.38 (CH), 123.87 (CH), 123.14 (CH), 118.39 (C), 117.17 (CH), 113.24 (CH), 111.57 (C), 110.14 (C), 103.89 (C), 47.15 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{22}H_{12}O_5SNa$ $[M+Na]^+$: 411.0303, found: 411.0305.

5-nitro-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3bk**). Yield 62%; White solid; Mp 265–266 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.57 (s, 1H), 8.41 (d, *J* = 9.2 Hz, 1H), 7.64-7.59 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.21-7.19 (m, 3H), 7.08 (s, 2H), 6.90 (d, *J* = 9.2 Hz, 1H), 5.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 192.51 (C), 172.82 (C), 165.17 (C), 158.19 (C), 155.41 (C), 143.90 (C), 134.57 (CH), 133.62 (CH), 130.41 (C), 128.79 (CH), 128.72 (CH), 124.54 (CH), 122.90 (CH), 121.84 (CH), 119.01 (C), 117.27 (CH), 113.93 (CH), 112.15 (C), 111.38 (C), 103.66 (C), 52.86 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}NO_7Na$ $[M+Na]^+$: 450.0590, found: 450.0596.

8′-nitro-3′-phenyl-3*H*,3′*H*,4′*H*-spiro[benzofuran-2,2′-furo[3,2-*c*]chromene]-3,4′-dione (**3bl**). Yield 81%; Yellow solid; Mp 315–317 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.56 (d, *J* = 2.4 Hz, 1H), 8.43 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 9.2 Hz, 1H), 7.41-7.37 (m, 1H), 7.24-7.22 (m, 2H), 7.15-7.10 (m, 3H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.65 (C), 170.44 (C), 164.07 (C), 158.40 (C), 156.86 (C), 143.77 (C), 140.12 (CH), 130.62 (C), 128.89 (CH), 128.64 (CH), 128.58 (CH), 127.80 (CH), 125.56 (CH), 124.07 (CH), 119.51 (CH), 118.35 (CH), 118.15 (C), 113.17 (CH), 112.06 (C), 110.92 (C), 105.86 (C), 51.78 (CH); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}NO_7Na$ $[M+Na]^+$: 450.0590, found: 450.0592.

4-Hydroxy-3-((4-nitrophenyl)(3-oxobenzofuran-2(3*H*)-ylidene)methyl)-2*H*-chromen-2-one (**4au**). Yield 78%; Yellow solid; Mp 238–239 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 11.46 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 2H), 7.96 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H),

7.67 (d, *J* = 8.8 Hz, 2H), 7.64–7.59 (m, 1H), 7.48–7.44 (m, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.83–6.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 186.27 (C), 163.66 (C), 158.81 (C), 156.53 (C), 153.71 (C), 148.10 (C), 147.67 (C), 137.47 (CH), 135.04 (C), 133.12 (CH), 131.76 (CH), 131.38 (CH), 131.03 (C), 125.26 (CH), 123.33 (CH), 121.86 (CH), 119.33 (CH), 118.83 (CH), 118.56 (C), 117.71 (CH), 111.66 (C), 110.01 (C); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}NO_7Na$ $[M+Na]^+$: 450.0590, found: 450.0589.

3-((2-Fluorophenyl)(3-oxobenzofuran-2(3*H*)-ylidene)methyl)-4-hydroxy-2*H*-chromen-2-one (**4ax**). Yield 77%; White solid; Mp 196–197 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.80 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.72–7.69 (m, 1H), 7.67–7.62 (m, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.38–7.34 (m, 1H), 7.32–7.26 (m, 2H), 7.24–7.20 (m, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 9.6 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 5.38 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.80 (C), 170.39 (C), 158.67 (C), 155.34 (C), 139.67 (CH), 133.43 (CH), 130.01 (d, *J* = 8.0 Hz, CH), 125.58 (CH), 124.42 (CH), 124.25 (d, *J* = 3.0 Hz, CH), 123.90 (CH), 123.09 (CH), 119.38 (d, *J* = 14.0 Hz, (C)), 118.16 (C), 117.15 (CH), 115.09 (d, *J* = 22.0 Hz, CH), 113.00 (CH), 111.61 (C), 110.59 (C); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{13}FO_5Na$ $[M+Na]^+$: 423.0645, found: 423.0644.

Methyl-4-((4-hydroxy-2-oxo-2*H*-chromen-3-yl)(3-oxobenzofuran-2(3*H*)-ylidene)methyl) benzoate (**4az**). Yield 16%; Yellow solid; Mp 214–215 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 11.51 (s, 1H), 8.02–8.00 (m, 2H), 7.96 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.62–7.58 (m, 1H), 7.56–7.53 (m, 2H), 7.45–7.41 (m, 2H), 7.40–7.36 (m, 1H), 6.96 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.75–6.71 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 186.79 (C), 166.60 (C), 163.44 (C), 158.75 (C), 156.62 (C), 153.67 (C), 147.32 (C), 137.22 (CH), 132.87 (CH), 132.84 (C), 132.07 (C), 131.95 (CH), 130.68 (C), 130.36 (CH), 129.42 (CH), 125.08 (CH), 121.86 (CH), 119.16 (CH), 118.61 (CH), 117.62 (CH), 111.82 (C), 110.09 (C), 52.32 (CH3), 29.74 (C); HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{16}O_7Na$ $[M+Na]^+$: 463.0794, found: 463.0791.

4-((4-Hydroxy-2-oxo-2*H*-chromen-3-yl)(3-oxobenzofuran-2(3*H*)-ylidene)methyl)benzo nitrile (**4ba**). Yield 26%; Yellow solid; Mp 259–260 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 11.46 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.78 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.65–7.59 (m, 5H), 7.48–7.44 (m, 2H), 7.39 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.80–6.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 186.41 (C), 163.59 (C), 158.82 (C), 156.55 (C), 153.70 (C), 147.53 (C), 137.41 (CH), 133.08 (C), 133.05 (CH), 131.86 (CH), 131.78 (CH), 131.28 (C), 131.08 (CH), 125.21 (CH), 121.85 (CH), 119.26 (CH), 118.78 (CH), 118.55 (C), 118.50 (C), 117.69 (CH), 113.01 (C), 111.69 (C), 109.93 (C); HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{13}NO_5Na$ $[M+Na]^+$: 430.0691, found: 430.0691.

4. Conclusions

In summary, we developed a new approach to the synthesis of spirocyclic benzofuran–furocoumarins. The simple method utilizes readily available 4-hydroxycoumarins and aurones as materials and employs an iodine-catalyzed cascade annulation reaction to obtain a series of spirocyclic benzofuran–furocoumarins in high yields (up to 99%) with excellent stereoselectivity (up to >20:1 dr). Additionally, this operationally simple and environmentally benign strategy shows great compatibility with different groups on the 4-hydroxycoumarins and aurones. Further research on the application of this strategy in other reactions is underway in our laboratory.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules29081701/s1.

Author Contributions: Conceptualization, X.W. and X.S.; methodology, C.Y., D.Y. and M.X.; formal analysis, S.D.; data curation, S.D.; writing—original draft preparation, X.W. and S.D.; writing—review and editing, X.W. and X.S.; supervision, X.W.; project administration, X.W. and X.S.; funding acquisition, X.W. and X.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Foundation of Yunnan Province (Nos. 202101BA070001-053, 202205AC160004, 202301BA070001-102) and the Program for Innovative Research Team in Qujing University.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in this article.

Conflicts of Interest: The authors declare no conflicts of interest.

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