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Note

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Diastereoselective Synthesis of Rauhut-Currier-Type Adducts *via* An Unexpected *α*-Addition of *α,β*-Unsaturated *γ*-Butyrolactams to Coumarin Derivatives

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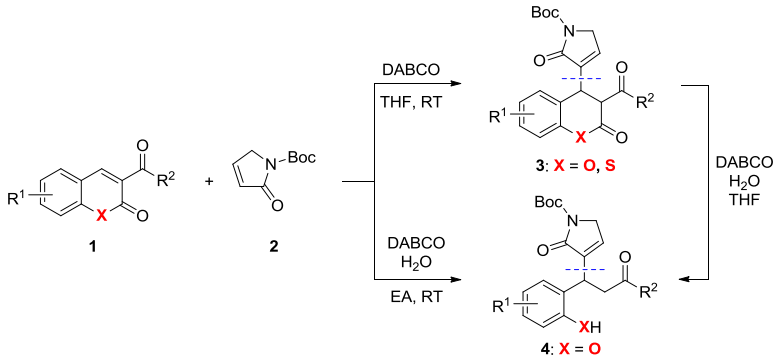
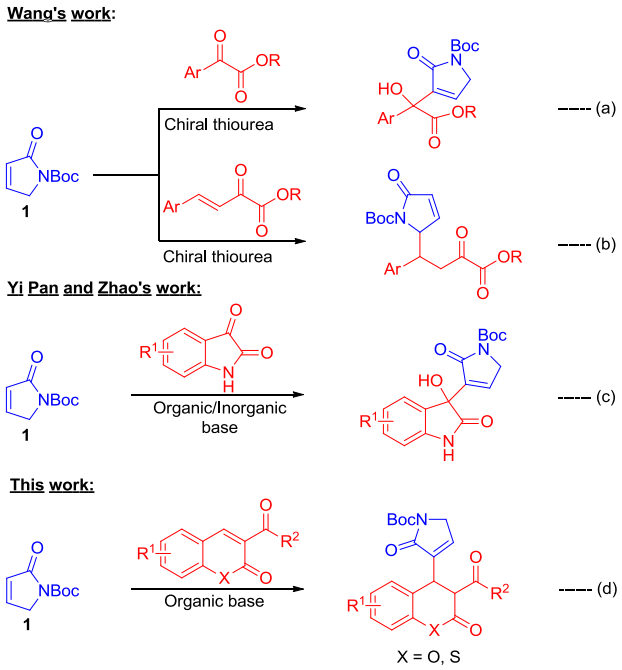


ABSTRACT: A novel, base-catalyzed and highly diastereoselective direct Michael addition-isomerization sequence is presented for the efficient synthesis of Rauhut-Currier-type adducts. An unexpected *α*-addition of *γ*-butyrolactam onto the 3-acyl coumarin derivatives was observed rather than the *γ*-addition, which is more common. The adducts could further undergo hydrolysis/decarboxylation to generate the products which are equivalent to those obtained by *α*-addition of *γ*-butyrolactam onto the corresponding chalcones.

A wide range of biologically active natural products are found to bear the nitrogen heterocycles in their core structures.[1] Among such heterocycles, the pyrrolidin-2-one ring systems are found to be the common entities.[2] For the synthesis of these ring systems, *α,β*-unsaturated *γ*-butyrolactams have served as common precursors in recent times. Although there are many reports on the *γ*-functionalization of *α,β*-unsaturated *γ*-butyrolactams with various electrophiles,[3] there are relatively few instances where the *α*-[4] or *β*-position[5] of these substrates is exploited for chemical transformations.

In 1994, Royer et. al. first reported the mono- and bis- *α*-alkylation of *α,β*-unsaturated *γ*-butyrolactams in presence of LDA.[4a] Later in 2013, Wang et. al. synthesized the Morita-Baylis-Hillman (MBH)-type adducts by a direct asymmetric aldol addition-isomerization reaction of *α,β*-unsaturated *γ*-butyrolactams with aryl *α*-ketoesters using a chiral thiourea catalyst (Scheme 1a).[4b] Following that, two groups have independantly reported the synthesis of MBH-type adducts from *α,β*-unsaturated *γ*-butyrolactams and isatins (Scheme 1c).[4c,4d] Very recently, Shibasaki et. al. reported the direct asymmetric Mannich-type reaction of *α,β*-unsaturated *γ*-butyrolactams with ketimines resulting in aza-MBH-type products.[4f] However, till date, there have been no reports on the 1,4-addition of *α,β*-unsaturated *γ*-butyrolactams on to the Michael acceptors resulting in Rauhut-Currier-type (RC) adducts. An attempt towards such transformation by Wang et. al. resulted in *γ*-addition leading to the vinylogous Michael addition products (Scheme 1b).[4b]



Scheme 1. *α*-functionalization of *α,β*-unsaturated *γ*-butyrolactams.

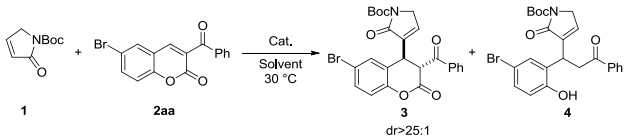
On the other hand, 3,4-dihydrocoumarin ring systems are the common motifs that are found in natural products and biologically active compounds.[6] But the coumarin derivatives have been infrequently used as Michael acceptors for the synthesis of such systems due to their reluctance in losing aromatic-like nature, hence requiring harsh reaction conditions.[7] Herein, we report an unprecedented *α*-addition of *α,β*-unsaturated *γ*-butyrolactams onto the 3-acyl coumarins for the generation of RC-type adducts (Scheme 1d). Further, these adducts could be subjected to hydrolysis/decarboxylation resulting in the products which are equivalent to those obtained by the *α*-addition of *α,β*-unsaturated *γ*-butyrolactams onto the chalcones, whose synthesis using alternative approaches appeared to be a challenging task.

We began our study towards the synthesis of RC adducts **3** by treating *α,β*-unsaturated *γ*-butyrolactam (**1**) with 3-acyl coumarin (**2aa**) in presence of triphenylphosphine, an ideal nucleophile for RC reaction (Table 1, entry 1). Unfortunately, the reaction did not proceed and the starting materials could be recovered after 95 h. So we tried a stronger nucleophile, PBu_3

which resulted in trace amounts of the expected product (entry 2). We then switched on to other nucleophilic bases and found that the results were optimistic with moderate yield of expected product as a single diastereomer (entries 3-7), with DABCO giving the best results (entry 7). It was observed that product **3** was susceptible towards hydrolysis and subsequent decarboxylation, which is a common phenomenon observed with β-keto acids. The structures of **3** and **4** were also confirmed by X-ray crystallographic analysis.[8]

A quick solvent screening revealed THF as ideal solvent to carry out the reaction (entry 9). In order to prevent the hydrolysis of product **3**, we then carried out the reaction in anhydrous solvents which increased the yield of the product **3** to a great extent (entries 10-12). Re-checking the efficiency of previously tested nucleophilic bases under anhydrous conditions confirmed that DABCO was still the best option (entry 12). Performing the reaction in presence of molecular sieves was not favorable (entry 15). Hence the optimal conditions for carrying out α-functionalization of **1** onto **2** were as established in entry 12, using 20 mol % of DABCO in anhydrous THF.

Table 1. Optimization of reaction conditions.[a]



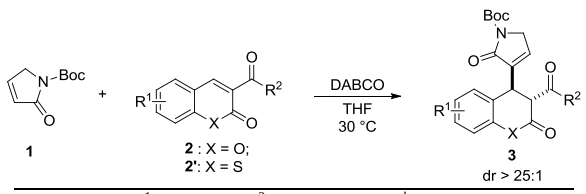
entry	cat.	solvent	time (h)	**3**/**4**, yield (%)[b]
1	PPh_3	DCM	95	NR[c]
2	PBu_3	DCM	3	10/0
3	DBU	DCM	57	48/0
4	Et_3N	DCM	6	64/9
5	DMAP	DCM	10	67/13
6	DPGN	DCM	12	55/16
7	DABCO	DCM	10	64/21
8	DABCO	Et_2O	8	72/2
9	DABCO	THF	8	74/11
10	DABCO	DCM[d]	3	73/12
11	DABCO	Toluene[d]	4	76/3
12	DABCO	THF[d]	5	99/0

13	DMAP	THF[d]	12	79/11
14	Et_3N	THF[d]	5	62/0
15[e]	DABCO	THF	5	67/0
16	K_2CO_3	THF[d]	9	10/0
17	K_2CO_3	THF[f]	24	60/0

[a] Unless otherwise specified, all the reactions were carried out using **1** (0.12 mmol), **2aa** (0.1 mmol), and catalyst (20 mol %) in the indicated solvent (0.2 mL) at 30 °C. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture using Ph_3CH as an internal standard. [c]No reaction. [d]Anhydrous solvent was used. [e]4 Å molecular sieves were used. [f]0.1 mL H_2O was added to the reaction mixture. DPGN = *N*,*N*-Diphenylguanidinium nitrate.

Under the optimized conditions, the scope of this reaction was studied by varying the substituents on coumarin ring as well as the acyl moiety and the results are presented in table 2. The reaction was highly diastereoselective and formation of a single diastereomer could be observed in all cases. Both the electron-withdrawing and electron-donating R^1 substituents on coumarin ring performed well resulting in the products in good to excellent yields (entries 1-4). However, varying the R^2 substitution of acyl moiety had an impact on the solubility of substrates and the reaction had to be carried out in increased dilutions or mixed solvents in some cases, which resulted in slightly varying results. Surprisingly, a 2-bromo substitution on the acyl group inhibited the reaction and could not furnish the product (entry 14). In contrast, a 2-naphthyl substitution or the heteroaromatic thienyl substitution could be tolerated well resulting in the products in good yields (entries 15 and 16). Even the presence of aliphatic cyclohexyl group resulted in the expected product albeit in the enolic form in slightly lower yield (entry 17).

Table 2. Substrate scope for the α-functionalization of **1** with **2**.[a]



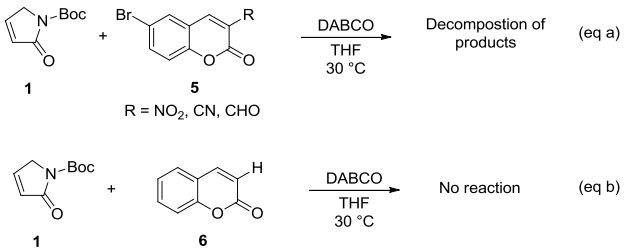
1 **2** : X = O; **2'**: X = S **3** dr > 25:1

entry	R^1	R^2	time (h)[b]	**3**, yield (%)[c]
1	6-Br	Ph	5	**3aa**, 99
2	6-Cl	Ph	4	**3ba**, 82

3	6,8-Cl	Ph	4	**3ca**, 91
4	6-OMe	Ph	3	**3da**, 98
5	H	Ph	6	**3ea**, 89
6	H	4-OMePh	7	**3eb**, 74
7	H	4-NO_2Ph	3	**3ec**, 83
8[d]	6-OMe	4-OMePh	16	**3db**, 96
9	6-OMe	4-NO_2Ph	6	**3dc**, 73
10[d]	6-Br	4-OMePh	13	**3ab**, 80
11[d]	6-Br	4-NO_2Ph	12	**3ac**, 66
12	6-Br	4-BrPh	3	**3ad**, 73
13	6-Br	3-BrPh	6	**3ae**, 80
14	6-Br	2-BrPh	8	**3af**, trace
15	6-Br	2-naphthyl	4	**3ag**, 85
16[e]	6-Br	2-thienyl	14	**3ah**, 85
17	6-Br	Cy	5	**3ai**, 59
18	6-Br	OEt	4	**3aj**, 70
19	6-OMe	OEt	7	**3dj**, 91
20[f]	H	Ph	7	**3ea'**, 94

[a] Unless otherwise specified, all the reactions were carried out using **1** (0.12 mmol), **2** (0.1 mmol), and DABCO (20 mol %) in anhydrous THF (0.2 mL) at 30 °C. [b]Indicates the time after which no further increase in the yield of **3** was observed. [c]Isolated yields. [d]0.6 mL of THF was used. [e]Mixed solvent (DCM:THF = 1:1) was used (0.6 mL). [f]Reaction with **2'** (X=S) instead of **2**.

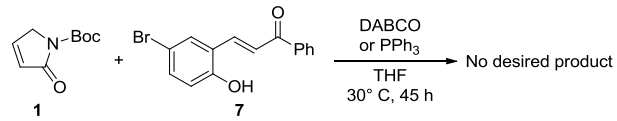
The reaction proceeded well even when the acyl functionality was replaced with an ester group (Table 2, entries 18 and 19). Interestingly, even the sulfur analog of **2** could participate in the reaction well resulting in the corresponding product in excellent yield (entry 20).



Scheme 2. Reaction with other EWGs on coumarin.

However, when the EWG was replaced by either a nitro, aldehyde or cyano group, corresponding products decomposed and could not be isolated (Scheme 2, eq a). On the other hand, the reaction did not work in the absence of an EWG indicating the importance of acyl or ester functionality for the activation of coumarin towards a nucleophilic attack (Scheme 2, eq b).

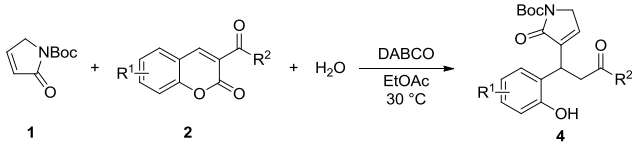
We were then interested in exploring the decarboxylated adduct **4** as there were no previous methods reported for their synthesis. Also, an attempt to synthesize these adducts by a straightforward Michael addition of **1** on to the chalcone **7** was not successful (Scheme 3), thereby enhancing the significance of the present protocol for their synthesis. This also highlights the importance of coumarin ring structure of the Michael acceptor, which could act as an additional EWG to activate the β-position towards a nucleophilic attack.



Scheme 3. Attempt towards a straightforward synthesis of hydrolysis/decarboxylation product **4** from **1** and **7**.

Hence, we carried out the reaction in presence of water to accelerate the hydrolysis/decarboxylation sequence under slightly modified reaction conditions.[8] Under the newly optimized conditions, substrate scope of this one-pot Michael addition/ Isomerization/Hydrolysis/Decarboxylation cascade was studied and the results are presented in table 3. In all the cases, this one-pot strategy furnished the decarboxylated products **4** in good yields.

Table 3. One-pot synthesis of the decarboxylated adduct **4**.[a]

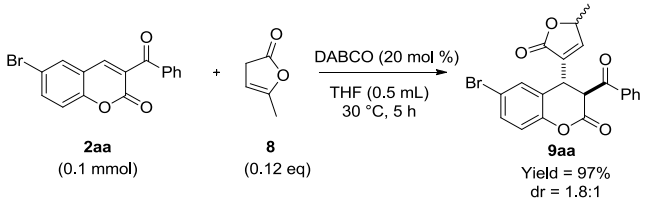


entry	R^1	R^2	time (h)[b]	**4**, yield (%)[c]
1	H	Ph	32	**4ea**, 86
2	6-Br	Ph	10	**4aa**, 82
3	6-Cl	Ph	10	**4ba**, 94
4	6,8-Cl	Ph	14	**4ca**, 98
5	H	4-OMePh	37	**4eb**, 74
6	6-Br	4-OMePh	13	**4ab**, 80
7	6-Br	2-naphthyl	12	**4ag**, 80

[a] Unless otherwise specified, all the reactions were carried out using **1** (0.12 mmol), **2** (0.1 mmol.), H_2O (0.4 mmol) and DABCO (40 mol %)

in EtOAc (0.2 mL) at 30 °C. [b]Indicates the time after which no further increase in the yield of **4** was observed. [c]Isolated yields.

The scope of the reaction was further extended towards α-angelica lactone (**8**) which was never been used as a nucleophile for its direct α-functionalization.[9] Under similar reaction conditions as in Table 2, α-angelica lactone (**8**) was treated with coumarin-derived Michael acceptor **2aa** which resulted in excellent yield of α-addition product **9aa** (Scheme 4). However, because of the generation of an additional methyl stereocenter which is away from the reactive site, the product was obtained with poor diastereoinduction.

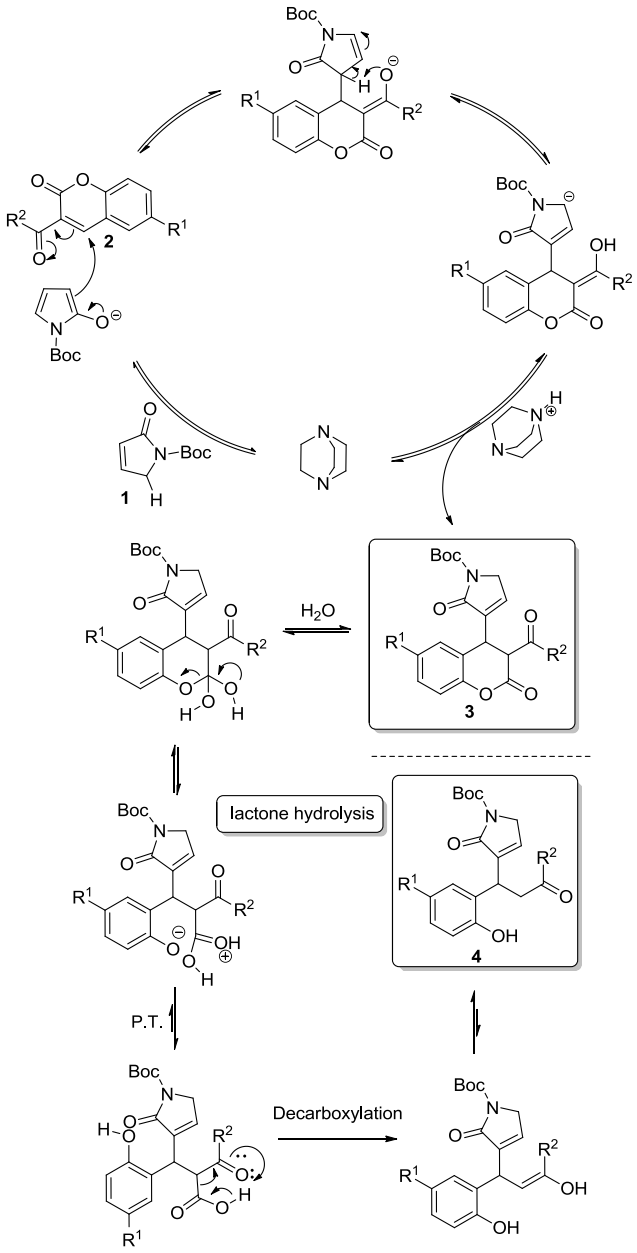


Scheme 4. Extension of the reaction towards α-angelica lactone.

Mechanistically, α-functionalization of **1** could be facilitated by either of the two pathways, a RC pathway or a Michael addition/isomerization sequence. However, the reaction could not be assisted by a phosphine but proceeded well with an inorganic base or a non-nucleophilic tertiary amine such as Et_3N (Table 1, entries 4, 16 and 17), although resulting in the product in lower yields. Moreover, the reaction was successful even with α-angelica lactone, which cannot act as an activated alkene for RC reaction. Hence it could be ascertained that the reaction followed the Michael addition/isomerization pathway furnishing the α-addition product (Scheme 5). The organic base enables deprotonation of **1**, resulting in the formation of a dienolate. This dienolate then adds on to Michael acceptor **2**, providing the intermediate which is susceptible towards

isomerization, resulting in the formal RC adduct **3**. This could undergo further hydrolysis and decarboxylation to afford the adduct **4**.

In conclusion, we have successfully demonstrated the synthesis of RC-type α–functionalization adducts of α,β-unsaturated γ-butyrolactam *via* a Michael addition-Isomerization sequence with 3-substituted coumarins. The present report happens to be the first one that involves the use of a Michael acceptor for the generation of RC-type α–functionalization adducts of α,β-unsaturated γ-butyrolactams *via* a 1,4-addition. The transformation was further applied for the analogous α-angelica lactone as well. More importantly, the decarboxylated products of the Michael addition-Isomerization cascade could also be furnished in good yields *via* a one-pot operation.



Scheme 5. Proposed mechanism for the Michael addition/Isomerization/Hydrolysis/Decarboxylation sequence.

EXPERIMENTAL SECTION:

General experimental methods:

All solvents and reagents were used as purchased from commercial suppliers without further purification. Analytical thin layer chromatography (TLC) was performed on precoated alumina-backed silica gel plates (0.2 mm thickness) which were developed using UV florescence and iodine. Flash-chromatography was performed on silica gel (230-400 mesh). Melting points were measured on a standard melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer, while ^{13}C NMR spectra were recorded on a 100 MHz instrument. Chemical shifts are reported in δ ppm referenced to an internal TMS standard for ^{1}H NMR and chloroform-d (δ = 77.0 ppm) for ^{13}C NMR. HRMS spectra were recorded using FAB (TOF analyzer) or ESI (TOF analyzer). The X-ray diffraction measurements were carried out at 298 K on a CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (k = 0.71073 Å).

Characterization data for new compounds.

The coumarin substrates **2aa**, **2ba**, **2ca**, **2ea**, **2ab**, **2ac**, **2aj** and **2ea'** were synthesized following the procedure reported in the literature.[7c] Likewise, the substrates **2da**, **2eb** and **2db** were prepared according to the method reported by Vina et. al.[10] The new coumarin substrates **2ec**, **2dc**, **2ad**-**2ai** and **2dj** were synthesized following a similar procedure which is mentioned below.

General procedure A for the synthesis of new coumarin substrates 2:

Piperidine (5 mol %) was added to a stirred solution of substituted salicylaldehyde (10 mmol) and corresponding ethyl benzoylacetate (1.25 equiv) or ethyl acetoacetate (1.25 equiv.) in CH_3CN (10 mL) at room temperature. After stirring for 5 min, the contents were heated to 80°C for 8h. After the reaction was completed, the reaction mixture was allowed to cool to room temperature, solvent was removed *in vacuo* and the crude product was purified by column

chromatography over silica gel using hexane/EtOAc as eluent to get the pure 3-acylcoumarin **2ec**, **2dc**, **2ad-2ai** or **2dj**.

*3-(4-Nitrobenzoyl)-2H-chromen-2-one (**2ec**):* Following the general procedure A, **2ec** was obtained after flash chromatography (EtOAc/Hex = 1/3) as a pale yellow solid (99% yield, 2.923 g). R_f 0.47 (EtOAc/Hex = 1/3); m.p.: 266.1-267.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.47-8.16 (m, 3H), 8.11-7.86 (m, 2H), 7.85-7.57 (m, 2H), 7.53-7.34 (m, 2H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ/ppm: 190.5, 150.4, 147.7, 144.5, 141.5, 134.6, 130.1, 129.7, 125.6, 125.3, 123.7, 118.1, 117.1; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 2067, 1638, 1520, 1351, 1234, 700; **HRMS** (ESI) calcd for $C_{16}H_{10}NO_5$, $[M+H]^+$ 296.0559, found: 296.0557.

*6-Methoxy-3-(4-Nitrobenzoyl)-2H-chromen-2-one (**2dc**):* Following the general procedure A, **2dc** was obtained after flash chromatography (EtOAc/Hex = 1/3) as a yellow solid (98% yield, 3.187 g). R_f 0.43 (EtOAc/Hex = 1/3); m.p.: 256.8-257.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.33 (d, *J* = 8.8 Hz, 2H), 8.25 (s, 1H), 7.99 (d, *J* = 8.9 Hz, 2H), 7.37 (d, *J* = 9.1 Hz, 1H), 7.28 (d, *J* = 9.1 Hz, 1H), 7.06 (d, *J* = 3.1 Hz, 1H), 3.89 (s, 3H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ/ppm: 190.6, 158.6, 156.6, 150.4, 149.8, 147.4, 141.5, 130.1, 125.8, 123.7, 122.8, 118.4, 118.2, 110.9, 56.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 2066, 1636, 1570, 1348, 685; **HRMS** (ESI) calcd for $C_{17}H_{12}NO_6$, $[M+H]^+$ 326.0665, found: 326.0663.

*6-Bromo-3-(4-Bromobenzoyl)-2H-chromen-2-one (**2ad**):* Following the general procedure A, **2ad** was obtained after flash chromatography (EtOAc/Hex = 1/8) as a white solid (73% yield, 2.978 g). R_f 0.48 (EtOAc/Hex = 1/8); m.p.: 261.3-262.7 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ/ppm: 8.40 (s, 1H), 8.11 (s, 1H), 7.94-7.83 (m, 3H), 7.77 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 8.7 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO- d_6) δ/ppm: 190.5, 157.5, 153.2, 144.4, 135.8, 134.9, 131.7,

131.6, 131.4, 128.1, 126.8, 120.1, 118.5, 116.2; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1750, 1732, 1606, 1234, 932, 767; **HRMS** (ESI) calcd for $C_{16}H_9Br_2O_3$, $[M+H]^+$ 406.8918, found: 406.8914.

*6-Bromo-3-(3-Bromobenzoyl)-2H-chromen-2-one (**2ae**):* Following the general procedure A, **2ae** was obtained after flash chromatography (EtOAc/Hex = 1/6) as a white solid (78% yield, 3.182 g). R_f 0.52 (EtOAc/Hex = 1/6); m.p.: 265.6-266.3 °C; **^{1}H NMR** (400 MHz, *d_6*-DMSO) δ/ppm: 8.40 (s, 1H), 8.13 (d, *J* = 9.0 Hz, 2H),7.92 (dd, *J* = 20.3, 7.7 Hz, 3H), 7.58-7.43 (m, 2H); **^{13}C NMR** (400 MHz, *d_6*-DMSO) δ/ppm: 190.3, 157.5, 153.4, 144.7, 138.1, 136.5, 135.9, 131.9, 131.7, 130.9, 128.4, 126.8, 122.0, 120.2, 118.6, 116.2; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 2068, 1636, 608; **HRMS** (ESI) calcd for $C_{16}H_8Br_2O_3Na$, $[M+Na]^+$ 428.8742, found: 428.8738.

*6-Bromo-3-(2-Bromobenzoyl)-2H-chromen-2-one (**2af**):* Following the general procedure A, **2af** was obtained after flash chromatography (EtOAc/Hex = 1/6) as a pale yellow solid (24% yield, 0.979 g). R_f 0.52 (EtOAc/Hex = 1/6); m.p.: 142.4-143.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.28 (s, 1H), 7.78 (d, *J* = 2.0 Hz, 1H) , 7.72 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ/ppm: 191.3, 157.2, 154.0, 145.9, 139.8, 136.9, 133.1, 132.4, 131.9, 129.9, 127.6, 126.5, 119.8, 119.6, 118.6, 117.4; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1750, 1732, 1606, 1234, 932, 767; **HRMS** (ESI) calcd for $C_{16}H_9Br_2O_3$, $[M+H]^+$ 406.8918, found: 406.8917.

*3-(2-Naphthoyl)-6-bromo-2H-chromen-2-one (**2ag**):* Following the general procedure A, **2ag** was obtained after flash chromatography (EtOAc/Hex = 1/6) as a white solid (61% yield, 2.313 g). R_f 0.46 (EtOAc/Hex = 1/6); m.p.: 205.8-206.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.33 (s, 1H), 8.01 (s, 1H), 7.99-7.85 (m, 4H), 7.79-7.69 (m, 2H),7.62 (t, *J* = 7.3 Hz, 1H) ,7.54 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 9.4 Hz, 1H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ/ppm: 191.0, 157.8, 153.6, 143.6, 136.2, 136.1, 133.3, 132.3, 132.1, 131.3, 129.7, 129.1, 128.7, 128.4, 127.9, 127.0, 124.5,

119.7, 118.7, 117.6; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1627, 1362, 1195, 657; **HRMS** (ESI) calcd for $C_{20}H_{12}BrO_3$, $[M+H]^+$ 378.9970, found: 378.9972.

*6-Bromo-3-(Thiophene-2-carbonyl)-2H-chromen-2-one (**2ah**):* Following the general procedure A, **2ah** was obtained after flash chromatography (EtOAc/Hex = 1/3) as a white solid (49% yield, 1.642 g). R_f 0.58 (EtOAc/Hex = 1/3); m.p. 205.1-206.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC) δ/ppm: 8.00 (s, 1H), 7.78 (d, J = 4.1 Hz, 1H), 7.77-7.68 (m, 3H), 7.31 (d, J = 9.7 Hz, 1H), 7.17 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ºC) δ/ppm: 182.4, 157.5, 153.4, 143.1, 142.6, 136.3, 136.0, 135.3, 131.2, 128.4, 127.9, 119.5, 118.7, 117.6; **IR** (ATR): $\tilde{\nu}$ (cm^{-1}) 2116, 1623, 1272, 696; **HRMS** (ESI) for $C_{14}H_7BrO_3SNa$ $[M+Na]^+$ calc.: 356.9197, found: 356.9196.

*6-Bromo-3-(Cyclohexanecarbonyl)-2H-chromen-2-one (**2ai**):* Following the general procedure A, **2ai** was obtained after flash chromatography (EtOAc/Hex = 1/12) as a white solid (28% yield, 0.938 g). R_f 0.54 (EtOAc/Hex = 1/12); m.p.: 237.1-238.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.29 (s, 1H), 7.76 (d , *J* = 1.8 Hz, 1H), 7.72 (d , *J* = 8.80 Hz, 1H), 7.27 (d , *J* = 2.8 Hz, 1H), 3.62-3.45 (m, 1H), 1.99-1.64 (m, 5H), 1.47-1.15 (m, 5H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ/ppm: 201.2, 158.2, 153.9, 145.7, 136.6, 131.9, 126.2, 119.9, 118.4, 117.4, 48.2, 28.5, 25.9, 25.6; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 2066, 1635, 694; **HRMS** (ESI) calcd for $C_{16}H_{16}BrO_3$, $[M+H]^+$ 335.0283, found: 335.0285.

*Ethyl 6-methoxy-2-oxo-2H-chromene-3-carboxylate (**2dj**):* Following the general procedure A, **2dj** was obtained after flash chromatography (EtOAc/Hex = 2/5) as a pale yellow solid (37% yield, 0.918 g). R_f 0.25 (EtOAc/Hex = 1/3); m.p.: 145.1-146.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.41 (s, 1H), 7.23-7.12 (m, 2H) , 6.95 (d, *J* = 2.8 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.40 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ/ppm: 162.9, 156.7, 156.1, 149.5,

148.2, 122.4, 118.2, 117.9, 117.6, 110.5, 61.7, 55.7, 14.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1750 (s), 1380 (w), 1300 (w), 796 (w); **HRMS** (ESI) calcd for $C_{13}H_{12}O_5$, $[M+Na]^+$ 271.0582, found: 271.0586.

General procedure B for the synthesis of Michael addition product 3:

A mixture of DABCO (0.02 mmol), *α,β*-unsaturated *γ*-butyrolactam **1** (0.12 mmol, 21.9 mg) and 3-acylcoumarin **2** (0.1 mmol) in 0.2 mL of anhydrous THF was stirred at 30 °C until the completion of the reaction (monitored by ^{1}H NMR). Then the solvent was removed under reduced pressure and the residue was purified by column chromatography over silica gel using hexane/EtOAc as eluent to give the desired product **3**.

*tert-Butyl 3-(3-Benzoyl-6-bromo-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3aa**):* Prepared according to the general procedure B using 3-benzoyl-6-bromo-2*H*-chromen-2-one **2aa** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/5) furnished the desired product **3aa** as a white solid (99% yield, 50.7 mg). R_f 0.34 (EtOAc/Hex = 1/3); m.p.: 186.2-187.1 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ*/ppm: 8.23 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.48 (dd, *J* = 8.7 Hz, 2.4 Hz, 1H), 7.16 (d, *J*= 2.4 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 6.51-6.50 (m, 1H), 5.29 (d, *J* = 2.3 Hz, 1H), 4.45-4.42 (m, 1H), 4.29 (pseudo dt, *J* = 20.3 Hz, 1.9 Hz, 1H), 4.23 (pseudo dt, *J* = 20.3 Hz, 2.2 Hz, 1H), 1.58 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 192.6, 167.7, 163.8, 150.6, 149.0, 141.1, 137.5, 134.6, 133.4, 133.0, 131.0, 129.5, 129.2, 121.7, 119.1, 117.7, 83.8, 52.5, 50.0, 37.5, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1781, 1718, 1480, 1325, 1154, 537; **HRMS** (MALDI) calcd for $C_{25}H_{22}BrNO_6Na$, $[M+Na]^+$ 534.0528, found: 534.0531.

*tert-Butyl 3-(3-Benzoyl-6-chloro-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3ba**):* Prepared according to the general procedure B using 3-benzoyl-6-chloro-2*H*-

chromen-2-one **2ba** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/3) furnished the desired product **3ba** as a white solid (82% yield, 38.3 mg). R_f 0.5 (EtOAc/Hex = 1/3); m.p.: 190.7-191.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.23 (d, J = 7.4 Hz, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.34 (dd, J = 8.7 Hz, 2.5 Hz, 1H), 7.15 (d, J= 8.7 Hz, 1H), 7.01 (d, J = 2.4 Hz, 1H), 6.54-6.47 (m, 1H), 5.30 (d, J = 2.5 Hz, 1H), 4.46-4.40 (m, 1H), 4.29 (pseudo dt, J = 20.4 Hz, 1.7 Hz, 1H), 4.23 (pseudo dt, J = 20.4 Hz, 2.2 Hz, 1H), 1.58 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 192.8, 167.9, 164.1, 150.3, 149.2, 141.4, 137.6, 134.8, 133.6, 130.5, 130.2, 129.7, 129.4, 128.4, 121.5, 119.0, 84.1, 52.7, 50.2, 37.8, 28.3; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1766, 1688, 1478, 1360, 1154, 684; **HRMS** (ESI) calcd for $C_{25}H_{21}NO_6Cl$, $[M-H]^-$ 466.1057, found: 466.1058.

*tert-Butyl 3-(3-Benzoyl-6,8-dichloro-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3ca**):* Prepared according to the general procedure B using 3-benzoyl-6,8-dichloro-2*H*-chromen-2-one **2ca** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/3) furnished the desired product **3ca** as a yellow solid (91% yield, 45.7 mg). R_f 0.49 (EtOAc/Hex = 1/3); m.p.: 184.4-185.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.21 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.44 (d, J= 2.4 Hz, 1H), 6.95 (d, J = 2.3 Hz, 1H), 6.63-6.55 (m, 1H), 5.33 (d, J = 2.5 Hz, 1H), 4.49-4.44 (m, 1H), 4.35-4.20 (m, 2H), 1.58 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 192.1, 167.6, 162.7, 148.9, 146.3, 141.3, 136.8, 134.7, 133.3, 130.4, 130.1, 129.5, 129.2, 126.6, 123.4, 122.7, 83.9, 52.1, 50.1, 37.8, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1757, 1645, 1449, 1288, 1158, 692; **HRMS** (ESI) calcd for $C_{25}H_{21}NO_6Cl_2Na$, $[M+Na]^+$ 524.0644, found: 524.0654.

*tert-Butyl 3-(3-Benzoyl-6-methoxy-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3da**):* Prepared according to the general procedure B using 3-benzoyl-6-methoxy-

2*H*-chromen-2-one **2da** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/5) furnished the desired product **3da** as a yellow solid (98% yield, 45.4 mg). R_f 0.23 (EtOAc/Hex = 1/3); m.p.: 188.0-189.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.24 (d, *J* = 7.4 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.14 (d, *J* = 9.0 Hz, 1H), 6.88 (dd, *J*= 9.0 Hz, 3.0 Hz, 1H), 6.51 (d, *J* = 3.0 Hz, 1H), 6.50-6.49 (m, 1H), 5.24 (d, *J* = 2.2 Hz, 1H), 4.42-4.39 (m, 1H), 4.27 (pseudo dt, *J* = 20.3 Hz, 1.8 Hz, 1H), 4.20 (pseudo dt, *J* = 20.3 Hz, 2.1 Hz, 1H), 3.73 (s, 3H) , 1.58 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 192.9, 168.0, 164.7, 156.6, 149.0, 145.3, 141.0, 138.0, 134.3, 133.6, 129.5, 129.1, 120.3, 118.2, 114.9, 113.3, 83.7, 55.6, 53.0, 50.0, 38.0, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1763, 1723, 1677, 1475, 1317, 1169; **HRMS** (MALDI) calcd for $C_{26}H_{25}NO_7Na$, $[M+Na]^+$ 486.1529, found: 486.1538.

*tert-Butyl 3-(3-Benzoyl-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3ea**):* Prepared according to the general procedure B using 3-benzoyl-2H-chromen-2-one **2ea** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/5) furnished the desired product **3ea** as a yellow solid (89% yield, 38.6 mg). R_f 0.33 (EtOAc/Hex = 1/3); m.p.: 155.4-156.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.24 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.42-7.34 (m, 1H), 7.22 (d, *J*= 8.1 Hz, 1H), 7.11 (td, *J* = 7.1 Hz, 1.0 Hz, 1H), 7.00 (d, *J* = 7.6, 1.2 Hz, 1H), 6.48-6.44 (m, 1H), 5.28 (d, *J*=2.2 Hz, 1H), 4.50-4.44 (m, 1H), 4.27 (pseudo dt, *J* = 20.2 Hz, 1.8 Hz, 1H), 4.20 (pseudo dt, *J* = 20.2 Hz, 1.8 Hz, 1H), 1.58 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 192.9, 168.0, 164.6, 151.5, 149.0, 141.0, 138.1, 134.4, 133.5, 130.0, 129.5, 129.1, 128.3, 125.2, 119.4, 117.4, 83.7, 53.1, 50.0, 37.7, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1773, 1720, 1460, 1355, 1156; **HRMS** (MALDI) calcd for $C_{25}H_{23}NO_6Na$, $[M+Na]^+$ 456.1423, found: 456.1416.

*tert-Butyl 3-(3-(4-Methoxybenzoyl)-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3eb**):* Prepared according to the general procedure B using 3-(4-methoxybenzoyl)-2*H*-chromen-2-one **2eb** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/5) furnished the desired product **3eb** as a white solid (74% yield, 34.3 mg). R_f 0.23 (EtOAc/Hex = 1/3); m.p.: 119.6-120.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.24 (d, *J* = 8.9 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.02-6.97 (m, 3H), 6.45-6.43 (m, 1H), 5.22 (d, *J*= 2.2 Hz, 1H), 4.45-4.42 (m, 1H), 4.27 (pseudo dt, *J* = 20.3 Hz, 1.8 Hz, 1H), 4.20 (pseudo dt, *J* = 20.3 Hz, 2.2 Hz, 1H), 3.88 (s, 3H), 1.58 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 191.2, 168.1, 164.7, 164.5, 151.6, 149.0, 140.9, 138.3, 131.9, 129.9, 128.3, 126.5, 125.1, 119.6, 117.3, 114.3, 83.7, 55.5, 52.9, 50.0, 37.9, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1774, 1726, 1675, 1601, 1459, 1320, 1156; **HRMS** (MALDI) calcd for $C_{26}H_{25}NO_7Na$, $[M+Na]^+$ 486.1523, found: 486.1529.

*tert-Butyl 3-(3-(4-Nitrobenzoyl)-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3ec**):* Prepared according to the general procedure B using 3-(4-nitrobenzoyl)-2*H*-chromen-2-one **2ec** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/5) furnished the desired product **3ec** as a yellow solid (83% yield, 39.7 mg). R_f 0.32 (EtOAc/Hex = 1/3); m.p.: 192.1-192.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.49-8.34 (m, 4H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.52-6.48 (m, 1H), 5.34 (d, *J* = 2.5 Hz, 1H), 4.44-4.39 (m, 1H), 4.30 (pseudo dt, *J* = 20.4 Hz, 1.7 Hz, 1H), 4.24 (pseudo dt, *J* = 20.4 Hz, 2.1 Hz, 1H), 1.59 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 191.7, 168.0, 163.6, 151.3, 151.0, 148.9, 141.6, 138.0, 137.5, 130.6, 130.2, 128.2, 125.5, 124.2, 118.9, 117.5, 84.0, 53.1, 50.1, 37.4, 28.0; **IR** (KBr) $\tilde{\nu}$

(cm^{-1}): 1772, 1718, 1522, 1458, 1359, 1320, 1155; **HRMS** (ESI) calcd for $C_{25}H_{22}N_2O_8$, $[M]^+$ 478.1376, found: 478.1378.

*tert-Butyl 3-(6-Methoxy-3-(4-Methoxybenzoyl)-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3db**):* Prepared according to the general procedure B using 6-methoxy-3-(4-methoxybenzoyl)-2*H*-chromen-2-one **2db** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/2) furnished the desired product **3db** as a yellow solid (96% yield, 47.4 mg). R_f 0.14 (EtOAc/Hex = 1/3); m.p.: 123.7-123.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.24 (d, J = 9.0 Hz, 2H), 7.13 (t, J = 9.0 Hz, 1H), 7.00 (t, J = 9.0 Hz, 2H), 6.88 (dd, J = 9.0 Hz, 3.0 Hz, 1H), 6.51 (d, J= 3.0 Hz, 1H), 6.50-6.46 (m, 1H), 5.17 (d, J = 2.2 Hz, 1H), 4.40-4.36 (m, 1H), 4.27 (pseudo dt, J = 20.2 Hz, 1.8 Hz, 1H), 4.20 (pseudo dt, J = 20.2 Hz, 2.2 Hz, 1H), 3.88 (s, 3H), 3.72 (s, 3H), 1.58 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 191.2, 168.1, 164.9, 164.5, 156.6, 149.0, 145.4, 140.9, 138.1, 132.0, 126.5, 120.4, 118.1, 114.9, 114.3, 113.3, 83.6, 55.6, 55.5, 52.8, 50.0, 38.1, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1772, 1672, 1599, 1457, 1320, 1157; **HRMS** (ESI) calcd for $C_{27}H_{26}NO_8$, $[M-H]^-$ 492.1658, found: 492.1674.

*tert-Butyl 3-(6-Methoxy-3-(4-Nitrobenzoyl)-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3dc**):* Prepared according to the general procedure B using 6-methoxy-3-(4-nitrobenzoyl)-2*H*-chromen-2-one **2dc** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/3) furnished the desired product **3dc** as a yellow solid (73% yield. 37.1 mg). R_f 0.43 (EtOAc/Hex = 1/3); m.p.: 180.9-181.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.49-8.33 (m, 4H), 7.15 (d, J = 9.0 Hz, 1H), 6.91 (dd, J = 9.0 Hz, 3.0 Hz, 1H), 6.56-6.52 (m, 1H), 6.50 (d, J = 3.0 Hz, 1H), 5.30 (d, J = 2.6 Hz, 1H), 4.39-4.34 (m, 1H), 4.30 (pseudo dt, J = 20.5 Hz, 1.9 Hz, 1H), 4.24 (pseudo dt, J = 20.5 Hz,

2.2 Hz, 1H), 3.74 (s, 3H), 1.58 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 191.7, 168.0, 163.8, 156.8, 151.0, 149.0, 145.1, 141.6, 138.0, 137.3, 130.7, 124.2, 119.8, 118.4, 115.1, 113.3, 84.0, 55.6, 53.1, 50.1, 37.6, 28.1; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1765, 1720, 1599, 1526, 1437, 1359, 1327, 1196; **HRMS** (ESI) calcd for $C_{26}H_{23}N_2O_9$, $[M-H]^-$ 507.1404, found: 507.1403.

*tert-Butyl 3-(6-Bromo-3-(4-Methoxybenzoyl)-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3ab**):* Prepared according to the general procedure B using 6-bromo-3-(4-methoxybenzoyl)-2*H*-chromen-2-one **2ab** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/2) furnished the desired product **3ab** as a yellow solid (80% yield, 43.4 mg). R_f 0.18 (EtOAc/Hex = 1/3); m.p.: 172.4-173.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ*/ppm: 8.23 (d, *J* = 8.9 Hz, 2H), 7.48 (dd, *J* = 8.8 Hz, 2.3 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 7.00 (d, *J*= 8.9 Hz, 2H), 6.50-6.46 (m, 1H), 5.22 (d, *J* = 2.2 Hz, 1H), 4.43-4.37 (m, 1H), 4.29 (pseudo dt, *J* = 20.3 Hz, 1.7 Hz, 1H), 4.22 (pseudo dt, *J* = 20.3 Hz, 2.2 Hz, 1H), 3.89 (s, 3H), 1.58 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 190.9, 167.8, 164.7, 164.1, 150.7, 149.0, 141.0, 137.7, 132.9, 132.0, 131.1, 126.3, 121.8, 119.1, 117.6, 114.4, 83.9, 55.6, 52.4, 50.0, 37.7, 28.1; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1780, 1723, 1602, 1478, 1357, 1154, 538; **HRMS** (MALDI) calcd for $C_{26}H_{24}BrNO_7Na$, $[M+Na]^+$ 564.0634, found: 564.0612.

*tert-Butyl 3-(6-Bromo-3-(4-Nitrobenzoyl)-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3ac**):* Prepared according to the general procedure B using 6-bromo-3-(4-nitrobenzoyl)-2*H*-chromen-2-one **2ac** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/5) furnished the desired product **3ac** as a yellow solid (66% yield, 36.8 mg). R_f 0.34 (EtOAc/Hex = 1/3); m.p.: 178.2-179.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ*/ppm: 8.47-8.32 (m, 4H), 7.52 (dd, *J* = 8.7 Hz, 2.3 Hz,

1H), 7.16 (d, *J* = 2.2 Hz, 1H), 7.12 (d, *J* = 8.7 Hz, 1H), 6.57-6.53 (m, 1H), 5.35 (d, *J* = 2.6 Hz, 1H), 4.41-4.37 (m, 1H), 4.33 (pseudo dt, *J* = 20.5 Hz, 1.7 Hz, 1H), 4.26 (pseudo dt, *J* = 20.5 Hz, 2.0 Hz, 1H), 1.59 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 191.4, 167.8, 162.9, 151.1, 150.4, 148.9, 141.8, 137.8, 136.8, 133.3, 131.0, 130.7, 124.3, 121.1, 119.3, 118.0, 84.1, 52.6, 50.1, 37.2, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1173, 1525, 1479, 1358, 1157; **HRMS** (MALDI) calcd for $C_{25}H_{21}BrN_2O_8$, $[M]^+$ 556.0481, found: 556.0467.

*tert-Butyl 3-(6-Bromo-3-(4-Bromobenzoyl)-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3ad**):* Prepared according to the general procedure B using 6-bromo-3-(4-bromobenzoyl)-2*H*-chromen-2-one **2ad** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/5) furnished the desired product **3ad** as a yellow solid (73% yield, 43.1 mg). R_f 0.33 (EtOAc/Hex = 1/3); m.p.: 166.1-166.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ*/ppm: 8.12 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.49 (dd, *J* = 8.7 Hz, 2.3 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 6.52-6.48 (m, 1H), 5.24 (d, *J* = 2.2 Hz, 1H), 4.41-4.35 (m, 1H), 4.30 (pseudo dt, *J* = 20.5 Hz, 1.7 Hz, 1H), 4.23 (pseudo dt, *J* = 20.5 Hz, 2.1 Hz, 1H), 1.59 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 191.7, 167.7, 163.4, 150.5, 148.9, 141.3, 137.2, 133.1, 132.6, 132.1, 131.0, 131.0, 130.2, 121.4, 119.2, 117.8, 84.0, 52.4, 50.1, 37.4, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1773, 1722, 1477, 1357, 1156, 537; **HRMS** (ESI) calcd for $C_{25}H_{20}NO_6Br_2$, $[M-H]^-$ 587.9657, found: 587.9655.

*tert-Butyl 3-(6-Bromo-3-(3-Bromobenzoyl)-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3ae**):* Prepared according to the general procedure B using 6-bromo-3-(3-bromobenzoyl)-2*H*-chromen-2-one **2ae** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/3) furnished the desired product **3ae** as a white solid (80% yield, 47.3 mg). R_f 0.57 (EtOAc/Hex = 1/3); m.p.: 136.3-137.6

°C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ*/ppm: 8.33 (d, *J* = 7.8 Hz, 1H), 8.21 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.76-7.52 (m, 2H), 7.16 (s, 1H), 7.10 (dd, *J* = 8.6 Hz, 2.0 Hz, 1H), 6.55-6.50 (m, 1H), 5.25 (d, *J* = 1.7 Hz, 1H), 4.42-4.38 (m, 1H), 4.30 (pseudo dt, *J* = 20.1 Hz, 1.3 Hz, 1H), 4.24 (pseudo dt, *J* = 20.1 Hz, 1.1 Hz, 1H), 1.58 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 191.4, 167.7, 163.3, 150.4, 148.9, 141.5, 137.4, 137.1, 135.1, 133.1, 132.1, 131.0, 130.8, 128.3, 123.5, 121.4, 119.2, 117.8, 83.9, 52.3, 50.0, 37.3, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1772, 1723, 1477, 1357, 1156; **HRMS** (ESI) calcd for $C_{25}H_{20}Br_2NO_6$, $[M-H]^-$ 587.9657, found: 587.9677.

*tert-Butyl 3-(3-(2-Naphthoyl)-6-Bromo-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3ag**):* Prepared according to the general procedure B using 3-(2-naphthoyl)-6-bromo-2*H*-chromen-2-one **2ag** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/3) furnished the desired product **3ag** as a white solid (85% yield, 47.8 mg). R_f 0.49 (EtOAc/Hex = 1/3); m.p.: 180.9-181.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ*/ppm: 9.02 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.09 (dd, *J* = 8.7 Hz, 1.7 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J*= 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.49 (dd, *J* = 8.6 Hz, 2.4 Hz, 1H), 7.15-7.09 (m, 2H), 6.54-6.49 (m, 1H), 5.45 (d, *J* = 2.6 Hz, 1H), 4.56-4.50 (m, 1H), 4.31 (pseudo dt, *J* = 20.3 Hz, 1.7 Hz, 1H), 4.24 (pseudo dt, *J* = 20.3 Hz, 2.1 Hz, 1H), 1.60 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 192.5, 167.8, 163.9, 150.6, 149.0, 141.2, 137.5, 136.1, 133.0, 132.5, 132.4, 131.0, 130.5, 130.4, 129.4, 129.0, 127.7, 127.0, 124.0, 121.7, 119.1, 117.7, 83.8, 52.7, 50.0, 37.8, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1773, 1723, 1676, 1477, 1357, 1154, 539; **HRMS** (ESI) calcd for $C_{29}H_{23}BrNO_6$, $[M-H]^-$ 560.0709, found: 560.0721.

*tert-Butyl 3-(6-Bromo-2-oxo-3-(Thiophene-2-carbonyl)chroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3ah**):* Prepared according to the general procedure B 6-bromo-3-

(thiophene-2-carbonyl)-2*H*-chromen-2-one **2ah** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/3) furnished the desired product **3ah** as a white solid (85% yield, 44.0 mg). R_f 0.43 (EtOAc/Hex = 1/3); m.p.: 169.7-170.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ*/ppm: 8.51 (d, *J* = 3.7 Hz, 1H), 7.76 (d, *J* = 5.4 Hz, 1H), 7.49 (dd, *J* = 8.7 Hz, 2.2 Hz, 1H), 7.23 (t, *J* = 4.4 Hz, 1H), 7.21 (d, *J*= 2.2 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 6.54-6.48 (m, 1H), 5.13 (d, *J* = 2.2 Hz, 1H), 4.50-4.44 (m, 1H), 4.29 (pseudo dt, *J* = 21.0 Hz, 1.8 Hz, 1H), 4.23 (pseudo dt, *J* = 21.0 Hz, 2.7 Hz, 1H), 1.58 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 185.0, 167.7, 163.2, 150.6, 149.0, 141.2, 140.7, 137.4, 136.4, 135.9, 133.0, 131.1, 129.1, 121.6, 119.1, 117.8, 83.9, 53.1, 50.0, 38.0, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1774, 1720, 1655, 1479, 1357, 1155, 528; **HRMS** (ESI) calcd for $C_{23}H_{19}BrNO_6S$, $[M-H]^-$ 516.0116, found: 516.0108.

*(E)-tert-Butyl 3-(6-Bromo-3-(Cyclohexyl(Hydroxy)methylene)-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3ai**):* Prepared according to the general procedure B using 6-bromo-3-(cyclohexanecarbonyl)-2*H*-chromen-2-one **2ai** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/3) furnished the desired product **3ai** as a white solid (59% yield, 30.6 mg). R_f 0.47 (EtOAc/Hex = 1/3); m.p.: 155.4-156.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ*/ppm: 13.58 (s, 1H), 7.65 (d, *J* = 2.3 Hz, 1H), 7.35 (dd, *J* = 8.8 Hz, 2.3 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.79-6.76 (m, 1H), 4.88 (s, 1H), 4.23 (pseudo dt, *J* = 20.2 Hz, 1.6 Hz, 1H), 4.15 (pseudo dt, *J* = 20.2 Hz, 2.0 Hz, 1H), 2.52 (t, *J* = 11.0 Hz, 1H), 1.89-1.62 (m, 5H), 1.55 (s, 9H), 1.47-1.19 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 185.8, 169.5, 167.3, 149.3, 148.9, 142.8, 138.2, 131.8, 131.6, 124.8, 118.8, 117.4, 91.5, 83.4, 49.5, 40.7, 33.2, 29.5, 29.0, 28.1, 25.6, 25.5, 25.4; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 3453, 1766, 1653,

1481, 1354, 1170, 623; **HRMS** (ESI) calcd for $C_{25}H_{28}NO_6BrNa$, $[M+Na]^+$ 540.0998, found: 540.1001.

*tert-Butyl 3-(6-Bromo-3-(Ethoxycarbonyl)-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3aj**):* Prepared according to the general procedure B using ethyl 6-bromo-2-oxo-2*H*-chromene-3-carboxylate **2aj** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/5) furnished the desired product **3aj** as a white solid (70% yield, 33.6 mg). R_f 0.30 (EtOAc/Hex = 1/3); m.p.: 72.4-73.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 7.46 (dd, J = 8.6 Hz, 2.3 Hz, 1H), 7.41 (d, J = 2.3 Hz, 1H), 7.01 (d, J = 8.6 Hz, 1H), 6.65-6.64 (m, 1H), 4.55-4.52 (m, 1H), 4.27 (pseudo dt, J = 21.0 Hz, 1.8 Hz, 1H), 4.22 (pseudo dt, J = 21.0 Hz, 1.6 Hz, 1H), 4.14 (m, 3H),1.56 (s, 9H), 1.15 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 166.7, 165.5, 162.7, 150.1, 149.3, 140.6, 136.7, 132.7, 131.5, 122.8, 118.9, 117.9, 83.7, 62.7, 49.7, 49.7, 36.2, 28.0, 13.8; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1774, 1736, 1477, 1368, 1155, 585; **HRMS** (MALDI) calcd for $C_{21}H_{22}BrNO_7Na$, $[M+Na]^+$ 502.0477, found: 502.0460.

*tert-Butyl 3-(3-(Ethoxycarbonyl)-6-methoxy-2-oxochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3dj**):* Prepared according to the general procedure B using ethyl 6-methoxy-2-oxo-2*H*-chromene-3-carboxylate **2dj** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/2) furnished the desired product **3dj** as a white solid (91% yield, 39.2 mg). R_f 0.19 (EtOAc/Hex = 1/3); m.p.: 134.4-135.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 7.05 (d, J = 8.9 Hz, 1H), 6.85 (dd, J = 8.9 Hz, 3.0 Hz, 1H), 6.78 (d, J = 3.0 Hz, 1H), 6.63-6.60 (m, 1H), 4.53-4.49 (m, 1H), 4.28-4.06 (m, 5H), 3.78 (s, 3H), 1.56 (s, 9H), 1.05 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 167.0, 165.9, 163.7, 156.7, 149.4, 144.8, 140.4, 137.2, 121.7, 118.0, 115.1, 113.4, 83.5, 62.5, 55.7, 50.2, 49.7, 36.6,

28.0, 13.8; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1773, 1734, 1496, 1156, 1033; **HRMS** (ESI) calcd for $C_{22}H_{24}NO_8$, $[M-H]^-$ 430.1502, found: 430.1501.

*tert-Butyl 3-(3-Benzoyl-2-oxothiochroman-4-yl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**3ea'**):* Prepared according to the general procedure B using 3-benzoyl-2*H*-thiochromen-2-one **2ea'** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/5) furnished the desired product **3ea'** as a white solid (94% yield, 42.2 mg). R_f 0.40 (EtOAc/Hex = 1/3); m.p.: 100.8-101.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.13 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.35-7.27 (m, 2H), 7.18 (t, *J*= 7.2 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.57-6.52 (m, 1H), 5.28 (d, *J* = 2.6 Hz, 1H), 4.63-4.58 (m, 1H), 4.28 (pseudo dt, *J* = 20.2 Hz, 1.5 Hz, 1H), 4.18 (pseudo dt, *J* = 20.2 Hz, 2.4 Hz, 1H), 1.58 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 195.5, 193.3, 168.3, 149.1, 141.3, 136.2, 134.4, 133.9, 131.2, 130.0, 129.7, 129.2, 128.9, 128.6, 127.7, 127.1, 83.5, 58.9, 49.9, 42.5, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1774, 1722, 1670, 1476, 1357, 1156; **HRMS** (ESI) calcd for $C_{25}H_{22}NO_5S$, $[M-H]^-$ 448.1219, found: 448.1205.

General Procedure C for the synthesis of hydrolyisis/decarboxylation product 4:

A mixture of DABCO (0.04 mmol), *α,β*-unsaturated *γ*-butyrolactam **1** (0.12 mmol), 3-acylcoumarin **2** (0.1 mmol) and H_2O (0.04 mmol) in 0.2 mL of EtOAc was stirred at 30 °C until the completion of the reaction (monitored by ^{1}H NMR). Then the solvent was removed under reduced pressure and the residue was purified by column chromatography to give the desired product **4**.

*tert-Butyl 3-(1-(2-Hydroxyphenyl)-3-oxo-3-phenylpropyl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**4ea**):* Prepared according to the general procedure C using 3-benzoyl-2*H*-chromen-

2-one **2ea** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/5) furnished the desired product **4ea** as a white solid (86% yield, 35.0 mg). R_f 0.40 (EtOAc/Hex = 1/3); m.p.: 69.1-70.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 7.96 (m, 3H), 7.56 (m, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.18 (dd, J = 7.8 Hz, 1.8 Hz, 1H), 7.11 (m, 1H), 6.94 (m, 2H), 6.88 (td, J = 7.6 Hz, 1.1 Hz, 1H), 4.77 (t, J = 6.7 Hz, 1H), 4.23 (m, 2H), 3.93 (dd, J = 17.5 Hz, 8.1 Hz, 1H), 3.67 (dd, J = 17.6 Hz, 6.5 Hz, 1H), 1.53 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 198.1, 170.4, 154.3, 149.3, 141.5, 138.0, 136.3, 133.5, 128.7, 128.4, 128.1, 128.0, 121.1, 118.9, 83.5, 50.1, 41.5, 31.8, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 3433, 2064, 1635, 1361, 1268, 1157, 750; **HRMS** (ESI) calcd for $C_{24}H_{25}NO_5Na$, $[M+Na]^+$ 430.1630, found: 430.1632.

*tert-Butyl 3-(1-(5-Bromo-2-hydroxyphenyl)-3-oxo-3-phenylpropyl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**4aa**):* Prepared according to the general procedure C using 3-benzoyl-6-bromo-2*H*-chromen-2-one **2aa** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/2) furnished the desired product **4aa** as a white solid (82% yield, 39.9 mg). R_f 0.38 (EtOAc/Hex = 1/2); m.p.: 79.2-80.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.22 (s, 1H), 7.98 (d, J = 7.4 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.23 (d, J = 2.4 Hz, 1H), 7.21 (dd, J= 8.5 Hz, 2.4 Hz, 1H), 6.96-6.91 (m, 1H), 6.85 (d, J = 8.5 Hz, 1H), 4.72 (t, J = 6.8 Hz, 1H), 4.35-4.19 (m, 2H), 3.91 (dd, J = 17.7 Hz, 8.3 Hz, 1H), 3.63 (dd, J = 17.7 Hz, 6.0 Hz, 1H), 1.54 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 197.5, 170.3, 153.7, 149.1, 141.2, 138.1, 136.2, 133.6, 131.3, 130.5, 130.4, 128.7, 128.2, 125.3, 121.0, 113.1, 83.6, 50.2, 41.3, 31.5, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 3447, 1768, 1677, 1363, 1156, 469; **HRMS** (MALDI) calcd for $C_{24}H_{24}BrNO_5Na$, $[M+Na]^+$ 508.0736, found: 508.0730.

*tert-Butyl 3-(1-(5-Chloro-2-hydroxyphenyl)-3-oxo-3-phenylpropyl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**4ba**):* Prepared according to the general procedure C using 3-benzoyl-6-chloro-2*H*-chromen-2-one **2ba** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/2) furnished the desired product **4ba** as a white solid (94% yield, 41.5 mg). R_f 0.40 (EtOAc/Hex = 1/2); m.p.: 79.1-80.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.22 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 4.7 Hz, 2H), 7.08 (d, *J* = 2.6 Hz, 1H), 7.03 (dd, *J* = 8.6 Hz, 2.6 Hz, 1H), 6.95 (s, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 4.74 (t, *J* = 7.0 Hz, 1H), 4.27 (d, *J* = 1.4 Hz, 2H), 3.85 (dd, *J* = 17.7 Hz, 8.3 Hz, 1H), 3.63 (dd, *J* = 17.7 Hz, 6.2 Hz, 1H), 1.53 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 197.5, 170.3, 153.1, 149.1, 141.1, 138.1, 136.1, 133.6, 129.9, 128.7, 128.3, 128.2, 127.6, 125.7, 120.4, 83.6, 50.2, 41.3, 31.5, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 3436, 2076, 1635, 1375, 1299, 1158, 991, 775, 685; **HRMS** (ESI) calcd for $C_{24}H_{24}NO_5ClNa$, $[M+Na]^+$ 464.1241, found: 464.1241.

*tert-Butyl 3-(1-(3,5-Dichloro-2-hydroxyphenyl)-3-oxo-3-phenylpropyl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**4ca**):* Prepared according to the general procedure C using 3-benzoyl-6,8-dichloro-2*H*-chromen-2-one **2ca** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/5) furnished the desired product **4ca** as a white solid (98% yield, 46.7 mg). R_f 0.32 (EtOAc/Hex = 1/3); m.p.: 197.5-198.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 7.97 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 2.2 Hz, 1H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.09 (s, 1H), 6.94 (s, 1H), 4.80 (t, *J* = 7.0 Hz, 1H), 4.29-4.21 (m, 2H), 3.90 (dd, *J* = 17.6 Hz, 7.6 Hz, 1H), 3.62 (dd, *J* = 17.6 Hz, 6.7 Hz, 1H), 1.54 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 197.3, 169.1, 149.4, 148.5, 139.9, 139.2, 136.2, 133.5, 130.4, 128.7, 128.1, 127.7, 127.3, 125.5, 122.6, 83.4, 49.8, 40.7, 32.8, 28.0; **IR**

(KBr) $\tilde{\nu}$ (cm^{-1}): 3419, 1633, 1464, 1268, 757; **HRMS** (ESI) calcd for $C_{24}H_{23}Cl_2NO_5Na$, $[M+Na]^+$ 498.0851, found: 498.0852.

*tert-Butyl 3-(1-(2-Hydroxyphenyl)-3-(4-Methoxyphenyl)-3-oxopropyl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**4eb**):* Prepared according to the general procedure C using 3-(4-methoxybenzoyl)-2*H*-chromen-2-one **2eb** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/3) furnished the desired product **4eb** as a yellow solid (74% yield, 32.4 mg). R_f 0.40 (EtOAc/Hex = 2/3); m.p.: 77.8-78.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.05 (s, 1H), 7.95 (d, J = 8.8 Hz, 2H), 7.17 (d, J = 7.6 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 6.98-6.83 (m, 5H), 4.75 (t, J = 6.9 Hz, 1H), 4.30-4.15 (m, 2H), 3.90-3.80 (m, 4H), 3.62 (dd, J = 17.3 Hz, 6.5 Hz, 1H), 1.53 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 196.7, 170.3, 163.8, 154.2, 149.3, 141.5, 138.1, 130.5, 129.3, 128.3, 128.2, 128.0, 121.0, 118.8, 113.8, 83.3, 55.5, 50.0, 41.2, 31.9, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 3418, 2924, 2076, 1633, 1356, 1260, 1169, 757; **HRMS** (ESI) calcd for $C_{25}H_{27}NO_6Na$, $[M+Na]^+$ 460.1736, found: 460.1736.

*tert-Butyl 3-(1-(5-Bromo-2-hydroxyphenyl)-3-(4-Methoxyphenyl)-3-oxopropyl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**4ab**):* Prepared according to the general procedure C using 6-bromo-3-(4-methoxybenzoyl)-2*H*-chromen-2-one **2ab** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 2/3) furnished the desired product **4ab** as a white solid (80% yield, 41.3 mg). White solid; R_f 0.40 (EtOAc/Hex = 2/3); m.p.: 55.5-56.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.30 (s, 1H), 7.95 (d, J = 8.9 Hz, 2H), 7.24-7.12 (m, 2H), 6.97-6.88 (m, 3H), 6.81 (t, J = 9.9 Hz, 1H), 4.71 (t, J = 7.0 Hz, 1H), 4.34-4.19 (m, 2H), 3.89-3.73 (m, 4H), 3.57 (dd, J = 17.4 Hz, 6.3 Hz, 1H), 1.52 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 196.2, 170.2, 163.9, 153.7, 149.2, 141.0, 138.4, 131.3, 130.6, 130.5, 129.3, 120.6, 113.9, 112.8, 83.5, 55.5, 50.1, 41.1, 31.7, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 1780,

1723, 1602, 1478, 1357; **HRMS** (MALDI) calcd for $C_{25}H_{26}BrNO_6Na$, $[M+Na]^+$ 538.0836, found: 538.0840.

*tert-Butyl 3-(1-(5-Bromo-2-hydroxyphenyl)-3-(Naphthalen-2-yl)-3-oxopropyl)-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (**4ag**):* Prepared according to the general procedure C using 3-(2-naphthoyl)-6-bromo-2*H*-chromen-2-one **2ag** and *tert*-butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate **1**. Purification by column chromatography (EtOAc/Hex = 1/2) furnished the desired product **4ag** as a white solid (80% yield, 42.9 mg). R_f 0.40 (EtOAc/Hex = 1/2); m.p.: 112.3-113.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.53 (s, 1H), 8026 (s, 1H), 8.05-7.93 (m, 2H), 7.93-7.78 (m, 2H), 7.61 (td, *J* = 6.8 Hz, 1.3 Hz, 1H), 7.56 (td, *J* = 5.6 Hz, 1.3 Hz, 1H), 7.29 (d, *J* = 2.3 Hz, 1H), 7.20 (dd, *J* = 8.6 Hz, 2.2 Hz, 1H), 6.97 (d, *J* = 1.0 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 4.79 (t, *J* = 7.0 Hz, 1H), 4.35-4.21 (m, 2H), 4.03 (dd, *J* = 17.6 Hz, 8.2 Hz, 1H), 3.76 (dd, *J* = 17.6 Hz, 6.0 Hz, 1H), 1.54 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm: 197.5, 170.4, 153.7, 149.2, 141.2, 138.3, 135.8, 133.5, 132.5, 131.3, 130.6, 130.5, 130.1, 129.7, 128.8, 128.7, 127.8, 127.0, 123.7, 120.9, 113.1, 83.7, 50.2, 41.4, 31.7, 28.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 3419, 2083, 1631, 1268, 757; **HRMS** (ESI) calcd for $C_{28}H_{26}BrNO_5Na$, $[M+Na]^+$ 558.0892, found: 558.0895.

General procedure D for the synthesis of 9aa:

A mixture of DABCO (0.02 mmol), *α*-angelica lactone **8** (0.12 mmol) and 3-benzoyl-6-bromo-2*H*-chromen-2-one **2aa** in 0.5 mL of anhydrous THF was stirred at 30 °C until the completion of the reaction (monitored by ^{1}H NMR). Then the solvent was removed under reduced pressure and the residue was purified by column chromatography to give the desired product **9aa** as a mixture of diastereomers (A small amount of pure diastereomer could be obtained after repeated column chromatography, which was used to record the analytical data).

3-Benzoyl-6-bromo-4-(5-Methyl-2-oxo-2,5-dihydrofuran-3-yl)chroman-2-one ***(9aa)****:* Prepared according to the general procedure D using 3-benzoyl-6-bromo-2*H*-chromen-2-one **2aa** and *α*-angelica lactone **8**. Purification by column chromatography using hexanes as eluent furnished the desired product **9aa** (inseparable mixture of diastereomers) as a white solid (97% yield, 1.8:1 diastereomeric ratio, 41.4 mg). After repeated column chromatography using toluene as eluent, a small fraction of pure diastereomer (**9aa**-major) was obtained which was used for spectroscopic analysis. R_f 0.37 (EtOAc/Hex = 1/3).

For the major diastereomer (**9aa**-major): m.p.: 192.8-193.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm : 8.17-8.11 (m, 2H), 7.69-7.62 (m, 1H), 7.57-7.46 (m, 3H), 7.20 (d, *J* = 2.2 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.84 (t, *J* = 1.4 Hz, 1H), 5.30 (d, J = 3.4 Hz, 1H), 5.14-5.06 (m, 1H), 4.44 (s, 1H), 1.38 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ/ppm : 192.3, 171.4, 163.5, 153.5, 150.3, 134.7, 133.6, 133.1, 131.8, 130.9, 129.4, 129.2, 129.0, 128.6, 121.8, 119.2, 117.8, 78.5, 52.0, 36.7, 19.0; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 2930 (w), 1751 (s), 1683 (m), 1479 (m), 1224 (m), 1156 (m), 1025 (w); **HRMS** (ESI) calcd for $C_{21}H_{16}BrO_5$, $[M+H]^+$ 427.0181, found: 427.0181.

For the mixture of diastereomers (**9aa**-major + minor): **^{1}H NMR** (400 MHz, $CDCl_3$,) δ/ppm: 8.13 (d, 2H+2H', *J* = 7.6 Hz), 7.61-7.69 (m, 1H+1H'), 7.61-7.46 (m, 3H+3H'),7.20 (d, 1H+1H', *J* = 2.2 Hz), 7.10 (d, 1H+1H', *J* = 8.8 Hz), 6.84-6.90 (m, 1H+1H'), 5.30 (d, 1H, *J* = 3.5 Hz), 5.28 (d, 1H', *J* = 3.0 Hz), 5.16-5.01 (m, 1H+1H'), 4.45 (s, 1H+1H'), 1.43 (d, 3H', *J* = 6.9 Hz), 1.38 (d, 3H, *J* = 6.9 Hz); **^{13}C NMR** (400 MHz, $CDCl_3$) δ/ppm : 192.4 (C), 192.3 (C'), 171.4 (C+C'), 163.6 (C), 163.5 (C'), 153.5 (C), 150.3 (C+C'), 134.6 (C+C'), 133.6 (C), 133.5 (C'), 133.0 (C+C'), 131.7 (C'), 131.6 (C), 130.9 (C'), 130.8 (C), 129.3 (C+C'), 129.1 (C+C'), 121.7 (C+C'), 119.1 (C+C'), 117.75 (C), 117.71 (C'), 78.4 (C+C'), 52.0 (C'), 51.7 (C), 36.8 (C), 36.6 (C'), 18.9 (C'), 18.7 (C).

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge via the Internet at http://pubs.acs.org.

Optimization data and copies of ^{1}H and ^{13}C NMR spectra for all new compounds (PDF)

X-ray crystallographic data for compound **3aa** (CIF)

X-ray crystallographic data for compound **4aa** (CIF)

X-ray crystallographic data for compound **9aa** (CIF)

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Notes

The authors declare no competing financial interest.

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