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# A novel one-pot synthesis of flavones†

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In this paper, a one-pot facile route for the $BiCl_3$/$RuCl_3$-mediated synthesis of functionalized flavones is described, including: (i) intermolecular *ortho*-acylation of substituted phenols with cinnamoyl chlorides, and (ii) intramolecular cyclodehydrogenation of the resulting *o*-hydroxychalcones. The reaction conditions are discussed herein.

## Introduction

For the flavonoid family, flavone (also called 2-arylchromone) with numerous biological activities is attracting many synthetic researchers to develop a number of versatile methodologies.[1] A recent review article[1a] has revealed the synthetic history of functionalized flavones from the traditional well-known named reactions (*e.g.*, Baker–Venkataraman,[2] Karl von-Auwers,[3] Algar–Flynn–Oyamada,[4] Allan–Robinson,[5] Kostanecki,[6] Mentzer[7] and Wittig[8]) to modern novel transition-metal promoted protocols (*e.g.*, Suzuki–Miyaura[9] and Sonogashira[10]). By the use of other reaction conditions such as microwave irradiation,[11] ionic liquids improvement[12] and photolytic annulation,[13] the unique methodologies of flavones and their derivatives have been established. For the synthetic chemistry of diversified flavones, the two-step process for (1) *ortho*-acylation of substituted phenols and (2) cyclodehydrogenation of the resulting *o*-hydroxychalcones is a general and direct route to provide access to the core structure, as shown in Scheme 1.

By the involvement of transition metals, various *ortho*-acylations of phenols have been well-developed, including $CuCl_2$,[14a] $FeCl_3$,[14b] $TiCl_4$,[14c] mercury lamp/photolysis,[14d] MsOH/microwave.[14e] For the following cyclodehydrogenation step, the uses of $InCl_3/SiO_2$,[15a] $FeCl_3 \cdot 6H_2O$/MeOH,[15b] and CuI/ionic liquids[15c] have been studied. In addition, transition metal-free oxidants-mediated reaction systems, for example, $I_2$/DMSO,[16a] DDQ/dioxane,[16b] $NaIO_4$/DMSO,[16c] $H_2O_2$/NaOH,[16d] $SeO_2$/dioxane[16e] and $Br_2$/NaOH[16f] have been investigated in the cyclodehydrogenation step.

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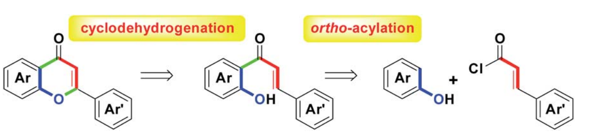
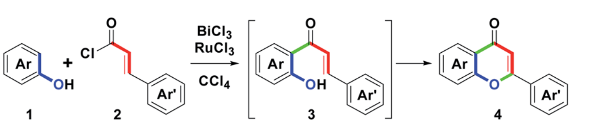
Among these reported routes with the synthetic sequence of intermolecular *ortho*-acylation followed by intramolecular cyclodehydrogenation, we found that all attempts adopted a two-step stepwise process as the major focused design in the flavone family formation. Despite the above elegant synthetic routes, to date, there are no reports on the one-pot synthesis of substituted flavones on the basis of the formal (3 + 3) annulation. Herein, we present metal chlorides-mediated one-pot synthesis of flavones **4** (Scheme 2) *via* the combination of $BiCl_3$ and$RuCl_3$-mediated intermolecular *ortho*-acylation of substituted phenols **1** with cinnamoyl chlorides **2** (one carbon–carbon bond formation, green), and intramolecular cyclodehydrogenation of the corresponding *o*-hydroxychalcones **3** (one carbon–oxygen bond formation, green). These starting materials, **1** and **2**, were obtained from commercial sources and used without further purification.

## Results and discussion

The initial study commenced with the treatment of the model substrate **1a** (Ar = Ph, 1.0 mmol) with **2a** (Ar′ = Ph, 1.0 mmol) and $AlCl_3$ (2.0 equiv.) in $CCl_4$ (20 mL) at reflux (77 °C) for 10 h. Only **3a** was produced at a 54% yield. The results are shown in




Scheme 1 Synthetic route of flavones.



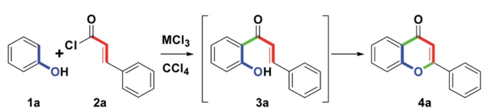

Scheme 2 Our synthetic route towards flavones.

Table 1, entry 1. Entries 2–7 show that six trivalent transition-metal chlorides (2.0 equiv., $InCl_3$, $FeCl_3$, $BiCl_3$, $CeCl_3$, $AuCl_3$ and $RuCl_3$) were studied in $CCl_4$ (20 mL) at reflux for 10 h. However, only $InCl_3$ and $FeCl_3$ obtained sole **3a** in 67% and 70% yields, respectively. $BiCl_3$ provided 65% yield of **3a** along with trace amount of **4a**. In particular, no reactions were observed for $CeCl_3$ and $AuCl_3$, while $RuCl_3$ produced a complex mixture. According to the experimental results, we understood that $InCl_3$ or $FeCl_3$-mediated *ortho*-acylation of **1a** proceeded well, but they could not promote the conversion from **3a** to **4a** (entries 2 and 3). In addition to forming **3a**, trace amount of **4a** (3%) could be obtained in the presence of $BiCl_3$ (entry 4). For $CeCl_3$ and $AuCl_3$, the reactivity of Lewis acid was weak to a degree that no desired reaction was initiated (entries 5 and 6). Compared with other $MCl_3$, $RuCl_3$ with strong oxidation ability could force the *ortho*-acylation of **1a** to complexation (entry 7). Next, we refocused the synthetic aim to study the equivalents of $BiCl_3$; however, after increasing the stoichiometric from 2.0 to 3.0 equiv., the conversion efficiency from **3a** to **4a** was similar to that of 2.0 equiv. (5%, entry 8).

In decreasing the equivalence of $BiCl_3$ from 2.0 to 1.0, no isolation of **4a** was observed (entry 9). On the basis of the above phenomenon, we found that excess amounts of $BiCl_3$ could not completely drive the conversion of **3a** to **4a**. For this reason, another promoter was required to enhance the reaction condition. Hence, we turned the synthetic focus to study the combination of $BiCl_3$ and $RuCl_3$-mediated synthesis of flavones. In entry 10, we found that the combination of $BiCl_3$ (1 equiv.) and $RuCl_3$ (1 equiv.) provided **4a** as the major product (68%) along with a 15% of **3a**. With these results in hand, we envisioned that $RuCl_3$ could trigger the cyclodehydrogenation step to accomplish the synthesis of **4a**. Three solvents having different boiling points, such as $MeNO_2$, $(CH_2Cl)_2$, $CH_2Cl_2$, and DMF were tested next. Using $MeNO_2$ (entry 11), complex unknown products were detected due to the high boiling temperature (101 °C). Entry 12 shows that $(CH_2Cl)_2$ produced a low conversion ratio (2/3) for **3a** and **4a**. For the low boiling point solvent, $CH_2Cl_2$ showed that only 10% of the amounts of **4a** were isolated, and **3a** was obtained as the major component (78%, entry 13). Among the three chloro-containing solvents, the temperature of boiling $CH_2Cl_2$ (40 °C) was low; as a result, the cyclodehydrogenation step could not be induced easier. Changing the solvent to DMF (entry 14), however, only unknown and unidentified complex mixture was isolated. Compared with $CH_2Cl_2$, $CCl_4$ and $(CH_2Cl)_2$ with higher boiling points (77 °C and 84 °C) could initiate the occurrence of the cyclodehydrogenation step, besides DMF (153 °C). According to the results, $CCl_4$ was the preferred solvent to obtain **4a**. To achieve the exhaustive conversion, the reaction time was examined next. Elongating the times to 15 h and 20 h respectively, showed that the transformation from **3a** to **4a** was complete, and the afforded yields of **4a** increased to 81% or 75%, respectively (entries 15 and 16). Even though the reaction time was elongated to 20 h, the yield of **4a** could not be enhanced. Remarkably, adjusting the temperature from reflux to room temperature (25 °C), no reactions were observed by the combination of $BiCl_3$ and $RuCl_3$. To increase the yield of **4a**, three combinations were examined next. In entry 17, the combination of $BiCl_3$ and $CuCl_2$ provided a 60% yield of **3a** along with trace amount of **4a** (8%). After changing $CuCl_2$ to $FeCl_3$, 72% yield of **3a** and 3% yield of **4a** were obtained for the combination of $BiCl_3$ and $CuCl_2$ (entry 18). The two results were similar to entries 4 and 8. Under the combination of $BiCl_3$ and $AuCl_3$ condition (entry 19), only **3a** was isolated in a 70% yield, and no desired **4a** was detected. Based on the results, we found that $CuCl_2$, $FeCl_3$ and $AuCl_3$ could not trigger the cyclodehydrogenation step easily. From the above screening reaction conditions, we envisioned that the combination of $BiCl_3$ (1.0 equiv.) and $RuCl_3$ (1.0 equiv.) could perform better for the formation of **4a** in refluxing $CCl_4$ for 15 h (entry 15). All the conditions were routinely carried out under an atmosphere of air (open-vessel conditions). The heating mantle was used to provide a stable heat source.

To study the scope and limitations of this one-pot route, substituted phenols **1a–1k** and cinnamoyl chlorides **2a–2o** were examined further. With optimal conditions established (Table 1, entry 14), we found that the one-pot two-step route could allow a direct synthesis of diversified flavones **4a–4y** in moderate to good yields (60–82%), as shown in Table 2, entries 1–26. For the electronic character of different Ar substituents on **1a–1k** and Ar′ substituents on **2a–2o**, these various substituents included: (1) electron-donating mono-, di- or trioxygenated aryl groups, (2) electron-neutral phenyl, biphenyl or naphthyl groups, (3) electron-withdrawing nitroaryl groups, (4) haloaryl

Table 1 Reaction conditions[a]



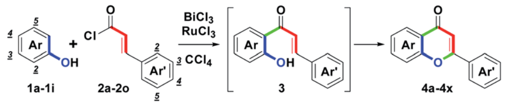

1a 2a 3a 4a

| Entry | $MCl_3$ (equiv.) | Solvent | Time (h) | **3a**/**4a**[b] % |
|---|---|---|---|---|
| 1 | $AlCl_3$ (2.0) | $CCl_4$ | 10 | 54/—[c] |
| 2 | $InCl_3$ (2.0) | $CCl_4$ | 10 | 67/—[c] |
| 3 | $FeCl_3$ (2.0) | $CCl_4$ | 10 | 70/—[c] |
| 4 | $BiCl_3$ (2.0) | $CCl_4$ | 10 | 65/3 |
| 5 | $CeCl_3$ (2.0) | $CCl_4$ | 10 | —[d] |
| 6 | $AuCl_3$ (2.0) | $CCl_4$ | 10 | —[d] |
| 7 | $RuCl_3$ (2.0) | $CCl_4$ | 10 | —[e] |
| 8 | $BiCl_3$ (3.0) | $CCl_4$ | 10 | 68/5 |
| 9 | $BiCl_3$ (1.0) | $CCl_4$ | 10 | 70/—[c] |
| 10 | $BiCl_3$ (1.0), $RuCl_3$ (1.0) | $CCl_4$ | 10 | 15/68 |
| 11 | $BiCl_3$ (1.0), $RuCl_3$ (1.0) | $MeNO_2$ | 10 | —[e] |
| 12 | $BiCl_3$ (1.0), $RuCl_3$ (1.0) | $(CH_2Cl)_2$ | 10 | 35/52 |
| 13 | $BiCl_3$ (1.0), $RuCl_3$ (1.0) | $CH_2Cl_2$ | 10 | 78/10 |
| 14 | $BiCl_3$ (1.0), $RuCl_3$ (1.0) | DMF | 10 | —[e] |
| **15** | **$BiCl_3$ (1.0), $RuCl_3$ (1.0)** | **$CCl_4$** | **15** | **3/81** |
| 16 | $BiCl_3$ (1.0), $RuCl_3$ (1.0) | $CCl_4$ | 20 | —[d]/75 |
| 17 | $BiCl_3$ (1.0), $CuCl_2$ (1.0) | $CCl_4$ | 15 | 60/8 |
| 18 | $BiCl_3$ (1.0), $FeCl_3$ (1.0) | $CCl_4$ | 15 | 72/3 |
| 19 | $BiCl_3$ (1.0), $AuCl_3$ (1.0) | $CCl_4$ | 15 | 70/—[c] |

[a] The reactions were run on a 1.0 mmol scale with phenol **1a**, cinnamoyl chloride **2a** (1.0 equiv.), metal chlorides ($MCl_3$, equiv.), solvent (20 mL), time (h), reflux. [b] Isolated yields. [c] No detection. [d] No reaction. [e] Unknown and unidentified complex mixture was isolated.

Table 2 Synthesis of 4a–4y [a]

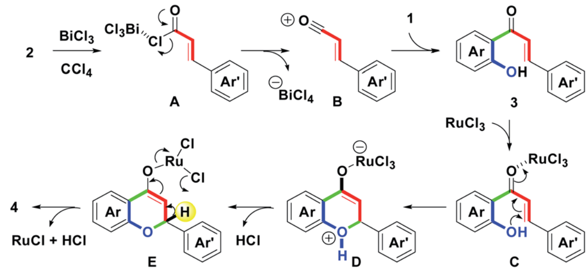



| Entry | 1, Ar = | 2, Ar′ = | $4^b$, (%) |
|---|---|---|---|
| 1 | **1a**, Ph | **2a**, Ph | **4a**, 81 |
| 2 | **1a**, Ph | **2b**, 4-MeOC$_6$H$_4$ | **4b**, 82 |
| 3 | **1a**, Ph | **2c**, 3-MeOC$_6$H$_4$ | **4c**, 80 |
| 4 | **1a**, Ph | **2d**, 3,4,5-(MeO)$_3$C$_6$H$_2$ | **4d**, 78 |
| 5 | **1a**, Ph | **2e**, 2,3,4-(MeO)$_3$C$_6$H$_2$ | **4e**, 72 |
| 6 | **1a**, Ph | **2f**, 3,4-CH$_2$O$_2$C$_6$H$_3$ | **4f**, 73 |
| 7 | **1a**, Ph | **2g**, 4-PhC$_6$H$_4$ | **4g**, 80 |
| 8 | **1a**, Ph | **2h**, 3,4-(MeO)$_2$C$_6$H$_3$ | **4h**, 72 |
| 9 | **1a**, Ph | **2i**, 3,4-Cl$_2$C$_6$H$_3$ | **4i**, 78 |
| 10 | **1a**, Ph | **2a**, Ph | **4j**, 80 |
| 11 | **1b**, 4-MeOC$_6$H$_4$ | **2a**, Ph | **4k**, 76 |
| 12 | **1c**, 3-MeOC$_6$H$_4$ | **2a**, Ph | **4l**, 68 |
| 13 | **1d**, 3-MeO-5-HOC$_6$H$_3$ | **2a**, Ph | **4m**, 64 |
| 14 | **1e**, 3,5-(MeO)$_2$C$_6$H$_3$ | **2j**, 4-NO$_2$C$_6$H$_4$ | **4n**, 76 |
| 15 | **1a**, Ph | **2k**, 2-naphthyl | **4o**, 70 |
| 16 | **1a**, Ph | **2l**, 2-FC$_6$H$_4$ | **4p**, 67 |
| 17 | **1a**, Ph | **2m**, 2-furyl | **4q**, 60[c] |
| 18 | **1a**, Ph | **2n**, 2-thienyl | **4r**, 62 |
| 19 | **1a**, Ph | **2o**, 1-naphthyl | **4s**, 75 |
| 20 | **1f**, 4-FC$_6$H$_4$ | **2h**, 3,4-(MeO)$_2$C$_6$H$_3$ | **4t**, 73 |
| 21 | **1g**, 4-ClC$_6$H$_4$ | **2h**, 3,4-(MeO)$_2$C$_6$H$_3$ | **4u**, 72 |
| 22 | **1h**, 4-BrC$_6$H$_4$ | **2h**, 3,4-(MeO)$_2$C$_6$H$_3$ | **4v**, 66 |
| 23 | **1i**, 4-MeC$_6$H$_4$ | **2h**, 3,4-(MeO)$_2$C$_6$H$_3$ | **4w**, 74 |
| 24 | **1c**, 3-MeOC$_6$H$_4$ | **2h**, 3,4-(MeO)$_2$C$_6$H$_3$ | **4x**, 64 |
| 25 | **1j**, 3-MeO-2-HOC$_6$H$_3$ | **2a**, Ph | **4y**, 60 |
| 26 | **1k**, 2-NO$_2$C$_6$H$_4$ | **2a**, Ph | **4z**, —[d] |

[a] All reactions were run on a 1.0 mmol scale with phenols **1a–1k**, cinnamoyl chlorides (**2a–2o**, 1.0 equiv.), BiCl$_3$ (315 mg, 1.0 equiv.), CCl$_4$ (20 mL), 10 h, reflux (77 °C); then RuCl$_3$·3H$_2$O (261 mg, 1.0 equiv.) was added into the reaction mixture, 5 h, reflux (monitored by TLC). [b] Isolated yields. [c] **3q** (10%) was obtained. [d] No detection.

groups and (5) heterocyclic furyl and thienyl groups were highly appropriate. However, when the Ar′ substituent was the 2-furyl group, the by-product **3q** was obtained in a 10% yield. Furthermore, with the use of RuCl$_3$, the conversion from **3q** to **4q** was successful. Therefore, efficient formation of **4a–4y** showed that these substituents (Ar and Ar′) did not affect the distribution of the provided yields, besides **4z** (Ar = 4-NO$_2$C$_6$H$_4$). The structures of **4a–4y** could be determined by $^1$H NMR analysis. The structure of **4t** was determined by single-crystal X-ray analysis.[17]

On the basis of the experimental results, a plausible mechanism for the formation of **4** is illustrated in Scheme 3. Initially, BiCl$_3$-mediated complexation of **2** forms **A** by one bismuth–chloro (Bi–Cl) bond formation. Then, by the removal of $^{\ominus}$BiCl$_4$, **B** with a styryl acylium center could be generated. Following the Friedel–Crafts *ortho*-acylation process, **B** reacts with **1** to lead **3** *via* one carbon–carbon (C–C) bond formation (green mark).[18a] Dubac *et al.* have reported similar reactions. In addition to BiCl$_3$, other bismuth salts-mediated Friedel–Crafts reactions have been well-documented.[18b–18d] Then, by the involvement of

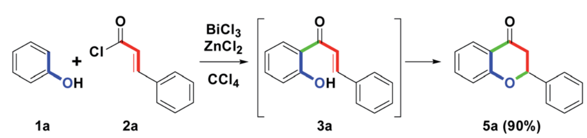



Scheme 3 Plausible mechanism.

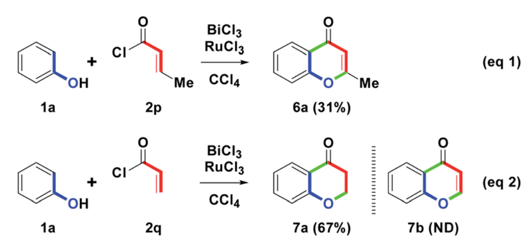
RuCl$_3$, **C** with a ruthenium(III)-chelated complex was produced. Furthermore, the intramolecular oxa-Michael addition provided **D** *via* one carbon-oxygen (C–O) bond formation (green mark). After the proton exchange, **E** could be formed along with the releasing HCl. Finally, dehydrogenation of **E** obtained **4** by the removal of RuCl and HCl.[19] Under the cyclodehydrogenation step, Laurenczy *et al.* reported the redox conversion between Ru(III) and Ru(I).[19a]

On the other hand, as an extension of the one-pot two-step synthetic route, changing the combination from BiCl$_3$/RuCl$_3$ to BiCl$_3$/ZnCl$_2$ was examined. However, the flavanone skeleton **5a** was isolated at a 90% yield, and no flavone **4a** was detected. A possible reason could be that ZnCl$_2$ lacks sufficient oxidative ability to completely promote the cyclodehydrogenation under the redox condition such that it only served a Lewis acid role in promoting the formation of **5a** *via* an intramolecular annulation of **3a**. Herein, we also developed the BiCl$_3$/ZnCl$_2$-mediated one-pot two-step, novel route for the synthesis of flavanone skeleton (Scheme 4).

With the results in mind, cinnamoyl chlorides **2a–2o** were adjusted next to crotonoyl chloride (**2p**) or acryloyl chloride (**2q**) under one-pot condition (Scheme 5). As shown in eqn (1), the BiCl$_3$/RuCl$_3$ mediated reaction of **1a** with **2p** provided **6a** with the chromen-4-one skeleton in only a 31% yield. Compared with **4a** (81%), the isolated yield of **6a** (31%) was low. The possible reason could be that with the hydrogen on **E** (yellow, Scheme 3),




Scheme 4 Synthesis of 5a.




Scheme 5 Synthesis of 6a and 7a.

the low acidity was not easy to abstract by the $RuCl_3$ for the dehydrogenation step to be triggered efficiently. On the basis of the results, we demonstrated that benzylic hydrogen was acidic and easily eliminated. Furthermore, by the removal of the β-methyl group on **2**, $BiCl_3/RuCl_3$ mediated reaction of **1a** with **2q** was shown in eqn (2). In particular, only **7a** was generated in a 67% yield. However, an intramolecular dehydrogenation step was not initiated so that the predicted **7b** was not obtained. The resulting phenomenon meant that cyclodehydrogenation only occurred in cinnamoyl substituents (with benzylic hydrogen). Although substrate **2** was limited to the cinnamoyl substituents, it still provided a novel one-pot synthesis of the flavone skeleton.

# Conclusion

In summary, we have developed a concise route for the effective synthesis of functionalized flavones *via* $BiCl_3/RuCl_3$ mediating the one-pot, direct intermolecular *ortho*-acylation of substituted phenols with cinnamoyl chlorides followed by intramolecular cyclodehydrogenation of the resulting *o*-hydroxychalcones under refluxing $CCl_4$ reaction conditions. The process provides a cascade pathway of one carbon–oxygen and one carbon–carbon bond formation. Related plausible mechanisms have been proposed. Further studies regarding the efficient synthetic routes towards flavones will be conducted and published in due course.

# Experimental

## General

All reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of air with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration *in vacuo*. Melting points were determined with a SMP3 melting apparatus. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and at 100 MHz, respectively. Chemical shifts ($\delta$) are reported in parts per million (ppm) and the coupling constants ($J$) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

## A representative synthetic procedure of compounds 4a–4y and 3q is as follows

$BiCl_3$ (315 mg, 1.0 mmol) was added to a solution of phenols **1a–1k** (1.0 mmol) in $CCl_4$ (20 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. Cinnamoyl chlorides **2a–2o** (1.0 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at reflux for 10 h (monitored by TLC). Then, $RuCl_3\cdot 3H_2O$ (261 mg, 1.0 mmol) was added to the reaction mixture (containing *o*-hydroxychalcones **3**) at reflux. The reaction mixture was stirred at reflux for 5 h (monitored by TLC). The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layers were washed with brine (2 × 20 mL), dried ($MgSO_4$), filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 20/1–4/1) afforded **4a–4y** and **3q**.

**2-Phenylchromen-4-one (4a).**[20] Yield = 81% (180 mg); white solid; mp = 90–92 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{11}O_2$ 223.0759, found 223.0768; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.24 (dd, $J$ = 1.6, 8.0 Hz, 1H), 7.94–7.92 (m, 2H), 7.71 (dt, $J$ = 2.0, 8.8 Hz, 1H), 7.57 (dd, $J$ = 0.8, 8.0 Hz, 1H), 7.55–7.50 (m, 3H), 7.42 (dt, $J$ = 0.8, 8.0 Hz, 1H), 6.86 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.4, 163.5, 156.3, 133.8, 131.7, 131.6, 129.0 (2×), 126.3 (2×), 125.7, 125.2, 123.9, 118.1, 107.5.

**2-(4-Methoxyphenyl)chromen-4-one (4b).**[21] Yield = 82% (207 mg); white solid; mp = 172–174 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{13}O_3$ 253.0865, found 253.0872; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.22 (dd, $J$ = 1.6, 8.0 Hz, 1H), 7.90 (d, $J$ = 9.2 Hz, 2H), 7.69 (dt, $J$ = 1.6, 8.4 Hz, 1H), 7.56 (dd, $J$ = 0.8, 8.4 Hz, 1H), 7.42 (dt, $J$ = 1.2, 8.0 Hz, 1H), 7.03 (d, $J$ = 9.2 Hz, 2H), 6.81 (s, 1H), 3.89 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.4, 163.7, 162.5, 156.2, 133.7, 128.6, 128.1 (2×), 125.7, 125.2, 123.9, 117.9, 114.5 (2×), 106.0, 55.5.

**2-(3-Methoxyphenyl)chromen-4-one (4c).**[22] Yield = 80% (202 mg); white solid; mp = 92–94 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{13}O_3$ 253.0865, found 253.0874; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.24 (dd, $J$ = 1.6, 8.0 Hz, 1H), 7.72 (dt, $J$ = 2.0, 8.4 Hz, 1H), 7.59 (dd, $J$ = 0.8, 8.4 Hz, 1H), 7.53 (dt, $J$ = 1.2, 8.0 Hz, 1H), 7.46–7.42 (m, 3H), 7.09 (ddd, $J$ = 0.8, 2.4, 8.8 Hz, 1H), 6.89 (s, 1H), 3.90 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.5, 160.0, 156.3, 134.0, 133.1, 130.2, 125.7 (2×), 125.4, 118.9, 118.1 (2×), 117.4, 111.8, 107.6, 55.5.

**2-(3,4,5-Trimethoxyphenyl)chromen-4-one (4d).**[23] Yield = 78% (243 mg); white solid; mp = 168–170 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{17}O_5$ 313.1076, found 313.1084; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.25 (dd, $J$ = 1.6, 8.0 Hz, 1H), 7.73 (dt, $J$ = 1.6, 8.4 Hz, 1H), 7.61 (d, $J$ = 8.0 Hz, 1H), 7.46 (dt, $J$ = 1.6, 7.6 Hz, 1H), 7.16 (s, 2H), 6.89 (s, 1H), 3.97 (s, 6H), 3.94 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.4, 163.4, 156.3, 153.6 (2×), 141.3, 134.0, 126.8, 125.7, 125.5, 123.9, 118.1, 107.1, 103.9 (2×), 61.1, 56.4 (2×).

**2-(2,3,4-Trimethoxyphenyl)chromen-4-one (4e).** Yield = 72% (225 mg); white solid; mp = 152–154 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{17}O_5$ 313.1076, found 313.1067; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.24 (dd, $J$ = 2.0, 8.4 Hz, 1H), 7.68 (dt, $J$ = 2.0, 8.4 Hz, 1H), 7.56 (d, $J$ = 9.2 Hz, 1H), 7.52 (dt, $J$ = 1.6, 8.4 Hz, 1H), 7.41 (dt, $J$ = 1.2, 8.0 Hz, 1H), 7.02 (s, 1H), 6.81 (d, $J$ = 8.8 Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 3.92 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.8, 161.5, 156.5, 156.3, 153.2, 133.5, 128.4, 125.7, 125.0, 124.2, 123.8, 119.1, 117.9, 111.1, 107.4, 61.2, 61.0, 56.1.

**2-Benzo[1,3]dioxol-5-ylchromen-4-one (4f).**[24] Yield = 73% (194 mg); white solid; mp = 200–202 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{11}O_4$ 267.0657, found 267.0650; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.22 (dd, $J$ = 1.6, 8.0 Hz, 1H), 7.70 (dt, $J$ = 1.6, 8.4 Hz, 1H), 7.55 (d, $J$ = 8.0 Hz, 1H), 7.51 (dd, $J$ = 1.6, 8.0 Hz, 1H), 7.42 (dt, $J$ = 0.8, 8.0 Hz, 1H), 7.38 (d, $J$ = 1.6 Hz, 1H), 6.94 (d, $J$ = 8.4 Hz, 1H), 6.81 (s, 1H), 6.08 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.3, 163.5, 156.1, 150.8, 148.5, 133.9, 125.7, 125.6, 125.3, 123.6, 121.7, 118.0, 108.8, 106.4, 106.3, 102.0.

**2-Biphenyl-4-ylchromen-4-one (4g).**[25] Yield = 80% (238 mg); white solid; mp = 141–143 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{15}O_2$ 299.1072, found 299.1077; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.26 (dd, $J$ = 1.6, 8.0 Hz, 1H), 8.03 (d, $J$ = 8.4 Hz, 2H), 7.76 (d, $J$ = 8.4 Hz, 2H), 7.74 (dt, $J$ = 1.6, 8.4 Hz, 1H), 7.67–7.61 (m, 3H), 7.51–7.40 (m, 4H), 7.00 (s, 1H), $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.4, 163.6, 156.3, 144.6, 139.7, 134.0, 130.3, 129.0 (2×), 128.3, 127.7 (2×), 127.2 (2×), 126.9 (2×), 125.7, 125.4, 123.7, 118.1, 107.1.

**2-(3,4-Dimethoxyphenyl)chromen-4-one (4h).**[26] Yield = 72% (203 mg); white solid; mp = 118–120 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{15}O_4$ 283.0970, found 283.0976; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.23 (dd, $J$ = 1.6, 8.0 Hz, 1H), 7.70 (dt, $J$ = 1.6, 8.4 Hz, 1H), 7.59 (d, $J$ = 8.4 Hz, 1H), 7.58 (d, $J$ = 8.4 Hz, 1H), 7.43 (dt, $J$ = 1.2, 8.0 Hz, 1H), 7.42 (d, $J$ = 8.0 Hz, 1H), 7.00 (d, $J$ = 8.4 Hz, 1H), 6.82 (s, 1H), 3.99 (s, 3H), 3.97 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.4, 163.6, 156.2, 152.2, 149.3, 133.7, 125.7, 125.2, 124.2, 123.8, 120.1, 118.0, 111.2, 108.9, 106.4, 56.1 (2×).

**2-(3,4-Dichlorophenyl)chromen-4-one (4i).**[26] Yield = 78% (226 mg); white solid; mp = 202–204 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_9Cl_2O_2$ 290.9980, found 290.9987; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.23 (dd, $J$ = 1.6, 8.0 Hz, 1H), 8.24 (d, $J$ = 1.6 Hz, 1H), 7.75–7.71 (m, 2H), 7.60 (dt, $J$ = 0.8, 8.4 Hz, 2H), 7.45 (dt, $J$ = 0.8, 8.0 Hz, 1H), 6.80 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.1, 160.9, 156.1, 136.0, 134.1, 133.7, 131.7, 131.1, 128.1, 125.8, 125.6, 125.3, 123.9, 118.1, 108.2.

**6-Methoxy-2-phenylchromen-4-one (4j).**[22] Yield = 80% (202 mg); white solid; mp = 165–167 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{13}O_3$ 253.0865, found 253.0873; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.94–7.90 (m, 2H), 7.59 (d, $J$ = 3.2 Hz, 1H), 7.54–7.49 (m, 4H), 7.29 (dd, $J$ = 3.2, 9.2 Hz, 1H), 6.87 (s, 1H), 3.90 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.3, 163.3, 157.0, 151.1, 131.8, 131.6, 129.0 (2×), 126.3 (2×), 124.4, 123.9, 119.5, 106.7, 104.8, 55.9.

**7-Methoxy-2-phenylchromen-4-one (4k).**[22] Yield = 76% (192 mg); white solid; mp = 106–108 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{13}O_3$ 253.0865, found 253.0860; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.12 (dd, $J$ = 0.4, 8.4 Hz, 1H), 7.91–7.88 (m, 2H), 7.53–7.48 (m, 3H), 6.99–6.96 (m, 2H), 6.80 (s, 1H), 3.93 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 177.8, 164.3, 163.2, 158.0, 131.7, 131.5, 129.0 (2×), 127.0, 126.2 (2×), 117.6, 114.5, 107.3, 100.4, 55.8.

**5-Hydroxy-7-methoxy-2-phenylchromen-4-one (4l).**[27] Yield = 68% (182 mg); white solid; mp = 167–169 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{13}O_4$ 269.0814, found 269.0821; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 10.81 (br s, 1H), 7.87–7.85 (m, 2H), 7.54–7.48 (m, 3H), 6.63 (s, 1H), 6.47 (d, $J$ = 2.4 Hz, 1H), 6.35 (d, $J$ = 2.4 Hz, 1H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 182.4, 165.5, 163.9, 162.1, 157.7, 131.8, 131.2, 129.0 (2×), 126.2 (2×), 105.8, 105.6, 98.1, 92.6, 55.7.

**5,7-Dimethoxy-2-phenylchromen-4-one (4m).**[22] Yield = 64% (181 mg); white solid; mp = 145–147 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{15}O_4$ 283.0970, found 283.0973; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.88–7.83 (m, 2H), 7.54–7.45 (m, 3H), 6.67 (s, 1H), 6.56 (d, $J$ = 2.4 Hz, 1H), 6.36 (d, $J$ = 2.0 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 177.6, 164.0, 160.9, 160.6, 159.9, 131.5, 131.1, 128.9 (2×), 125.9 (2×), 109.3, 109.0, 96.2, 92.8, 56.4, 55.7.

**2-(4-Nitrophenyl)chromen-4-one (4n).**[21] Yield = 76% (203 mg); white solid; mp = 128–130 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{10}NO_4$ 268.0610, found 268.0618; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.39 (d, $J$ = 9.2 Hz, 2H), 8.24 (dd, $J$ = 1.6, 8.0 Hz, 1H), 8.11 (d, $J$ = 9.2 Hz, 2H), 7.76 (dt, $J$ = 1.6, 8.8 Hz, 1H), 7.61 (dd, $J$ = 0.8, 8.4 Hz, 1H), 7.47 (dt, $J$ = 1.2, 8.0 Hz, 1H), 6.92 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.0, 160.6, 156.2, 149.4, 137.6, 134.4, 127.2 (2×), 125.9, 125.8, 124.2 (2×), 123.6, 118.1, 109.6.

**2-Naphthalen-2-ylchromen-4-one (4o).**[28] Yield = 70% (190 mg); white solid; mp = 141–143 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{13}O_2$ 273.0916, found 273.0925; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.52 (s, 1H), 8.23 (dd, $J$ = 1.6, 8.0 Hz, 1H), 8.02–7.90 (m, 4H), 7.76 (dt, $J$ = 1.6, 8.4 Hz, 1H), 7.67 (dd, $J$ = 0.8, 8.4 Hz, 1H), 7.64–7.57 (m, 2H), 7.47 (dt, $J$ = 1.2, 7.6 Hz, 1H), 7.07 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.5, 163.7, 156.4, 134.8, 134.0, 132.9, 129.1, 129.0, 128.8, 128.1, 127.9, 127.1 (2×), 125.8, 125.4, 123.8, 122.6, 118.1, 107.7.

**2-(2-Fluorophenyl)chromen-4-one (4p).**[29] Yield = 67% (161 mg); white solid; mp = 100–102 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{10}FO_2$ 241.0665, found 241.0669; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.25 (dd, $J$ = 1.6, 8.0 Hz, 1H), 7.94 (dt, $J$ = 1.6, 8.0 Hz, 1H), 7.72 (dt, $J$ = 1.6, 8.0 Hz, 1H), 7.57–7.50 (m, 2H), 7.44 (dt, $J$ = 1.2, 7.6 Hz, 1H), 7.33 (dt, $J$ = 1.2, 8.0 Hz, 1H), 7.24 (dd, $J$ = 1.2, 8.4 Hz, 1H), 6.96 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.5, 160.6 (d, $J$ = 254.0 Hz), 158.9, 156.4, 133.9, 132.9 (d, $J$ = 9.1 Hz), 129.1, 125.8, 125.3 (2×), 124.6 (d, $J$ = 3.8 Hz), 123.8, 118.1, 117.0 (d, $J$ = 22.7 Hz), 112.4 (d, $J$ = 10.6 Hz).

**2-Furan-2-ylchromen-4-one (4q).**[30] Yield = 60% (127 mg); white solid; mp = 122–124 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{13}H_9O_3$ 213.0552, found 213.0559; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.22 (dd, $J$ = 2.0, 8.0 Hz, 1H), 7.68 (dt, $J$ = 2.0, 8.4 Hz, 1H), 7.63 (dd, $J$ = 0.8, 2.0 Hz, 1H), 7.50 (dd, $J$ = 0.8, 8.4 Hz, 1H), 7.41 (dt, $J$ = 0.8, 8.0 Hz, 1H), 7.15 (d, $J$ = 3.2 Hz, 1H), 6.76 (s, 1H), 6.62 (dd, $J$ = 2.0, 3.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 177.9, 155.8, 155.2, 146.4, 145.8, 133.8, 125.8, 125.2, 124.1, 117.9, 113.1, 112.5, 105.5.

**3-Furan-2-yl-1-(2-hydroxyphenyl)propenone (3q).** Yield = 10% (21 mg); white solid; mp = 105–107 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{11}O_3$ 215.0708, found 215.0714; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 12.89 (s, 1H), 7.92 (dd, $J$ = 2.0, 8.4 Hz, 1H), 7.68 (d, $J$ = 14.8 Hz, 1H), 7.560 (dd, $J$ = 0.8, 1.2 Hz, 1H), 7.558 (d, $J$ = 14.8 Hz, 1H), 7.49 (dt, $J$ = 1.6, 8.8 Hz, 1H), 7.02 (dd, $J$ = 0.8, 8.4 Hz, 1H), 6.94 (dt, $J$ = 1.2, 8.4 Hz, 1H), 6.77 (d, $J$ = 3.2 Hz, 1H), 6.54 (dd, $J$ = 1.6, 3.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 193.3, 163.5, 151.5, 145.4, 136.3, 131.1, 129.6, 120.0, 118.8, 118.5, 117.6, 117.1, 112.9.

**2-Thiophen-2-ylchromen-4-one (4r).**[30] Yield = 62% (141 mg); white solid; mp = 93–95 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{13}H_9O_2S$ 229.0323, found 229.0332; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.21 (dd, $J$ = 1.6, 7.6 Hz, 1H), 7.34 (dd, $J$ = 1.2, 3.6 Hz, 1H), 7.69 (dt, $J$ = 1.6, 8.4 Hz, 1H), 7.58 (dd, $J$ = 1.2, 4.8 Hz, 1H), 7.54 (dd, $J$ = 0.8, 8.4 Hz, 1H), 7.42 (dt, $J$ = 1.2, 8.4 Hz, 1H), 7.19 (dd, $J$ = 3.6, 4.8 Hz, 1H), 6.72 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 177.9, 159.1, 155.9, 135.2, 133.8, 130.3, 128.5, 128.5, 125.7, 125.3, 124.0, 117.9, 106.2.

**2-Naphthalen-1-ylchromen-4-one (4s).**[20] Yield = 75% (204 mg); white solid; mp = 139–141 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{13}O_2$ 273.0916, found 273.0910; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.32 (dd, $J$ = 1.6, 8.0 Hz, 1H), 8.16–8.12 (m, 1H), 8.04 (d, $J$ = 8.4 Hz, 1H), 7.98–7.94 (m, 1H), 7.78 (d, $J$ = 6.4 Hz, 1H), 7.74 (dt, $J$ = 1.6, 8.8 Hz, 1H), 7.61–7.54 (m, 4H), 7.49 (dt, $J$ = 1.2, 8.0 Hz, 1H), 6.73 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.3, 165.6, 156.8, 134.0, 133.8, 131.6, 130.6, 130.4, 128.7, 128.0, 127.5, 126.6, 125.9, 125.4, 125.1, 124.9, 124.0, 118.3, 113.0.

**2-(3,4-Dimethoxyphenyl)-6-fluorochromen-4-one (4t).** Yield = 73% (219 mg); white solid; mp = 168–170 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{14}FO_4$ 301.0876, found 301.0879; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.86 (dd, $J$ = 2.8, 8.0 Hz, 1H), 7.60–7.55 (m, 2H), 7.42 (dt, $J$ = 3.2, 8.8 Hz, 1H), 7.38 (br s, 1H), 6.99 (d, $J$ = 8.0 Hz, 1H), 6.81 (s, 1H), 3.98 (s, 3H), 3.97 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 177.5 (d, $J$ = 2.3 Hz), 163.9, 160.8, 158.4, 152.4, 149.4, 124.9 (d, $J$ = 7.6 Hz), 123.8, 121.8 (d, $J$ = 25.7 Hz), 120.2, 120.0 (d, $J$ = 7.6 Hz, 1H), 111.2, 110.6 (d, $J$ = 23.5 Hz), 108.9, 105.7, 56.13, 56.11. Single-crystal X-ray diagram: crystal of compound **4t** was grown by slow diffusion of EtOAc into a solution of compound **4t** in $CH_2Cl_2$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group *Pn*, $a$ = 4.0051(3) Å, $b$ = 10.1298(8) Å, $c$ = 16.3327(12) Å, $V$ = 662.13(9) Å$^3$, $Z$ = 2, $d_{calcd}$ = 1.506 g cm$^{-3}$, $F(000)$ = 312, 2$\theta$ range 2.010–26.380°, $R$ indices (all data) $R1$ = 0.0307, w$R2$ = 0.0827.

**6-Chloro-2-(3,4-dimethoxyphenyl)chromen-4-one (4u).**[31] Yield = 72% (228 mg); white solid; mp = 199–201 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{14}ClO_4$ 317.0581, found 317.0588; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.20 (d, $J$ = 2.4 Hz, 1H), 7.63 (d, $J$ = 2.8 Hz, 1H), 7.56 (dd, $J$ = 2.4, 8.4 Hz, 1H), 7.54 (dd, $J$ = 0.4, 8.8 Hz, 1H), 7.37 (d, $J$ = 2.0 Hz, 1H), 6.99 (d, $J$ = 8.4 Hz, 1H), 6.78 (s, 1H), 3.99 (s, 3H), 3.97 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 177.1, 163.8, 154.5, 152.4, 149.4, 133.8, 131.1, 125.2, 124.9, 123.8, 120.2, 119.7, 111.2, 108.9, 106.3, 56.1 (2×).

**6-Bromo-2-(3,4-dimethoxyphenyl)chromen-4-one (4v).**[32] Yield = 66% (238 mg); white solid; mp = 206–208 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{14}BrO_4$ 361.0076, found 361.0081; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.34 (d, $J$ = 2.4 Hz, 1H), 7.77 (dd, $J$ = 2.4, 8.8 Hz, 1H), 7.55 (dd, $J$ = 2.0, 8.4 Hz, 1H), 7.47 (d, $J$ = 8.8 Hz, 1H), 7.36 (d, $J$ = 2.0 Hz, 1H), 6.98 (d, $J$ = 8.4 Hz, 1H), 6.81 (s, 1H), 3.98 (s, 3H), 3.97 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 176.9, 163.9, 154.9, 152.5, 149.4, 136.6, 128.3, 125.1, 123.7, 120.3, 119.9, 118.7, 111.2, 108.9, 106.2, 56.1 (2×).

**2-(3,4-Dimethoxyphenyl)-6-methylchromen-4-one (4w).**[33] Yield = 74% (219 mg); white solid; mp = 182–184 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{17}O_4$ 297.1127, found 297.1138; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.05 (br s, 1H), 7.64–7.52 (m, 3H), 7.44 (br s, 1H), 7.15 (br s, 1H), 7.00 (s, 1H), 3.98 (s, 6H), 2.50 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.4, 164.8, 154.6, 152.7, 149.4, 135.7, 125.6, 125.0, 123.8, 123.1, 120.8, 117.9, 117.6, 111.3, 109.1, 56.3, 56.2, 21.0.

**2-(3,4-Dimethoxyphenyl)-7-methoxychromen-4-one (4x).**[34] Yield = 64% (200 mg); white solid; mp = 172–174 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{17}O_5$ 313.1076, found 313.1085; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.14 (d, $J$ = 8.8 Hz, 1H), 7.57 (dd, $J$ = 2.0, 8.8 Hz, 1H), 7.38 (d, $J$ = 2.0 Hz, 1H), 7.02–6.97 (m, 3H), 6.89 (s, 1H), 3.99 (s, 3H), 3.97 (s, 3H), 3.95 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 177.7, 164.4, 163.8, 158.0, 152.3, 149.3, 127.0, 124.0, 120.2, 117.1, 114.7, 111.2, 108.9, 105.8, 100.4, 56.13, 56.10, 55.9.

**8-Hydroxy-7-methoxy-2-phenylchromen-4-one (4y).** Yield = 60% (161 mg); white solid; mp = 236–238 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{13}O_4$ 269.0814, found 269.0816; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.01–7.99 (m, 2H), 7.80 (d, $J$ = 9.2 Hz, 1H), 7.56–7.50 (m, 3H), 7.06 (d, $J$ = 9.2 Hz, 1H), 6.96 (s, 1H), 4.05 (s, 3H), 2.80 (br s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.3, 150.0, 144.9, 134.0, 131.6, 130.8, 129.1 (3×), 126.4 (2×), 116.5 (2×), 108.6, 106.7, 56.7.

**2-Phenylchroman-4-one (5a).**[35] $BiCl_3$ (315 mg, 1.0 mmol) was added to a solution of phenol **1a** (94 mg, 1.0 mmol) in $CCl_4$ (20 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. Cinnamoyl chloride **2a** (167 mg, 1.0 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at reflux for 10 h. Then, $ZnCl_2$ (136 mg, 1.0 mmol) was added to the reaction mixture at reflux. The reaction mixture was stirred at reflux for 5 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layers were washed with brine (2 × 20 mL), dried ($MgSO_4$), filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 20/1–4/1) afforded **5a**. Yield = 90% (202 mg); colorless solid; mp = 77–79 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{13}O_2$ 225.0916, found 225.0924; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.95

(dd, $J$ = 2.0, 8.0 Hz, 1H), 7.54–7.38 (m, 6H), 7.08–7.04 (m, 2H), 5.49 (dd, $J$ = 2.8, 13.2 Hz, 1H), 3.10 (dd, $J$ = 13.2, 16.8 Hz, 1H), 2.90 (dd, $J$ = 2.8, 16.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 191.9, 161.5, 138.7, 136.2, 128.8 (2×), 128.7, 127.0, 126.1 (2×), 121.6, 120.9, 118.1, 79.6, 44.6.

**2-Methyl-chromen-4-one (6a).**[36] **and chroman-4-one (7a).**[37] $BiCl_3$ (315 mg, 1.0 mmol) was added to a solution of phenol **1a** (94 mg, 1.0 mmol) in $CCl_4$ (20 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. Crotonoyl chloride **2p** (104 mg, 1.0 mmol) or acryloyl chloride **2q** (90 mg, 1.0 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at reflux for 10 h. Then, $RuCl_3 \cdot 3H_2O$ (261 mg, 1.0 mmol) was added to the reaction mixture at reflux. The reaction mixture was stirred at reflux for 5 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layers were washed with brine (2 × 20 mL), dried ($MgSO_4$), filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 20/1–4/1) afforded **6a** and **7a**. For **6a**: yield = 31% (50 mg); colorless solid; mp = 62–64 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) $m/z$: $[M + H]^+$ calcd for $C_{10}H_9O_2$ 161.0603, found 161.0612; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.17 (dd, $J$ = 1.6, 8.0 Hz, 1H), 7.63 (dt, $J$ = 1.6, 8.8 Hz, 1H), 7.41 (dd, $J$ = 0.8, 8.0 Hz, 1H), 7.35 (dt, $J$ = 0.8, 8.0 Hz, 1H), 6.17 (s, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 178.2, 166.2, 156.5, 133.4, 125.6, 124.9, 123.6, 117.8, 110.6, 20.6. For **7a**: yield = 67% (99 mg); colorless liquid; HRMS (ESI-TOF) $m/z$: $[M + H]^+$ calcd for $C_9H_9O_2$ 161.0603, found 161.0612; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.86 (dd, $J$ = 2.0, 8.0 Hz, 1H), 7.44 (dt, $J$ = 1.6, 8.4 Hz, 1H), 6.98 (dt, $J$ = 1.2, 8.0 Hz, 1H), 6.94 (dd, $J$ = 1.2, 8.4 Hz, 1H), 4.50 (t, $J$ = 6.4 Hz, 2H), 2.78 (t, $J$ = 6.4 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 191.7, 161.8, 135.8, 127.0, 121.2 (2×), 117.8, 66.9, 37.7.

## Conflicts of interest

There are no conflicts to declare.

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