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TMSI-Promoted Vinylogous Michael Addition of Siloxyfuran to 2-Substituted Chromones: A General Approach for the Total Synthesis of Chromanone Lactone Natural Products

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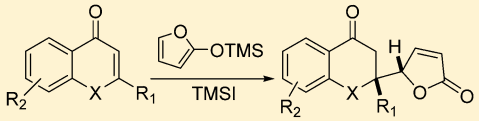
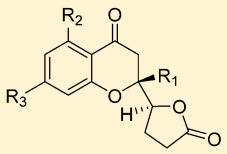
Supporting Information





Microdiplodiasone, R_1 = Me, R_2 = R_3 = OH
Lachnone C, R_1 = Me, R_2 = OH, R_3 = CH_2OH
Gonytolide C, R_1 = CO_2Me, R_2 = OH, R_3 = Me
Gonytolide G, R_1 = CO_2Me, R_2 = OH, R_3 = CH_2OH

ABSTRACT: A concise and facile synthetic protocol for the construction of the 2-γ-lactone chromanone skeleton has been achieved through a TMSI-promoted diastereoselective vinylogous Michael addition of siloxyfuran to 2-substituted chromones. The applicability of this method is demonstrated through the rapid access to the total syntheses of (±)-microdiplodiasone, (±)-lachnone C, and (±)-gonytolides C and G.

INTRODUCTION

The chromanone core[1] substituted with the γ-lactone moiety constitutes a privileged scaffold of numerous natural products (Figure 1).[2] Most of these compounds exhibited promising biological activities. For example, gonytolide A,[2a] which is composed of two monomeric units of gonytolide C,[2b] showed interesting immune response promoting activity, xanthoquinodin A4 was active against human cancer cells,[2c] and microdiplodiasone displayed significant antimicrobial activity.[2d]

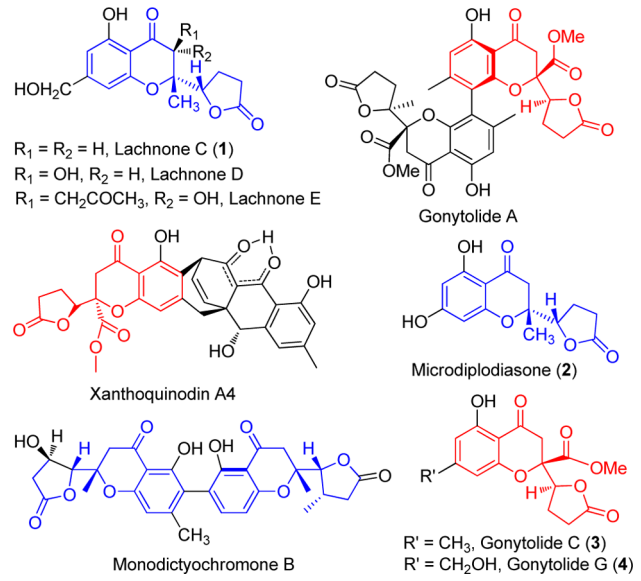


Figure 1. Structures of natural products possessing the 2-γ-lactone chromanone skeleton.

As a consequence of these intriguing bioactivities, together with their distinguished molecular structures, several groups have been interested in the syntheses of these natural products.[3] The Bräse group reported the enantioselective synthesis of lachnone C via a domino vinylogous aldol-oxa-Michael reaction.[3a] Recently, a domino approach to the enantioselective total syntheses of blennolide C and gonytolide C was reported by Tietze et al.[3b] The stereoselective total synthesis of gonytolide C has been accomplished by Sudhakar and co-workers via diastereoselective intramolecular cyclization.[3c] Despite the various synthetic strategies reported, a general strategy for the efficient synthesis of these types of compounds through a common intermediate is still lacking. The main challenge lies in the construction of the two contiguous stereogenic centers which contain a γ-lactone moiety attached to the substituted chromanone skeleton.

Vinylogous Mukaiyama–Michael (VMM) reactions of the α,β-unsaturated carbonyl compounds[4] and 2-(trialkylsilyloxy)-furans have been extensively studied and proven to be a valuable and straightforward method for introducing γ-butenolides.[3d,5] Even though great progress has been achieved in this area in recent years, the synthesis of the 2-γ-lactone

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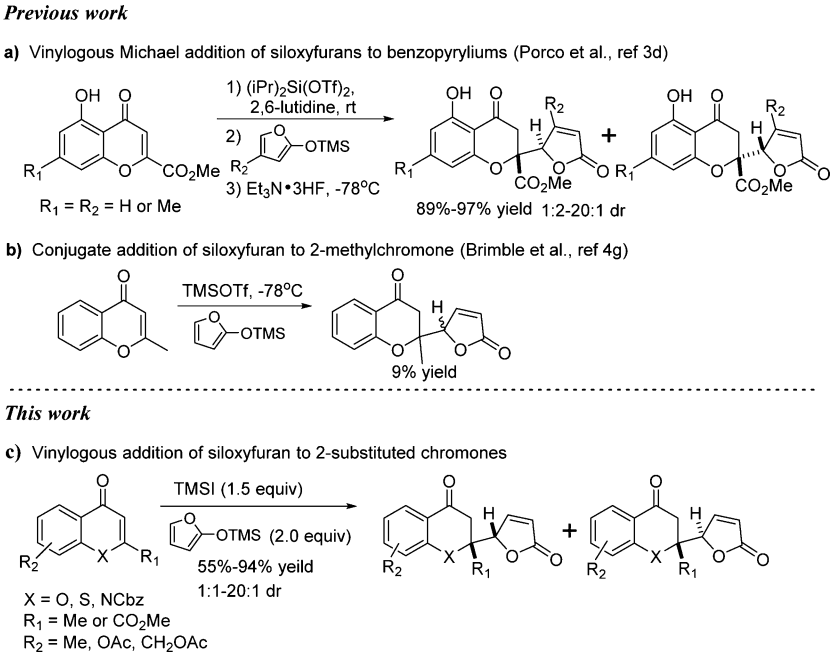
Scheme 1. Syntheses of 2-γ-Lactone Chromanones



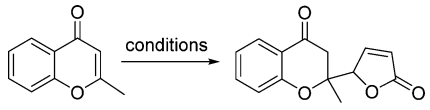
chromanone core via a conjugate addition approach still remains a formidable challenge. The difficulties mainly come from the substituent, especially the alkyl substituent at C_2 of chromone, which would lead to lower reactivity in the conjugate addition.[4d] Porco and co-workers recently have made remarkable contribution in this field by developing a novel dialkylsilyl triflate assisted vinylogous Michael addition of siloxyfurans to benzopyryliums. This method offers a direct access to 2-methoxycarbonyl 2-γ-lactone chromanone skeletons (Scheme 1a).[3d] However, efficient methods for the construction of more challenging 2-methyl 2-γ-lactone chromanone skeletons,[6] which are also the privileged core components of numerous biologically active natural products (such as microdiplodiasone, lachnones C−E,[2e] and monodictyochromone B[2f]), still remain more elusive. To our knowledge, only Brimble et al.[4d] have recently reported the construction of a 2-methyl 2-γ-lactone chromanone skeleton through the conjugate addition of 2-methylchromone with 2-trimethylsilyloxyfuran; however, the desired addition product was obtained in low yield (Scheme 1b).

In this regard, we explored a general access to the syntheses of 2-γ-lactone chromanone skeletons, especially those substituted with methyl at C_2. Accordingly, in this paper, we report a general strategy for the construction of 2-γ-lactone chromanone skeletons via a TMSI-promoted vinylogous Michael addition of siloxyfuran to C_2-substituted chromones (Scheme 1c). This protocol has a broad substrate scope and tolerates a large range of functional groups. Moreover, the applicability of this sequence is demonstrated through the efficient total syntheses of (±)-lachnone C (**1**), (±)-microdiplodiasone (**2**), and (±)-gonytolides C (**3**) and G (**4**).

RESULTS AND DISCUSSION

We initiated our studies using 2-methylchromone **5a** as a model substrate to explore the reaction conditions. Selected representative screening results for this model reaction are presented in Table 1. Unfortunately, frequently used Lewis acids, such as $TiCl_4$, $BF_3{\cdot}OEt_2$, $Sc(OTf)_3$, and $Cu(OTf)_2$, did not promote the desired vinylogous Michael addition. Recently, iodine has been used as a Lewis acid catalyst for the activation of carbonyl compounds, including α,β-unsaturated compounds, in excellent yields with high diastereoselctivity.[7] As expected, a catalytic amount of I_2 could promote this vinylogous Michael addition (Table 1, entry 1), resulting in the addition product **6a** in 15% yield. Increasing the amount of I_2 to 1.2 equiv led to a slightly reduced yield (Table 1, entry 2). The use of ICl[8] instead of I_2 could dramatically increase the yield to 60% (Table 1, entry 3). To our delight, in the presence of 1.2 equiv of iodotrimethylsilane (TMSI),[9] the desired product could be isolated in 76% yield (Table 1, entry 4). Thus, TMSI turned out to be the effective Lewis acid for vinylogous Michael

Table 1. Vinylogous Michael Addition of 2-Trimethylsilyloxyfuran to 2-Methylchromone 5a[a]



5a **6a**

entry	Lewis acid (amt (equiv))	temp (°C)	time (h)	yield[b] (%)	dr[c]
1	I_2 (0.1)	room temp	24	15	1:1
2	I_2	room temp	24	13	1:1
3	ICl	room temp	4	60	1:1
4	TMSI[d] (1.2)	room temp	4	76	1:1
5	**TMSI[d] (1.5)**	**room temp**	**4**	**81**	**1:1**
6	TMSI[d] (1.5)	0	4	78	1:1
7	TMSI[d] (1.5)	room temp	24	73	1:1
8	TMSI[d] (2.0)	room temp	4	80	1:1
9	TMSI[e]	room temp	4	79	1:1

[a]Unless otherwise noted, all reactions were carried out with 0.2 mmol of **5a**, 2.0 equiv of 2-trimethylsilyloxyfuran, and 1.2 equiv of Lewis acid at room temperature in 2 mL of anhydrous DCM. [b]Isolated yields. [c]Determined by ^1H NMR spectroscopy. [d]TMSI was generated in situ from TMSCl and NaI in anhydrous DCM. [e]TMSI was purchased from a commercial supplier.

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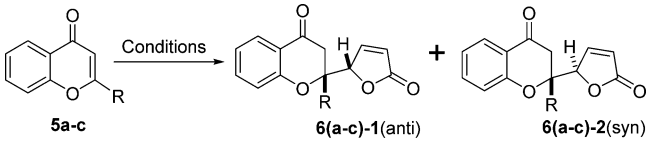
addition of 2-trimethylsilyloxyfuran to 2-methylchromone. Encouraged by this result, we further examined the reaction conditions. When the amount of TMSI was increased to 1.5 equiv, a slightly increased yield was obtained (Table 1, entry 5). Further extension of the reaction time to 24 h led to a reduced yield (Table 1, entry 7). This may be attributed to the gradual decomposition of 2-trimethylsilyloxyfuran, which was unstable at room temperature. In addition, increasing the amount of TMSI to 2.0 equiv (Table 1, entry 8) did not promote the yield of **6a**. Notably, commercially available TMSI just led to a slightly reduced yield (Table 1, entry 9). When the reaction temperature was reduced to 0 °C, the yield of **6a** was slightly reduced (Table 1, entry 6).

Having established the optimal reaction conditions (Table 1, entry 5), we further evaluated the effect of temperature and substituents at C_2 of chromones on this vinylogous Michael addition, as shown in Table 2. The chromone **5b**, which is not substituted at C_2, showed high activity, and the adduct was obtained in 82% yield with a 1:1 diastereoselectivity at −60 °C within 1 h (Table 2, entry 2). When the reaction temperature was raised to 0 °C or reduced to −80 °C (even on prolonging the reaction time to 24 h), the yield of **6b** was slightly reduced, while the diastereoselectivity presented no differences due to less hindrance at C_2 (Table 2, entries 1 and 3). In contrast, 2-methylchromone **5a** is much less active. The vinylogous Michael addition of **5a** and 2-trimethylsilyloxyfuran proceeded smoothly at room temperature, and the adduct **6a** could be obtained in 81% yield with a 1:1 diastereoselectivity (Table 2, entry 4). When the reaction temperature was reduced to 0 °C, the yield of **6a** was slightly reduced, but the diastereoselectivity was not improved (Table 2, entry 5). Further reducing the temperature to −60 °C led to the suppression of the reaction, and only a trace of the desired product could be observed (Table 2, entry 6). Chromone **5c** substituted with an electron-withdrawing and more sterically hindering CO_2Me group at C_2 showed higher activity and diastereoselectivity. The adduct could be obtained in 94% yield with a 2:1 diastereoselectivity at −60 °C within 1 h (Table 2, entry 8). Increasing the reaction temperature to 0 °C led to a reduced diastereoselectivity (Table 2, entry 7). Reducing the temperature to −80 °C could not further promote the diastereoselectivity (Table 2, entry 9).

Table 2. Vinylogous Michael Addition of 2-Trimethylsilyloxyfuran to Chromones Substituted with Different Groups at C_2[a]



entry	substrate	R	temp (°C)	time (h)	yield[b] (%)	dr[c]
1	**5b**	H	0	1	75	1:1
2	**5b**	H	−60	1	82	1:1
3	**5b**	H	−80	4	80	1:1
4	**5a**	Me	room temp	4	81	1:1
5	**5a**	Me	0	4	78	1:1
6	**5a**	Me	−60	24	trace	nd[d]
7	**5c**	CO_2Me	0	1	88	1:1
8	**5c**	CO_2Me	−60	1	94	2:1
9	**5c**	CO_2Me	−80	4	86	2:1

[a]All reactions were carried out with 0.2 mmol of **5**, 2.0 equiv of 2-trimethylsilyloxyfuran, and 1.5 equiv of TMSI in 2 mL of anhydrous DCM at the corresponding time and temperature. TMSI was generated in situ from TMSCl and NaI in anhydrous DCM. [b]Isolated yields. [c]Determined by ^{1}H NMR spectroscopy. [d]Not detected.

Next, the scope and generality of this vinylogous Michael addition reaction were investigated (Table 3). For various chromones with different substituents, the desired products **6a−o** were obtained in moderate to high yield (55−94%) as diastereomeric mixtures (1:1 to 20:1 dr). In general, the electron density of the benzene ring has an obvious effect on the reaction activity, while the steric hindrance at C_2 had a positive impact on the diastereoselectivity of the adduct. For 2-methylchromone substrates bearing one or two electron-donating substituents (such as OMe) on the benzene ring, the reaction could not proceed even at room temperature for 24h (**6d,e**). To our delight, when the hydroxyl group was protected by acetyl, the reaction proceeded smoothly and the desired products were obtained in moderate yield with 3:1 to 20:1 diastereoselectivities (**6f−i**). 2-Methoxycarbonyl chromones bearing an acetoxyl group, a methyl group, or a hydroxymethyl group on the benzene ring underwent addition with excellent efficiency (**6j−l**). 2-Methoxycarbonyl chromone with a methoxy group and a methyl group on the benzene ring displayed low activity, giving the addition product (**6m**) in moderate yield (60%) and diastereoselectivity (1:1). This result suggested again that the activities of 2-methoxycarbonyl chromones were higher than those of 2-methylchromones, as mentioned in Table 2. Furthermore, we also examined the vinylogous Michael addition of thiochromone and Cbz-protected 4-quinolone[10] with 2-trimethylsilyloxyfuran. The desired products (**6n,o**) were generated in moderate yields. These results serve to illustrate the applicability and generality of this TMSI-promoted vinylogous Michael addition of siloxyfuran to chromones.

To determine the relative configurations of the major and minor isomers of **6**, ^{1}H and ^{13}C NMR spectra of the isolated main product **6h** were assigned using NOESY NMR techniques.[7c,11] The strong NOE signal between H_a and H_b in the major isomer is in accordance with the predominant formation of the anti product. The representative NOE signals for *anti*-**6h** are summarized in Figure 2. Therefore, the major diastereomers of **6** were assigned as the anti isomers, while the minor diastereomers were assigned as the syn isomers.

With various chromanone butenolides in hand, we then turned our attention to the utilization of these synthetic building blocks in the total syntheses of (±)-lachnones C (**1**), (±)-microdiplodiasone (**2**) (Scheme 2), and (±)-gonytolides C (**3**) and G (**4**) (Scheme 3). Starting from chromanone butenolides **6h,i,k,l**, these four natural products could be succinctly synthesized through a general two-step deprotection/conjugate reduction sequence,[3d] respectively. It is noteworthy that this work is the first total synthesis of (±)-microdiplodiasone (**2**). These synthetic applications further demonstrated the high efficiency and applicability of our methodology.

CONCLUSION

In conclusion, we have developed a novel and efficient approach for the concise syntheses of 2-γ-lactone chromanone skeletons through a TMSI-promoted diastereoselective vinylogous Michael addition of siloxyfuran to 2-substituted chromones. This protocol exhibits a wide range of applications for various chromones, thiochromone, and quinolone, giving the corresponding addition products in moderate to good

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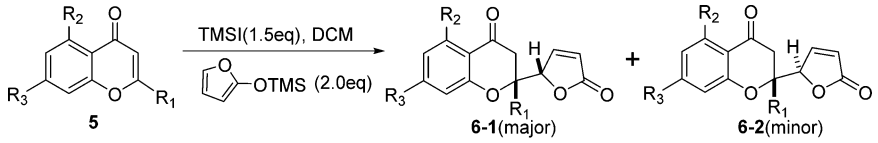
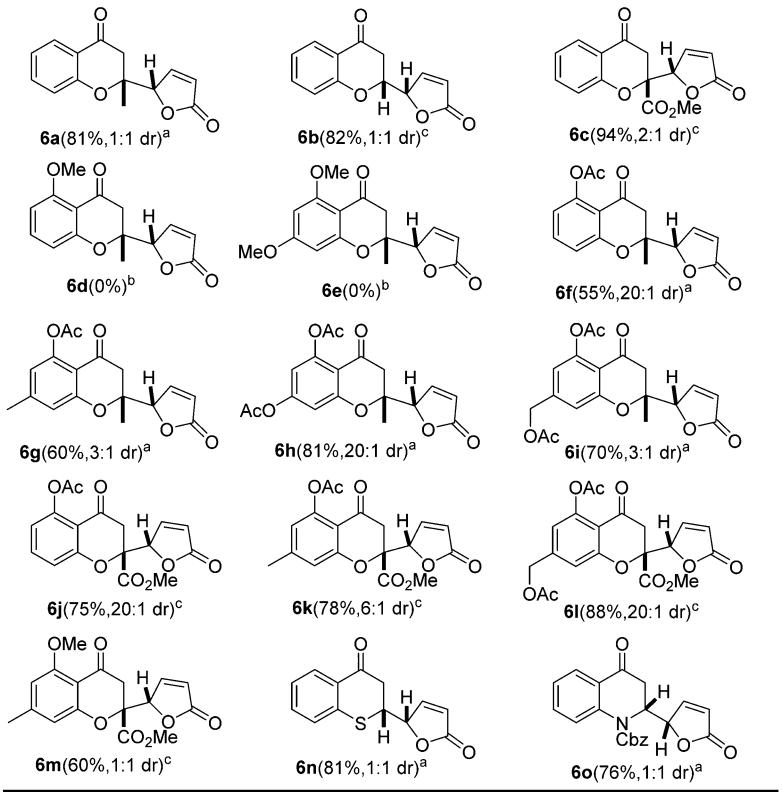
Table 3. Substrate Scope of TMSI-Promoted Vinylogous Michael Addition of Siloxyfuran to 2-Substituted Chromones[a]





[a]Unless otherwise noted, all reactions were carried out with 0.2 mmol of **5**, 2.0 equiv of 2-trimethylsilyloxyfuran, and 1.5 equiv of TMSI in 2 mL of anhydrous DCM at room temperature for 4 h. TMSI was generated in situ from TMSCl and NaI in anhydrous DCM. Major isomers of **6** and isolated yields are given. dr values were determined by ^{1}H NMR spectroscopy. [b]At room temperature for 24 h. [c]At −60 °C for 1 h.

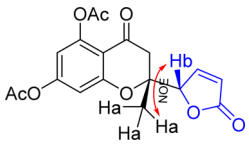


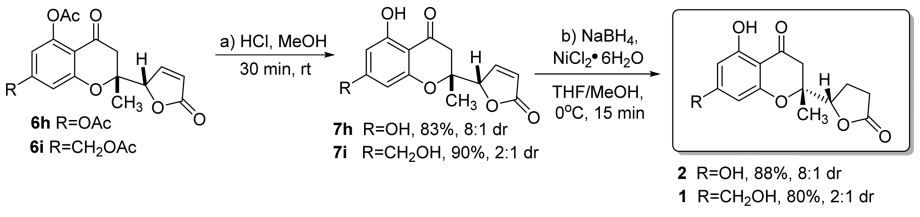
Figure 2. Representative NOE responses for the anti isomer of **6**.

yields with moderate to high diastereoselectivity. In addition, the effectiveness and utility of this method have been fully demonstrated through the total syntheses of (±)-lachnone C, (±)-microdiplodiasone, and (±)-gonytolides C and G. Further research toward the development of the asymmetric variant of the reported reaction and the utilization of this reaction for the total syntheses of other natural products containing 2-γ-lactone chromanone skeletons are currently under investigation in our laboratory.

EXPERIMENTAL SECTION

General Experimental Methods. All manipulations were conducted with a round-bottom flask in dry air. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on GF254 plates. Silica gel (200−300 mesh) was used for column chromatography. Unless otherwise noted, commercially available reagents and solvents were used without any purification. The distillation range of petroleum ether was 60−90 °C. DCM was freshly distilled from CaH_2. ^{1}H and ^{13}C NMR spectra were recorded on 400 (100) MHz instruments, and spectral data were reported in

Scheme 2. Total Syntheses of (±)-Lachnones C (1) and (±)-Microdiplodiasone (2)



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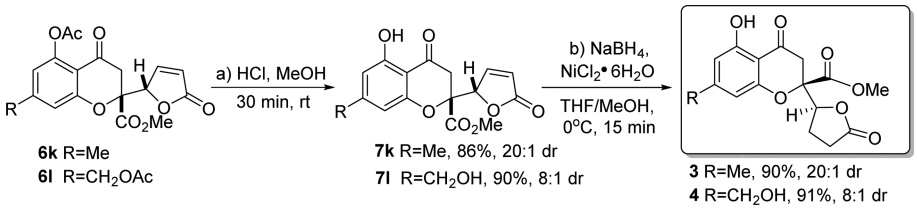
Scheme 3. Total Syntheses of (±)-Gonytolides C (3) and G (4)



ppm relative to tetramethylsilane (TMS) as the internal standard. High-resolution mass spectra (HRMS) were obtained on a mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time of flight (QTof). IR spectra were recorded on a FT-IR spectrometer, and only major peaks are reported (in cm^{-1}). Melting points were determined on a microscopic apparatus and are uncorrected. The following abbreviations are used for the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br s, broad singlet for proton spectra. Coupling constants (J) are reported in hertz (Hz).

General Procedure A for the Preparation of 2-Substituted Chromones. To a solution of the corresponding 2-hydroxyacetophenone (1 equiv) in dry ethyl formate or ethyl acetate was added sodium (6 equiv). The reaction mixture was stirred at room temperature for 18 h. Cold 0.5 N HCl was then added, the aqueous layer was separated, and the remaining organic layer was dried and evaporated in vacuo to give the crude diketone. A solution of the crude diketone with 2 drops of concentrated HCl in methanol was stirred at room temperature for 4 h. The methanol was removed in vacuo to give a residue, followed by adding ethyl acetate and washing with brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford a crude product, which was purified via silica gel flash column chromatography to give the title compound.

General Procedure B for the Preparation of 2-Substituted Chromones. The corresponding 2-hydroxyacetophenone (1 equiv) was dissolved in acetic anhydride. Anhydrous sodium acetate (3 equiv) was added. The mixture was stirred and refluxed for 24 h. The reaction mixture was cooled, diluted with H_2O, and then extracted with EtOAc. The combined organic extracts were washed with H_2O until the aqueous washes were neutral to pH paper, dried over anhydrous Na_2SO_4, and then concentrated. The residue was dissolved in water, and anhydrous sodium carbonate (5 equiv) was added. The mixture was refluxed for 2 h. The reaction mixture was cooled and neutralized with concentrated HCl. The aqueous layers were extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel flash column chromatography.

General Procedure C for the Preparation of 2-Substituted Chromones.[3d] The corresponding 2-hydroxyacetophenone (1 equiv) and dimethyl oxalate (5 equiv) were dissolved in MeOH/MeONa solution (freshly prepared by dissolving Na (5 equiv) in MeOH), and the reaction mixture was heated to reflux overnight. After the mixture was cooled, the solvent was removed in vacuo and H_2O was added. A yellow precipitate was formed immediately upon acidification with concentrated HCl. The resulting solid was collected by vacuum filtration and dissolved in MeOH. More concentrated HCl was added, and the solution was refluxed for 2 h. The aqueous phase was extracted three times with EtOAc. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel flash column chromatography.

General Procedure D for the Acetylation of Chromones and Hydroxyacetophenones. To a solution of the corresponding hydroxyacetophenone or hydroxychromone (1 equiv) in dry DCM were added successively triethylamine (1.5 equiv), acetyl chloride (1.5 equiv), and a catalytic amount of DMAP. The resulting solution was stirred at room temperature for the appropriate time. After the reaction was complete (detected by TLC), the solution was then diluted with DCM and poured into ice-cold 1 M aqueous hydrochloric acid. The organic phase was separated and washed with dilute aqueous $NaHCO_3$ solution and brine in turn. The organic phase was dried with anhydrous Na_2SO_4, the solvent was removed under reduced pressure, and the resultant crude product was purified by silica gel flash column chromatography.

General Procedure E for the Syntheses of Brominated Chromones and Ketones. To a mixture of chromone or ketone (1.0 equiv) and AIBN (0.1 equiv) in CCl_4 (10 mL) was added NBS (1.5 equiv). The resulting mixture was stirred and heated to reflux for 8 h. The reaction mixture was quenched with water and diluted with DCM, and the separated organic layer was washed with 1 M aqueous hydrochloric acid, dried with anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by silica gel flash column chromatography.

*2-Methyl-4H-chromen-4-one (**5a**).* This compound was prepared according to general procedure A from 2-hydroxyacetophenone (2.7 g, 20 mmol, 1 equiv) and sodium (2.8 g, 120 mmol, 6 equiv) in dry ethyl acetate (30 mL). The crude product was purified via flash column chromatography (silica gel, PE/EtOAc 8/1 v/v as eluent) to give the title compound **5a** (2.3 g, 71% in two steps) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, 1H, J = 8.0 Hz, 1.6 Hz), 7.61 (td, 1H, J = 8.4 Hz, 1.6 Hz), 7.39−7.32 (m, 2H), 6.16 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.1, 166.2, 156.4, 133.4, 125.5, 124.8, 123.4, 117.7, 110.4, 20.5. All spectroscopic data were consistent with previously reported data.[4g]

*Chromone (1-Benzopyran-4-one) (**5b**).* This compound was prepared according to general procedure A from 2-hydroxyacetophenone (2.7 g, 20 mmol, 1 equiv) and sodium (2.8 g, 120 mmol, 6 equiv) in dry ethyl formate (30 mL). The crude product was purified via flash column chromatography (silica gel, PE/EtOAc 8/1 v/v as eluent) to give the title compound **5b** (2.1 g, 73% in two steps) as pale yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, 1H, J = 8.0 Hz, 1.6 Hz), 7.86 (d, 1H, J = 6.0 Hz), 7.67−7.63 (m, 1H), 7.44−7.36 (m, 2H), 6.33 (d, 1H, J = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 156.2, 155.2, 133.5, 125.4, 125.0, 124.6, 117.9, 112.7. All spectroscopic data were consistent with previously reported data.[4g]

*Methyl 4-Oxo-4H-chromene-2-carboxylate (**5c**).* This compound was prepared according to general procedure C from 2-hydroxyacetophenone (5.5 g, 40 mmol, 1 equiv), dimethyl oxalate (11.8 g, 100 mmol, 2.5 equiv), and 200 mL of MeOH/MeONa solution (freshly prepared by dissolving Na (2.3 g, 100 mmol, 2.5 equiv) in 200 mL of MeOH) to afford a bright yellow solid. The crude product was purified by flash column chromatography (silica gel, PE/EtOAc 8/1 v/v as eluent) to afford **5c** (4.9 g, 60%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, 1H, J = 8.0 Hz, J = 1.6 Hz), 7.74 (td, 1H, J = 8.4 Hz, 1.6 Hz), 7.60 (d, 1H, J = 8.0 Hz), 7.47−7.43 (m, 1H), 7.11 (s, 1H), 4.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.3, 161.0, 155.9, 151.9, 134.7, 125.9, 125.7, 124.4, 118.7, 114.9, 53.5. All spectroscopic data were consistent with previously reported data.[12]

*5-Hydroxy-2-methyl-4H-chromen-4-one (**8**).* This compound was prepared according to general procedure A from 2,6-dihydroxyacetophenone (1.5 g, 10.0 mmol, 1 equiv) and sodium (1.4 g, 60 mmol, 6 equiv) in dry ethyl acetate (15 mL). The crude product was purified via flash column chromatography (silica gel, PE/EtOAc 4/1 v/v as eluent) to give the title compound **8** (1.1 g, 65% in two steps) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.53 (s, 1H), 7.46 (t, 1H, J = 8.4 Hz), 6.83 (dd, 1H, J = 8.0 Hz, 0.8 Hz), 6.74 (dd, 1H, J = 8.0 Hz, 0.8 Hz), 6.08 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.4, 167.6, 160.7, 156.7, 135.0, 111.1, 110.3, 109.0, 106.7,

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20.5. All spectroscopic data were consistent with previously reported data.[13]

*5-Methoxy-2-methyl-4H-chromen-4-one (**5d**).* A solution of **8** (352 mg, 2.0 mmol, 1.0 equiv) in anhydrous DMF was added to NaH (57.6 mg, 2.4 mmol, 1.2 equiv) at room temperature, and the resulting suspension was stirred for 10 min. Iodomethane (340.8 mg, 2.4 mmol, 1.2 equiv) was then added dropwise, and the mixture was stirred at room temperature until completion as determined by TLC. The reaction mixture was then diluted with ethyl acetate, washed twice with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, PE/EtOAc 2/1 v/v as eluent) to give **5d** (285.1 mg, 75%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (t, 1H, J = 8.4 Hz), 6.98 (dd, 1H, J = 8.4 Hz, J = 0.8 Hz,), 6.78 (d, 1H, J = 8.4 Hz), 6.09 (s, 1H), 3.97 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.2, 163.7, 159.7, 158.6, 133.4, 114.2, 112.1, 109.9, 106.2, 56.4, 19.9. All spectroscopic data were consistent with previously reported data.[4g]

*2-Methyl-4-oxo-4H-chromen-5-yl Acetate (**5f**).* This compound was prepared according to general procedure D from chromone **8** (467 mg, 2.7 mmol, 1 equiv), triethylamine (0.6 mL, 4.0 mmol, 1.5 equiv), acetyl chloride (0.3 mL, 4.0 mmol, 1.5 equiv), and DMAP (catalytic equiv) to afford an orange solid. The crude product was purified by flash column chromatography (silica gel, PE/EtOAc 2/1 v/v as eluent) to afford **5f** (543.0 mg, 94%) as a white solid. Mp: 91−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (t, 1H, J = 8.0 Hz), 7.33 (dd, 1H, J = 0.8 Hz, J = 8.4 Hz), 6.99 (dd, 1H, J = 0.4 Hz, J = 8.0 Hz), 6.05 (s, 1H), 2.43 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9, 169.8, 165.0, 157.7, 149.2, 133.1, 118.9, 116.7, 116.0, 111.6, 21.1, 20.2. HRMS-ESI (m/z): calcd for $C_{12}H_{11}O_4$ $[M + H]^+$ 219.0652, found 219.0650. IR (neat): 3341, 3077, 2956, 2925, 2375, 1768, 1658, 1618, 1511, 1469, 1391, 1365, 1248, 1201, 1041, 995, 955, 877, 790, 785, 686 cm^{-1}.

*5-Hydroxy-2,7-dimethyl-4H-chromen-4-one (**9**).* This compound was prepared according to general procedure B from 2,6-dihydroxy-4-methylacetophenone (1.7 g, 10 mmol, 1 equiv) in acetic anhydride (4.5 mL), anhydrous sodium acetate (2.5 g, 30 mmol, 3 equiv), and anhydrous sodium carbonate (5.3 g, 50 mmol, 5 equiv). The crude product was purified by flash column chromatography (silica gel, PE/EtOAc 8/1 v/v as eluent) to give the title compound **9** (1.1 g, 60% in two steps) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.44 (s, 1H), 6.66 (s, 1H), 6.59 (s, 1H), 6.05 (s, 1H), 2.39 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.1, 167.2, 160.4, 156.7, 146.9, 112.0, 108.9, 108.3, 107.2, 22.3, 20.5. All spectroscopic data were consistent with previously reported data.[14]

*2,7-Dimethyl-4-oxo-4H-chromen-5-yl Acetate (**5g**).* This compound was prepared according to general procedure D from chromone **9** (380 mg, 2.0 mmol, 1 equiv), triethylamine (0.4 mL, 3.0 mmol, 1.5 equiv), acetyl chloride (0.2 mL, 3.0 mmol, 1.5 equiv), and DMAP (catalytic equiv) to afford an orange solid. The crude product was purified by flash column chromatography (silica gel, PE/EtOAc 2/1 v/v as eluent) to afford **5g** (422.2 mg, 91%) as a white solid. Mp: 154−155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (s, 1H), 6.80 (s, 1H), 6.00 (s, 1H), 2.43 (s, 3H), 2.41 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 169.9, 164.7, 157.6, 148.8, 144.7, 120.1, 115.8, 114.3, 111.4, 21.6, 21.1, 20.1. HRMS-ESI (m/z): calcd for $C_{13}H_{13}O_4$ $[M + H]^+$ 233.0808, found 233.0813. IR (neat): 3421, 2920, 2846, 1771, 1656, 1613, 1486, 1389, 1364, 1199, 1172, 1064, 933, 867 cm^{-1}.

*5,7-Dihydroxy-2-methyl-4H-chromen-4-one (**10**).* This compound was prepared according to general procedure B from a mixture of 2,4,6-trihydroxyacetophenone (2.7 g, 16.1 mmol, 1 equiv) in acetic anhydride (8.1 mL), anhydrous sodium acetate (4.0 g, 48.3 mmol, 3 equiv), and anhydrous sodium carbonate (8.5 g, 80.6 mmol, 5 equiv). The crude product was purified by flash column chromatography (silica gel, PE/EtOAc 4/1 v/v as eluent) to give the title compound **10** (1.80 g, 59% in two steps) as a beige powder. Mp:256−259 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.81 (s, 1H), 10.79 (s, 1H), 6.30 (s, 1H), 6.16 (s, 1H), 6.15 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 181.8, 167.7, 164.1, 161.5, 157.8, 107.9, 103.4, 98.7, 93.7, 19.9. HRMS-ESI (m/z): calcd for $C_{10}H_9O_4$ $[M + H]^+$ 193.0495, found 193.0493. IR (neat): 3438, 2936, 2253, 2127, 1658, 1450, 1388, 1353, 1270, 1167, 1051, 1027, 1005, 825, 763, 630 cm^{-1}. All spectroscopic data were consistent with previously reported data.[15]

*5,7-Dimethoxy-2-methyl-4H-chromen-4-one (**5e**).* To a refluxing solution of **10** (384 mg, 2.0 mmol, 1.0 equiv) and K_2CO_3 (607 mg, 4.4 mmol, 2.2 equiv) in acetone (10 mL) was added $(CH_3)_2SO_4$ (605 mg, 4.8 mmol, 2.4 equiv) dropwise. The mixture was stirred at reflux for 4 h and cooled. The solution was filtered, and the solvent was evaporated to afford the crude product, which was purified by flash chromatography (silica gel, PE/EtOAc 2/1 v/v as eluent) to give **5e** (317 mg, 72%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.41 (s, 1H), 6.33 (s, 1H), 6.00 (s, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 163.7, 162.9, 160.8, 160.0, 111.8, 108.8, 95.8, 92.6, 56.2, 55.5, 19.6. All spectroscopic data were consistent with previously reported data.[16]

*2-Methyl-4-oxo-4H-chromene-5,7-diyl Diacetate (**5h**).* This compound was prepared according to general procedure D from chromone **10** (384 mg, 2.0 mmol, 1 equiv), triethylamine (0.4 mL, 3.0 mmol, 1.5 equiv), acetyl chloride (0.2 mL, 3.0 mmol, 1.5 equiv), and DMAP (catalytic equiv) to afford a colorless solid. The crude product was purified by flash column chromatography (silica gel, PE/EtOAc 2/1 v/v as eluent) to afford **5h** (469.2 mg, 85%) as a white solid. Mp: 115−117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, 1H, J = 2.4 Hz), 6.79 (d, 1H, J = 2.0 Hz), 6.02 (s, 1H), 2.40 (s, 3H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 169.3, 167.9, 165.1, 157.8, 153.6, 150.1, 114.5, 113.4, 111.5, 108.7, 21.1, 21.0, 20.0. HRMS-ESI (m/z): calcd for $C_{14}H_{13}O_6$ $[M + H]^+$ 277.0707, found 277.0711. IR (neat): 3439, 3072, 2940, 2361, 1772, 1664, 1621, 1390, 1367, 1197, 1130, 1060, 1027, 937, 902, 851, 708, 666, 572 cm^{-1}.

*2-Acetyl-5-methyl-1,3-phenylene Diacetate (**11**).* This compound was prepared according to general procedure D from 2,6-dihydroxy-4-methylacetophenone (498 mg, 3.0 mmol, 1 equiv), triethylamine (1.0 mL, 7.5 mmol, 2.5 equiv), acetyl chloride (0.53 mL, 7.5 mmol, 2.5 equiv), and DMAP (catalytic equiv) to afford a white solid. The crude product was purified by flash column chromatography (silica gel, PE/EtOAc 4/1 v/v as eluent) to afford **11** (712.5 mg, 95%) as a white solid. Mp: 38−39 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (s, 2H), 2.42 (s, 3H), 2.35 (s, 3H) 2.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 168.7, 147.7, 142.1, 124.7, 121.0, 31.0, 21.2, 20.8. HRMS-ESI (m/z): calcd for $C_{13}H_{15}O_5$ $[M + H]^+$ 251.0914, found 251.0926. IR (neat): 3404, 2919, 2857, 1767, 1694, 1620, 1419, 1366, 1247, 1183, 1119, 1048, 879, 666, 577 cm^{-1}.

*2-Acetyl-5-(bromomethyl)-1,3-phenylene Diacetate (**12**).* This compound was prepared according to general procedure E from compound **11** (4.5 g, 18 mmol, 1 equiv), NBS (4.8 g, 27 mmol, 1.5 equiv), and AIBN (0.30 g, 1.8 mmol, 0.1 equiv) to afford a yellow solid. The crude product was purified by gel column chromatography (PE/EtOAc 8/1 v/v as eluent) to give **12** (5.0 g, 85%) as a yellow solid. Mp: 56−57 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (s, 2H), 4.42 (s, 2H), 2.46 (s, 3H), 2.28 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 168.5, 147.9, 141.0, 127.4, 120.9, 31.1, 31.0, 20.9. HRMS-ESI (m/z): calcd for $C_{13}H_{14}BrO_5$ $[M + H]^+$ 329.0019, found 329.0033. IR (neat): 3434, 2922, 2852, 1772, 1697, 1649, 1548, 1422, 1380, 1245, 1181, 1047, 950, 886, 754, 661 cm^{-1}.

*5-Hydroxy-7-(hydroxymethyl)-2-methyl-4H-chromen-4-one (**13**).* This compound was prepared according to general procedure B from benzyl bromide acetophenone **12** (4.2 g, 12.8 mmol, 1 equiv), anhydrous sodium acetate (3.2 g, 38.4 mmol, 3 equiv), acetic anhydride (20 mL), and anhydrous sodium carbonate (6.8 g, 64 mmol, 5 equiv) to afford a yellow solid, which was purified by silica gel flash column chromatography (PE/EtOAc 8/1 v/v as eluent) to give compound **13** (2.0 g, 75% in two steps) as a pale yellow solid. Mp: 84−86 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 12.64 (s, 1H), 6.96 (s, 1H), 6.74 (s, 1H), 6.17 (s, 1H), 4.70 (d, 1H, J = 5.2 Hz), 4.53 (t, 1H, J = 5.6 Hz), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ 184.1, 169.4, 161.6, 157.9, 152.8, 109.8, 109.5, 109.1, 104.9, 64.0, 20.5. HRMS-ESI (m/z): calcd for $C_{11}H_{11}O_4$ $[M + H]^+$ 207.0652, found 207.0648. IR (neat): 3434, 2918, 2852, 1658, 1623, 1585, 1506, 1382, 1293, 1263, 1155, 1054, 1001, 846 cm^{-1}.

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*(5-Acetoxy-2-methyl-4-oxo-4H-chromen-7-yl)methyl Acetate (**5i**).* This compound was prepared according to general procedure D from chromone **13** (412 mg, 2 mmol, 1 equiv), triethylamine (0.7 mL, 5 mmol, 2.5 equiv), acetyl chloride (0.4 mL, 5 mmol, 2.5 equiv), and DMAP (catalytic equiv) to afford a white solid. The crude product was purified by gel column chromatography (PE/EtOAc 4/1 v/v as eluent) to give **5i** (465 mg, 80%) as a white solid. Mp: 59−61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (s,1H), 6.95 (s, 1H), 6.04 (s, 1H), 5.16 (s, 2H), 2.41 (s, 3H), 2.33 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 170.4, 169.7, 165.1, 157.6, 149.4, 142.1, 117.8, 116.0, 114.5, 111.6, 64.4, 21.0, 20.8, 20.1. HRMS-ESI (m/z): calcd for $C_{15}H_{15}O_6$ $[M + H]^+$ 291.0863, found 291.0868. IR (neat): 3433, 2969, 2922, 2851, 1770, 1742, 1652, 1432, 1389, 1364, 1220, 1196, 1048, 1021, 935, 868, 771, 695, 573 cm^{-1}.

*Methyl 5-Hydroxy-4-oxo-4H-chromene-2-carboxylate (**14**).* This compound was prepared according to general procedure C from 2,6-dihydroxyacetophenone (1.5 g, 9.9 mmol), dimethyl oxalate (5.8 g, 49.3 mmol, 5 equiv), and 100 mL of MeOH/MeONa solution (freshly prepared by dissolving Na (1.1 g, 49.3 mmol, 5 equiv) in 100 mL of MeOH) to afford a yellow solid. The crude product was purified by flash column chromatography (silica gel, PE/EtOAc 4/1 v/v as eluent) to afford **14** (1.0 g, 46%) as a bright yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.10 (s, 1H), 7.59 (t, 1H, J = 8.4 Hz), 7.03 (s, 1H), 7.02 (dd, 1H, J = 8.4 Hz, J = 0.8 Hz), 6.83 (dd, 1H, J = 8.4 Hz, 0.8 Hz), 4.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 160.6, 160.3, 156.0, 152.7, 136.5, 113.6, 112.0, 111.7, 107.7, 53.6. All spectroscopic data were consistent with previously reported data.[3d]

*Methyl 5-Acetoxy-4-oxo-4H-chromene-2-carboxylate (**5j**).* This compound was prepared according to general procedure D from chromone **14** (440 mg, 2 mmol, 1.0 equiv), triethylamine (0.4 mL, 3 mmol, 1.5 equiv), acetyl chloride (0.2 mL, 3 mmol, 1.5 equiv), and DMAP (catalytic equiv) to afford white crystal. The crude product was purified by flash column chromatography (silica gel, PE/EtOAc 4/1 v/v as eluent) to give **5j** (482.1 mg, 92%) as a white solid. Mp: 120−122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (t, 1H, J = 8.0 Hz), 7.51 (d, 1H, J = 8.4 Hz), 7.06 (d, 1H, J = 8.0 Hz), 6.97 (s, 1H), 4.00 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9, 169.6, 160.7, 157.1, 151.0, 149.2, 134.4, 119.8, 117.8, 116.8, 115.8, 53.5, 21.0. HRMS-ESI (m/z): calcd for $C_{13}H_{11}O_6$ $[M + H]^+$ 263.0550, found 263.0557. IR (neat): 3465, 2957, 2854, 2372, 1773, 1657, 1471, 1449, 1285, 1196, 1115, 1028, 1002, 978, 877, 765, 703 cm^{-1}.

*Methyl 5-Hydroxy-7-methyl-4-oxo-4H-chromene-2-carboxylate (**15**).* This compound was prepared according to general procedure C from 4-methyl-2,6-dihydroxyacetophenone (1.0 g, 6 mmol), dimethyl oxalate (3.5 g, 30 mmol, 5 equiv), and 100 mL of a MeOH/NaOMe solution (freshly prepared by dissolving Na metal (552 mg, 24 mmol, 4 equiv) in 100 mL of MeOH) to afford a yellow solid. The crude product was purified by flash column chromatography (silica gel, PE/EtOAc 4/1 v/v as eluent) to afford chromone **15** (916 mg, 65%) as a bright yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.02 (s, 1H), 7.01 (s, 1H), 6.87 (s, 1H), 6.68 (s, 1H), 4.01 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.1, 160.5, 160.3, 156.0, 152.5, 148.8, 113.6, 112.9, 109.8, 108.1, 53.6, 22.5. All spectroscopic data were consistent with previously reported data.[3d]

*Methyl 5-Acetoxy-7-methyl-4-oxo-4H-chromene-2-carboxylate (**5k**).* This compound was prepared according to general procedure D from chromone **15** (468 mg, 2 mmol, 1 equiv), triethylamine (0.4 mL, 3 mmol, 1.5 equiv), acetyl chloride (0.2 mL, 3 mmol, 1.5 equiv), and DMAP (catalytic equiv) to afford a white solid. The crude product was purified by flash column chromatography (silica gel, PE/EtOAc 4/1 v/v as eluent) to give **5k** (502 mg, 91%) as a white solid. Mp: 113−114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (s, 1H), 6.92 (s, 1H), 6.87 (s, 1H), 3.99 (s, 3H), 2.47 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6, 169.6, 160.7, 156.9, 150.7, 148.7, 146.3, 121.0, 116.5, 115.7, 115.4, 53.4, 21.7, 20.9. HRMS-ESI (m/z): calcd for $C_{14}H_{13}O_6$ $[M + H]^+$ 277.0707, found 277.0710. IR (neat): 3084, 2959, 2362, 1767, 1740, 1658, 1623, 1449, 1387, 1367, 1271, 1200, 1108, 1019, 960, 904, 868, 773, 718, 669, 580, 494 cm^{-1}.

*Methyl 5-Methoxy-7-methyl-4-oxo-4H-chromene-2-carboxylate (**5m**).* A solution of chromone **15** (468 mg, 2.0 mmol, 1.0 equiv) in anhydrous DMF was added to NaH (57.6 mg, 2.4 mmol, 1.2 equiv) at room temperature, and the resulting suspension was stirred for 10 min. Iodomethane (340.8 mg, 2.4 mmol, 1.2 equiv) was then added dropwise, and the mixture was stirred at room temperature until completion as determined by TLC. The reaction mixture was then diluted with ethyl acetate and washed twice with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (silica gel, PE/EtOAc 2/1 v/v as eluent) to give **5m** (386.9 mg, 78%) as a yellow solid. Mp: 124−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (m, 2H), 6.65 (s, 1H), 3.98 (s, 3H), 3.97 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 161.1, 159.4, 157.9, 149.8, 146.4, 116.5, 113.1, 110.5, 108.2, 56.4, 53.3, 22.3. HRMS-ESI (m/z): calcd for $C_{13}H_{13}O_5$ $[M + H]^+$ 249.0757, found 249.0760. IR (neat): 3435, 2956, 2925, 2853, 1731, 1659, 1615, 1465, 1394, 1265, 1118, 1026, 953, 904, 867, 826, 793, 768, 739, 703 cm^{-1};

*Methyl 5-Acetoxy-7-(bromomethyl)-4-oxo-4H-chromene-2-carboxylate (**16**).* This compound was prepared according to general procedure E from chromone **5k** (166 mg, 0.6 mmol, 1.0 equiv), NBS (160 mg, 0.9 mmol, 1.5 equiv), and AIBN (10 mg, 0.06 mmol, 0.1 equiv) to afford a colorless solid. The crude product was purified by gel column chromatography (PE/EtOAc 8/1 v/v as eluent) to give **16** (159 mg, 75%) as a colorless solid. Mp: 102−103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, 1H, J = 1.6 Hz), 7.08 (d, 1H, J = 1.6 Hz), 6.96 (s, 1H), 4.48 (s, 2H), 4.00 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 169.5, 160.6, 156.9, 151.1, 149.4, 147.6, 144.8, 120.5, 116.9, 116.0, 53.6, 30.5, 21.0. HRMS-ESI (m/z): calcd for $C_{14}H_{12}BrO_6$ $[M + H]^+$ 354.9812, found 354.9820. IR (neat): 3425, 2922, 2840, 1770, 1742, 1655, 1630, 1475, 1434, 1388, 1258, 1190, 1104, 1043, 959, 900, 872, 768 cm^{-1}.

*Methyl 5-Acetoxy-7-(acetoxymethyl)-4-oxo-4H-chromene-2-carboxylate (**5l**).* Under an argon atmosphere at 21 °C, benzyl bromide **16** (70.8 mg, 0.2 mmol, 1 equiv) was dissolved in DMF (5 mL) followed by the addition of sodium acetate (24.6 mg, 0.3 mmol, 1.5 equiv). After 4 h, the reaction mixture was quenched with water and extracted with EtOAc (15 mL × 3). The organic layer was separated and washed with water (20 mL × 5) to remove DMF. The organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography (PE/EtOAc 4:1 v/v as eluent) to afford **5l** (63 mg, 94%) as a yellow solid. Mp: 126−128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (t, 1H, J = 0.4 Hz), 7.02 (d, 1H, J = 1.6 Hz), 6.97 (s, 1H), 5.20 (s, 2H), 4.00 (s, 3H), 2.43 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6, 170.3, 169.5, 160.6, 157.1, 151.0, 149.4, 143.8, 118.6, 117.1, 116.0, 115.0, 64.2, 53.6, 21.0, 20.8. HRMS-ESI (m/z): calcd for $C_{16}H_{15}O_8$ $[M + H]^+$ 335.0761, found 335.0765. IR (neat): 3439, 2921, 2829, 1770, 1740, 1655, 1632, 1433, 1382, 1256, 1220, 1190, 1105, 1038, 950, 900, 870, 768, 749, 723, 664, 585 cm^{-1}.

*1-(2-Mercaptophenyl)ethan-1-one (**17**).* This compound was prepared according to a reported procedure.[17] A mixture of thiosalicylic acid (6.0 g, 0.04 mol) and finely dispersed LiH (0.8 g, 0.1 mol) in anhydrous THF (20 mL) was refluxed for 0.5 h. Then the mixture was cooled to room temperature, and 100 mL of 1 M methyllithium in Et_2O was added under a nitrogen atmosphere. The mixture was allowed to stand at room temperature for 4 h. It was then poured into water (100 mL), the aqueous layer was saturated with ammonium chloride, and the organic phase was separated. The organic phase was dried over anhydrous Na_2SO_4 and evaporated to provide **17** (3.55 g, 60%), which was used directly in the next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 1H, J = 8.0 Hz), 7.32−7.30 (m, 2H), 7.23−7.19 (m, 1H), 4.50 (s, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 137.5, 132.8, 132.3, 131.7, 131.6, 124.7, 27.7. All spectroscopic data were consistent with previously reported data.[17]

*4H-Thiochromen-4-one (**5n**).* This compound was prepared according to general procedure A from **17** (1.5 g, 10.0 mmol, 1 equiv) and sodium (1.4 g, 60 mmol, 6 equiv) in dry ethyl formate (20 mL). The crude product was purified via flash column chromatography (silica gel, PE/EtOAc 8/1 v/v as eluent) to give the title compound **5n** (1.1 g, 70% in two steps) as pale brown crystals. ^{1}H NMR (400 MHz,

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$CDCl_3$): δ 8.55 (d, 1H, *J* = 8.0 Hz), 7.83 (d, 1H, *J* = 10.4 Hz), 7.62−7.61 (m, 2H), 7.57−7.53 (m, 1H), 7.01 (d, 1H, *J* = 10.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.7, 137.8, 137.5, 132.3, 131.4, 128.7, 127.8, 126.7, 125.9. All spectroscopic data were consistent with previously reported data.[18]

*Quinolin-4(1H)-one (**18**).* This compound was prepared according to a reported procedure.[19] A stirred mixture of Meldrum's acid (51.5 g, 0.35 mol) and trimethyl orthoformate (150.7 g, 1.4 mol) was refluxed for 30 min. Then aniline (29.8 g, 0.3 mol) was added dropwise at the same temperature, and the solution was stirred for 40 min. After the solution was cooled to room temperature, the resulting precipitate was filtered off, washed with *n*-hexane, and dried in vacuo to provide 5-anilinomethylene-2,2-dimethyl-1,3-dioxane-4,6-dione (57.7 g, 72%), which was used directly in the next step. ^1H NMR (400 MHz, DMSO-d_6): δ 11.27 (d, 1H, *J* = 14.6 Hz), 8.59 (d, 1H, *J* = 14.6 Hz), 7.57 (d, 2H, *J* = 8.0 Hz), 7.46−7.42 (m, 2H), 7.28 (t, 1H, *J* = 7.4 Hz), 1.68 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.0, 162.8, 153.3, 138.6, 129.6, 126.3, 119.0, 104.2, 86.6, 26.5. All spectroscopic data were consistent with previously reported data.[19] Diphenyl ether (140 mL) was heated to 250 °C and stirred vigorously under a nitrogen atmosphere. 5-Anilinomethylene-2,2-dimethyl-1,3-dioxane-4,6-dione (26.3 g, 0.1 mol) was added portionwise, and the reaction mixture was stirred for 30 min at this temperature. The resulting solution was cooled to 70 °C and diluted with *n*-hexane (200 mL). The precipitate was filtered off, washed with *n*-hexane, and dried in vacuo. The title compound **18** was obtained as a brown solid (14.0 g, 90%). ^1H NMR (400 MHz, DMSO-d_6): δ 11.79 (br s, 1H), 8.12 (dd, 1H, *J* = 8.0 Hz, *J* = 1.2 Hz), 7.92 (d, 1H, *J* = 7.2 Hz), 7.67−7.63 (m, 1H), 7.56 (d, 1H, *J* = 8.0 Hz), 7.35−7.31 (m, 1H), 6.06 (d, 1H, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 177.0, 140.1, 139.5, 131.7, 125.8, 125.0, 123.1, 118.3, 108.7. All spectroscopic data were consistent with previously reported data.[19]

*Benzyl 4-Oxoquinoline-1(4H)-carboxylate (**5o**).* This compound was prepared according to a reported procedure.[20] A solution of 4(1*H*)-quinolone **18** (451 mg, 3.11 mmol) in THF (10 mL) was added to a suspension of NaH (346 mg, 8.7 mmol, 60 wt % in mineral oil) in THF (15 mL) at room temperature, and the resulting mixture was stirred for 15 min at 55 °C. Benzyl chloroformate (790 mg, 4.6 mmol) was then added dropwise, and the mixture was stirred for 21 h at room temperature. The reaction mixture was quenched with water and extracted with Et_2O. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified via flash column chromatography (with Et_2O/hexane 2/1 v/v as eluent) to afford compound **5o** as a white solid (607 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, 1H, *J* = 9.2 Hz), 8.36 (dd, 2H, *J* = 8.5 Hz, *J* = 1.6 Hz), 7.69−7.64 (m, 1H), 7.50−7.42 (m, 6H), 6.26 (d, 1H, *J* = 8.8 Hz), 5.47 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.9, 151.2, 138.4, 138.2, 133.9, 132.9, 129.2, 128.9, 128.8, 126.9, 126.5, 125.4, 119.9, 112.4, 70.4. All spectroscopic data were consistent with previously reported data.[20]

Typical Procedure for the Syntheses of 2-γ-Lactone Chromanones. NaI (0.3 mmol, 1.5 equiv) and TMSCl (0.3 mmol, 1.5 equiv) were added to a solution of the correspounding chromone (0.2 mmol, 1.0 equiv) in anhydrous DCM (2 mL), and the mixture was stirred for 10 min at room temperature. Then the reaction mixture was brought to the appropriate temperature, and 2-(trimethylsilyloxy)-furan (0.4 mmol, 2.0 equiv) was added dropwise. The reaction mixture was stirred at this temperature until the reaction was complete, as indicated by thin-layer chromatography (TLC). The reaction mixture was quenched by H_2O and extracted with DCM. The combined organic layers were washed with saturated $Na_2S_2O_3$ and brine in turn, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the pure product using petroleum ether/ethyl acetate as eluent.

*2-Methyl-2-(5-oxo-2,5-dihydrofuran-2-yl)chroman-4-one (**6a**).* This compound was prepared from **5a** and purified by gel column chromatography (PE/EtOAc 2/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6a** (1:1) as a pale yellow solid (40 mg, 81%). Mp: 99−101 °C. Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 69.19; H, 5.31. ^1H NMR (400 MHz, $CDCl_3$): δ 7.90−7.85 (m, 1H), 7.62−7.56 (m, 1H), 7.54−7.48 (m, 1H), 7.07−7.02 (m, 1H), 7.98−6.93 (m, 1H), 6.32−6.29 (m, 1H), 5.22 (t, 0.47H, *J* = 1.76 Hz), 5.13* (t, 0.46H, *J* = 1.76 Hz), 3.03 (d, 0.5H, *J* = 16.7 Hz), 2.94* (d, 0.5H, *J* = 16.6 Hz), 2.80 (d, 0.5H, *J* = 16.7 Hz), 2.64* (d, 0.5H, *J* = 16.6 Hz), 1.54 (s, 1.5H), 1.34* (s, 1.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.2*, 190.0, 171.8*, 171.7, 158.5, 152.3*, 151.8, 136.60*,136.55, 126.7*, 126.6, 123.86*, 123.79, 121.8*, 121.7, 120.20*, 120,17, 118.2*, 118.0, 86.2*, 85.3, 80.8, 80.5*, 44.7, 43.0*, 21.2, 19.1*. HRMS-ESI (*m*/*z*): calcd for $C_{14}H_{12}O_4Na$ $[M + Na]^+$ 267.0628, found 267.0631. IR (neat): 3365, 3100, 2922, 2862, 1759, 1691, 1608, 1463, 1384, 1308, 1231, 1159, 1098, 1038, 963, 893, 814, 767, 660, 592 cm^{-1}. * = diastereomer. All spectroscopic data were consistent with previously reported data.[4g]

*2-(5-Oxo-2,5-dihydrofuran-2-yl)chroman-4-one (**6b**).* This compound was prepared from **5b** and purified by gel column chromatography (PE/EtOAc 2/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6b** (1:1) as a pale yellow solid (38 mg, 82%). Mp: 117−119 °C. Anal. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38. Found: C, 67.43; H, 4.66. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88−7.86 (m, 1H), 7.69* (dd, 0.4H, *J* = 5.8 Hz, *J* = 1.5 Hz), 7.60−7.57 (m, 0.6H), 7.53−7.47 (m, 1H), 7.09−7.03 (m, 1H), 7.01−6.94 (m, 1H), 6.34−6.30 (m, 1H), 5.29 (br s, 1H), 4.78 (dt, 0.6H, *J* = 13.4 Hz, *J* = 3.4 Hz), 4.60−4.55*(m, 0.4H), 3.02−2.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 190.0*, 171.9, 171.8*, 160.4, 160.3*, 152.7*, 152.1, 136.5, 136.4*, 127.12*, 127.06, 123.8, 123.4*, 122.3*, 122.2, 120.9*, 120.7, 117.82*, 117.77, 82.8, 82.6*, 75.6, 38.8*, 38.7. HRMS-ESI (*m*/*z*): calcd for $C_{13}H_{11}O_4$ $[M + H]^+$ 231.0652, found 231.0658. IR (neat): 3432, 2969, 2920, 2840, 1755, 1688, 1605, 1462, 1305, 1224, 1155, 1109, 1043, 995, 961, 892, 820, 771 cm^{-1}. * = diastereomer. All spectroscopic data were consistent with previously reported data.[4g]

*Methyl 4-Oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)chromane-2-carboxylate (**6c**).* This compound was prepared from **5c** and purified by gel column chromatography (PE/EtOAc 2/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6c** (2:1) as a colorless gum (54 mg, 94%). Anal. Calcd for $C_{15}H_{12}O_6$: C, 62.50; H, 4.20. Found: C, 62.14; H, 4.13. ^1H NMR (400 MHz, $CDCl_3$): δ 7.86−7.83 (m, 1H), 7.61−7.50 (m, 2H), 7.11−6.99 (m, 2H), 7.36 (dd, 0.6H, *J* = 5.8 Hz, *J* = 2.0 Hz), 7.32* (dd, 0.4H, *J* = 5.8 Hz, *J* = 2.0 Hz), 5.44 (dt, 1H, *J* = 12.5 Hz, *J* = 1.8 Hz), 3.76 (s, 1.7H), 3.70* (s, 1.3H), 3.28−3.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.2, 187.7*, 171.2, 171.1*, 168.8, 168.2*, 159.1*, 158.9, 150.9, 150.7*, 136.8*, 136.6, 126.8*, 126.7, 124.1, 123.9*, 122.6*, 122.5, 120.3*, 120.2, 118.0*, 117.8, 83.7, 83.4*, 83.3*, 82.8, 53.7, 53.6*, 40.4, 40.3*. HRMS-ESI (*m*/*z*): calcd for $C_{15}H_{13}O_6$ $[M + H]^+$ 289.0707, found 289.0711. IR (neat): 3370, 3103, 3014, 2956, 2843, 1791, 1760, 1695, 1609, 1462, 1304, 1276, 1204, 1158, 1104, 1035, 990, 886, 824, 764, 621, 586 cm^{-1}. * = minor diastereomer.

*2-Methyl-4-oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)chroman-5-yl Acetate (**6f**).* This compound was prepared from **5f** and purified by gel column chromatography (PE/EtOAc 2/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6f** (20:1) as a colorless gum (33 mg, 55%). Anal. Calcd for $C_{16}H_{14}O_6$: C, 63.58; H, 4.67. Found: C, 63.21; H, 5.17. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, 1H, *J* = 5.8 Hz, *J* = 1.6 Hz), 7.48 (t, 1H, *J* = 8.2 Hz), 6.86 (dd, 1H, *J* = 8.5 Hz, *J* = 1.0 Hz), 6.69 (dd, 1H, *J* = 8.0 Hz, *J* = 1.0 Hz), 5.11 (t, 1H, *J* = 1.8 Hz), 2.91 (d, *J* = 16.4 Hz, 1H), 2.55 (d, *J* = 16.4 Hz, 1H), 2.37 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.4, 171.7, 169.6, 159.6, 152.6, 151.6, 149.7, 136.2, 123.9, 116.3, 116.2, 113.3, 85.9, 80.5, 43.7, 21.0. HRMS-ESI (*m*/*z*): calcd for $C_{16}H_{14}O_6Na$ $[M + Na]^+$ 325.0683, found 325.0688. IR (neat): 3530, 3366, 3092, 3022, 2980, 2940, 2412, 2255, 1773, 1692, 1619, 1578, 1434, 1370, 1270, 1128, 1074, 1025, 942, 907, 822, 762, 666, 584 cm^{-1}.

*2,7-Dimethyl-4-oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)chroman-5-yl Acetate (**6g**).* This compound was prepared from **5g** and purified by gel column chromatography (PE/EtOAc 2/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6g** (3:1) as a colorless gum (38 mg, 60%). Anal. Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10. Found: C, 64.93; H, 5.47. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56* (dd, 0.26H, *J* =

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5.8 Hz, J = 1.5 Hz), 7.52 (dd, 0.74H, J = 5.8 Hz, J = 1.6 Hz), 6.70* (s, 0.25H), 6.68 (s, 0.75H), 6.51 (m, 1H), 6.28 (m, 1H), 5.16* (t, 0.24H, J = 1.7 Hz), 5.09 (t, 0.76H, J = 1.7 Hz), 2.95* (d, 0.25H, J = 16.4 Hz), 2.86 (d, 0.75H, J = 16.4 Hz), 2.69* (d, 0.25H, J = 16.4 Hz), 2.52 (d, 0.78H, J = 16.4 Hz), 2.36* (s, 0.8H), 2.35 (s, 2.23H), 2.34* (s, 0.76H), 2.33 (s, 2.35H), 1.51 (s, 2.26H), 1.33* (s, 0.74H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.0, 187.9*, 171.8*, 171.7, 169.7*, 169.6, 159.5*, 159.4, 152.1*, 151.6, 149.7*, 149.6, 148.3*, 148.2, 123.9, 123.7*, 117.4*, 117.35, 116.4, 116.2*, 111.0, 85.9, 85.2*, 80.5*, 80.4, 45.4*, 43.6, 21.9, 21.1, 21.0*, 19.2. HRMS-ESI (m/z): calcd for $C_{17}H_{17}O_6$ $[M + H]^+$ 317.1020, found 317.1029. IR (neat): 3444, 2917, 1757, 1687, 1623, 1563, 1455, 1340, 1267, 1198, 1076, 1018, 890, 832, 692 cm^{-1}. * = minor diastereomer.

*2-Methyl-4-oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)chromane-5,7-diyl Diacetate (**6h**).* This compound was prepared from **5h** and purified by gel column chromatography (PE/EtOAc 1/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6h** (20:1) as a colorless gum (58 mg, 81%). Anal. Calcd for $C_{18}H_{16}O_8$: C, 60.00; H, 4.48. Found: C, 59.62; H, 4.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, 1H, J = 5.6 Hz, J = 1.6 Hz), 6.69 (d, 1H, J = 2.0 Hz), 6.50 (d, 1H, J = 2.0 Hz), 6.27 (dd, 1H, J = 6.0 Hz, J = 2.0 Hz), 5.08 (t, 1H, J = 1.6 Hz), 2.89 (d, 1H, J = 16.0 Hz), 2.52 (d, 1H, J = 16.4 Hz), 2.33 (s, 3H), 2.28 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 171.6, 169.1, 167.9, 160.2, 156.2, 151.5, 150.8, 124.0, 111.2, 110.5, 109.1, 85.8, 80.9, 43.4, 21.2, 21.10, 20.98. HRMS-ESI (m/z): calcd for $C_{18}H_{17}O_8$ $[M + H]^+$ 361.0918, found 361.0923. IR (neat): 3366, 3096, 3023, 2926, 2850, 2256, 1762, 1692, 1618, 1578, 1433, 1369, 1269, 1189, 1130, 1075, 1026, 892, 831, 756, 663, 583 cm^{-1}.

*(5-Acetoxy-2-methyl-4-oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)-chroman-7-yl)methyl Acetate (**6i**).* This compound was prepared from **5i** and purified by gel column chromatography (PE/EtOAc 2/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6i** (3:1) as a colorless gum (52 mg, 70%). Anal. Calcd for $C_{19}H_{18}O_8$: C, 60.96; H, 4.85. Found: C, 60.64; H, 4.57. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57* (dd, 0.32H, J = 5.6 Hz, J = 1.2 Hz), 7.53 (dd, 0.71H, J = 5.6 Hz, J = 1.2 Hz), 6.87* (s, 0.25H), 6.85 (s, 0.74H), 6.67* (s, 0.23H), 6.66 (s, 0.77H), 6.30 (dd, 1H, J = 6.0 Hz, J = 2.0 Hz), 5.17* (s, 0.22H), 5.10 (t, 0.77H, J = 1.6 Hz), 5.07 (m, 2H), 2.97* (d, 0.23H, J = 16.0 Hz), 2.91 (d, 0.77H, J = 16.4 Hz), 2.72* (d, 0.22H, J = 16.4 Hz), 2.55 (d, 0.80H, J = 16.4 Hz), 2.38* (s, 0.67H), 2.37 (s, 2.24H), 2.16 (s, 3H), 1.53 (s, 2.36H), 1.35* (s, 0.63H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.9, 171.6, 170.4, 169.5, 159.7, 151.4, 150.0, 145.3, 124.1, 115.0, 114.6, 112.7, 85.8, 80.7, 64.5, 43.7, 21.04, 21.00, 20.8. HRMS-ESI (m/z): calcd for $C_{19}H_{19}O_8$ $[M + H]^+$ 375.1074, found 375.1078. IR (neat): 3396, 2956, 2922, 2851, 1750, 1689, 1627, 1564, 1434, 1377, 1226, 1195, 1147, 1073, 889, 816 cm^{-1}. * = minor diastereomer.

*Methyl 5-Acetoxy-4-oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)-chromane-2-carboxylate (**6j**).* This compound was prepared from **5j** and purified by gel column chromatography (PE/EtOAc 2/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6j** (20:1) as a colorless gum (52 mg, 75%). Anal. Calcd for $C_{17}H_{14}O_8$: C, 58.96; H, 4.08. Found: C, 58.59; H, 4.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 2H), 6.92 (d, 1H, J = 8.4), 6.72 (d, 1H, J = 7.6), 6.35 (dd, 1H, J = 5.8 Hz, J = 2.0 Hz), 5.40 (t, 1H, J = 1.7 Hz), 3.77 (s, 3H), 3.22 (d, 1H, J = 16.6 Hz), 3.05 (d, 1H, J = 16.6 Hz), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 171.1, 169.3,168.5, 159.8, 150.7, 149.8, 136.2, 124.2, 117.2, 115.9, 113.6, 83.0, 82.6, 53.8, 41.1, 21.0. HRMS-ESI (m/z): calcd for $C_{17}H_{15}O_8$ $[M + H]^+$ 347.0761, found 347.0769. IR (neat): 3419, 2920, 2846, 1749, 1684, 1653, 1558, 1522, 1457, 1200, 1155, 1040, 518 cm^{-1}.

*Methyl 5-Acetoxy-7-methyl-4-oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)chromane-2-carboxylate (**6k**).* This compound was prepared from **5k** and purified by gel column chromatography (PE/EtOAc 2/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6k** (6:1) as a colorless gum (56 mg, 78%). Anal. Calcd for $C_{18}H_{16}O_8$: C, 60.00; H, 4.48. Found: C, 60.37; H, 4.19. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56* (dd, 0.14H, J = 5.8 Hz, J = 1.6 Hz), 7.50 (dd, 0.86H, J = 5.8 Hz, J = 1.6 Hz), 6.82* (d, 0.12H, J = 0.6 Hz), 6.74 (d, 0.88H, J = 0.6 Hz), 6.54 (d, 1H, J = 0.8 Hz), 6.33 (dd, 0.82H, J = 5.8 Hz, J = 2.0 Hz), 6.28* (dd, 0.16H, J = 5.8 Hz, J = 2.0 Hz), 5.40* (t, 0.14H, J = 1.8 Hz), 5.37 (t, 0.83H, J = 1.8 Hz), 3.76 (s, 2.52H), 3.72 (s, 0.40H), 3.18 (d, 1H, J = 16.6 Hz), 3.17 (d, 1H, J = 16.6 Hz), 2.35* (s, 0.43H), 2.34 (s, 3H), 2.33 (s, 2. 76H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.0, 171.1, 169.3, 168.6, 159.6, 150.8, 149.6, 148.4, 124.0, 118.2, 116.1, 111.2, 83.0, 82.5, 53.8, 40.9, 21.9, 21.0. HRMS-ESI (m/z): calcd for $C_{18}H_{16}O_8Na$ $[M + Na]^+$ 383.0737, found 383.0742. IR (neat): 3365, 3122, 3017, 2956, 2923, 2852, 1794, 1761, 1691, 1625, 1564, 1436, 1370, 1266, 1198, 1093, 1024, 883, 841, 757, 580 cm^{-1}. * = minor diastereomer.

*Methyl 5-Acetoxy-7-(acetoxymethyl)-4-oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)chromane-2-carboxylate (**6l**).* This compound was prepared from **5l** and purified by gel column chromatography (PE/EtOAc 2/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6l** (20:1) as a colorless gum (74 mg, 88%). Anal. Calcd for $C_{20}H_{18}O_{10}$: C, 57.42; H, 4.34. Found: C, 57.21; H, 4.42. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, 1H, J = 5.8 Hz, J = 1.6 Hz), 6.90 (d, 1H, J = 0.4 Hz), 6.69 (d, 1H, J = 0.8 Hz), 6.35 (dd, 1H, J = 6.0 Hz, J = 2.0 Hz), 5.39 (t, 1H, J = 1.8 Hz), 5.07 (s, 2H), 3.78 (s, 3H), 3.22 (d, 1H, J = 16.6 Hz), 3.04 (d, 1H, J = 16.6 Hz), 2.36 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.0, 171.1, 170.5, 169.3, 168.5, 159.9, 150.7, 150.1, 145.5, 124.3, 115.9, 114.3, 112.9, 83.0, 82.8, 64.5, 54.0, 41.2, 21.1, 20.9. HRMS-ESI (m/z): calcd for $C_{20}H_{19}O_{10}$ $[M + H]^+$ 419.0973, found 419.0977. IR (neat): 3423, 2921, 2857, 2358,1792, 1746, 1628, 1430, 1383, 1155, 1068, 1026, 669, 647, 619 cm^{-1}.

*Methyl 5-Methoxy-7-methyl-4-oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)chromane-2-carboxylate (**6m**).* This compound was prepared from **5m** and purified by gel column chromatography (PE/EtOAc 2/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6m** (1:1) as a colorless gum (40 mg, 60%). Anal. Calcd for $C_{17}H_{16}O_7$: C, 61.45; H, 4.85. Found: C, 61.07; H, 4.57. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, 0.70H, J = 5.6 Hz, J = 1.2 Hz), 7.49* (dd, 0.42H, J = 5.6 Hz, J = 1.2 Hz), 6.51 (s, 0.4H), 6.43 (s, 0.4H), 6.34 (s, 1H), 6.33* (dd, 0.49H, J = 5.6 Hz, J = 2.0 Hz), 6.29 (dd, 0.51H, J = 5.6 Hz, J = 2.0 Hz), 5.40* (t, 0.44H, J = 1.6 Hz), 5.37 (t, 0.49H, J = 1.6 Hz), 3.88 (s, 2.57H), 3.86* (s, 0.54H), 3.76* (s, 1.45H), 3.71 (s, 1.56H), 3.23−2.98 (m, 2H), 2.34* (s, 1.35H), 2.32 (s, 1.64H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2*, 185.7, 171.2*, 171.1, 168.8*, 168.2, 160.4*, 160.24, 160.18*, 160.1, 150.8, 150.7*, 148.7*, 148.4, 123.79*, 123.75, 110.3*, 110.2, 108.5, 108.3*, 106.02, 106.01*, 83.7, 83.1*, 82.6, 82.2*, 56.0, 55.8*, 53.6*, 53.4, 41.5*, 41.3, 22.4, 22.3*. HRMS-ESI (m/z): calcd for $C_{17}H_{17}O_7$ $[M + H]^+$ 333.0969, found 333.0966. IR (neat): 3357, 2925, 2854, 2373, 1792, 1743, 1638, 1606, 1571, 1461, 1416, 1219, 1160, 1116, 1044, 882, 826, 736, 702, 628 cm^{-1}. * = diastereomer.

*5-(4-Oxothiochroman-2-yl)furan-2(5H)-one (**6n**).* This compound was prepared from **5n** and purified by gel column chromatography (PE/EtOAc 4/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6n** (1:1) as a brown gum (40 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (dd, 0.60H, J = 8.0 Hz, J = 1.2 Hz), 8.08* (dd, 0.40H, J = 2.0 Hz, J = 1.6 Hz), 7.57 (dd, 0.63H, J = 5.6 Hz, J = 1.6 Hz), 7.45−7.40 (m, 1H), 7.37* (dd, 0.38H, J = 6.0 Hz, J = 1.6 Hz), 7.28−7.20 (m, 2H), 6.22 (td, 1H, J = 6.0 Hz, J = 1.6 Hz), 5.28* (dt, 0.35H, J = 5.2 Hz, J = 1.7 Hz), 5.14 (dt, 0.60H, J = 8.0 Hz, J = 1.6 Hz), 3.93−3.89* (m, 0.35H), 3.62−3.57 (m, 0.59H), 3.12−3.19 (m, 1H), 3.10−2.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2*, 192.0, 171.5, 171.2*, 153.2, 152.1*, 139.2*, 138.8, 134.0, 133.9*, 130.5, 130.3*, 129.1, 129.0*, 127.6, 127.5*, 125.8, 125.6*, 123.9*, 123.3; 83.4*, 82.6, 43.1, 42.4*, 41.1, 40.7*. HRMS-ESI (m/z): calcd for $C_{13}H_{10}O_3SNa$ $[M + Na]^+$ 269.0243, found 269.0235. IR (neat): 3343, 3091, 2923, 2375, 1786, 1756, 1679, 1589, 1460, 1437, 1288, 1264, 1234, 1158, 1110, 1089, 1028, 884, 823, 802, 767 cm^{-1}. * = diastereomer.

*Benzyl 4-Oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)-3,4-dihydroquinoline-1(2H)-carboxylate (**6o**).* This compound was prepared from **5o** and purified by gel column chromatography (PE/EtOAc 4/1 v/v as eluent) to give an inseparable mixture of diastereomers of **6o** (1:1) as a brown gum (55 mg, 76%). Anal. Calcd for $C_{21}H_{17}NO_5$: C, 69.41; H, 4.72; N, 3.85. Found: C, 69.38; H, 4.38; N, 3.67. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, 1H, J = 7.6 Hz), 7.71 (d, 1H, J = 8.4 Hz), 7.51 (t, 1H, J = 8.4 Hz), 7.38 (s, 5H), 7.26−7.18 (m, 2H), 6.06 (dd, 1H, J =

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8.4 Hz, J = 5.7 Hz), 5.30 (d, 2H, J = 3.4 Hz), 5.26 (t, 1H, J = 6.0 Hz), 5.16 (d, 1H, J = 6.0 Hz), 3.18 (dd, 1H, J = 18.2 Hz, J = 7.1 Hz), 2.84 (d, 1H, J = 18.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 171.1, 153.7, 152.7, 152.0, 140.9, 135.2, 134.8, 128.8, 128.7, 128.3, 127.1, 124.9, 124.8, 124.0, 123.4, 121.7, 72.1, 68.9, 55.0, 39.4. HRMS-ESI (m/z): calcd for $C_{21}H_{21}N_2O_5$ $[M+NH_4]^+$ 381.1445, found 381.1442. IR (neat): 3362, 2957, 2925, 1759, 1688, 1601, 1481, 1460, 1390, 1320, 1296, 1266, 1224, 1157, 1043, 945, 885, 822, 766, 736, 700. * = diastereomer.

General Procedure for the Deacetylation of Chromanone Butenolides. Chromone butenolide (**6h,i,k,l**; 0.2 mmol, 1.0 equiv) was dissolved in methanol (2.0 mL). One drop of concentrated HCl was then added, and the mixture was stirred at room temperature for 30 min until the reaction was completed as indicated by TLC. The solvent was removed under reduced pressure. The residue was diluted with EtOAc (10.0 mL) and washed with saturated $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4 ,and then the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography to afford chromanone butenolides using petroleum ether/ethyl acetate as eluent.

*5,7-Dihydroxy-2-methyl-2-(5-oxo-2,5-dihydrofuran-2-yl)-chroman-4-one (**7h**).* This compound was prepared from **6h** and purified by gel column chromatography (PE/EtOAc 1/1 v/v as eluent) to give an inseparable mixture of diastereomers of **7h** (8:1) as a yellow gum (46 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.90* (s, 0.11H), 11.83 (s, 0.88H), 7.60* (dd, 0.15H, J = 6.0 Hz, J = 1.6 Hz), 7.57 (dd, 0.87H, J = 6.0 Hz, J = 1.6 Hz), 7.32 (br, 1H), 6.30 (dd, 1H, J = 6.0 Hz, J = 2.0 Hz), 6.00 (dd, 1H, J = 5.6 Hz, J = 2.0 Hz), 5.95* (d, 0.11H, J = 2.0 Hz), 5.90 (d, 0. 89H, J = 2.0 Hz), 5.22* (s, 0.1H), 5.12 (t, 0. 89H, J = 1.6 Hz), 3.00* (d, 0.12H, J = 17.2 Hz), 2.93 (d, 0. 89H, J = 16.8 Hz), 2.74* (d, 0.13H, J = 17.2 Hz), 2.57 (d, 0.90H, J = 17.2 Hz), 1.57 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD): δ 195.6, 174.6, 168.7, 165.3, 162.0, 154.8, 124.0, 102.7, 97.3, 96.7, 88.6, 81.6, 43.6, 21.3. HRMS-ESI (m/z): calcd for $C_{14}H_{16}NO_6$ $[M+NH_4]^+$ 294.0972, found 294.0970. IR (neat): 3399, 2927, 2512, 2243, 2138, 2074, 1755, 1625, 1453, 1386, 1324, 1171, 1120, 976, 831, 542 cm^{-1}. * = minor diastereomer.

*5-Hydroxy-7-(hydroxymethyl)-2-methyl-2-(5-oxo-2,5-dihydrofuran-2-yl)chroman-4-one (**7i**).* This compound was prepared from **6i** and purified by gel column chromatography (PE/EtOAc 1/1 v/v as eluent) to give an inseparable mixture of diastereomers of **7i** (2:1) as a yellow gum (52 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.59* (s, 0.35H), 11.53 (s, 0.63H), 7.60* (dd, 0.36H, J = 6.0 Hz, J = 1.6 Hz), 7.56 (dd, 0.65H, J = 6.0 Hz, J = 1.6 Hz), 6.54* (s, 0.34H), 6.53 (s, 0.64H),6.50* (s, 0.36H), 6.45 (s, 0.64H), 6.32−6.30 (m, 1H), 5.21* (s, 0.33H), 5.10 (t, 0.64H, J = 1.6 Hz), 4.66* (s, 0.70H), 4.64 (s, 1.31H), 3.08* (d, 0.35H, J = 17.2 Hz), 2.98 (d, 0.65H, J = 17.2 Hz), 2.82* (d, 0.35H, J = 17.2 Hz), 2.62 (d, 0.64H, J = 17.2 Hz), 1.57 (s, 2.06H), 1.33 (s, 0.94H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 195.4*, 171.8*, 171.7, 162.0*, 161.8, 158.5, 153.5*, 153.4, 152.3*, 151.7, 123.9, 123.8*, 107.2*, 107.1, 106.27*, 106.25, 105.2, 105.0*, 86.2, 84.9*, 80.4*, 80.2, 64.3, 44.0*, 42.1, 21.6, 19.2*. HRMS-ESI (m/z): calcd for $C_{15}H_{15}O_6$ $[M + H]^+$ 291.0863, found 291.0870. IR (neat): 3439, 2920, 2840, 1754, 1645, 1562, 1439, 1381, 1307, 1203, 1155, 1055, 897, 756, 664, 546 cm^{-1}. * = minor diastereomer.

*Methyl 5-Hydroxy-7-methyl-4-oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)chromane-2-carboxylate (**7k**).* This compound was prepared from **6k** and purified by gel column chromatography (PE/EtOAc 2/1 v/v as eluent) to give an inseparable mixture of diastereomers of **7k** (20:1) as a yellow gum (55 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.40 (s, 1H), 7.50 (dd, 1H, J = 5.6 Hz, J = 1.6 Hz), 6.38 (s, 1H), 6.35 (dd, 1H, J = 5.6 Hz, J = 2.0 Hz), 6.31 (s, 1H), 5.37 (t, 1H, J = 1.8 Hz), 3.79 (s, 3H), 3.24 (d, 1H, J = 16.8 Hz), 3.14 (d, 1H, J = 17.2 Hz), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.4, 171.0, 168.7, 161.7, 158.2, 151.2, 150.7, 124.1, 111.3, 108.3, 105.4, 83.0, 82.3, 53.9, 39.4, 22.5. HRMS-ESI (m/z): calcd for $C_{16}H_{15}O_7$ $[M + H]^+$ 319.0812, found 319.0822. IR (neat): 3441, 2958, 2924, 2840, 2359, 1791, 1758, 1714, 1640, 1573, 1457, 1380, 1260, 1205, 1099, 1073, 1026, 882, 826, 734, 672, 551 cm^{-1}.

*Methyl 5-Hydroxy-7-(hydroxymethyl)-4-oxo-2-(5-oxo-2,5-dihydrofuran-2-yl)chromane-2-carboxylate (**7l**).* This compound was prepared from **6l** and purified by gel column chromatography (PE/EtOAc 1/1 v/v as eluent) to give an inseparable mixture of diastereomers of **7l** (8:1) as a yellow gum (60 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.44 (s, 1H), 7.59* (dd, 0.08H, J = 6.0 Hz, J = 1.6 Hz), 7.51 (dd, 0.94H, J = 5.6 Hz, J = 1.6 Hz), 6.58* (s, 0.12H), 6.55 (s, 0.87H), 6.50 (s, 1H), 6.35 (dd, 1H, J = 5.6 Hz, J = 2.0 Hz), 5.41* (t, 0.09H, J = 2.0 Hz), 5.38 (t, 0.93H, J = 1.8 Hz), 4.64 (s, 2H), 3.84* (s, 0.21H), 3.79 (s, 2.86H), 3.27 (d, 1H, J = 17.2 Hz), 3.16 (d, 1H, J = 17.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 171.0, 168.6, 161.9, 158.6, 153.5, 150.7, 124.2, 107.9, 106.4, 104.9, 83.0, 82.4, 64.3, 53.9, 39.5. HRMS-ESI (m/z): calcd for $C_{16}H_{15}O_8$ $[M + H]^+$ 335.0761, found 335.0766. IR (neat): 3431, 2924, 2357, 1789, 1750, 1639, 1433, 1380, 1192, 1152, 1069, 835, 714, 650, 419 cm^{-1}. * = minor diastereomer.

General Procedure for the Reduction of the Chromanone Butenolides.[3d] Chromanone butenolides (**7h,i,k,l**; 1.0 equiv) and nickel chloride hexahydrate (1.1 equiv) were dissolved in THF/MeOH (3/1 v/v). After the mixture was cooled to 0 °C, $NaBH_4$ (2.1 equiv) was added in one portion. After 15 min, the reaction was quenched with saturated NH_4Cl and extracted twice with EtOAc. The combined organic phase was washed twice with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by silica gel chromatography to afford the corresponding natural products using petroleum ether/ethyl acetate as eluent.

*(±)-Lachnone C (**1**).* This compound was prepared according to the general procedure for the reduction of the chromanone butenolides from chromanone butenolide **7i** (40 mg, 0.14 mmol 1.0 equiv), nickel chloride hexahydrate (36.1 mg, 0.15 mmol, 1.1 equiv), and $NaBH_4$ (10.9 mg, 0.30 mmol, 2.1 equiv) in THF/MeOH (3/1 v/v, 4.0 mL) at 0 °C for 15 min to afford a yellow gum. The crude product was purified by silica gel chromatography (PE/EtOAc 2/1 v/v) to afford (±)-lachnone C (**1**; 33 mg, 80%) as a yellow gum as a 2:1 mixture of diastereomers. Anal. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.26; H, 5.66. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.56 (s, 1H), 6.52* (s, 0.32H), 6.50 (s, 0.68H), 6.44 (s, 1H), 4.63 (s, 2H), 4.58* (t, 0.31H, J = 7.6 Hz), 4.46 (dd, 0.76H, J = 8.0 Hz, J = 6.0 Hz), 3.35 (d, 0.73H, J = 16.8 Hz), 2.98* (d, 0.27H, J = 17.6 Hz), 2.53 (d, 1H, J = 17.0 Hz), 2.78−2.69 (m, 1H), 2.64−2.57 (m, 1H), 2.56−2.46 (m, 1H), 2.41−2.34 (m, 1H), 1.45* (s, 0.99H), 1.39 (s, 2.0H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 196.0*, 176.2, 176.1*, 162.0, 161.8*, 158.87*, 158.85, 153.3*, 153.0, 106.9, 106.8*, 106.4, 106.3*, 105.28, 105.25*, 82.8, 82.6*, 80.8, 64.4, 43.3, 42.8*, 28.24, 28.18*, 22.7*, 22.3, 19.5, 19.1*. HRMS-ESI (m/z): calcd for $C_{15}H_{17}O_6$ $[M + H]^+$ 293.1020, found 293.1026. IR (neat): 3391, 2921, 2851, 1772, 1644, 1569, 1438, 1375, 1270, 1165, 1058, 987, 848, 726 cm^{-1}. * = minor diastereomer.

*(±)-Microdiplodiasone (**2**).* This compound was prepared according to the general procedure for the reduction of the chromanone butenolides from chromanone butenolide **7h** (30.4 mg, 0.1 mmol, 1.0 equiv), nickel chloride hexahydrate (28.52 mg, 0.12 mmol, 1.1 equiv), and $NaBH_4$ (8.70 mg, 0.23 mmol, 2.1 equiv) in THF/MeOH (3/1 v/v, 4.0 mL) at 0 °C for 15 min to afford a yellow gum. The crude product was purified by silica gel chromatography (PE/EtOAc 1/1 v/v) to afford (±)-microdiplodiasone (**2**; 24 mg, 88%) as a yellow gum as a 8:1 mixture of diastereomers. Anal. Calcd for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.08; H, 4.78. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.88* (s, 0.12H), 11.87 (s, 0.84H), 7.14 (br, 1H), 5.99* (d, 0.12H, J = 2.4 Hz), 5.97 (d, 0.87H, J = 2.4 Hz), 5.90* (d, 0.10H, J = 2.4 Hz), 5.87 (d, 0.89H, J = 2.0 Hz), 4.58* (t, 0.09H, J = 7.2 Hz), 4.50 (dd, 0.91H, J = 8.0 Hz, J = 6.0 Hz), 3.71* (d, 0.12H, J = 11.2 Hz), 3.26 (d, 0.89H, J = 17.2 Hz), 2.92* (d, 0.09H, J = 16.8 Hz), 2.47 (d, 1H, J = 17.2 Hz), 2.78−2.70 (m, 1H), 2.66−2.57 (m, 1H), 2.54−2.44 (m, 1H), 2.40−2.34 (m, 1H), 1.45* (s, 0.24H), 1.38 (s, 2.88H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.6, 177.5, 165.4, 163.9, 160.3, 102.0, 96.7, 95.9, 83.3, 80.8, 42.7, 28.5, 21.5, 19.6. HRMS-ESI (m/z): calcd for $C_{14}H_{15}O_6$ $[M + H]^+$ 279.0863, found 279.0859. IR (neat): 3371, 2924, 1767, 1728, 1638, 1452, 1384, 1332, 1270, 1158, 1069, 1029, 876, 750, 598 cm^{-1}. * = minor diastereomer.

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*(±)-Gonytolide C (**3**).* This compound was prepared according to the general procedure for the reduction of the chromanone butenolides from chromanone butenolide **7k** (47.7 mg, 0.15 mmol, 1.0 equiv), nickel chloride hexahydrate (40.4 mg, 0.17 mmol, 1.1 equiv), and $NaBH_4$ (12.2 mg, 0.32 mmol, 2.1 equiv) in THF/MeOH (3/1 v/v, 4.0 mL) at 0 °C for 15 min to afford a yellow gum. The crude product was purified by silica gel chromatography (PE/EtOAc 1/1 v/v) to afford (±)-gonytolide C (**3**; 43 mg, 90%) as a yellow gum as a 20:1 mixture of diastereomers. Anal. Calcd for $C_{16}H_{16}O_7$: C, 60.00; H, 5.04. Found: C, 59.66; H, 4.68. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.42 (s, 0.9H), 6.38 (s, 1H), 6.37 (s, 1H), 4.78 (dd, 1H, J = 8.6 Hz, J = 4.2 Hz), 3.75 (s, 3H), 3. 46 (d, 1H, J = 17.2 Hz), 3.07 (d, 1H, J = 17.2 Hz), 2.86−2.77 (m,1H), 2.62−2.46 (m,2H), 2.39−2.34 (m,1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0, 176.0, 169.1, 161.7, 158.9, 151.2, 111.0, 108.3, 105.4, 84.6, 79.7, 53.6, 40.3, 27.7, 22.5, 21.7. HRMS-ESI (m/z): calcd for $C_{16}H_{17}O_7$ $[M + H]^+$ 321.0969, found 321.0976. IR (neat): 3398, 2921, 2851, 1785, 1755, 1646, 1570, 1457, 1367, 1268, 1202, 1161, 1061, 939, 836, 747, 675, 554 cm^{-1}.

*(±)-Gonytolide G (**4**).* This compound was prepared according to the general procedure for the reduction of the chromanone butenolides from chromanone butenolide **7l** (64 mg, 0.19 mmol, 1.0 equiv), nickel chloride hexahydrate (50 mg, 0.21 mmol, 1.1 equiv), and $NaBH_4$ (15.5 mg, 0.40 mmol, 2.1 equiv) in THF/MeOH (3/1 v/v, 4.0 mL) at 0 °C for 15 min to afford a yellow gum. The crude product was purified by silica gel chromatography (PE/EtOAc 2/1 v/v) to afford (±)-gonytolide G (**4**; 58 mg, 91%) as a colorless gum as an 8:1 mixture of diastereomers. Anal. Calcd for $C_{16}H_{16}O_8$: C, 57.14; H, 4.80. Found: C, 57.46; H, 5.17. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.47 (s, 0.89H), 11.43* (s, 0.09H), 6.60* (s, 0.13H), 6.57 (s, 1H), 6.5 (s, 1H), 4.88* (dd, 0.1H, J = 8.0 Hz, J = 6.0 Hz), 4.80 (dd, 0.9H, J = 8.6 Hz, J = 4.2 Hz), 4.67 (s, 2H), 3.76* (s, 0.19H), 3.75 (s, 2.80H), 3.49 (d, 1H, J = 17.2 Hz), 3.09 (d, 0.91H, J = 17.2 Hz), 2.99* (d, 0.11H, J = 17.2 Hz), 2.87−2.78 (m, 1H), 2.63−2.46 (m, 2H), 2.40−2.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 176.0, 169.0, 162.0, 159.3, 153.4, 107.6, 106.5, 104.9, 84.7, 79.7, 64.4, 53.7, 40.4, 27.7, 21.7. HRMS-ESI (m/z): calcd for $C_{16}H_{17}O_8$ $[M + H]^+$ 337.0918, found 337.0928. IR (neat): 3434, 2958, 2921, 2835, 2357, 1647, 1457, 1381, 1203, 1152, 1054, 892, 703, 672 cm^{-1}. * = minor diastereomer.

■ ASSOCIATED CONTENT

Supporting Information

Text and figures giving general information, schemes for general procedures A−E, schemes for the syntheses of chromones **8**, **9**, **10**, **5i**, **14**, **15**, and **5l**, thiochromone **5n**, and quinolone **5o**, and NMR spectra of all compounds prepared in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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