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Ruthenium(II)-catalyzed C–H activation of chromones with maleimides to synthesize succinimide/ maleimide-containing chromones

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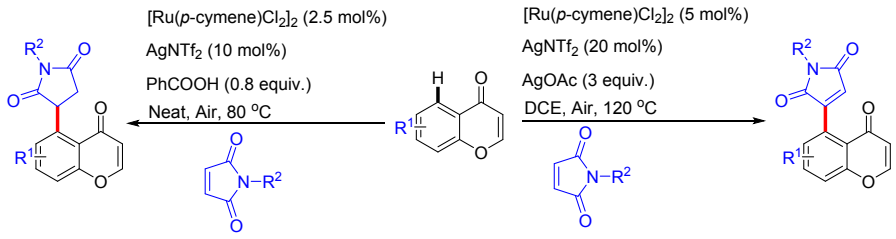


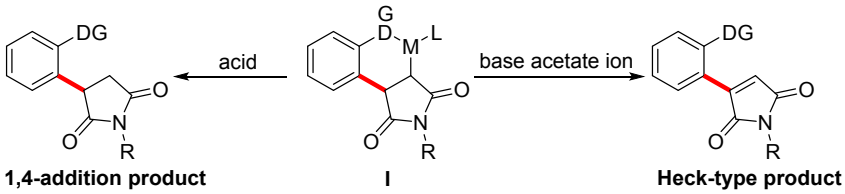
- 1,4-Addition product
- Heck-type product
- Short reaction time
- Solvent-free conditons
- Functional group compatibility
- Mechanistic investigation
- 50 Examples
- Yields up to 95%

ABSTRACT: An efficient route for the coupling of maleimides with chromones at the C5-position has been developed under Ru(II) catalysis. It could provide 1,4-addition products and oxidative Heck-type products by switching additives. Benzoic acid led to the formation of 1,4-addition products under solvent-free conditions, and silver acetate promoted to the generation of oxidative Heck-type products. Various maleimides and chromones were suitable for this transformation, affording the desired products with good to excellent yields in a short reaction time. In order to understand the mechanism of this reaction, deuteration studies and control experiments have been performed.

Introduction

The succinimide and maleimide motifs are prevalent in many natural products and drug candidates, exhibiting a broad spectrum of biological activities.[1] Therefore, development of efficient and practical methods for the preparation of these compounds has drawn considerable attention from chemists. Transition-metal-catalyzed C–H bond activation is considered as a direct way to construct structurally diverse molecules. In recent years, several directing groups assisted coupling reactions of maleimides and (hetero)arenes have been accomplished by transition-metal-catalyzed C–H bond activation.[2–5] According to the mechanism (scheme 1), the intermediate **I** is formed in the coupling reactions of arenes and maleimides, it does not have β-hydrogen in the *syn*-periplanar position. There are two ways for the transformation of intermediate **I**: one way is acid-promoted protodemetallation**,** affording 1,4-addition products; the other way is base acetate ion-promoted deprotonation**,** giving Heck-type products. In the most of reported reactions, maleimides underwent hydroarylation, providing 1,4-addition products.[3] Different metal catalysts (such as Rhodium, Ruthenium, Cobalt, Manganese) were successfully applied in this transformation. In 2018, the Prabhu group reported the first Heck-type coupling of maleimides with ketones by Rh(III) catalyzed direct C–H bond activation, the desired

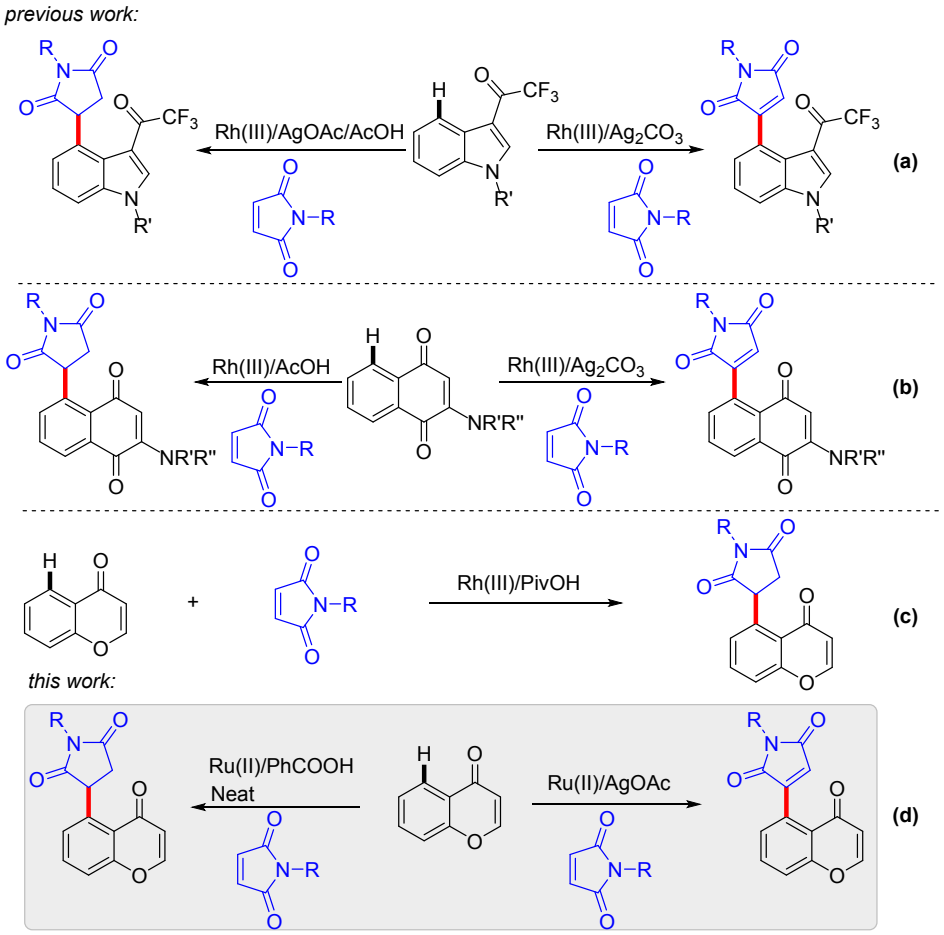
Scheme 1. Formation of 1,4-Addition Product and Heck-Type Product from Intermediate I



products were obtained in moderate yields.[4] Later, they developed an elegant method for the coupling of maleimides with indoles at the C4-position under Rh(III) catalysis. In this protocol, 1,4-addition products and Heck-type products could be obtained by switching the additives (scheme 2(a)).[3e] In 2019, a Rh(III)-catalyzed alkenylation of maleimides with arylacetamides was achieved by Jeganmohan's group.[5] Very recently, Sharma and co-workers reported a method on the regioselective C–H alkylation and alkenylation at the C5-position of 2-amino-1,4-naphthoquinones with maleimides under Rh(III) catalysis (scheme 2(b)).[3f] Obviously, approaches for the preparation of 1,4-addition products and Heck-type products of maleimides with (hetero)arenes *via* direct C–H bond activation are highly in demand.

The chromone scaffold is a core structure and ubiquitously present in numerous bioactive compounds and pharmaceuticals, their derivatives have gained considerable attention in new drug discovery.[6] So far, several strategies have been developed for the functionalization of different positions of chromone ring to synthesize their derivatives.[3b,7,8,9,10] The C5-position of chromones could be functionalized by chelation-assisted transition-metal-catalyzed transformation. In this case, the keto group of chromones, which has weakly coordinating ability, was used as a directing group. On the basis of this strategy, the Jeganmohan group and Antonchick group successfully developed elegant methods of oxidative cross-coupling of olefins with chromones at the C5-position using Ru(II) and

Scheme 2. Comparison of Previous Work with Current Work



Rh(III) catalysts, respectively.[8,9] Subsequently, several research groups finished the C5-amination of chromones with sulfonyl azides using different transition-metal catalysts.[10] In 2015, a Ru(II)-catalyzed hydroxylation of chromones at the C5-position was accomplished by Hong's group.[11] However, the methods for the coupling of chromones at the C5-position with maleimides are rare. Only one method was reported for the C5-alkylation of chromones with maleimides under Rh(III) catalysis (scheme (2c)).[3b] The protocols for the alkenylation of chromones at the C5-position with maleimides has never been reported.

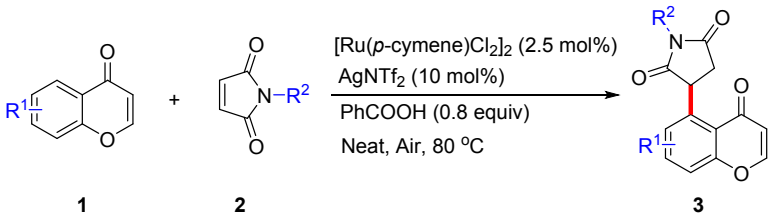
In continuation of our studies on the direct functionalization of unactivated C–H bonds,[7d,12] we are

interested in the exploration of transition-metal-catalyzed protocols for the coupling of maleimides with chromones at the C5-position. Inspired by the aforementioned background, and our experiences in this field,[12] we herein wish to disclose a Ru(II)-catalyzed novel protocol for hydroarylation and oxidative Heck-type coupling of chromones at the C5-position with maleimides by switching the additives (scheme (2d)).

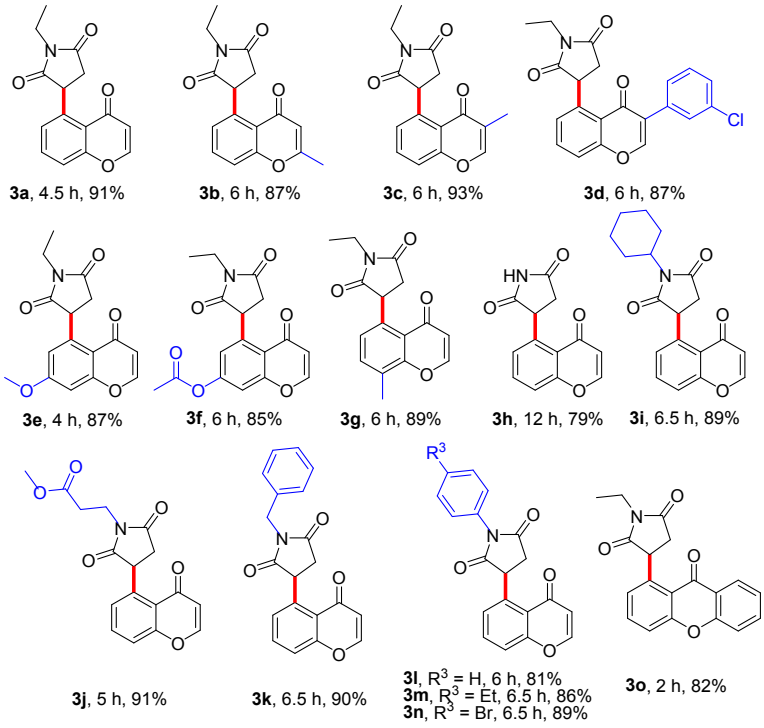
We started our exploration using chromone **1a** and maleimide **2a** as model substrates. Different additives, solvents, amounts of the additive, reaction temperature, equivalents of maleimide and catalysts were screened for this transformation (Table S1–S5, ESI†). Finally, the optimal conditions for the hydroarylation of maleimides and chromones were obtained: *N*-ethylmaleimide (2.5 equiv.), $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol%), $AgNTf_2$ (10 mol%), benzoic acid (0.8 equiv.) without solvent at 80 °C in air (entry 3, Table S3, ESI†); the optimal conditions for the Heck-type coupling of maleimides and chromones were obtained: *N*-ethylmaleimide (2.5 equiv.), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), $AgNTf_2$ (20 mol%), and AgOAc (3 equiv.) in DCE (2 mL) at 120 °C in air (entry 1, Table S5, ESI†). Moreover, gram-scale reactions were carried out under the optimal conditions, the desired products **3a** and **4a** were obtained in 84% and 81% yields, respectively (entry 11, Table S3; entry 13, Table S5, ESI†). The structure of product **4a** was further confirmed by single-crystal X-ray analysis (CCDC 1901928, see the ESI†).

Having the optimized conditions in hand, we explored the scope for the hydroarylation reaction. Chromones and maleimides with diverse substituents were examined under the solvent-free reaction conditions. Various substituents were tolerated in this transformation, and the desired products were obtained in good to excellent yields in 5-8 h (Table 1, **3b**–**3n**). The reaction of xanthone gave the desired in 82% yield in 2 h (Table 1, **3o**).[13]

Table 1. Hydroarylation of Chromones and Maleimides[a]



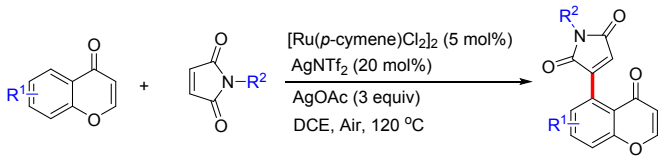
1 **2** **3**



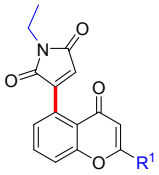
[a]Reaction conditions: **1** (0.2 mmol, 1 equiv), **2** (0.5 mmol, 2.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (0.005 mmol, 0.025 equiv), $AgNTf_2$ (0.02 mmol, 0.1 equiv), benzoic acid (0.16 mmol, 0.8 equiv.) without solvent at 80 °C in air.

Next, we turned our attention to evaluate the generality for the Heck-type coupling reaction. Chromone derivatives with diverse electron-donating or -withdrawing groups at the different positions were tested with *N*-ethylmaleimide under optimum conditions. Generally, the reactions proceeded smoothly, providing the corresponding products in good to excellent yields in a short reaction time (Table 2, **4b**–**4q**). Notably, chromone derivatives containing halogens or ester groups were tolerated in

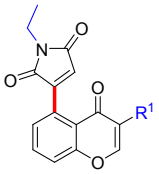
Table 2. Heck-Type Coupling of Chromones and Maleimides[a]



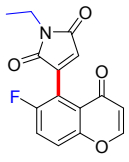
1 2 4



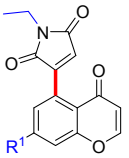
4a, R^1 = H, 1 h, 92%
4b, R^1 = Me, 0.5 h, 95%
4c[b], R^1 = Ph, 0.5 h, 75%



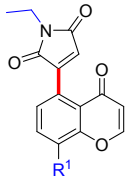
4d, R^1 = Me, 0.5 h, 92%
4e[b], R^1 = Br, 4 h, 92%
4f, R^1 = Ph, 1 h, 93%
4g, R^1 = 2-Me-Ph, 1 h, 93%
4h, R^1 = 3-Cl-Ph, 1.5 h, 92%



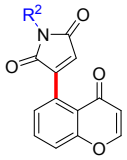
4i[b], 1 h, 79%



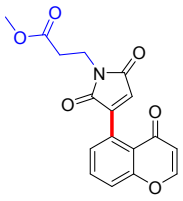
4j, R^1 = Me, 0.5 h, 91%
4k, R^1 = OMe, 0.5 h, 90%
4l, R^1 = OAc, 1 h, 95%
4m, R^1 = F, 2 h, 94%
4n, R^1 = Cl, 2 h, 83%
4o[b], R^1 = Br, 1 h, 84%



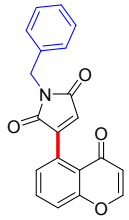
4p, R^1 = Me, 0.5 h, 93%
4q, R^1 = Cl, 1 h, 85%



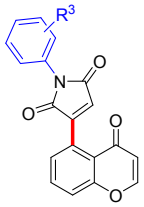
4r, R^2 =H, 12 h, 62%
4s, R^2 = Me, 0.5 h, 89%
4t, R^2 = *t*-Bu, 1 h, 69%
4u, R^2 = Cy, 1 h, 88%



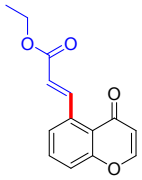
4v, 3.5 h, 88%



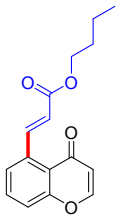
4w, 0.5 h, 87%



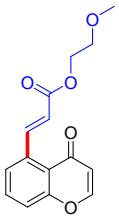
4x, R^3 = H, 2 h, 78%
4y[b], R^3 = 2-Br, 1 h, 86%
4z, R^3 = 4-Et, 0.5 h, 79%
4aa[b], R^3 = 4-Ac, 1 h, 73%
4ab, R^3 = 4-Br, 0.5 h, 75%
4ac, R^3 = 4-NO_2, 4 h, 61%



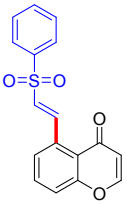
4ad, 1 h, 80%



4ae, 1 h, 81%



4af, 1 h, 90%

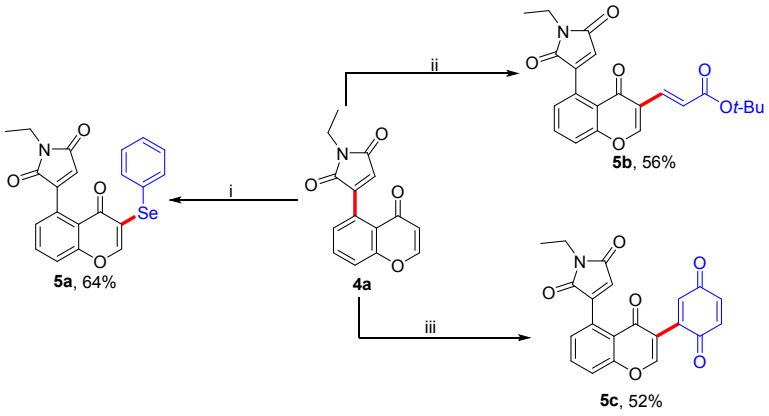


4ag, 0.5 h, 93%

[a]Reaction conditions: **1** (0.2 mmol, 1 equiv), **2** (0.5 mmol, 2.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (0.01 mmol, 0.05 equiv), $AgNTf_2$ (0.04 mmol, 0.2 equiv), AgOAc (0.6 mmol, 3 equiv) in DCE (2 mL, 0.1 M) at 120 °C in air. [b]0.015 mmol (0.075 equiv) of [Ru(*p*-cymene)Cl_2]$_2$ and 0.06 mmol (0.3 equiv) of $AgNTf_2$ were used.

this transformation, providing an opportunity for further modification of the related products at the remaining reactive sites (**4e**, **4h**, **4i**, **4l**–**4o**, **4q**). Subsequently, we turned our attention to investigate the scope of the reaction with respect to maleimide reactants with chromone under the optimal conditions. Changing the ethyl group to hydrogen or other alkyl groups at the nitrogen position of maleimides, the related products were gained in good yields (**4r**–**4v**). *N*-benzylmaleimide as well as *N*-phenylmaleimides with various substituents (bromo, ethyl, acetyl, nitro) were tolerated in this transformation, furnishing the desired products in good yields in a short reaction time (**4w**–**4ac**). To our delight, this protocol was also suitable for acrylates, the corresponding products were obtained in good yields in 1 h (**4ad**–**4af**). Furthermore, application of phenyl vinyl sulfone was successful, providing the desired product in 93% yield in 0.5 h (**4ag**).

Scheme 3. Synthetic Applications



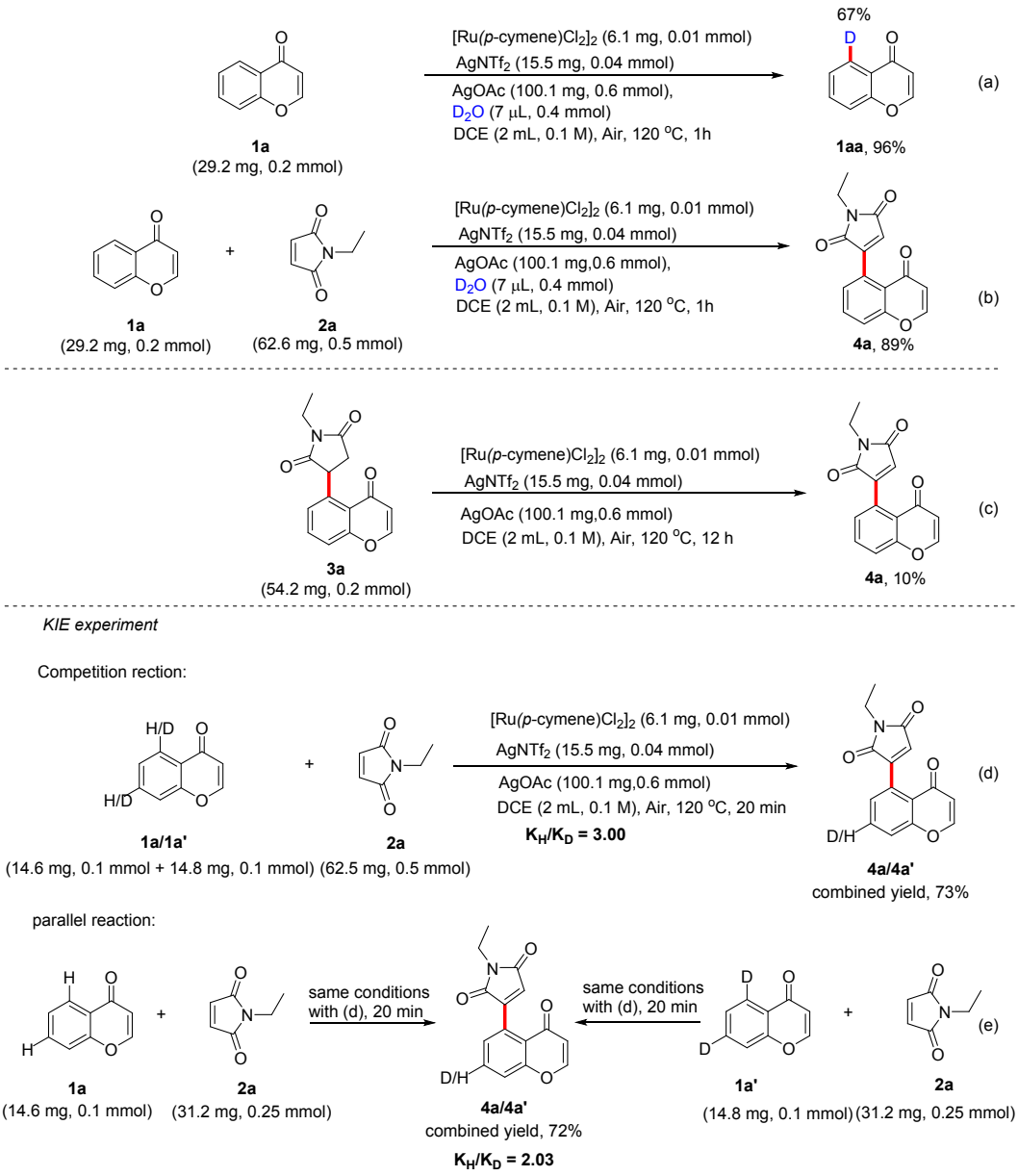
[a]Reaction conditions: (i) **4a** (53.8 mg, 0.2 mmol), diphenyl diselenide (31.2 mg, 0.1 mmol), NIS (6.7 mg, 0.03 mmol), TBHP (70% in H_2O, 11 μL, 0.8 mmol), DMF (2 mL, 0.1 M), 70 °C, 12 h; (ii) **4a** (53.8 mg, 0.2 mmol),*tert*-butyl acrylate (58 μL, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), $Cu(OAc)_2$ (109.0 mg, 0.6 mmol), Ag_2CO_3 (165.4 mg, 0.6 mmol), PivOH (2 mL, 0.1 M), 120 °C, 8 h; (iii) **4a** (53.8 mg, 0.2 mmol),1,4-benzoquinone (86.5 mg, 0.8 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), AgOAc (83.4 mg, 0.5 mmol), PivOH (46 μL, 0.4 mmol), 1,4-dioxane (2 mL, 0.1 M), 100 °C, 12 h.

After successfully developing the protocol for the preparation of Heck-type products of succinimides with chromones, we tried to modify the C3-position of chromone ring of the products using reported methods to demonstrate their further synthetic utility (Scheme 3). Selenation of the product **4a** with diphenyl diselenide employing the method from our group was successful,[7d] affording the desired product **5a** in 68% isolated yield. The product **4a** could be further alkenylated with *tert*- butyl acrylate[7a] or benzoquinone[7b] by palladium catalysis, the expected products **5b** and **5c** were obtained in moderate yields.

In order to gain some insights into the mechanism of this interesting approach, we conducted the deuterium labelling experiments. **1a** was treated with 2 equiv of D_2O under the optimal conditions in the absence of maleimide, leading to the incorporation of deuterium at the C5-position of **1a** according to the proton NMR spectrum (Scheme 4 (a), see the ESI† for details). Then we performed the same reaction with 2.2 equiv of **2a**. No incorporation of deuterium was observed for the isolated product (Scheme 4 (b), see the ESI† for details). These results suggest that the initial C–H activation step might be reversible, and the C–H activation exclusively occurs at the C5-position with the assistance of the keto group. Moreover, 1,4-addition product **3a** was examined under the optimum conditions. After 12 h, 84% of **3a** was recovered, **4a** was obtained in 10% isolated yield (Scheme 4 (c), see the ESI† for details). The result of this experiment indicates that **4a** is not formed by the oxidation of **3a** in this transformation. Additionally, the kinetic isotope effect (KIE) value of the parallel and competitive reactions were obtained, these results suggest that the C–H metallation might be involved in the rate-determining step (Scheme 4 (d), see the ESI† for details).

On the basis of control studies and the reported literatures,[2–5,8–14] a plausible mechanism of the reactions of maleimides with chromones at the C5-position was proposed (Scheme 5). Initially,

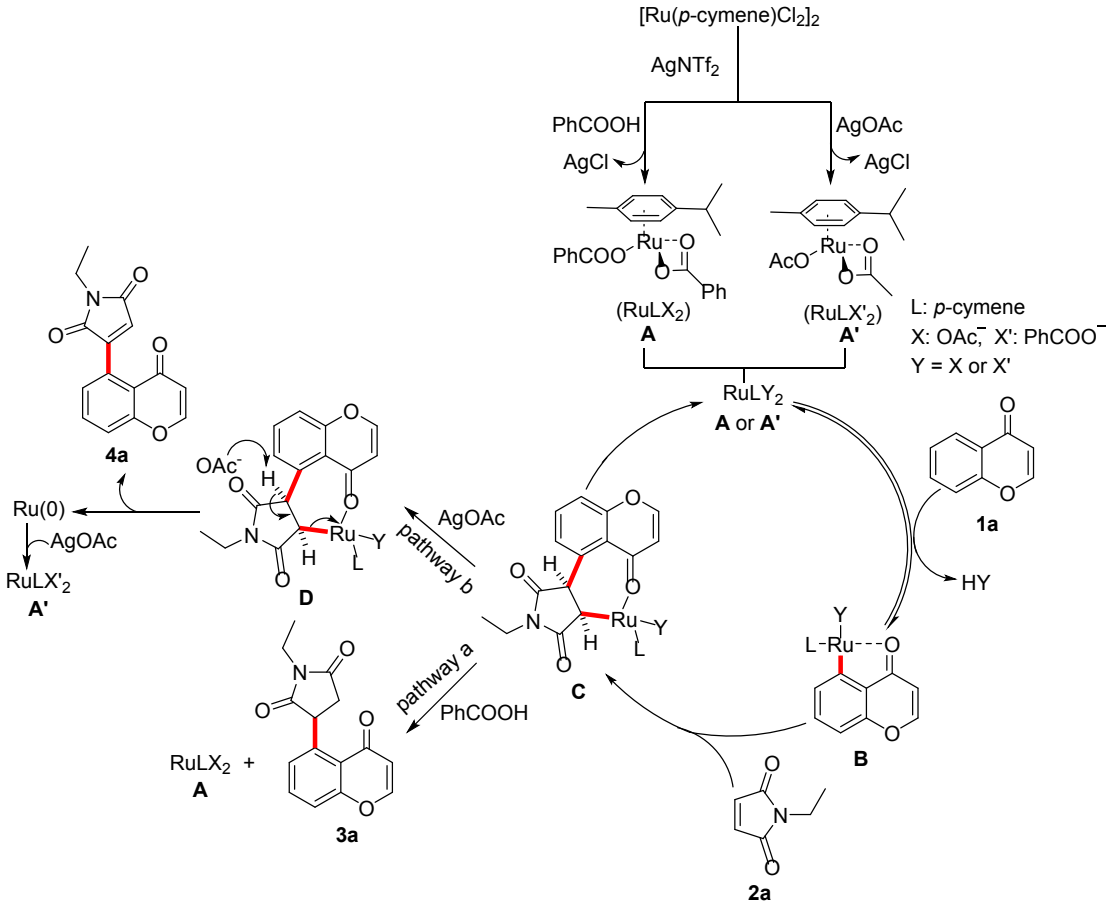
Scheme 4. Mechanistic Investigation



$[Ru(p\text{-cymene})Cl_2]_2$ reacts with $AgNTf_2$ and benzoic acid or AgOAc to generate a more active monomeric **A or A'** and AgCl. Coordination between ruthenium species and the oxygen atom of keto group, followed by C–H bond activation provides a five membered metallocycle **B**. Subsequently, maleimide **2a** inserts into the carbon–ruthenium bond of **B** and produces a bicyclic intermediate **C**, in which the *β*-hydride elimination is restricted due to the lack of *β*-hydrogen in a *syn*-periplanar manner.

If the additive is benzoic acid, the reaction gives 1,4-addition product **3a** along with the species **A** by protodemetallation. If the additive is silver acetate, the Heck-type product **4a** along with Ru(0) species are generated by deprotonation of the acidic *β*-hydrogen of intermediate **C** by OAc^-. Oxidation of Ru(0) species by silver acetate regenerates the active Ru(II) catalyst.

Scheme 5. Proposed Mechanism



In conclusion, we have reported a Ru(II)-catalyzed coupling reaction of chromones at the C5-position with maleimides using keto as a weak directing group. Succinimide-containing chromones and maleimide-containing chromones can be generated by switching the additives in this transformation: benzoic acid leads to the formation of 1,4-addition products under solvent-free conditions; silver acetate furnishes Heck-type products. This protocol features short

reaction time, good tolerance with various functional groups as well as wide substrate scopes, providing the desired products in good to excellent yields.

Experimental Section

1. General Information:

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade. Column chromatography was performed using silica gel Merck 60 (particle size 0.040-0.063 mm). Solvent mixtures are understood as volume/volume. ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR were recorded on a Bruker DRX500 (500 MHz) spectrometer in $CDCl_3$ (δ = 7.26 ppm for 1H, δ = 77.00 ppm for ^{13}C) and in DMSO-d_6 (δ = 2.50 ppm for ^{1}H, δ = 39.43 ppm for ^{13}C). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are given in Hertz (Hz). High resolution mass spectra were recorded on a ESI-Q-TOF mass spectrometer. Chemical yields refer to isolated pure substances.

2. General procedure for synthesis:

(1) General procedure for the preparation of substituted chromones (others are commercially available):

1) General Procedure for the preparation of 3-(*o*-tolyl)-4*H*-chromen-4-one and 3-(3-chlorophenyl)-4*H*-chromen-4-one[15]

3-Bromochromone (0.5 mmol, 1 equiv), phenylboronic acid (1.5 mmol, 3 equiv) and (2M) Na_2CO_3 solution were taken in toluene (3 mL, 0.17 M) in a 25 mL round bottom flask. The solvent was purged with argon for 30 min to remove the dissolved oxygen from solvent. Then $Pd(PPh_3)_4$ (0.025 mmol, 0.05 equiv) was added to the reaction mixture and it was refluxed for

18-24 h. After completion of the reaction, it was allowed to come to room temperature. The reaction mixture was extracted with ethyl acetate, washed with water, brine and dried over anhydrous $MgSO_4$. Purified by normal silica gel column chromatography (20-30% ethyl acetate/pet. Ether) to afford the corresponding isoflavones.

2) General procedure for the preparation of 7-methyl-4*H*-chromen-4-one, 7-chloro-4*H*-chromen-4-one, 8-methyl-4*H*-chromen-4-one, and 8-chloro-4*H*-chromen-4-one[16]

The corresponding 1-(2-hydroxyphenyl)ethan-1-one (0.5 mmol, 1 equiv) was placed in a flame-dried flask with stir bar in 0.5 M ethyl formate and cooled to 0 °C. NaH (60% in mineral oil, 3 mmol, 6 equiv) was added portion-wise to the cooled solution over 2 hours. If necessary for stirring, minimal amounts of dry THF were added to the flask in portions as needed. After addition of all of the NaH, the solution was warmed to room temperature and quenched with methanol (5 mm0l, 10 equiv). Concentrated HCl (25 mmol, 50 equiv) was then added slowly and allowed to stir overnight at room temperature. The reaction was then diluted with ethyl acetate, washed with water, $NaHCO_3$ (sat. aq.), and brine, dried with Na_2SO_4, and concentrated under vacuum to afford the crude chromone. The chromones were then recrystallized with ethyl acetate/hexanes or dichloromethane/hexanes to afford pure materials.

3) General procedure for the preparation of 4-oxo-4*H*-chromen-7-yl acetate[16,17]

i) 7-hydroxy-4*H*-chromen-4-one was prepared according to the procedure 2).

ii) Acetyl chloride (0.282 mL, 3.96 mmol) was added dropwise to a solution of 4-oxo-4*H*-chromen-7-yl acetate (0.5 g, 3.3 mmol) and pyridine (0.294 mL, 3.63mmol) in dichloromethane (2.5 mL). After 3 h, the mixture was washed, in sequence, with water (2.5 mL), 10% HCl (2.5 mL), water (1.2 mL), and a saturated solution of $NaHCO_3$ (2.5 mL). The organic

phase was dried and concentrated to give the desired product.

(2) General procedure for the synthesis of products 3:

Chromones **1** (0.2 mmol, 1 equiv), maleimides **2** (0.5 mmol, 2.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (0.005 mmol, 0.025 equiv), $AgNTf_2$ (0.02 mmol, 0.1 equiv) and benzoic acid (0.16 mmol, 0.8 equiv) were added in a 12 mL screw capped tube at room temperature in air. The reaction mixture was allowed to warm up to 80 °C in heating mantle and stirred for 1-12 h. When the reaction was completed, it was mixed with water and ethyl acetate. The reaction mixture was extracted three times with ethyl acetate. The combined organic layer was washed two times with a little amount of water, dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated under vacuum and the residue was purified by flash column chromatography on silica gel (eluting with petroleum ether-ethyl acetate) to provide the desired products **3**.

(3) General procedure for the synthesis of products 4:

Chromones **1** (0.2 mmol, 1 equiv) and maleimides **2** (0.5 mmol, 2.5 equiv) were dissolved in a 12 mL screw capped tube with 2 mL of DCE (0.1 M). Then [Ru(*p*-cymene)Cl_2]$_2$ (0.01 mmol, 0.05 equiv), $AgNTf_2$ (0.04 mmol, 0.2 equiv) and AgOAc (0.6 mmol, 3 equiv) were added to the reaction mixture at room temperature in air. The reaction mixture was allowed to warm up to 120 °C in heating mantle and stirred for 1-12 h. After finishing the reaction, the reaction mixture was directly loaded on a silica gel column and purified with petroleum ether/EtOAc mixture to provide the desired products **4**.

(4) **Procedure for the synthesis of product 5a:**[7d]

A mixture of **4a** (53.8 mg, 0.2 mmol), diphenyl diselenide (31.2 mg, 0.1 mmol), NIS (6.7 mg, 0.03 mmol), TBHP (70% in H_2O, 11 μL, 0.8 mmol) and DMF (2 mL, 0.1 M) were added in a 5 mL

glass tube, which was stirred at 70 °C for 12 h. When the reaction was completed, it was mixed with water and ethyl acetate. The reaction mixture was extracted three times with ethyl acetate. The combined organic layer was washed two times with a little amount of water, dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated under vacuum and the residue was purified by flash column chromatography on silica gel (eluting with petroleum ether-ethyl acetate) to provide the desired product **5a**.

(5) **Procedure for the synthesis of product 5b:**[7a]

4a (53.8 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), $Cu(OAc)_2$ (109.0 mg, 0.6 mmol), and Ag_2CO_3 (165.4 mg, 0.6 mmol) were combined in PivOH (2 mL, 0.1 M). The *tert*-butyl acrylate (58 μL, 0.4 mmol) was added slowly and the reaction mixture was heated to 120 °C. The reaction was monitored by TLC using EtOAc/petroleum ether as the mobile phase. The reaction mixture was diluted with CH_2Cl_2 and the excess $NaHCO_3$ was added to neutralize PivOH. After stirring the mixture for 10 min, the residue was washed with sequentially aqueous $NaHCO_3$ and NH_4Cl. The organic layer was dried over $MgSO_4$. After removal of solvent, the residue was purified by flash chromatography on silica gel to give the desired product **5b**.

(6) **Procedure for the synthesis of product 5c:**[7b]

4a (53.8 mg, 0.2 mmol), 1,4-benzoquinone (86.5 mg, 0.8 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), AgOAc (83.4 mg, 0.5 mmol) and PivOH (46 μL, 0.4 mmol) were combined in 1,4-dioxane (2 mL, 0.1 M) in a cap test tube. The reaction mixture was heated to 100 °C. The reaction was stirred for 12 h until **4a** disappeared (monitored by TLC using EtOAc/petroleum ether as the mobile phase).

After cooled to room temperature, the 1,4-dioxane solvent was removed under reduced pressure. The reaction mixture was diluted with CH_2Cl_2 and the aqueous $NaHCO_3$ was added to neutralize the PivOH. After stirring the mixture for 10 min, the residue was extracted with aqueous NH_4Cl. The organic layer was dried over $MgSO_4$. After removal of solvent, the residue was purified by flash chromatography on silica gel to give the desired product **5c**.

3. Characterization of synthesized substituted chromones:

3-(o-tolyl)-4H-chromen-4-one.[18] The isolated yield is 77%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.89 (s, 1H), 7.75 – 7.68 (m, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.27 – 7.23 (m, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 2.27 (s, 3H) ppm.

3-(3-chlorophenyl)-4H-chromen-4-one.[19] The isolated yield is 45%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 – 8.29 (m, 1H), 8.04 (s, 1H), 7.74 – 7.68 (m, 1H), 7.59 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.39 – 7.37 (m, 2H) ppm.

7-methyl-4H-chromen-4-one.[20] The isolated yield is 60%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 6.0 Hz, 1H), 7.25 – 7.19 (m, 2H), 6.30 (d, *J* = 6.0 Hz, 1H), 2.48 (s, 3H) ppm.

4-oxo-4H-chromen-7-yl acetate.[21] The isolated yield is 48%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 1H), 7.83 (d, *J* = 6.0 Hz, 1H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.14 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.32 (d, *J* = 6.0 Hz, 1H), 2.34 (s, 3H) ppm.

7-chloro-4H-chromen-4-one.[22] The isolated yield is 52%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 6.0 Hz, 1H), 7.47 (d, *J* = 1.9 Hz, 1H), 7.36 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.33 (d, *J* = 6.0 Hz, 1H) ppm. ^{13}C{1H}NMR (151 MHz, $CDCl_3$) δ 176.69, 156.53, 155.29, 139.81, 127.19, 126.11, 123.35, 118.19, 113.24 ppm. HRMS (EI) m/z: [M] calcd for $C_9H_5ClO_2$: 179.9978, found: 179.9981.

8-methyl-4H-chromen-4-one.[22] The isolated yield is 57%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.88 (dd, *J* = 5.9, 3.0 Hz, 1H), 7.48 (d, *J* = 6.5 Hz, 1H), 7.27 (td, *J* = 7.7, 2.9 Hz, 1H), 6.32 (dd, *J* = 5.9, 2.9 Hz, 1H), 2.45 (d, *J* = 2.6 Hz, 3H) ppm. ^{13}C{1H}NMR (151 MHz, $CDCl_3$) δ 177.95, 155.02, 154.98, 134.61, 127.57, 124.71, 124.68, 123.28, 112.72, 15.53 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_8O_2$: 161.0602, found: 161.0598.

8-chloro-4H-chromen-4-one.[22] The isolated yield is 61%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.92 (d, *J* = 6.0 Hz, 1H), 7.71 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 6.36 (d, *J* = 6.0 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.76, 155.16, 152.17, 134.02, 126.13, 125.21, 124.38, 123.14, 113.17 ppm. HRMS (EI) m/z: [M] calcd for $C_9H_5ClO_2$: 179.9978, found: 179.9980.

4. Characterization of products 3, 4 and 5:

(S)-1-Ethyl-3-(4-oxo-4H-chromen-5-yl)pyrrolidine-2,5-dione. The product **3a** was obtained as a white solid (49.3 mg, 91%) after purification through a chromatography column (elution: 17% EtOAc in petroleum ether), mp 136–137 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.26 (d, *J* = 5.9 Hz, 1H), 7.77 –

7.74 (m, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.38 (m, 1H), 6.30 (d, *J* = 5.9 Hz, 1H), 4.40 (m, 1H), 3.50 – 3.45 (m, 2H), 2.98 (m, 1H), 2.57 (dd, *J* = 17.3, 6.5 Hz, 1H), 1.14 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$ NMR (126 MHz, DMSO-d_6) δ 177.5, 176.9, 176.0, 157.6, 155.8, 136.2, 133.6, 130.8, 121.6, 119.0, 112.9, 47.0, 36.8, 32.9, 12.6 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{14}NO_4$, 272.0923; found, 272.0918.

(S)-1-Ethyl-3-(2-methyl-4-oxo-4H-chromen-5-yl)pyrrolidine-2,5-dione. The product **3b** was obtained as a white solid (49.5 mg, 87%) after purification through a chromatography column (elution: 50% EtOAc in petroleum ether), mp 164–165 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.4, 7.5 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.18 (s, 1H), 6.09 (s, 1H), 4.05 (m, 1H), 3.72 – 3.63 (m, 2H), 3.02 (m, 1H), 2.76 (m, 1H), 2.35 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (151 MHz, $CDCl_3$) δ 178.6, 177.5, 176.3, 165.1, 158.2, 135.7, 133.0, 130.4, 120.8, 119.1, 111.3, 48.4, 37.3, 33.8, 20.0, 12.9 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}NO_4$: 286.1079, found: 286.1073.

(S)-1-Ethyl-3-(3-methyl-4-oxo-4H-chromen-5-yl)pyrrolidine-2,5-dione. The product **3c** was obtained as a white solid (53.0 mg, 93%) after purification through a chromatography column (elution: 40% EtOAc in petroleum ether), mp158–159 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.58 (t, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.18 (s, 1H), 4.06 (m, 1H), 3.69 (q, *J* = 7.0 Hz, 2H), 2.99 (m, 1H), 2.79 (m, 1H), 1.93 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (151 MHz, $CDCl_3$) δ 178.7, 177.3, 176.4, 158.4, 150.7, 132.8, 130.3, 128.1, 121.4, 121.0, 119.3, 48.6, 37.6, 34.0, 12.8, 11.1 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}NO_4$: 286.1079, found: 286.1072.

(S)-3-(3-(3-Chlorophenyl)-4-oxo-4H-chromen-5-yl)-1-ethylpyrrolidine-2,5-dione. The product **3d** was obtained as an amorphous solid (66.4 mg, 87%) after purification through a chromatography column (elution: 40% EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.33 – 7.26 (m, 4H), 4.10 (m, 1H), 3.67 (dd, *J* = 14.0, 6.9 Hz, 2H), 3.02 (m, 1H), 2.81 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 177.3, 176.6, 176.1.0, 157.9, 152.3, 135.4, 134.2, 133.4, 133.1, 121.0, 129.6, 129.0, 128.4, 127.0, 124.8, 121.9, 119.1, 77.2, 77.0, 76.8, 48.6, 37.6, 34.0, 12.8 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}ClNO_4$: 382.0846, found: 382.0841.

(S)-1-Ethyl-3-(7-methoxy-4-oxo-4H-chromen-5-yl)pyrrolidine-2,5-dione. The product **3e** was obtained as a white solid (52.4 mg, 87%) after purification through a chromatography column (elution: 40% EtOAc in petroleum ether), mp 164–165 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 5.8 Hz, 1H), 6.83 (s, 1H), 6.79 (s, 1H), 6.19 (d, *J* = 5.7 Hz, 1H), 3.89 (s, 3H), 3.71 – 3.63 (m, 2H), 2.99 (m, 1H), 2.75 (m, 1H), 1.82 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C{1H}NMR (151 MHz, $CDCl_3$) δ 177.3, 176.8, 176.3, 162.9, 160.2, 153.7, 137.2, 120.5, 116.0, 113.6, 100.8, 55.8, 48.6, 37.1, 33.9, 12.9 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}NO_5$: 302.1028, found: 302.1021.

(S)-5-(1-Ethyl-2,5-dioxopyrrolidin-3-yl)-4-oxo-4H-chromen-7-yl acetate. The product **3f** was obtained as a white solid (55.9 mg, 85%) after purification through a chromatography column (elution: 50% EtOAc in petroleum ether), mp 118–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 5.9 Hz, 1H), 7.32 (d, *J* = 2.0 Hz, 1H), 6.99 (s, 1H), 6.25 (d, *J* = 5.9 Hz, 1H), 4.01 (m, 1H), 3.71

– 3.62 (m, 2H), 3.05 (m, 1H), 2.74 (m, 1H), 2.33 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (151 MHz, $CDCl_3$) δ 177.5, 176.6, 176.0, 168.2, 158.7, 154.3, 153.5, 137.5, 124.7, 119.9, 113.8, 111.8, 48.2, 37.1, 33.9, 21.1, 12.9 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}NO_6$: 330.0978, found: 330.0970.

(S)-1-Ethyl-3-(8-methyl-4-oxo-4H-chromen-5-yl)pyrrolidine-2,5-dione. The product **3g** was obtained as a white solid (50.7 mg, 89%) after purification through a chromatography column (elution: 40% EtOAc in petroleum ether), mp 165–166 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 5.8 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.08 (s, 1H), 6.23 (d, *J* = 5.4 Hz, 1H), 4.00 (m, 1H), 3.69 – 3.60 (m, 2H), 2.97 (m, 1H), 2.71 (m, 1H), 2.41 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (151 MHz, $CDCl_3$) δ 178.5, 177.3, 176.4, 156.6, 154.1, 134.2, 133.1, 130.3, 128.9, 122.0, 113.6, 48.4, 37.4, 33.8, 15.9, 12.9 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}NO_4$: 286.1079, found: 286.1072.

(S)-3-(4-Oxo-4H-chromen-5-yl)pyrrolidine-2,5-dione. The product **3h** was obtained as a white solid (38.4 mg, 79%) after purification through a chromatography column (elution: 70% EtOAc in petroleum ether), mp 153–154 °C. ^1H NMR (600 MHz, DMSO-d_6) δ 11.05 (brs, 1H), 8.27 (d, *J* = 5.6 Hz, 1H), 7.75 (t, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 5.6 Hz, 1H), 6.39 – 6.23 (m, 1H), 4.41 (m, 1H), 2.91 (m, 1H), 2.57 (dd, *J* = 17.3, 6.6 Hz, 1H) ppm. $^{13}C\{1H\}$NMR (151 MHz, DMSO-d_6) δ 179.1, 178.3, 178.1, 158.1, 156.4, 136.9, 134.2, 131.2, 122.2, 119.5, 113.5, 49.1, 38.6 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{10}NO_4$: 244.0610, found: 244.0605.

(S)-1-Cyclohexyl-3-(4-oxo-4H-chromen-5-yl)pyrrolidine-2,5-dione. The product **3i** was obtained as a white solid (57.9 mg, 89%) after purification through a chromatography column (elution: 40% EtOAc in petroleum ether), mp 92–93 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.26 (d, J = 5.8 Hz, 1H), 7.75 (t, J = 7.9 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.38 (s, 1H), 6.30 (d, J = 5.9 Hz, 1H), 4.34 (m, 1H), 3.86 (t, J = 12.2 Hz, 1H), 2.90 (m, 1H), 2.56 – 2.51 (m, 1H), 2.12 – 2.03 (m, 2H), 1.78 (d, J = 12.9 Hz, 2H), 1.69 (t, J = 14.3 Hz, 2H), 1.61 (d, J = 12.6 Hz, 1H), 1.25 (dd, J = 24.4, 11.1 Hz, 2H), 1.12 (dd, J = 26.0, 13.0 Hz, 1H) ppm. ^{13}C{1H}NMR (151 MHz, DMSO-d_6) δ 177.4, 177.1, 176.3, 157.7, 155.9, 136.5, 133.7, 130.9, 121.6, 119.2, 113.1, 50.8, 46.8,36.6, 28.6, 28.2, 25.5, 25.4, 25.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}NO_4$: 326.1392, found: 326.1385.

Methyl (S)-3-(2,5-dioxo-3-(4-oxo-4H-chromen-5-yl)pyrrolidin-1-yl)propanoate. The product **3j** was obtained as a white solid (59.9 mg, 91%) after purification through a chromatography column (elution: 40% EtOAc in petroleum ether), mp 122–123 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.25 (t, J = 5.5 Hz, 1H), 7.75 (t, J = 7.9 Hz, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.40 (s, 1H), 6.31 – 6.30 (m, 1H), 4.39 (m, 1H), 3.69 (t, J = 7.5 Hz, 2H), 3.60 (s, 3H), 3.01 (m, 1H), 2.69 – 2.60 (m, 2H), 2.56 (dd, J = 17.5, 6.3 Hz, 1H) ppm. ^{13}C{1H}NMR (151 MHz, DMSO-d_6) δ 177.8, 177.0, 176.2, 171.2, 157.8, 156.1, 136.1, 133.8, 131.0, 121.6, 119.3, 113.0, 51.6, 47.0, 36.8, 34.0, 31.4 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}NO_6$: 330.0978, found: 330.0971.

(S)-1-Benzyl-3-(4-oxo-4H-chromen-5-yl)pyrrolidine-2,5-dione. The product **3k** was obtained as a white solid (60.0 mg, 90%) after purification through a chromatography column (elution: 40% EtOAc in petroleum ether), mp 125–126 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (d, J = 5.9 Hz, 1H), 7.78 (t, J = 7.9 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.40 – 7.26 (m, 6H), 6.32 (d, J = 5.9 Hz, 1H),

4.65 (dd, *J* = 47.1, 15.0 Hz, 2H), 3.08 (m, 1H), 2.66 (dd, *J* = 17.4, 6.5 Hz, 1H), 2.54 (m, 1H) ppm. ^{13}C{1H}NMR (151 MHz, DMSO-d_6) δ 177.7, 177.2, 176.3, 157.7, 156.1, 136.5, 133.8, 130.9, 129.6, 128.4, 127.5, 127.2, 121.6, 119.3, 113.0, 47.2, 41.4, 36.8 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}NO_4$: 334.1079, found: 334.1072.

(S)-3-(4-Oxo-4H-chromen-5-yl)-1-phenylpyrrolidine-2,5-dione. The product **3l** was obtained as a white solid (51.7 mg, 81%) after purification through a chromatography column (elution: 40% EtOAc in petroleum ether), mp 135–136 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.31 (d, *J* = 5.9 Hz, 1H), 7.80 (dd, *J* = 8.4, 7.5 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 7.0 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.3 Hz, 2H), 6.39 (d, *J* = 5.9 Hz, 1H), 4.62 (m, 1H), 3.17 (m, 1H), 2.76 (dd, *J* = 17.5, 6.7 Hz, 1H) ppm. ^{13}C{1H}NMR (151 MHz, DMSO-d_6) δ 177.8, 176.3, 175.5, 157.8, 156.1, 136.1, 133.8, 133.2, 130.9, 128.8, 128.1, 127.3, 121.5, 119.3, 113.0, 47.2, 4.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{14}NO_4$: 320.0923, found: 320.0916.

(S)-1-(4-Ethylphenyl)-3-(4-oxo-4H-chromen-5-yl)pyrrolidine-2,5-dione. The product **3m** was obtained as a white solid (59.7 mg, 86%) after purification through a chromatography column (elution: 40% EtOAc in petroleum ether), mp 201–202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 5.9 Hz, 1H), 7.65 (t, *J* = 8.0 Hz,1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.33 – 7.29 (m, 3H), 6.32 (d, *J* = 5.9 Hz, 1H), 4.28 (m, 1H), 3.18 (m, 1H), 2.97 (m, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H) ppm. ^{13}C{1H}NMR (151 MHz, $CDCl_3$) δ 178.2, 176.2, 175.8, 158.4, 154.4, 144.5, 135.8, 133.4, 130.8, 130.3, 128.6, 126.9, 122.1, 119.6, 113.8, 48.4, 37.4, 28.6, 15.4 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{18}NO_4$: 348.1236, found: 348.1228.

(S)-1-(4-Bromophenyl)-3-(4-oxo-4H-chromen-5-yl)pyrrolidine-2,5-dione. The product **3n** was obtained as a white solid (70.8 mg, 89%) after purification through a chromatography column (elution: 40% EtOAc in petroleum ether), mp 184–185 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.32 (d, J = 5.9 Hz, 1H), 7.2 (t, J = 7.2 Hz, 1H), 7.75 – 7.73 (m, 2H), 7.70 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 7.0 Hz, 1H), 7.34 (d, J = 8.5 Hz, 2H), 6.39 (d, J = 5.9 Hz, 1H), 4.61 (m, 1H), 3.18 (dd, J = 16.1, 8.8 Hz, 1H), 2.75 (dd, J = 17.6, 6.7 Hz, 1H) ppm. ^{13}C{1H}NMR (151 MHz, $CDCl_3$) δ 178.2, 175.8, 175.2, 158.4, 154.5, 135.4, 133.4, 132.2, 131.8, 130.8, 128.7, 122.2, 121.9, 119.7, 113.6, 48.25, 37.3 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{13}BrNO_4$: 398.0028, found: 398.0024.

Ethyl-3-(9-oxo-9H-xanthen-1-yl)pyrrolidine-2,5-dione. The product **3o** was obtained as a white solid (52.7 mg, 82%) after purification through a chromatography column (elution: 25% EtOAc in petroleum ether), mp 230–231 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, J = 5.6 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.52 (d, J = 8.2 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.19 (m, 1H), 4.12 (m, 1H), 3.73 (q, J = 7.1 Hz, 2H), 3.07 (m, 1H), 2.86 (m, 1H), 1.34 (m, 3H) ppm. ^{13}C{1H}NMR (151 MHz, $CDCl_3$) δ 177.80, 177.41, 176.49, 158.00, 155.21, 137.01, 135.02, 134.37, 130.04, 128.39, 126.88, 124.09, 122.06, 119.21, 117.47, 48.71, 37.27, 34.09, 12.97 ppm. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{15}NO_4$: 344.0898, found: 344.0896.

1-Ethyl-3-(4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4a** was obtained as a white solid (49.5 mg, 92%) after purification through a chromatography column (elution: 10% EtOAc in petroleum ether), mp 159–160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 6.0 Hz, 1H), 7.71 –7.67 (m, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.22 (d, J = 7.3 Hz, 1H), 6.42 (s, 1H), 6.28 (d, J = 6.0 Hz, 1H), 3.63

(q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 177.0, 170.5, 169.3, 157.0, 154.8, 149.4, 133.2, 129.5, 126.9, 124.5, 123.4, 120.5, 113.7, 33.2, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}NO_4$: 270.0766, found: 270.0762.

1-*Ethyl-3-(2-methyl-4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione.* The product **4b** was obtained as a white solid (53.8 mg, 95%) after purification through a chromatography column (elution: 13% EtOAc in petroleum ether), mp 182–183 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.65 (t, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 7.3 Hz, 1H), 6.40 (s, 1H), 6.10 (s, 1H), 3.62 (q, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 177.6, 170.5, 169.3, 165.8, 157.0, 149.6, 132.8, 129.2, 126.6, 124.3, 122.2, 120.1, 111.3, 33.1, 20.3, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}NO_4$: 284.0923, found: 284.0916.

1-Ethyl-3-(4-oxo-2-phenyl-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4c** was obtained as a white solid (51.8 mg, 75%) after purification through a chromatography column (elution: 8% EtOAc in petroleum ether), mp 235–236 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.3 Hz, 2H), 7.76 – 7.70 (m, 2H), 7.58 – 7.53 (m, 3H), 7.27 (d, *J* = 6.9 Hz, 1H), 6.78 (s, 1H), 6.48 (s, 1H), 3.68 (t, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 177.9, 170.6, 169.4, 163.1, 156.8, 149.5, 133.2, 131.9, 131.3, 129.4, 129.2, 126.9, 126.4, 124.5, 122.6, 120.4, 108.3, 33.2, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NO_4$: 346.1079, found: 346.1073.

1-Ethyl-3-(3-methyl-4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4d** was obtained as a white solid (52.1 mg, 92%) after purification through a chromatography column (elution: 10% EtOAc

in petroleum ether), mp 193–194 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 6.41 (s, 1H), 3.65 (q, *J* = 7.2 Hz, 2H), 1.95 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 177.8, 170.5, 169.4, 157.2, 151.3, 149.9, 132.7, 129.4, 126.5, 124.3, 122.1, 121.6, 120.4, 33.2, 14.0, 11.1 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}NO_4$: 284.0923, found: 284.0915.

3-(3-Bromo-4-oxo-4H-chromen-5-yl)-1-ethyl-1H-pyrrole-2,5-dione. The product **4e** was obtained as a white solid (63.7 mg, 92%) after purification through a chromatography column (elution: 8% EtOAc in petroleum ether), mp 214–215 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.75 (t, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 6.45 (s, 1H), 3.66 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 171.8, 170.4, 169.2, 156.7, 153.4, 148.8, 133.6, 130.0, 127.6, 125.1, 121.5, 120.4, 111.3, 33.4, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{11}BrNO_4$: 347.9872, found: 347.9865.

1-Ethyl-3-(4-oxo-3-phenyl-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4f** was obtained as a white solid (64.2 mg, 93%) after purification through a chromatography column (elution: 6% EtOAc in petroleum ether), mp 158–159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.73 – 7.70 (m, 1H), 7.62 – 7.61 (m, 1H), 7.48 – 7.46 (m, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.27 – 7.25 (m, 1H), 6.43 (s, 1H), 3.65 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 176.0, 170.6, 169.4, 156.8, 152.5, 149.8, 133.1, 131.3, 130.0, 129.0, 128.6, 128.4, 127.1, 126.3, 124.2, 123.2, 120.5 33.3, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NO_4$: 346.1079, found: 346.1072.

1-Ethyl-3-(4-oxo-3-o-tolyl-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4g** was obtained as a white solid (66.8 mg, 93%) after purification through a chromatography column (elution: 8% EtOAc in petroleum ether), mp 165–166 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.69 (t, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 6.38 (s, 1H), 3.56 (q, *J* = 7.1 Hz, 2H), 2.18 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 175.9, 170.6, 169.4, 157.0, 153.0, 149.7, 138.2, 133.1, 131.0, 130.4, 130.3, 130.0, 128.9, 127.4, 127.0, 125.9, 124.0, 123.0, 120.5, 33.2, 20.0, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{18}NO_4$: 360.1236, found: 360.1228.

3-(3-(3-Chlorophenyl)-4-oxo-4H-chromen-5-yl)-1-ethyl-1H-pyrrole-2,5-dione. The product **4h** was obtained as a white solid (69.8 mg, 92%) after purification through a chromatography column (elution: 8% EtOAc in petroleum ether), mp 195–196 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.75 – 7.71 (m, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.47 (d, 1H), 7.38 – 7.35 (m, 1H), 7.34 – 7.33 (m, 2H), 7.28 – 7.27 (m, 1H), 6.44 (s, 1H), 3.65 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 175.6, 170.5, 169.3, 156.7, 152.8, 149.6, 134.4, 133.3, 133.0, 130.0, 129.8, 128.9, 128.5, 127.3, 127.2, 125.1, 124.4, 123.1, 120.5, 33.3, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{15}ClNO_4$: 380.0690, found: 380.0684.

1-Ethyl-3-(6-fluoro-4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4i** was obtained as a white solid (45.4 mg, 79%) after purification through a chromatography column (elution: 12% EtOAc in petroleum ether), mp 193–194 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 5.9 Hz, 1H), 7.60 – 7.58 (m, 1H), 7.50 (t, *J* = 8.7 Hz, 1H), 6.57 (s, 1H), 6.28 (d, *J* = 5.9 Hz, 1H), 3.66 (q, *J* = 7.2 Hz, 2H),

1.27 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 176.8 (d, J = 1.9 Hz), 170.2, 169.1, 156.6 (d, J = 249.7 Hz), 154.9, 153.2 (d, J = 1.3 Hz), 141.1, 127.7 (d, J = 2.3 Hz), 124.3 (d, J = 1.3 Hz), 121.9 (d, J = 1.5 Hz), 121.9 (d, J = 32.3 Hz), 114.9 (d, J = 17.2 Hz), 113.2, 33.3, 14.0 ppm. ^{19}F NMR (471 MHz,) δ -116.10 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{11}FNO_4$: 288.0672, found: 288.0664.

1-Ethyl-3-(7-methyl-4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4j** was obtained as a white solid (51.5 mg, 91%) after purification through a chromatography column (elution: 10% EtOAc in petroleum ether), mp 212–213 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 6.0 Hz, 1H), 7.35 (s, 1H), 7.04 (s, 1H), 6.40 (s, 1H), 6.24 (d, J = 5.9 Hz, 1H), 3.63 (q, J = 7.2 Hz, 2H), 2.47 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 176.9, 170.5, 169.3, 157.15, 154.6, 149.5, 144.6, 129.2, 128.3, 124.4, 121.2, 120.1, 113.6, 33.1, 21.6, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}NO_4$: 284.0923, found: 284.0915.

1-Ethyl-3-(7-methoxy-4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4k** was obtained as a white solid (53.8 mg, 90%) after purification through a chromatography column (elution: 13% EtOAc in petroleum ether), mp 222–223 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 6.0 Hz, 1H), 6.94 (d, J = 2.4 Hz, 1H), 6.81 (d, J = 2.4 Hz, 1H), 6.41 (s, 1H), 6.23 (d, J = 6.0 Hz, 1H), 3.92 (s, 3H), 3.65 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 176.4, 170.5, 169.2, 163.1, 158.9, 154.4, 149.2, 130.9, 124.6, 117.3, 116.5, 113.6, 102.1, 56.1, 33.2, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}NO_5$: 300.0872, found: 300.0865.

5-(1-Ethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)-4-oxo-4H-chromen-7-yl acetate. The product **4l** was obtained as a white solid (65.4 mg, 95%) after purification through a chromatography column (elution: 12% EtOAc in petroleum ether), mp 158–159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 6.0 Hz, 1H), 7.41 (d, *J* = 2.2 Hz, 1H), 7.02 (d, *J* = 2.2 Hz, 1H), 6.45 (s, 1H), 6.28 (d, *J* = 6.0 Hz, 1H), 3.65 (q, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 176.4, 170.2, 168.9, 168.2, 157.6, 154.9, 153.6, 148.5, 130.9, 125.1, 121.2, 121.1, 113.8, 113.0 33.2, 21.1, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{14}NO_6$: 328.0821, found: 328.0814.

1-Ethyl-3-(7-fluoro-4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4m** was obtained as a white solid (54.0 mg, 94%) after purification through a chromatography column (elution: 10% EtOAc in petroleum ether), mp 146–147 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 6.0 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.01 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.46 (s, 1H), 6.28 (d, *J* = 6.0 Hz, 1H), 3.65 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 171.4 (s), 165.3 (s), 164.0 (s), 159.6 (d, *J* = 256.9 Hz), 153.4 (d, *J* = 13.6 Hz), 150.1 (s), 143.5 (d, *J* = 1.6 Hz), 127.4 (d, *J* = 10.7 Hz), 120.4 (s), 115.7 (d, *J* = 2.6 Hz), 111.1 (d, *J* = 24.1 Hz), 109.1 (s), 102.0 (d, *J* = 24.6 Hz), 28.5, 9.2 ppm; ^{19}F NMR (471 MHz,) δ -107.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{11}FNO_4$: 288.0672, found: 288.0665.

3-(7-Chloro-4-oxo-4H-chromen-5-yl)-1-ethyl-1H-pyrrole-2,5-dione. The product **4n** was obtained as a white solid (50.3 mg, 83%) after purification through a chromatography column (elution: 10% EtOAc in petroleum ether), mp 205–206 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 6.0 Hz, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.22 (d, *J* = 1.9 Hz, 1H), 6.46 (s, 1H), 6.28 (d, *J* = 6.0 Hz, 1H), 3.64 (q, *J* = 7.2 Hz, 2H),

1.25 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 176.2, 170.0, 168.8, 157.2, 154.8, 148.0, 139.2, 131.0, 127.4, 125.2, 122.0, 120.2, 114.0, 33.3, 13.9 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{11}ClNO_4$: 304.0377, found: 304.0370.

3-(7-Bromo-4-oxo-4H-chromen-5-yl)-1-ethyl-1H-pyrrole-2,5-dione. The product **4o** was obtained as a white solid (58.1 mg, 84%) after purification through a chromatography column (elution: 7% EtOAc in petroleum ether), mp 187–188 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 6.0 Hz, 1H), 7.76 (s, 1H), 7.37 (s, 1H), 6.46 (s, 1H), 6.29 (d, J = 6.0 Hz, 1H), 3.64 (q, J = 7.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 176.3, 170.0, 168.8, 156.9, 154.7, 147.8, 130.9, 130.0, 127.2, 125.1, 123.2, 122.3, 114.0, 33.2, 13.9 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{11}BrNO_4$: 347.9872, found: 347.9865.

1-Ethyl-3-(8-methyl-4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4p** was obtained as a white solid (52.6 mg, 93%) after purification through a chromatography column (elution: 10% EtOAc in petroleum ether), mp 157–158 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 5.8 Hz, 1H), 7.53 (d, J = 7.4 Hz, 1H), 7.12 (d, J = 7.4 Hz, 1H), 6.38 (s, 1H), 6.29 (d, J = 5.8 Hz, 1H), 3.63 (q, J = 7.1 Hz, 2H), 2.49 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 177.4, 170.6, 169.4, 155.5, 154.6, 149.8, 134.0, 130.4, 126.9, 126.4, 124.0, 123.3, 113.6, 33.1, 15.9, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}NO_4$: 284.0923, found:284.0915.

3-(8-Chloro-4-oxo-4H-chromen-5-yl)-1-ethyl-1H-pyrrole-2,5-dione. The product **4q** was obtained as a white solid (51.5 mg, 85%) after purification through a chromatography column (elution: 7% EtOAc in

petroleum ether), mp 156–157 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 5.9 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.43 (s, 1H), 6.34 (d, *J* = 5.9 Hz, 1H), 3.63 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 176.5, 170.2, 169.0, 154.8, 152.8, 148.6, 133.5, 128.0, 126.7, 125.7, 124.8, 124.6, 114.0, 33.2, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{11}ClNO_4$: 304.0377, found: 304.0370.

3-(4-Oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4r** was obtained as a white solid (29.9 mg, 62%) after purification through a chromatography column (elution: 50% EtOAc in petroleum ether), mp 167–168 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.95 (brs, 1H), 8.31 (d, *J* = 5.9 Hz, 1H), 7.87 (t, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 7.3 Hz, 1H), 6.70 (s, 1H), 6.33 (d, *J* = 5.9 Hz, 1H) ppm. ^{13}C{1H}NMR (151 MHz, DMSO-d_6) δ 176.3, 172.0, 170.5, 156.6, 156.3, 149.6, 133.7, 128.8, 127.3, 125.3, 122.5, 120.4, 112.8 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_8NO_4$: 242.0453, found: 242.0447.

1-Methyl-3-(4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4s** was obtained as a white solid (45.4 mg, 89%) after purification through a chromatography column (elution: 13% EtOAc in petroleum ether), mp 216–217 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 5.9 Hz, 1H), 7.71 (t, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 6.46 (s, 1H), 6.30 (d, *J* = 5.9 Hz, 1H), 3.10 (s, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 177.2, 170.7, 169.5, 157.1, 154.9, 149.6, 133.2, 129.4, 127.0, 124.6, 123.5, 120.6, 113.8, 24.1 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{10}NO_4$: 256.0610, found: 256.0603.

1-Tert-butyl-3-(4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4t** was obtained as a white solid (41.0 mg, 69%) after purification through a chromatography column (elution: 8% EtOAc in petroleum ether), mp 100–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 6.0 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 6.29 (s, 2H), 1.63 (s, 9H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 177.0, 171.8, 170.6, 157.0, 154.7, 148.6, 133.1, 129.7, 127.0, 124.7, 123.5, 120.3, 113.8, 57.4, 29.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}NO_4$: 298.1079, found: 298.1073.

1-Cyclohexyl-3-(4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4u** was obtained as a white solid (56.8 mg, 88%) after purification through a chromatography column (elution: 7% EtOAc in petroleum ether), mp 120–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 6.0 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.57 – 7.54 (m, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 6.37 (s, 1H), 6.28 (d, *J* = 6.0 Hz, 1H), 4.00 – 3.92 (m, 1H), 2.16 – 2.05 (m, 2H), 1.83 – 1.77 (m, 4H), 1.63 (d, *J* = 12.2 Hz, 1H), 1.36 – 1.13 (m, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 177.0, 170.7, 169.4, 157.0, 154.8, 148.9, 133.1, 129.6, 126.9, 124.4, 123.4, 120.4, 113.7, 51.1, 30.0, 26.0, 25.2 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{18}NO_4$: 324.1236, found: 324.1229.

Methyl 3-(2,5-dioxo-3-(4-oxo-4H-chromen-5-yl)-2,5-dihydro-1H-pyrrol-1-yl)propanoate. The product **4v** was obtained as a white solid (57.5 mg, 88%) after purification through a chromatography column (elution: 17% EtOAc in petroleum ether), mp 130–131 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 6.0 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.59 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.24 (dd, *J* = 7.3, 0.8 Hz, 1H), 6.45 (s, 1H), 6.29 (d, *J* = 6.0 Hz, 1H), 3.91 (t, *J* = 7.4 Hz, 2H), 3.68 (s, 3H), 2.72 (t, *J* = 7.4 Hz, 2H) ppm.

$^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 177.0, 171.4, 170.1, 169.0, 157.0, 154.9, 149.6, 133.3, 129.2, 126.98, 124.6, 123.4, 120.7, 113.7, 51.9, 33.9, 33.0 ppm. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{13}NO_6Na$: 350.0641, found: 350.0633.

1-Benzyl-3-(4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4w** was obtained as a white solid (57.6 mg, 87%) after purification through a chromatography column (elution: 10% EtOAc in petroleum ether), mp 203–204 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 5.8 Hz, 1H), 7.74 (t, J = 7.8 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.48 (d, J = 7.3 Hz, 2H), 7.38 (t, J = 7.2 Hz, 2H), 7.29 (dd, J = 18.2, 7.2 Hz, 2H), 6.52 (s, 1H), 6.36 (d, J = 5.8 Hz, 1H), 4.83 (s, 2H) ppm. $^{13}C\{1H\}$NMR (151 MHz, $CDCl_3$) δ 177.2, 170.4, 169.3, 157.2, 155.0, 149.7, 136.7, 133.4, 129.4, 128.8, 128.4, 127.8, 127.2, 124.7, 123.6, 120.8, 113.9, 41.9 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{14}NO_4$: 332.0923, found: 332.0915.

3-(4-Oxo-4H-chromen-5-yl)-1-phenyl-1H-pyrrole-2,5-dione. The product **4x** was obtained as a light yellow solid (49.4 mg, 78%) after purification through a chromatography column (elution: 13% EtOAc in petroleum ether), mp 195–196 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 6.0 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.61 (d, J = 8.5 Hz, 1H), 7.47 – 7.46 (m, 4H), 7.36 – 7.34 (m, 1H), 7.31 (d, J = 7.3 Hz, 1H), 6.60 (s, 1H), 6.31 (d, J = 6.0 Hz, 1H) ppm. $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 177.1, 169.4, 168.2, 157.1, 155.0, 149.5, 133.3, 131.9, 129.2, 129.0, 127.7, 127.0, 126.4, 124.5, 123.5, 120.8, 113.8 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{12}NO_4$: 318.0766, found: 318.0760.

1-(2-Bromophenyl)-3-(4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4y** was obtained as

a white solid (67.8 mg, 86%) after purification through a chromatography column (elution: 13% EtOAc in petroleum ether), mp 199–200 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 6.0 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.61 (d, J = 8.5 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.34 (d, J = 7.3 Hz, 1H), 7.32 – 7.28 (m, 1H), 6.63 (s, 1H), 6.32 (d, J = 6.0 Hz, 1H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 177.1, 168.5, 167.5, 157.0, 154.9, 149.9, 133.5, 133.3, 131.5, 131.3, 130.7, 129.0, 128.4, 127.2, 124.8, 123.5, 120.84, 113.8 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{11}BrNO_4$: 395.9872, found: 395.9868.

1-(4-Ethylphenyl)-3-(4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4z** was obtained as a white solid (54.5 mg, 79%) after purification through a chromatography column (elution: 10% EtOAc in petroleum ether), mp 181–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 6.0 Hz, 1H), 7.72 (t, J = 7.9 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.37 – 7.35 (m, 2H), 7.32 – 7.28 (m, 3H), 6.59 (s, 1H), 6.31 (d, J = 6.0 Hz, 1H), 2.67 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 177.0, 169.5, 168.3, 157.1, 154.9, 149.4, 143.9, 133.3, 129.4, 129.3, 128.5, 127.0, 126.4, 124.5, 123.5, 120.7, 113.8, 28.6, 15.5 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NO_4$: 346.1079, found: 346.1072.

1-(4-Ecetylphenyl)-3-(4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4aa** was obtained as an amorphous solid (52.4 mg, 73%) after purification through a chromatography column (elution: 10% EtOAc in petroleum ether). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 (d, J = 6.0 Hz, 1H), 8.10 (d, J = 8.7 Hz, 2H), 7.96 – 7.92 (m, 1H), 7.87 – 7.85 (m, 1H), 7.56 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 7.2 Hz, 1H), 7.10 (s, 1H), 6.40 (d, J = 6.0 Hz, 1H), 2.61 (s, 3H) ppm. ^{13}C{1H}NMR (126 MHz, DMSO-d_6) δ 197.1, 176.5, 168.9, 167.7, 156.8, 156.4, 149.1, 135.9, 135.4, 133.9, 129.0, 128.3, 127.4, 125.8, 125.0, 122.6,

120.9, 112.9, 26.7 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{14}NO_5$:360.0872, found: 360.0865.

1-(4-Bromophenyl)-3-(4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4ab** was obtained as a light yellow solid (59.1 mg, 75%) after purification through a chromatography column (elution: 8% EtOAc in petroleum ether), mp 213–214 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 6.0 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.64 – 7.62 (m, 1H), 7.59 – 7.57 (m, 2H), 7.39 – 7.37 (m, 2H), 7.31 (d, J = 7.2 Hz, 1H), 6.60 (s, 1H), 6.33 (d, J = 6.0 Hz, 1H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 177.1, 168.9, 167.8, 157.1, 155.0, 149.6, 133.3, 132.1, 131.1, 129.0, 127.7, 127.0, 124.5, 123.5, 121.3, 120.9, 113.8 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{11}BrNO_4$: 395.9872, found: 395.9868.

1-(4-Nitrophenyl)-3-(4-oxo-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **4ac** was obtained as a light yellow solid (44.2 mg, 61%) after purification through a chromatography column (elution: 17% EtOAc in petroleum ether), mp 158–159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 – 8.41 (m, 1H), 8.40 – 8.39 (m, 1H), 8.37 (d, J = 6.0 Hz, 1H), 7.97 – 7.94 (m, 1H), 7.87 (dd, J = 8.5, 1.1 Hz, 1H), 7.75 – 7.72 (m, 2H), 7.50 (dd, J = 7.3, 1.0 Hz, 1H), 7.14 (s, 1H), 6.40 (d, J = 6.0 Hz, 1H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 177.2, 168.3, 167.4, 157.1, 155.2, 150.0, 146.0, 137.8, 133.5, 128.5, 127.0, 125.7, 124.6, 124.4, 123.4, 121.2, 113.7 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{11}N_2O_6$: 363.0617, found: 363.0611.

(E)-Ethyl 3-(4-oxo-4H-chromen-5-yl)acrylate. The product **4ad** was obtained as a white solid (39.0 mg, 80%) after purification through a chromatography column (elution: 10% EtOAc in petroleum ether),

mp 119–120 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, *J* = 15.9 Hz, 1H), 7.78 (d, *J* = 5.9 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 6.30 (d, *J* = 5.9 Hz, 1H), 6.21 (d, *J* = 15.9 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 178.7, 166.4, 157.5, 154.1, 144.6, 137.3, 133.0, 124.8, 122.4, 121.7, 119.6, 114.3, 60.6, 14.3 ppm. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{12}O_4Na$: 267.0633, found: 267.0627.

(E)-Butyl 3-(4-oxo-4H-chromen-5-yl)acrylate. The product **4ae** was obtained as an amorphous solid (44.1 mg, 81%) after purification through a chromatography column (elution: 6% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.89 (d, *J* = 16.0 Hz, 1H), 8.24 (d, *J* = 5.9 Hz, 1H), 7.75 (t, *J* = 8.0 Hz, 1H), 7.67 – 7.64 (m, 2H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.33 (d, *J* = 5.9 Hz, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 1.64 – 1.58 (m, 2H), 1.41 – 1.34 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C{1H}NMR (126 MHz, DMSO-d_6) δ 178.6, 166.4, 157.5, 156.3, 144.5, 135.9, 134.0, 125.4, 121.9, 121.3, 120.7, 114.0, 64.2, 30.7, 19.1, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{16}O_4Na$: 295.0946, found: 295.0939.

(E)-Methoxyethyl 3-(4-oxo-4H-chromen-5-yl)acrylate. The product **4af** was obtained as an amorphous solid (49.3 mg, 90%) after purification through a chromatography column (elution: 17% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (d, *J* = 15.9 Hz, 1H), 7.79 (d, *J* = 5.9 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 6.31 (d, *J* = 5.9 Hz, 1H), 6.26 (d, *J* = 15.9 Hz, 1H), 4.41 – 4.34 (m, 2H), 3.73 – 3.62 (m, 2H), 3.42 (s, 3H) ppm. ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 178.8, 166.4, 157.5, 154.3, 145.3, 137.1, 133.1, 124.9, 122.4, 121.2, 119.8, 114.2, 70.5, 63.7, 59.1 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}O_5$: 297.0739, found: 297.0732.

(E)-5-(2-(Phenylsulfonyl)vinyl)-4H-chromen-4-one. The product **4ag** was obtained as a light yellow solid (58.0 mg, 93%) after purification through a chromatography column (elution: 12% EtOAc in petroleum ether), mp 149–150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (d, *J* = 15.3 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 2H), 7.81 (d, *J* = 5.9 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 15.3 Hz, 1H), 6.32 (d, *J* = 5.9 Hz, 1H) ppm. ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 178.4, 157.4, 154.6, 143.9, 140.5, 134.8, 133.4, 133.3, 130.0, 129.3, 128.0, 125.1, 122.5, 120.5, 114.1 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{13}O_4S$: 313.0535, found: 313.0527.

1-Ethyl-3-(4-oxo-3-(phenylselanyl)-4H-chromen-5-yl)-1H-pyrrole-2,5-dione. The product **5a** was obtained as a white solid (54.3 mg, 64%) after purification through a chromatography column (elution: 12% EtOAc in petroleum ether), mp 172–173 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.59 (s, 1H), 7.93 (dd, *J* = 8.5, 7.3 Hz, 1H), 7.85 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.46 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.43 – 7.41 (m, 2H), 7.32 – 7.26 (m, 3H), 6.85 (s, 1H), 3.48 (q, *J* = 7.1 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 174.8, 170.5, 169.2, 156.9, 154.6, 149.0, 134.0, 133.2, 129.8, 129.6, 128.3, 127.6, 127.2, 124.6, 121.5, 120.4, 119.2, 33.3, 13.9 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NO_4Se$: 426.0245, found: 426.0238.

(E)-Tert-butyl3-(5-(1-ethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)-4-oxo-4H-chromen-3-yl)acrylate. The product **5b** was obtained as a white solid (44.2 mg, 56%) after purification through a chromatography column (elution: 12% EtOAc in petroleum ether), mp 135–136 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.92 (s, 1H), 7.94 – 7.91 (m, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.46 (d, *J* = 7.1 Hz, 1H),

7.33 (d, J = 16.0 Hz, 1H), 6.90 (d, J = 16.0 Hz, 1H), 6.86 (s, 1H), 3.53 (q, J = 7.1 Hz, 2H), 1.46 (s, 9H), 1.14 (t, J = 7.1 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 175.5, 170.4, 169.2, 166.3, 156.1, 156.0, 149.4, 133.4, 133.3, 129.9, 127.5, 124.5, 124.5, 122.8, 120.4, 120.4, 80.6, 33.3, 28.123, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{22}NO_6$: 396.1447, found: 396.1444.

4-(3-(3,6-Dioxocyclohexa-1,4-dienyl)-4-oxo-4H-chromen-5-yl)-1-ethyl-1H-pyrrole-2,5-dione. The product **5c** was obtained as a yellow solid (39.0 mg, 52%) after purification through a chromatography column (elution: 12% EtOAc in petroleum ether), mp 170–171 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 8.54 (s, 1H), 7.97 – 7.93 (m, 1H), 7.89 (dd, J = 8.5, 1.2 Hz, 1H), 7.47 (dd, J = 7.1, 1.2 Hz, 1H), 7.05 (d, J = 2.6 Hz, 1H), 7.00 (d, J = 10.2 Hz, 1H), 6.93 (dd, J = 10.2, 2.6 Hz, 1H), 6.85 (s, 1H), 3.49 (q, J = 7.1 Hz, 2H), 1.10 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$NMR (126 MHz, DMSO-d_6) δ 187.3, 185.0, 174.1, 170.3, 168.9, 157.1, 155.8, 148.7, 138.2, 137.1, 136.3, 134.8, 134.3, 129.1, 128.0, 125.0, 121.7, 120.6, 117.5, 32.4, 13.7 ppm. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{13}NO_6Na$: 398.0641, found: 398.0637.

ASSOCIATED CONTENT

Supporting information contains: optimization of reaction conditions, study on reaction mechanism, X-ray structure of **4a**, copies of ^1H, ^{13}C NMR spectra of synthesized substituted chromones, copies of ^1H, ^{13}C and ^{19}F NMR spectra of products **3, 4** and **5**. The supporting information is available free of charge on the ACS Publications website at DOI:

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Notes

The authors declare no competing financial interest.

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