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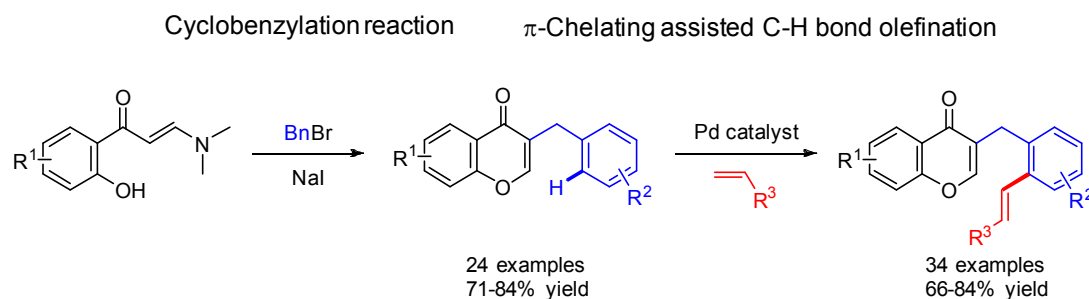
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Synthesis of 3-(2-Olefinbenzyl)-4*H*-chromen-4-one through Cyclobenzylation and Catalytic C–H Bond Functionalization Using Palladium (II)

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ABSTRACT

An efficient strategy for synthesizing 3-(2-olefinbenzyl)-4*H*-chromen-4-one in two steps was developed. The first step is a cyclobenzylation reaction between (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one and benzyl bromide to produce homoisoflavonoid. The second step involves intermolecular Pd-catalyzed π -chelating-assisted C–H bond olefination. Using the C-2/C-3 double bond of chromone, palladium-catalyzed aryl C–H bond activation can be functionalized to generate *ortho*-olefination derivatives in moderate to high yields.

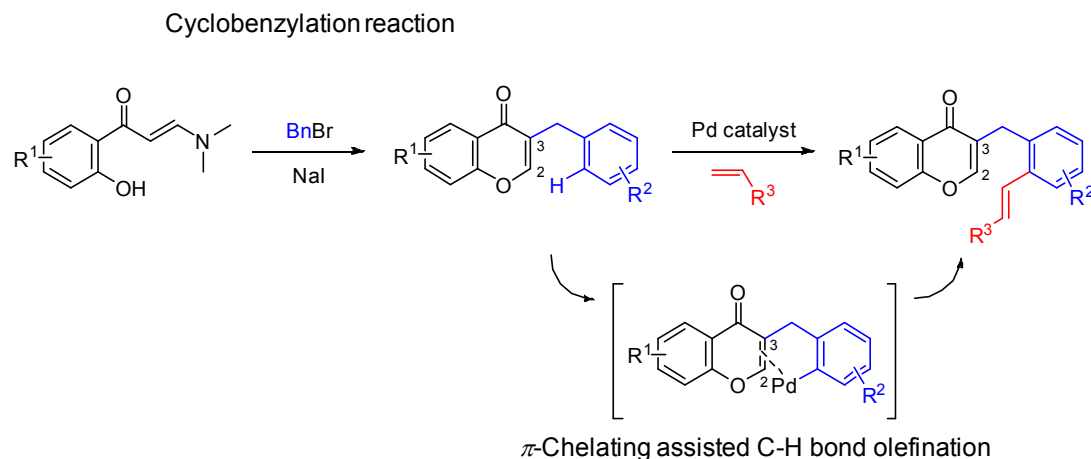
INTRODUCTION

The directed activation of C–H bonds catalyzed by transition metal complexes into useful functional groups has proven extremely valuable, and the versatility and practicality of this strategy in organic synthesis has been demonstrated.¹ The methodology involved in the directed activation of C–H bonds is attractive to synthetic chemists because the transformation is simple and the synthetic route is efficient (i.e. does not include extra steps). The C–H bond functionalization between arenes and olefins can be achieved through the introduction of a directing group, and this is commonly known as the Fujiwara–Moritani reaction.² The directing group comprises an *N*- or *O*-containing functional group, such as an acylamino, carboxylic acid, oxazoline, or *N*-heteroaryl group.^{3–5} Most directing groups involve the σ -coordination of metal catalysts; however, few researchers have reported on C=C double bond (π -chelating)-assisted C–H bond olefination using a palladium catalyst.^{6–7} Moreover, a small number of studies have reported intermolecular C–H olefination reactions assisted by π -chelating C=C bonds, most of which have limited their focus to reactions involving an allylbenzene substrate.

Chromone forms the core structure of several flavonoids, and chromone and its derivatives are found in numerous natural products.⁸ Chromone fragments are highly versatile building blocks that are used in the construction of various heterocyclic compounds. Furthermore, chromone is classified as a “privileged structure” and is found in a wide variety of pharmacologically active compounds (e.g. homoisoflavonoids) that are used in the treatment of angiogenesis-mediated diseases and in the development of anticancer agents.^{9–10} Recently, allylic groups have been successfully employed in the *ortho*-alkenylation of arenes, which prompted us to explore whether the C-2/C-3 double bond of chromone could be used as a directing group in intermolecular C–H activation and olefination reactions. Herein, we report an efficient process that can be applied to synthesize 3-(2-olefinbenzyl)-4*H*-chromen-4-one for use as a biologically active

compound. The olefin reduction products of 3-(2-olefinbenzyl)-4*H*-chromen-4-ones have been shown to inhibit aldose reductase, which is a potential target in the treatment of diabetes complications.¹¹ Our proposed synthesis method involves a two-step reaction, as follows: (1) the cyclobenzylation of (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one using benzyl bromide to produce homoisoflavonoid, followed by (2) Pd-catalyzed π -chelating-assisted C–H bond olefination. We found that employing the C-2/C-3 double bond of chromone allows palladium-catalyzed aryl C–H bonds to be functionalized efficiently to generate *ortho*-olefination derivatives in moderate to high yields (Scheme 1).

Scheme 1. Strategy for synthesis of 3-(2-olefinbenzyl)-4*H*-chromen-4-one

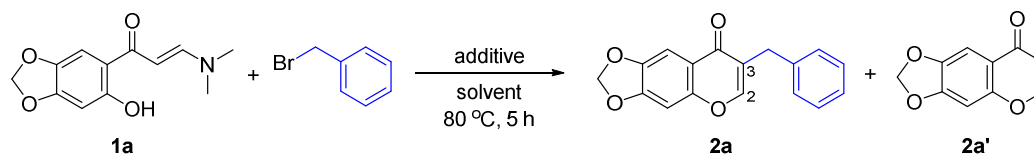


RESULTS AND DISCUSSION

Synthesis was initiated by directly converting (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** and benzyl bromide into homoisoflavonoid **2a** through electrophilic cyclobenzylation.¹² To achieve this, **1a** was heated with benzyl bromide in DMF to produce cyclobenzylation product **2a** and cyclization product **2a'** at a ratio of approximately 2:1. Additive(s) (listed in Table 1) were then used to optimize the reaction (i.e. to increase the yield of cyclobenzylation product **2a** and to reduce the yield of cyclization product **2a'**). To elucidate the effects of

various additives, NaI and KI were individually examined under the same reaction conditions. We determined that **2a** was produced in satisfactory yields when NaI was used as an additive in acetone under heating conditions. The presence of alkaline metal iodide might undergo the Finkelstein reaction, which results in a halide exchange involving benzyl bromide. This further improved the yield of the cyclobenzylation product. We next sought to determine whether using an additive of NaI combined with silver salt or TMSCl as an activator could further optimize reaction conditions; however, the presence of silver salt was found to hamper cyclobenzylation and cyclization, and the addition of TMSCl did not improve the cyclobenzylation yield. Results of these evaluations are summarized in Table 1.

Table 1. Optimization studies for the cyclobenzylation reaction of **1a** and benzyl bromide^a



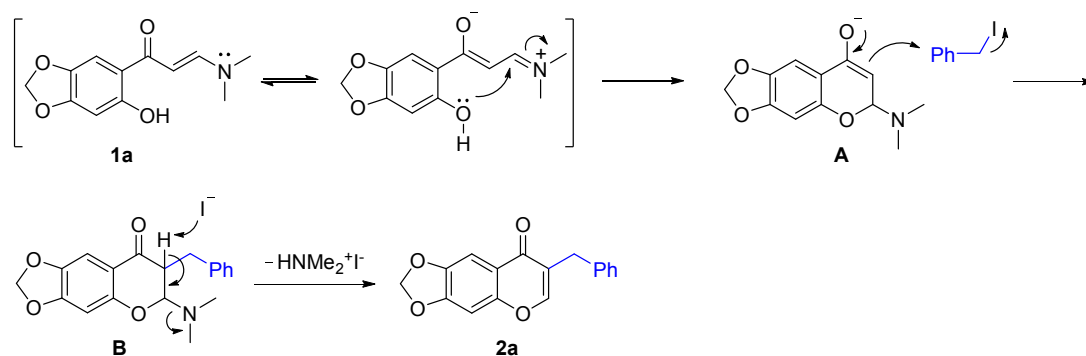
entry	additive(s)	solvent	2a yield (%) ^b	2a' yield (%) ^b
1	-	DMF	54 ^c	26 ^c
2	-	CH ₃ CN	46	35
3	-	CH ₂ Cl ₂	48	29
4	-	acetone	57	25
5	NaI	DMF	72 ^c	12 ^c
6	NaI	CH ₂ Cl ₂	69	14
7	NaI	acetone	80 ^c	-
8	KI	DMF	68 ^c	10 ^c
9	NaI + TMSCl	DMF	64	13
10	NaI + AgNO ₃	DMF	42	34
11	NaI + AgOTf	DMF	51	20

^aUnless otherwise mentioned, all reactions were carried out using **1a** (1.0 mmol), benzyl bromide (1.0 mmol), additive(s) (3.0 mmol), 4Å molecular sieves, and solvent at 80 °C

for 5 h. ^bYields were determined by the ¹H NMR integration method using mesitylene as the internal standard. ^cIsolated yield.

Results of both the current study (shown in Table 1) and previous studies suggest a plausible mechanism for the cyclobenzylation of **1a** and benzyl bromide, which is shown in Scheme 2.¹² In brief, intramolecular cycloaddition of a hydroxy group with iminium generates intermediate **A**, and intermediate **A** is then benzylated with benzyl iodide to produce intermediate **B**. Finally, elimination of dimethyl amine generates the desired homoisoflavone **2a**.

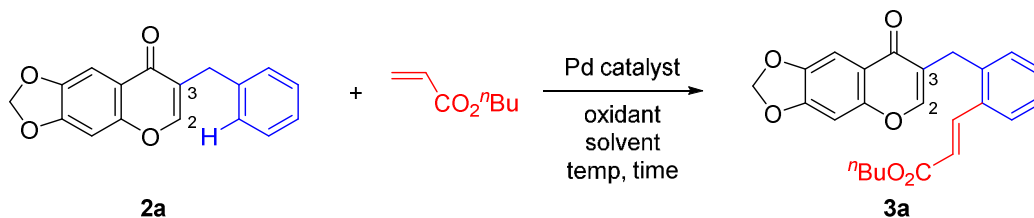
Scheme 2. Proposed mechanism underlying cyclobenzylation reaction



Having obtained the cyclobenzylation product **2a**, we next sought to perform π -chelating-assisted C–H bond catalytic olefination in Pd. This reaction was initiated by adding homoisoflavonoid **2a** and *n*-butyl acrylate to dichloromethane in the presence of Pd(OAc)₂ (10 mol%) and TFA (20 equiv). We then evaluated the ability of various combinations of oxidants and solvents to increase the reaction yield of **3a**. Among the oxidants, O₂ and K₂S₂O₈ were found to be most effective. The other oxidants were far less effective, leading to the production of **3a** in the following yields: Cu(OAc)₂ (22%), Ag₂O (15%), AgOAc (trace), PhI(OAc)₂ (0%), and O₂ + Cu(OAc)₂ (41%). Using DCE as a cosolvent achieved yields that were similar to those obtained when DCM was used (Table 2, entries 7 and 8), whereas other cosolvents (DMF, ACN, toluene, and THF) reduced

reaction yields. The structure of **3a** was confirmed by ^1H and ^{13}C NMR spectra as well as by mass data.¹³

Table 2. Screening conditions for Pd-catalyzed olefination of homoisoflavonoid **2a** with *n*-butyl acrylate^a



entry	Pd catalyst	oxidant	solvent	temp °C/time h	yield % ^c
1	Pd(OAc) ₂	O ₂	TFA/DCM	25/36	76 ^{b,d}
2	Pd(OAc) ₂	Cu(OAc) ₂	TFA/DCM	80/36	22
3	Pd(OAc) ₂	Ag ₂ O	TFA/DCM	80/36	15
4	Pd(OAc) ₂	AgOAc	TFA/DCM	80/36	trace
5	Pd(OAc) ₂	PhI(OAc) ₂	TFA/DCM	80/36	-
6	Pd(OAc) ₂	O ₂ + Cu(OAc) ₂	TFA/DCM	80/36	41 ^b
7	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA/DCM	80/36	83 ^d
8	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA/DCE	80/36	82 ^d
9	Pd(PPh ₃) ₂ Cl ₂	K ₂ S ₂ O ₈	TFA/DCM	80/36	18
10	PdCl ₂	K ₂ S ₂ O ₈	TFA/DCM	80/36	-
11	Pd(OAc) ₂	K ₂ S ₂ O ₈	AcOH/DCM	80/36	-
12	Pd(OAc) ₂	K ₂ S ₂ O ₈	PivOH/DCM	80/36	-
13	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA/DCM	80/36	62 ^{d,e}
14	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA	80/36	-
15	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFE/DCM	80/36	trace
16	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA/DCM	80/12	44
17	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA/DCM	80/24	72
18	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA/DCM	80/48	76
19	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA/DCE	80/48	69
20	Cu(OAc) ₂	-	TFA/DCM	80/36	-
21	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA(30 eq)/DCM	80/36	67
22	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA(10 eq)/DCM	80/36	78
23	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA(5 eq)/DCM	80/36	58
24	Pd(OAc) ₂	K ₂ S ₂ O ₈	DCM	80/36	-

^aUnless otherwise mentioned, all reactions were carried out using **2a** (1.0 mmol), *n*-butyl

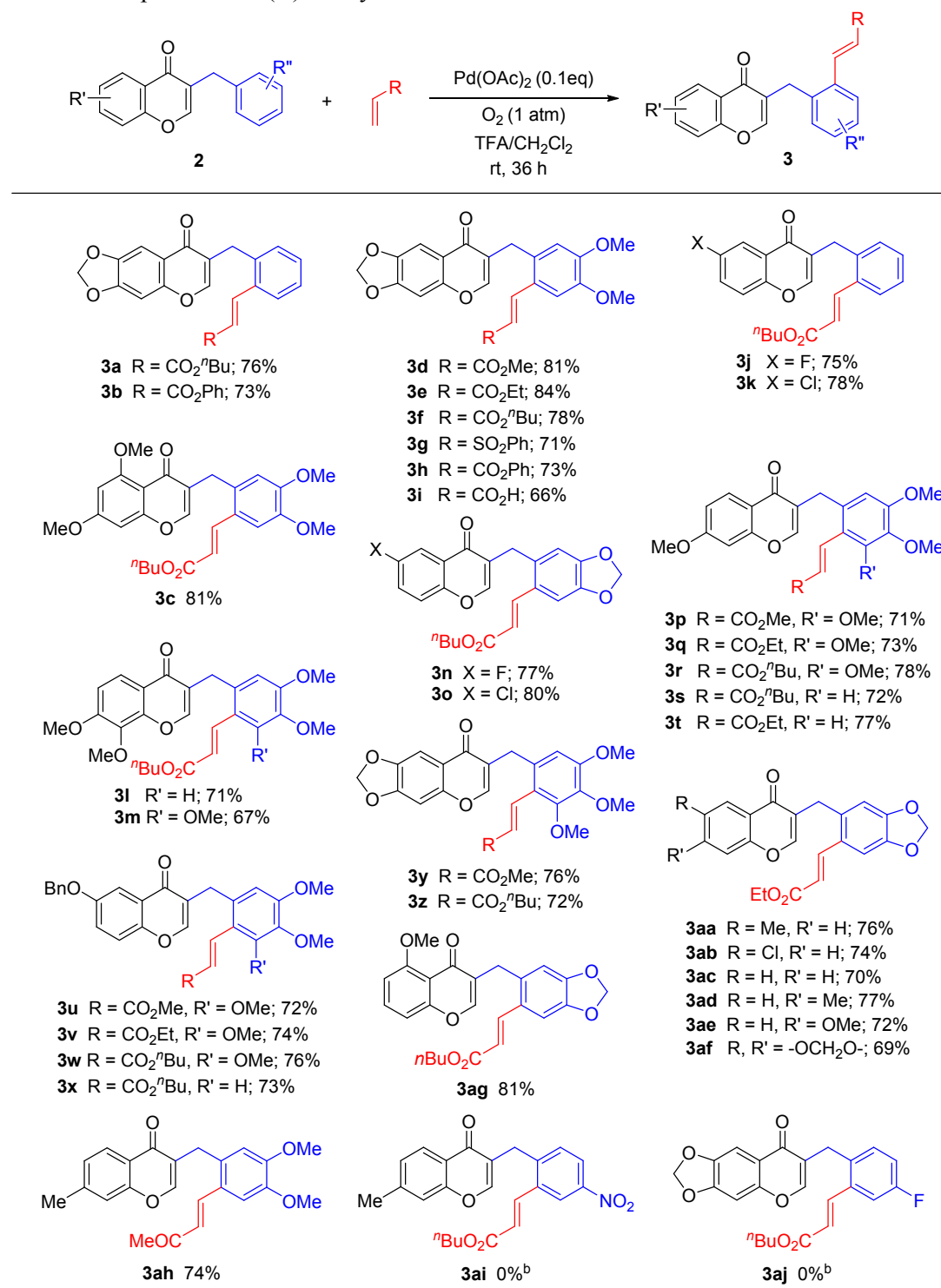
acrylate (1.0 mmol), Pd catalyst (10 mol %), oxidant (2.0 mmol), TFA (20 eq), and solvent (6.0 mL). ^bReaction was performed under one atmosphere of O₂. ^cYields were determined by the ¹H NMR integration method using mesitylene as the internal standard. ^dIsolated yield. ^e4Å molecular sieves were added.

Results of these tests revealed that the highest yield of **3a** (83%) was obtained when the reaction was conducted in TFA/DCM in the presence of the oxidant K₂S₂O₈ at a temperature of 80 °C. However, when the reaction was conducted under mild conditions and molecular oxygen was employed as the terminal oxidant, the yield was only slightly lower. Moreover, a higher concentration of TFA resulted in a slight decrease in the yield of **3a**, whereas weaker acids (AcOH or PivOH) greatly inhibited **3a** formation. We also investigated the efficiency of various Pd catalysts, including PdCl₂, Pd(PPh₃)₂Cl₂, and Pd(OH)₂/C. Of these, only Pd(PPh₃)₂Cl₂ presented catalytic activity, resulting in an 18% yield of **3a**. The other catalysts were completely inactive. In addition, the olefination process was observed to be largely insensitive to the presence of water, and the yield was not improved when the reaction was performed using molecular sieves (Table 2, entry 7 vs. entry 13). Considering all screening tests, the best results were obtained when **2a** was treated with 10 mol% of Pd(OAc)₂ and 2 equiv. of K₂S₂O₈ in TFA/DCM under heating (80 °C) over a period of 36 h. Nonetheless, molecular oxygen was only slightly less efficient than K₂S₂O₈ as a terminal oxidant. Oxygen is more environmentally friendly, and it also provides milder reaction conditions. Therefore, oxygen was employed as the terminal oxidant in subsequent reactions.

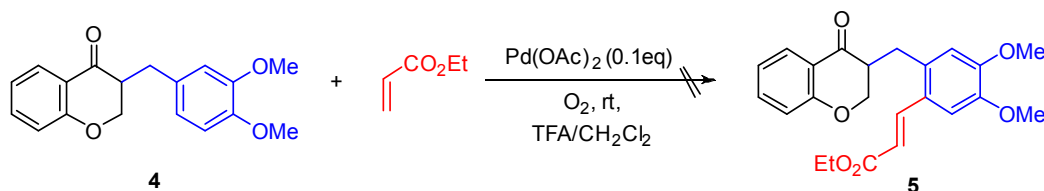
Having determined the optimal reaction conditions, we next investigated the ability of various olefins to facilitate the olefination of homoisoflavonoids **2**. Olefins including methyl acrylate, ethyl acrylate, *n*-butyl acrylate, phenyl acrylate, acrylic acid, 3-buten-2-one, and phenyl vinyl sulfone all produced the desired products at satisfactory yields (Table 3). However, other olefins, such as styrene,

1,2,3-trimethoxy-5-vinylbenzene, and methyl 2-((*tert*-butoxycarbonyl)amino)acrylate, failed to produce the corresponding *ortho*-olefination products under the same reaction conditions. The substitution effect of this reaction with respect to the Pd catalytic π -chelating-assisted reaction was then investigated. Incorporating an additional methoxy group on the benzyl ring was found to slightly reduce the yield compared with compounds **3l**, **3m** and **3r**, **3s** (Table 3). Conversely, a substitution in the sixth or seventh position of 4*H*-chromen-4-one had almost no effect on product yield (**3p** to **3x**). Notably, incorporating an additional fluoro or chloro atom on the 4*H*-chromen-4-one ring (compounds **3j**, **3k**, **3n**, and **3o**) did not alter the yield; however, **3n** and **3o**, both of which contained a 3,4-dimethoxy group on the benzyl ring, delivered a higher yield than did **3j** or **3k**. Furthermore, 3-benzyl-4*H*-chromen-4-ones that contained an electron-withdrawing NO₂ group (i.e. compound **2ai**) or a halogen F (i.e. compound **2aj**) at the *para*-position of the benzyl ring failed to undergo *ortho*-olefination. The methyl ester group and other halogens (Cl and Br) on the benzyl ring were given in trace amounts of olefination products. Generally, we found that chromone π -bond directed C-H bond functionalization was able to generate the olefination products of a broad variety of homoisoflavonoids in good yields. However, it is worth noting that, when the reaction was carried out with excessive ethyl acrylate (up to 5 equiv.), no difunctionalization products were observed.

The olefination of 4-chromanone **4** was also investigated using ethyl acrylate and the Pd catalyst under the same reaction conditions as those described earlier. However, olefination product **5** was not obtained (Scheme 3). This finding as well as findings related to the Pd-catalyzed olefination of homoisoflavonoids **2** indicate that the chromone C=C π -bond is an influential directing group in the olefination reactions. Therefore, we posit that the reaction pathway associated with the olefination of homoisoflavonoids **2** is likely similar to the pathway associated with the olefination of allyl benzene, as outlined in previous reports.

Table 3. Scope of the Pd(II)-catalyzed olefination of homoisoflavonoids^a

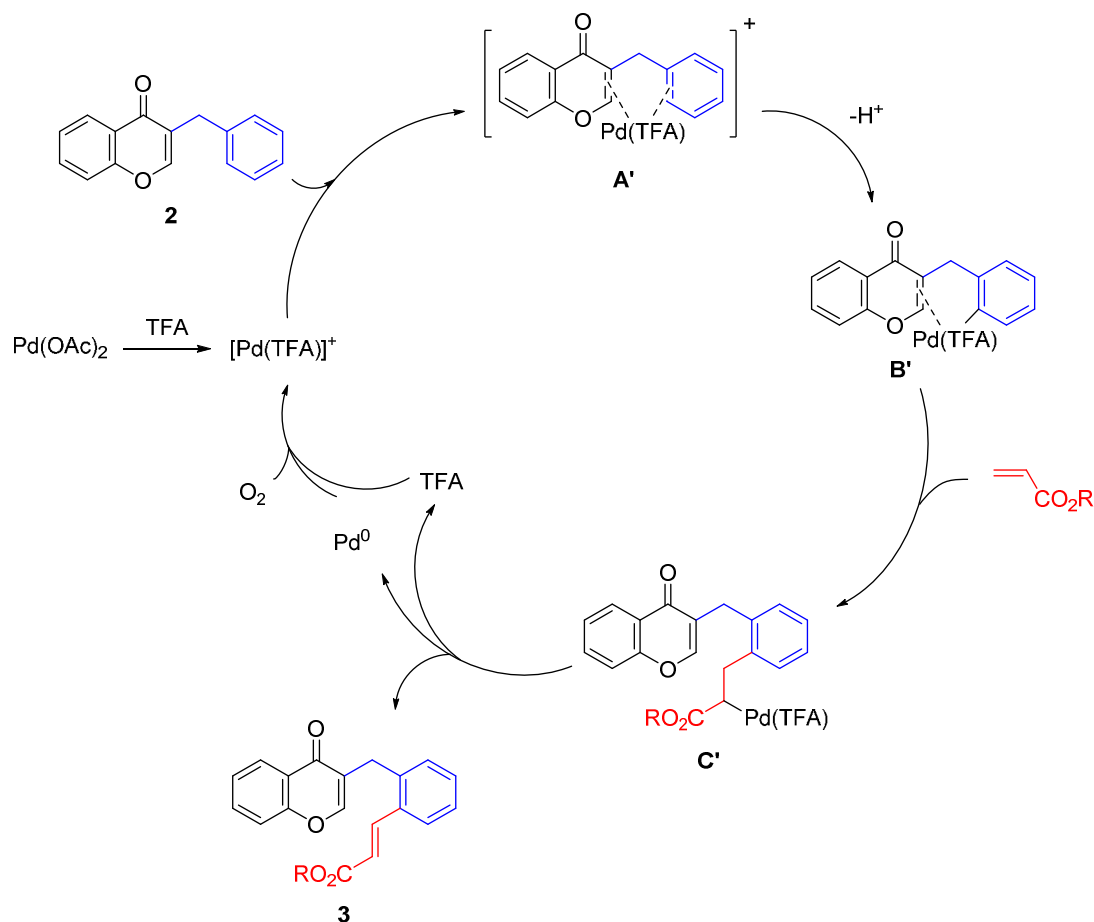
^aUnless otherwise mentioned, all reactions were performed using **2** (1.0 mmol), olefin (1.0 mmol), Pd catalyst (10 mol %), O_2 (1 atm), TFA (20 eq), and solvent (6.0 mL). ^bStarting material was recovered.

Scheme 3. Pd(II)-catalyzed olefination of 4-chromanone

One possible mechanism underlying the π -assisted olefination reaction is outlined in Scheme 4. Based on the results obtained in the current study and known Pd-catalyzed C–H activation reactions, we posit that electrophilic $[\text{Pd}(\text{TFA})]^+$ species should form in the presence of Pd(OAc)₂ and TFA.^{7,14-15} Indeed, the highly electrophilic Pd(II) species generated from this reaction for the coordination of the C=C π -bond in **2** leads to the formation of the intermediate **A'**. Subsequently, metalation of the aryl C–H bond forms the Pd(II) σ -aryl complex **B'**. The oxidative addition of the activated olefin to Pd(II)-complex **B'** followed by the elimination of β -hydride then yields the corresponding product **3** as well as the Pd(0) species. Finally, Pd(0) is reoxidized to form the catalytically active $[\text{Pd}(\text{TFA})]^+$ species using molecular oxygen, which completes the catalytic cycle.

Conversely, olefination of the chromanone **4** product was not observed under the same reaction conditions. This indicates that the carbonyl group of 3-benzyl-4*H*-chromen-4-one did not act as the directing group in the *ortho*-metalation of the benzylic ring (through a seven-membered-ring palladacycle) (Scheme 3).¹⁶

Scheme 4. Proposed mechanism underlying the Pd-catalyzed olefination of homoisoflavonoids



CONCLUSIONS

This study demonstrated the synthesis of 3-(2-olefinbenzyl)-4*H*-chromen-4-one in a two-step process involving cyclobenzylation and Pd-catalyzed π -chelating-assisted C–H bond olefination. Specifically, a homoisoflavonoid scaffold was constructed through the cyclobenzylation of (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one and benzyl bromide. Subsequently, with the assistance of the C-2/C-3 double bond of chromone π -chelation, the Pd-catalyzed benzyl C–H bonds were functionalized to generate *ortho*-olefination derivatives.

EXPERIMENTAL SECTION

General information. All reagents were used as received from commercial suppliers

unless otherwise stated. Dichloromethane (DCM) and *N,N'*-dimethylformamide (DMF) were dried over calcium hydride for 48 h prior to distillation. The proton NMR spectra were obtained on Varian Unity Inova 500 (500 MHz) and Varian VNMRS 600 (600 MHz) spectrometers. All NMR chemical shifts were reported as δ values in parts per million (ppm), and coupling constants (*J*) were given in hertz (Hz). The splitting pattern abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; br, broad; m, unresolved multiplet due to the field strength of the instrument; dd, doublet of doublet; and dt, doublet of triplet. Melting points were measured on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. Fourier transform infrared spectra were collected with an Avatar 320 spectrometer. High-resolution mass spectra were obtained by using electrospray ionization (ESI-Quadrupole). Purification was performed using preparative separations in flash column chromatography (Merck silica gel 60, particle size of 230-400 mesh). Analytical TLC was carried out on precoated plates (Merck silica gel 60, F254). The compounds analyzed on the TLC plates were visualized using a UV light, I_2 vapor, or basic aqueous potassium permanganate ($KMnO_4$) with heating.

General procedure for the synthesis of 3-benzyl-4*H*-chromen-4-one 2a-2ai through cyclobenzylation of (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one and benzyl bromide.

(*E*)-3-(Dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one was synthesized in accordance with a previously reported method.¹⁷ To a solution of (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one (191 mg, 1.0 mmol), NaI (450 mg, 3.0 mmol) and 4Å molecular sieves in acetone (15 mL) was added benzyl bromide (0.12 mL, 1.0 mmol) dropwise. The reaction mixture was then heated to reflux over a period of 5 h, as verified using thin layer chromatography (TLC). The reaction was then quenched by addition of water, and the reaction mixture was filtered and extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with brine

solution (15 mL), dried over MgSO_4 , and concentrated in vacuo. Finally, the residue was purified by flash column chromatography (EtOAc/hexanes = 1:4) to yield the desired 3-benzyl-4*H*-chromen-4-one.

General procedure for the Pd-catalyzed olefination of 3-benzyl-4*H*-chromen-4-ones 2a-2aj with alkenes.

In a 100 mL two-necked flask was placed 3-benzyl-4*H*-chromen-4-one **2a-2aj** (1.0 mmol) and $\text{Pd}(\text{OAc})_2$ (10 mol%), which was evacuated and then filled with oxygen gas. Dichloromethane (6.0 mL) and trifluoroacetic acid (TFA) (1.5 mL, 20 equiv) were then sequentially added to the flask. Following the addition of alkene (1.0 mmol), the mixture was stirred under an oxygen atmosphere until the reaction had completed. The mixture was then filtered through a Celite pad and washed with CH_2Cl_2 (20 mL). Finally, the filtrate was concentrated, and the residue was purified by flash column chromatography (EtOAc/hexanes = 1/4) to yield the desired olefination product. All the compounds shown in Table 3 were prepared according to this procedure.

*7-Benzyl-8*H*-[1,3]dioxolo[4,5-*g*]chromen-8-one (2a).* Yellow solid; yield: 224 mg (80%); R_f = 0.55 (EtOAc/hexanes = 1:4); mp 155-157 °C; IR (KBr) ν_{max} 3064, 2909, 1639, 1611, 1473, 1390, 1131, 1039 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.51 (s, 1H), 7.49 (s, 1H), 7.30-7.26 (m, 4H), 7.21-7.18 (m, 1H), 6.77 (s, 1H), 6.05 (s, 2H), 3.77 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.4, 153.8, 152.5, 152.4, 146.0, 138.7, 129.0, 128.6, 126.5, 123.9, 118.8, 102.4, 102.3, 97.8, 31.6; HRMS (ESI-quadrupole) m/z : $[\text{M} + 23]^+$ calcd for $\text{C}_{17}\text{H}_{12}\text{O}_4\text{Na}$ 303.0633; Found 303.0624.

*3-(3,4-Dimethoxybenzyl)-5,7-dimethoxy-4*H*-chromen-4-one (2c).* Yellow solid; yield: 288 mg (81%); R_f = 0.45 (EtOAc/hexanes = 1:4); mp 133-135 °C; IR (KBr) ν_{max} 2936, 2360, 1610, 1513, 1207, 1082 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.32 (s, 1H), 6.80-6.76 (m, 3H), 6.34 (d, J = 2.4 Hz, 1H), 6.30 (d, J = 2.4 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 3.82 (s, 3H), 3.65 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.2, 163.7, 161.1,

160.0, 150.5, 148.9, 147.5, 131.4, 125.8, 121.1, 112.4, 111.2, 109.3, 95.9, 92.4, 56.2, 55.9, 55.8, 55.6, 31.0; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{20}H_{21}O_6$ 357.1333; Found 357.1321.

7-(3,4-Dimethoxybenzyl)-8H-[1,3]dioxolo[4,5-g]chromen-8-one (2d). Yellow solid; yield: 272 mg (80%); R_f = 0.45 (EtOAc/hexanes = 1:4); mp 141-143 °C; IR (KBr) $\nu_{\max}$ 3003, 1463, 1257, 1030 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.52 (s, 1H), 7.48 (s, 1H), 6.81-6.78 (m, 4H), 6.06 (s, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.72 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.4, 153.8, 152.5, 152.4, 149.0, 147.7, 146.0, 131.2, 124.2, 120.9, 118.8, 112.3, 111.3, 102.4, 102.3, 97.8, 55.9, 55.8, 31.2; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{19}H_{17}O_6$ 341.1020; Found 341.1010.

3-Benzyl-6-fluoro-4H-chromen-4-one (2j). Yellow solid; yield: 195 mg (77%); R_f = 0.60 (EtOAc/hexanes = 1:4); mp 200-202 °C; IR (KBr) $\nu_{\max}$ 3069, 2921, 1634, 1476, 1393, 1132 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.84 (dd, J = 7.8, 3.0 Hz, 1H), 7.59 (s, 1H), 7.40 (dd, J = 9.0, 4.2 Hz, 1H), 7.36-7.33 (m, 1H), 7.31-7.26 (m, 4H), 7.21 (dt, J = 6.6, 1.8 Hz, 1H), 3.80 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.7 (d, $^4J_{C-F}$ = 2.3 Hz), 159.4 (d, $^1J_{C-F}$ = 245.5 Hz), 153.3, 152.6, 138.3, 129.0, 128.6, 126.6, 124.8 (d, $^3J_{C-F}$ = 6.9 Hz), 124.1, 121.7 (d, $^2J_{C-F}$ = 25.2 Hz), 120.2, 110.7 (d, $^2J_{C-F}$ = 23.6 Hz), 31.6; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{16}H_{12}O_2F$ 255.0816; Found 255.0814.

3-Benzyl-6-chloro-4H-chromen-4-one (2k). Colorless solid; yield: 216 mg (80%); R_f = 0.65 (EtOAc/hexanes = 1:4); mp 97-99 °C; IR (KBr) $\nu_{\max}$ 3023, 2926, 1638, 1465, 1381,

1315, 1153 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.17 (d, J = 3.0 Hz, 1H), 7.57-7.54 (m, 2H), 7.35 (d, J = 9.0 Hz, 1H), 7.30-7.26 (m, 4H), 7.23-7.20 (m, 1H), 3.79 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.3, 154.7, 153.2, 138.2, 133.7, 130.9, 129.0, 128.7, 126.6, 125.4, 124.8, 124.7, 119.8, 31.6; HRMS (ESI-quadrupole) m/z : $[\text{M} + 23]^+$ calcd for $\text{C}_{16}\text{H}_{11}\text{O}_2\text{ClNa}$ 293.0340; Found 293.0335.

3-(3,4-Dimethoxybenzyl)-7,8-dimethoxy-4H-chromen-4-one (2l). Yellow solid; yield: 277 mg (78%); R_f = 0.45 (EtOAc/hexanes = 1:4); mp 106-108 $^\circ\text{C}$; IR (KBr) ν_{max} 2923, 1600, 1454, 1284, 1171, 1078 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.93 (d, J = 9.0 Hz, 1H), 7.59 (s, 1H), 7.00 (d, J = 9.0 Hz, 1H), 6.81-6.77 (m, 3H), 3.95 (s, 3H), 3.91 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 3.72 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.0, 156.2, 152.8, 150.8, 149.0, 147.7, 136.5, 131.1, 124.2, 121.3, 120.9, 118.7, 112.3, 111.3, 110.0, 61.5, 56.4, 55.9, 55.8, 31.2; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{20}\text{H}_{21}\text{O}_6$ 357.1333; Found 357.1329.

7,8-Dimethoxy-3-(3,4,5-trimethoxybenzyl)-4H-chromen-4-one (2m). Yellow solid; yield: 274 mg (71%); R_f = 0.30 (EtOAc/hexanes = 1:4); mp 119-121 $^\circ\text{C}$; IR (KBr) ν_{max} 2929, 1641, 1601, 1507, 1454, 1400, 1285, 1126 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.93 (d, J = 9.0 Hz, 1H), 7.61 (s, 1H), 7.0 (d, J = 9.0 Hz, 1H), 6.48 (s, 2H), 3.95 (s, 3H), 3.91 (s, 3H), 3.80 (s, 6H), 3.78 (s, 3H), 3.70 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.9, 156.2, 153.2, 152.8, 150.8, 136.5, 136.5, 134.3, 123.8, 121.3, 118.6, 109.9, 105.9, 61.5, 60.8,

56.4, 56.0, 31.8; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{21}H_{23}O_7$ 387.1438;
Found 387.1434.

3-(Benzo[d][1,3]dioxol-5-ylmethyl)-6-fluoro-4H-chromen-4-one (2n). Yellow solid;
yield: 241 mg (81%); R_f = 0.55 (EtOAc/hexanes = 1:4); mp 127-129 °C; IR (KBr) $\nu_{\max}$
2921, 2852, 1642, 1478, 1321, 1245, 1177, 1037 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.83
(dd, J = 8.4, 3.0 Hz, 1H), 7.61 (s, 1H), 7.40 (dd, J = 9.6, 4.2 Hz, 1H), 7.36-7.32 (m, 1H),
6.73 (d, J = 13.2 Hz, 1H), 6.72 (s, 2H), 5.90 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (150 MHz,
 CDCl_3) δ 176.7 (d, $^4J_{\text{C-F}}$ = 2.4 Hz), 160.2, 158.6, 153.2, 152.6 (d, $^4J_{\text{C-F}}$ = 1.2 Hz), 147.0 (d,
 $^1J_{\text{C-F}}$ = 232.8 Hz), 132.0, 124.9 (d, $^3J_{\text{C-F}}$ = 7.5 Hz), 124.1, 121.8, 121.7, 120.1 (d, $^3J_{\text{C-F}}$ =
8.0 Hz), 110.6 (d, $^2J_{\text{C-F}}$ = 23.6 Hz), 109.4, 108.3, 100.9, 31.3; HRMS (ESI-quadrupole)
 m/z : $[M + 1]^+$ calcd for $C_{17}H_{12}O_4\text{F}$ 299.0714; Found 299.0712.

3-(Benzo[d][1,3]dioxol-5-ylmethyl)-6-chloro-4H-chromen-4-one (2o). Yellow solid;
yield: 264 mg (84%); R_f = 0.55 (EtOAc/hexanes = 1:4); mp 133-135 °C; IR (KBr) $\nu_{\max}$
2922, 1643, 1500, 1464, 1245, 1145, 1036 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.16 (d, J
= 3.0 Hz, 1H), 7.59 (t, J = 1.2 Hz, 1H), 7.55 (dd, J = 9.0, 2.4 Hz, 1H), 7.35 (d, J = 9.0 Hz,
1H), 6.74-6.72 (m, 3H), 5.90 (s, 2H), 3.70 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.3,
154.7, 153.2, 147.8, 146.3, 133.7, 131.9, 130.9, 125.3, 124.9, 124.7, 121.9, 119.8, 109.4,
108.4, 100.9, 31.3; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{17}H_{12}O_4\text{Cl}$
315.0419; Found 315.0414.

7-Methoxy-3-(3,4,5-trimethoxybenzyl)-4H-chromen-4-one (2p). White solid; yield: 274 mg (77%); R_f = 0.35 (EtOAc/hexanes = 1:4); mp 109-111 °C; IR (KBr) $\nu_{\max}$ 2938, 2838, 1637, 1608, 1440, 1239, 1125 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.12 (d, J = 9.0 Hz, 1H), 7.53 (s, 1H), 6.95 (dd, J = 9.0, 2.4 Hz, 1H), 6.78 (d, J = 2.4 Hz, 1H), 6.49 (s, 2H), 3.87 (s, 3H), 3.82 (s, 6H), 3.80 (s, 3H), 3.72 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.8, 163.9, 158.2, 153.3, 152.7, 136.6, 134.5, 127.4, 124.3, 117.8, 114.5, 106.0, 100.1, 60.8, 56.1, 55.8, 31.9. HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{20}\text{H}_{21}\text{O}_6$ 357.1333; Found 357.1330.

3-(3,4-Dimethoxybenzyl)-7-methoxy-4H-chromen-4-one (2s). Yellow solid; yield: 248 mg (76%); R_f = 0.38 (EtOAc/hexanes = 1:4); mp 100-102 °C; IR (KBr) $\nu_{\max}$ 2956, 2360, 1607, 1514, 1440, 1240, 1139, 1027 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.11 (d, J = 9.0 Hz, 1H), 7.49 (s, 1H), 6.94 (dd, J = 9.0, 2.4 Hz, 1H), 6.81-6.79 (m, 3H), 6.76 (d, J = 2.4 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.72 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.9, 163.9, 158.2, 152.6, 149.0, 147.7, 131.2, 127.4, 124.7, 121.0, 117.8, 114.4, 112.4, 111.3, 100.0, 55.9, 55.8, 55.7, 31.2; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{O}_5$ 327.1227; Found 327.1227.

6-(Benzyloxy)-3-(3,4,5-trimethoxybenzyl)-4H-chromen-4-one (2u). Yellow solid; yield: 350 mg (81%); R_f = 0.52 (EtOAc/hexanes = 1:4); mp 114-116 °C; IR (KBr) $\nu_{\max}$ 3481, 2937, 1637, 1482, 1322, 1240, 1162, 1009 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.68

(d, $J = 3.0$ Hz, 1H), 7.61 (s, 1H), 7.44 (d, $J = 7.2$ Hz, 2H), 7.38-7.30 (m, 3H), 7.33-7.29 (m, 2H), 6.50 (s, 2H), 5.13 (s, 2H), 3.82 (s, 6H), 3.81 (s, 3H), 3.74 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.2, 155.9, 153.3, 153.0, 151.4, 136.6, 136.2, 134.4, 128.6, 128.2, 127.7, 124.4, 124.2, 123.6, 119.6, 106.2, 106.0, 70.6, 60.8, 56.1, 32.1; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{O}_6$ 433.1646; Found 433.1640.

6-(Benzyloxy)-3-(3,4-dimethoxybenzyl)-4H-chromen-4-one (2x). Yellow solid; yield: 305 mg (76%); $R_f = 0.57$ (EtOAc/hexanes = 1:4); mp 95-97 °C; IR (KBr) ν_{max} 2925, 1639, 1482, 1451, 1322, 1261, 1139, 1027 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.67 (d, $J = 3.0$ Hz, 1H), 7.56 (s, 1H), 7.43 (d, $J = 7.2$ Hz, 2H), 7.37 (t, $J = 7.2$ Hz, 2H), 7.34-7.27 (m, 3H), 6.83-6.77 (m, 3H), 5.10 (s, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.74 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.2, 155.8, 152.9, 151.3, 148.9, 147.6, 136.2, 131.1, 128.6, 128.1, 127.6, 124.3, 124.0, 123.9, 120.9, 119.4, 112.2, 111.2, 106.0, 70.5, 55.8, 55.7, 31.3; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{25}\text{H}_{23}\text{O}_5$ 403.1540; Found 403.1538.

7-(3,4,5-Trimethoxybenzyl)-8H-[1,3]dioxolo[4,5-g]chromen-8-one (2y). Yellow solid; yield: 299 mg (81%); $R_f = 0.37$ (EtOAc/hexanes = 1:4); mp 189-191 °C; IR (KBr) ν_{max} 2938, 1641, 1590, 1464, 1256, 1125 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.52 (s, 1H), 7.51 (s, 1H), 6.79 (s, 1H), 6.48 (s, 2H), 6.07 (s, 2H), 3.82 (s, 6H), 3.80 (s, 3H), 3.71 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.4, 153.8, 153.3, 152.6, 152.4, 146.1, 136.6, 134.4, 123.8, 118.8, 106.0, 102.4, 102.3, 97.8, 60.8, 56.1, 31.9; HRMS (ESI-quadrupole)

m/z : $[M + 1]^+$ calcd for $C_{20}H_{19}O_7$ 371.1125; Found 371.1115.

3-(Benzo[d][1,3]dioxol-5-ylmethyl)-5-methoxy-4H-chromen-4-one (*2ag*). Yellow solid; yield: 232 mg (75%); R_f = 0.53 (EtOAc/hexanes = 1:4); mp 115-117 °C; IR (KBr) $\nu_{\max}$ 2895, 1646, 1475, 1360, 1246, 1159, 1075 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.50-7.47 (m, 2H), 6.94 (dd, J = 9.0, 0.6 Hz, 1H), 6.77-6.70 (m, 4H), 5.89 (s, 2H), 3.97 (s, 3H), 3.65 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.0, 160.0, 158.5, 151.0, 147.6, 146.0, 133.5, 132.6, 125.8, 122.0, 114.6, 110.0, 109.6, 108.2, 105.9, 100.8, 56.3, 31.3; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{18}H_{15}O_5$ 311.0914; Found 311.0907.

3-(3,4-Dimethoxybenzyl)-7-methyl-4H-chromen-4-one (*2ah*). Yellow solid; yield: 220 mg (71%); R_f = 0.20 (EtOAc/hexanes = 1:4); mp 142-145 °C; IR (KBr) $\nu_{\max}$ 3070, 2933, 2834, 1643, 1513, 1426, 1352, 1261, 1139 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.07 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 1.2 Hz, 1H), 7.17-7.15 (m, 2H), 6.81-6.78 (m, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 3.72 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.3, 156.5, 152.8, 149.0, 147.6, 144.7, 131.2, 126.4, 125.6, 124.6, 121.6, 120.9, 117.6, 112.3, 111.3, 55.9, 55.8, 31.2, 21.7; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{19}H_{19}O_4$ 311.1278; Found 311.1278.

3-(3-Chlorobenzyl)-4H-chromen-4-one (*2ak*). Yellow solid; yield: 189 mg (70%); R_f = 0.67 (EtOAc/hexanes = 1:4); mp 105-107 °C; IR (KBr) $\nu_{\max}$ 3067, 2922, 1643, 1609, 1466, 1350, 1141 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.15 (dd, J = 8.0, 1.2 Hz, 1H), 7.63

(s, 1H), 7.57 (dt, $J = 8.4, 1.2$ Hz, 1H), 7.35-7.28 (m, 2H), 7.24 (s, 1H), 7.17-7.12 (m, 3H), 3.72 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.9, 156.2, 152.9, 140.7, 134.1, 133.3, 129.6, 128.7, 127.0, 126.5, 125.6, 124.8, 123.6, 123.5, 117.9, 31.2; HRMS (ESI-quadrupole) m/z : $[\text{M} + 23]^+$ calcd for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{Cl}$ 271.0519; Found 271.0520.

3-(4-Bromobenzyl)-4H-chromen-4-one (2al). Yellow solid; yield: 226 mg (72%); R_f = 0.65 (EtOAc/hexanes = 1:4); mp 157-159 °C; IR (KBr) ν_{max} 3065, 2921, 1635, 1486, 1465, 1351, 1141 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.19 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.65-7.61 (m, 2H), 7.41-7.35 (m, 4H), 7.16 (d, $J = 6.5$ Hz, 2H), 3.74 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 177.3, 156.4, 153.0, 137.7, 133.5, 131.6, 130.7, 125.9, 125.0, 124.0, 123.8, 120.4, 118.0, 31.2. HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{Br}$ 315.0015; Found 315.0014.

Methyl 4-((4-oxo-4H-chromen-3-yl)methyl)benzoate (2am). Yellow solid; yield: 229 mg (78%); R_f = 0.45 (EtOAc/hexanes = 1:4); mp 174-176 °C; IR (KBr) ν_{max} 3060, 2952, 1710, 1633, 1609, 1467, 1282, 1106 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.20 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.95 (d, $J = 6.5$ Hz, 2H), 7.66-7.62 (m, 2H), 7.42-7.34 (m, 4H), 3.88 (s, 3H), 3.85 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 177.3, 166.7, 156.5, 153.1, 144.2, 133.6, 129.9, 128.9, 128.5, 126.0, 125.1, 123.8, 118.1, 110.0, 52.0, 31.8; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{18}\text{H}_{15}\text{O}_4$ 295.0965; Found 295.0965

Butyl (E)-3-(2-((8-oxo-8H-[1,3]dioxolo[4,5-g]chromen-7-yl)methyl)phenyl)acrylate

(3a). White solid; yield: 308 mg (76%); R_f = 0.50 (EtOAc/hexanes = 1:4); mp 156-158 °C; IR (KBr) $\nu_{\max}$ 3065, 2910, 1612, 1475, 1391, 1262, 1199, 1132, 1040 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) 7.92 (d, J = 15.6 Hz, 1H), 7.59 (dd, J = 7.2, 1.2 Hz, 1H), 7.53 (s, 1H), 7.33-7.27 (m, 4H), 6.77 (s, 1H), 6.35 (d, J = 15.6 Hz, 1H), 6.06 (s, 2H), 4.15 (t, J = 6.6 Hz, 2H), 3.93 (d, J = 1.2 Hz, 2H), 1.64-1.60 (m, 2H), 1.38-1.34 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) 176.2, 166.8, 153.7, 152.6, 152.6, 146.1, 141.6, 137.5, 133.7, 131.0, 130.3, 128.8, 127.4, 126.8, 123.0, 120.3, 118.7, 102.4, 97.8, 64.5, 30.7, 29.0, 19.2, 13.7; HRMS (ESI-quadrupole) m/z : $[\text{M} + 23]^+$ calcd for $\text{C}_{24}\text{H}_{22}\text{O}_6\text{Na}$ 429.1309; Found 429.1308.

Phenyl

(*E*)-3-(2-((8-oxo-8H-[1,3]dioxolo[4,5-g]chromen-7-yl)methyl)phenyl)acrylate (3b). White solid; yield: 311 mg (73%); R_f = 0.25 (EtOAc/hexanes = 1:4); mp 190-192 °C; IR (KBr) $\nu_{\max}$ 2922, 1462, 1257, 1137 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.14 (d, J = 16.2 Hz, 1H), 7.67 (d, J = 7.2 Hz, 1H), 7.51 (s, 1H), 7.38-7.30 (m, 5H), 7.21 (t, J = 7.2 Hz, 2H), 7.12 (d, J = 5.4 Hz, 2H), 6.78 (s, 1H), 6.54 (d, J = 16.2 Hz, 1H), 6.06 (s, 2H), 3.96 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.2, 165.1, 153.8, 152.7, 152.6, 150.7, 146.1, 143.6, 137.9, 133.4, 131.1, 130.7, 129.4, 127.5, 127.0, 125.8, 123.0, 121.6, 119.3, 118.7, 102.4, 97.8, 97.8, 29.0; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{26}\text{H}_{19}\text{O}_6$ 427.1176; Found 427.1177.

Butyl

(*E*)-3-(2-((5,7-dimethoxy-4-oxo-4*H*-chromen-3-yl)methyl)-4,5-dimethoxyphenyl)acrylate

(3*c*). Yellow solid; yield: 390 mg (81%); R_f = 0.18 (EtOAc/hexanes = 1:2); mp 140-142

°C; IR (KBr) $\nu_{\max}$ 2926, 1706, 1609, 1514, 1166 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.83

(d, J = 15.6 Hz, 1H), 7.07 (d, J = 3.0 Hz, 2H), 6.80 (s, 1H), 6.33 (dd, J = 7.8, 2.4 Hz, 2H),

6.24 (d, J = 15.6 Hz, 1H), 4.14 (t, J = 6.6 Hz, 2H), 3.92 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H),

3.84 (s, 3H), 3.83 (s, 3H), 1.63-1.59 (m, 2H), 1.38-1.34 (m, 2H), 0.85 (t, J = 6.6 Hz, 3H);

^{13}C NMR (150 MHz, CDCl_3) δ 176.1, 167.1, 163.8, 161.1, 160.0, 151.0, 150.8, 148.1,

141.2, 131.6, 125.7, 125.0, 117.5, 113.7, 109.1, 108.7, 96.0, 92.4, 64.3, 56.3, 56.0, 55.9,

55.7, 30.7, 29.7, 19.2, 13.7; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{27}\text{H}_{31}\text{O}_8$

483.2013; Found 483.2012.

Methyl

(*E*)-3-(4,5-dimethoxy-2-((8-oxo-8*H*-[1,3]dioxolo[4,5-*g*]chromen-7-yl)methyl)phenyl)acryl

ate (3*d*). Yellow solid; the X-ray structure of this compound was obtained; yield: 343 mg

(81%); R_f = 0.25 (EtOAc/hexanes = 1:2); mp 200-202 °C; IR (KBr) $\nu_{\max}$ 2921, 1709, 1641,

1463, 1256, 1168 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.85 (d, J = 15.6 Hz, 1H), 7.52 (s,

1H), 7.20 (s, 1H), 7.07 (s, 1H), 6.80 (s, 1H), 6.76 (s, 1H), 6.26 (d, J = 15.6 Hz, 1H), 6.06

(s, 2H), 3.89 (s, 6H), 3.86 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.3,

167.4, 153.7, 152.7, 152.6, 151.1, 148.2, 146.1, 141.3, 131.4, 125.6, 123.4, 118.6, 117.2,

113.5, 108.8, 102.4, 102.3, 97.8, 56.0, 55.9, 51.7, 28.5; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{23}H_{21}O_8$ 425.1231; Found 425.1231.

Ethyl

(E)-3-(4,5-dimethoxy-2-((8-oxo-8H-[1,3]dioxolo[4,5-g]chromen-7-yl)methyl)phenyl)acrylate (3e). Colorless solid; yield: 368 mg (84%); R_f = 0.45 (EtOAc/hexanes = 1:2); mp 187-189 °C; IR (KBr) $\nu_{\max}$ 2922, 1704, 1641, 1463, 1256, 1171 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.86 (d, J = 16.2 Hz, 1H), 7.53 (s, 1H), 7.23 (s, 1H), 7.08 (s, 1H), 6.81 (s, 1H), 6.76 (s, 1H), 6.23 (d, J = 16.2 Hz, 1H), 6.06 (d, J = 2.4 Hz, 2H), 4.21 (q, J = 7.2 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.86 (s, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.2, 167.0, 153.7, 152.6, 152.6, 151.0, 148.2, 146.1, 141.1, 131.4, 125.7, 123.4, 118.7, 117.7, 113.6, 108.6, 102.4, 102.3, 97.8, 60.4, 56.0, 55.9, 29.7, 14.3; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{24}H_{23}O_8$ 439.1387; Found 439.1391.

Butyl

(E)-3-(4,5-dimethoxy-2-((8-oxo-8H-[1,3]dioxolo[4,5-g]chromen-7-yl)methyl)phenyl)acrylate (3f). Yellow solid; yield: 363 mg (78%); R_f = 0.58 (EtOAc/hexanes = 1:4); mp 137-139 °C; IR (KBr) $\nu_{\max}$ 2927, 2359, 1704, 1463, 1255, 1167 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.86 (d, J = 15.6 Hz, 1H), 7.53 (s, 1H), 7.27 (s, 1H), 7.10 (s, 1H), 6.83 (s, 1H), 6.26 (s, 1H), 6.27 (d, J = 15.6 Hz, 1H), 6.07 (s, 2H), 4.15 (t, J = 7.2 Hz, 2H), 3.90 (s, 6H), 3.88 (s, 2H), 1.65-1.62 (m, 2H), 1.42-1.37 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR

(150 MHz, CDCl₃) δ 176.1, 167.0, 153.6, 152.6, 151.0, 148.1, 146.0, 141.0, 131.3, 125.6, 123.3, 118.5, 117.5, 113.5, 108.7, 102.3, 102.2, 97.7, 64.3, 55.9, 30.7, 29.6, 19.1, 13.6;

HRMS (ESI-quadrupole) m/z : [M + 1]⁺ calcd for C₂₆H₂₇O₈ 467.1700; Found 467.1704.

7-(4,5-Dimethoxy-2-((E)-2-(phenylsulfonyl)vinyl)benzyl)-8H-[1,3]dioxolo[4,5-g]chr

omen-8-one (3g). Yellow solid; yield: 359 mg (71%); R_f = 0.21 (EtOAc/hexanes = 1:4);

mp 198-200 °C; IR (KBr) $\nu_{\max}$ 1640, 1511, 1463, 1142 cm⁻¹; ¹H NMR (600 MHz, CDCl₃)

δ 7.88-7.85 (m, 3H), 7.56-7.52 (m, 2H), 7.47-7.32 (m, 2H), 7.33 (s, 1H), 6.92 (s, 1H),

6.85 (s, 1H), 6.79 (s, 1H), 6.66 (d, J = 15.0 Hz, 1H), 6.09 (s, 2H), 3.88 (s, 2H), 3.87 (s,

3H), 3.84 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 176.1, 153.7, 152.8, 152.5, 151.7, 148.3,

146.2, 140.8, 139.5, 133.2, 132.5, 129.3, 127.6, 126.3, 123.4, 123.0, 118.7, 113.8, 103.1,

102.4, 102.3, 97.8, 56.1, 56.0, 28.8; HRMS (ESI-quadrupole) m/z : [M + 1]⁺ calcd for

C₂₇H₂₃O₈S 507.1108; Found 507.1108.

Phenyl

(E)-3-(4,5-dimethoxy-2-((8-oxo-8H-[1,3]dioxolo[4,5-g]chromen-7-yl)methyl)phenyl)acryl

ate (3h). Yellow solid; yield: 355 mg (73%); R_f = 0.30 (EtOAc/hexanes = 1:2); mp

162-164 °C; IR (KBr) $\nu_{\max}$ 2923, 1720, 1600, 1462, 1139 cm⁻¹; ¹H NMR (600 MHz,

CDCl₃) δ 8.06 (d, J = 15.6 Hz, 1H), 7.51 (s, 1H), 7.35 (t, J = 7.8 Hz, 2H), 7.28 (s, 1H),

7.20 (t, J = 7.8 Hz, 1H), 7.15 (s, 1H), 7.10 (d, J = 7.8 Hz, 2H), 6.85 (s, 1H), 6.76 (s, 1H),

6.45 (d, J = 15.6 Hz, 1H), 6.05 (s, 2H), 3.92 (s, 3H), 3.88 (s, 3H), 3.88 (s, 2H); ¹³C NMR

(150 MHz, CDCl₃) δ 176.2, 165.4, 153.7, 152.7, 152.6, 151.4, 150.8, 148.2, 146.1, 143.0, 132.0, 129.3, 125.7, 125.3, 123.3, 121.6, 118.6, 116.4, 113.6, 108.8, 102.3, 102.2, 97.8, 56.0, 55.9, 28.6; HRMS (ESI-quadrupole) m/z : [M + 1]⁺ calcd for C₂₈H₂₃O₈ 487.1387; Found 487.1380.

(E)-3-(4,5-Dimethoxy-2-((8-oxo-8H-[1,3]dioxolo[4,5-g]chromen-7-yl)methyl)phenyl)acrylic acid (3i). Yellow solid; yield: 270 mg (66%); R_f = 0.45 (EtOAc/hexanes = 2:1); mp 150-152 °C; IR (KBr) $\nu_{\max}$ 2936, 1712, 1636, 1482, 1390, 1129, 1044 cm⁻¹; ¹H NMR (600 MHz, CD₃OD) δ 7.85 (d, J = 15.6 Hz, 1H), 7.55 (s, 1H), 7.40 (s, 1H), 7.23 (s, 1H), 6.97 (s, 1H), 6.95 (d, J = 15.6 Hz, 1H), 6.85 (s, 1H), 6.11 (s, 2H), 4.57 (br, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.83 (s, 2H); ¹³C NMR (150 MHz, CD₃OD) δ 178.4, 155.6, 155.5, 152.3, 149.7, 148.6, 141.6, 132.5, 130.3, 129.4, 127.4, 124.6, 119.4, 115.0, 114.5, 110.7, 104.3, 102.1, 98.9, 56.5, 56.4, 29.3; HRMS (ESI-quadrupole) m/z : [M + 1]⁺ calcd for C₂₂H₁₉O₈ 411.1074; Found 411.1075.

Butyl (E)-3-(2-((6-fluoro-4-oxo-4H-chromen-3-yl)methyl)phenyl)acrylate (3j). Orange solid; yield: 285 mg (75%); R_f = 0.25 (EtOAc/hexanes = 1:8); mp 64-66 °C; IR (KBr) $\nu_{\max}$ 3446, 2924, 1646, 1480, 1316, 1173 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.92 (d, J = 15.6 Hz, 1H), 7.86 (dd, J = 8.4, 3.0 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.41-7.27 (m, 6H), 6.35 (d, J = 15.6 Hz, 1H), 4.15 (t, J = 6.6 Hz, 2H), 3.95 (s, 2H), 1.65-1.60 (m, 2H), 1.38-1.33 (m, 2H), 0.91 (t, J = 6.6 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 176.5, 166.8,

159.4 (d, $^1J_{C-F}$ = 245.6 Hz), 153.5, 152.6, 141.4, 137.1, 133.7, 131.0, 130.3, 127.5, 126.9, 124.7 (d, $^3J_{C-F}$ = 7.5 Hz), 123.1, 121.9 (d, $^2J_{C-F}$ = 25.8 Hz), 120.5, 120.2 (d, $^3J_{C-F}$ = 8.1 Hz), 110.7 (d, $^2J_{C-F}$ = 23.6 Hz), 64.5, 30.7, 29.0, 19.2, 13.7; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{23}H_{22}O_4F$ 381.1497; Found 381.1492.

Butyl (E)-3-(2-((6-chloro-4-oxo-4H-chromen-3-yl)methyl)phenyl)acrylate (3k).

Yellow solid; yield: 309 mg (78%); R_f = 0.30 (EtOAc/hexanes = 1:8); mp 83-85 °C; IR (KBr) $\nu_{\max}$ 2920, 2360, 1711, 1646, 1465, 1313, 1172 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.19 (d, J = 2.4 Hz, 1H), 7.91 (d, J = 12.0 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.56 (dd, J = 9.0, 2.4 Hz, 1H), 7.35-7.27 (m, 5H), 6.35 (d, J = 12.0 Hz, 1H), 4.15 (t, J = 6.6 Hz, 2H), 3.95 (s, 2H), 1.64-1.60 (m, 2H), 1.39-1.32 (m, 2H), 0.90 (t, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.1, 166.8, 154.7, 153.5, 141.4, 137.0, 133.8, 133.7, 131.0, 130.3, 127.6, 126.9, 125.4, 124.5, 123.9, 120.5, 119.8, 64.5, 31.9, 29.0, 19.1, 13.7; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{23}H_{22}O_4Cl$ 397.1201; Found 397.1198.

Butyl

(E)-3-(2-((7,8-dimethoxy-4-oxo-4H-chromen-3-yl)methyl)-4,5-dimethoxyphenyl)acrylate

(3l). Yellow solid; yield: 342 mg (71%); R_f = 0.25 (EtOAc/hexanes = 1:2); mp 115-117 °C; IR (KBr) $\nu_{\max}$ 2957, 1704, 1602, 1514, 1429, 1284 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.92 (d, J = 9.0 Hz, 1H), 7.84 (d, J = 15.6 Hz, 1H), 7.29 (s, 1H), 7.07 (s, 1H), 6.99 (d, J = 9.0 Hz, 1H), 6.80 (s, 1H), 6.25 (d, J = 15.6 Hz, 1H), 4.12 (t, J = 6.6 Hz, 2H), 3.93 (s,

3H), 3.87 (s, 6H), 3.86 (s, 3H), 3.84 (s, 2H), 1.62-1.57 (m, 2H), 1.36-1.32 (m, 2H), 0.85 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.7, 167.0, 156.2, 153.0, 150.9, 150.7, 148.1, 141.0, 136.4, 131.2, 125.6, 123.3, 121.2, 118.4, 117.6, 113.5, 109.9, 108.7, 64.3, 61.4, 56.3, 55.9, 55.8, 30.6, 28.3, 19.0, 13.6; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{27}\text{H}_{31}\text{O}_8$ 483.2013; Found 483.2008.

Butyl

(E)-3-(6-((7,8-dimethoxy-4-oxo-4H-chromen-3-yl)methyl)-2,3,4-trimethoxyphenyl)acrylate (3m). Yellow solid; yield: 343 mg (67%); $R_f = 0.43$ (EtOAc/hexanes = 1:2); mp 113-115 °C; IR (KBr) ν_{max} 2958, 2926, 1735, 1167 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.94 (d, $J = 9.0$ Hz, 1H), 7.70 (d, $J = 16.2$ Hz, 1H), 7.39 (s, 1H), 7.01 (d, $J = 9.0$ Hz, 1H), 6.66 (d, $J = 9.0$, 1H), 6.58 (d, $J = 16.2$ Hz, 1H), 4.12 (t, $J = 7.2$ Hz, 2H), 3.96 (s, 3H), 3.90 (s, 3H), 3.84 (s, 9H), 3.83 (s, 2H), 1.63-1.57 (m, 2H), 1.36-1.31 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.7, 167.9, 156.3, 154.4, 153.9, 153.1, 150.8, 141.3, 137.8, 136.5, 134.3, 122.9, 121.4, 121.3, 121.2, 120.4, 118.4, 109.9, 64.2, 61.5, 60.9, 60.5, 56.4, 56.0, 30.7, 29.7, 19.1, 13.7; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{28}\text{H}_{33}\text{O}_9$ 513.2119; Found 513.2116.

Butyl

(E)-3-(6-((6-fluoro-4-oxo-4H-chromen-3-yl)methyl)benzo[d][1,3]dioxol-5-yl)acrylate (3n). Colorless solid; yield: 326 mg (77%); $R_f = 0.38$ (EtOAc/hexanes = 1:4); mp 156-158

°C; IR (KBr) $\nu_{\max}$ 3443, 2923, 2360, 1646, 1480, 1259, 1173, 1038 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.86-7.83 (m, 2H), 7.40-7.34 (m, 3H), 7.07 (s, 1H), 6.78 (s, 1H), 6.22 (d, $J = 15.6$ Hz, 1H), 5.97 (s, 2H), 4.14 (t, $J = 6.6$ Hz, 2H), 3.87 (s, 2H), 1.64-1.59 (m, 2H), 1.37-1.32 (m, 2H), 0.89 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.5, 167.0, 159.4 (d, $^1J_{\text{C-F}} = 245.4$ Hz), 153.5, 152.6, 152.5, 149.6, 147.3, 140.8, 132.4, 127.1, 124.7, 124.6, 123.2, 121.8 (d, $^2J_{\text{C-F}} = 25.2$ Hz), 120.2 (d, $^3J_{\text{C-F}} = 8.1$ Hz), 110.7 (d, $^2J_{\text{C-F}} = 23.6$ Hz), 105.9, 101.6, 64.4, 30.7, 29.7, 19.2, 13.7; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{24}\text{H}_{22}\text{O}_6\text{F}$ 425.1395; Found 425.1392.

Butyl

(E)-3-(6-((6-chloro-4-oxo-4H-chromen-3-yl)methyl)benzo[d][1,3]dioxol-5-yl)acrylate

(3o). White solid; yield: 352 mg (80%); $R_f = 0.65$ (EtOAc/hexanes = 1:4); mp 140-142 °C; IR (KBr) $\nu_{\max}$ 3421, 1647, 1465, 1259, 1174, 1038 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.18 (d, $J = 2.4$ Hz, 1H), 7.83 (d, $J = 15.6$ Hz, 1H), 7.57 (dd, $J = 9.0, 2.4$ Hz, 1H), 7.83 (s, 1H), 7.35 (d, $J = 9.0$ Hz, 1H), 7.07 (s, 1H), 6.78 (s, 1H), 6.21 (d, $J = 15.6$ Hz, 1H), 5.97 (s, 2H), 4.14 (t, $J = 6.6$ Hz, 2H), 3.87 (s, 2H), 1.63-1.60 (m, 2H), 1.38-1.33 (m, 2H), 0.89 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.1, 167.0, 154.7, 153.5, 149.7, 147.3, 140.8, 133.8, 132.3, 131.0, 127.1, 125.3, 124.5, 123.9, 119.8, 118.2, 110.8, 106.0, 101.6, 64.4, 30.7, 28.9, 19.2, 13.7; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{24}\text{H}_{22}\text{O}_6\text{Cl}$ 441.1099; Found 441.1100.

Methyl

(*E*)-3-(2,3,4-trimethoxy-6-((7-methoxy-4-oxo-4*H*-chromen-3-yl)methyl)phenyl)acrylate

(3*p*). Yellow solid; yield: 312 mg (71%); R_f = 0.35 (EtOAc/hexanes = 1:2); mp 148-150

°C; IR (KBr) $\nu_{\max}$ 2923, 2359, 1713, 1610, 1439, 1168, 1128 cm^{-1} ; ^1H NMR (600 MHz,

CDCl_3) δ 8.10 (d, J = 9.0 Hz, 1H), 7.72 (d, J = 16.2 Hz, 1H), 7.34 (s, 1H), 6.92 (dd, J =

6.6, 2.4 Hz, 1H), 6.73 (d, J = 2.4 Hz, 1H), 6.67 (s, 1H), 6.58 (d, J = 16.2 Hz, 1H), 3.86 (s,

2H), 3.84 (s, 3H), 3.83 (s, 6H), 3.82 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ

176.6, 168.2, 163.9, 158.1, 154.4, 153.8, 152.9, 141.2, 138.2, 134.4, 127.2, 123.3, 120.7,

120.3, 117.5, 114.5, 110.0, 100.0, 60.8, 60.4, 55.9, 55.7, 51.5, 29.6; HRMS

(ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{O}_8$ 441.1544; Found 441.1546.

Ethyl

(*E*)-3-(2,3,4-trimethoxy-6-((7-methoxy-4-oxo-4*H*-chromen-3-yl)methyl)phenyl)acrylate

(3*q*). Yellow solid; yield: 331 mg (73%); R_f = 0.32 (EtOAc/hexanes = 1:2); mp 117-119

°C; IR (KBr) $\nu_{\max}$ 2925, 1610, 1440, 1170, 1128 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.10

(d, J = 9.0 Hz, 1H), 7.70 (d, J = 16.2 Hz, 1H), 7.35 (t, J = 1.2 Hz, 1H), 6.92 (dd, J = 9.0,

2.4 Hz, 1H), 6.73 (d, J = 2.4 Hz, 1H), 6.68 (s, 1H), 6.56 (d, J = 16.2 Hz, 1H), 4.17 (q, J =

7.2 Hz, 2H), 3.86 (s, 2H), 3.85 (s, 3H), 3.84 (s, 6H), 3.83 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H);

^{13}C NMR (150 MHz, CDCl_3) δ 176.6, 167.8, 163.9, 158.0, 154.3, 153.8, 153.0, 141.2,

137.9, 134.4, 127.2, 123.3, 121.2, 120.3, 117.5, 114.5, 110.0, 100.0, 60.8, 60.5, 60.3, 55.9,

55.7, 29.8, 14.2; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{25}H_{27}O_8$ 455.1700;
Found 455.1701.

Butyl

(E)-3-(2,3,4-trimethoxy-6-((7-methoxy-4-oxo-4H-chromen-3-yl)methyl)phenyl)acrylate

(3r). Yellow solid; yield: 376 mg (78%); R_f = 0.45 (EtOAc/hexanes = 1:2); mp 98-100 °C;
IR (KBr) $\nu_{\max}$ 2917, 1706, 1611, 1440, 1128 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.10 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 15.6 Hz 1H), 7.34 (s, 1H), 6.92 (dd, J = 9.0, 1.2 Hz, 1H), 6.74 (d, J = 1.8 Hz, 1H), 6.68 (s, 1H), 6.58 (d, J = 15.6 Hz, 1H), 4.11 (t, J = 6.6 Hz, 2H), 3.87 (s, 2H), 3.85 (s, 3H), 3.84 (s, 6H), 3.83 (s, 3H), 1.67-1.56 (m, 2H), 1.35-1.30 (m, 2H), 0.86 (t, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.6, 167.9, 163.9, 158.1, 154.3, 153.8, 153.0, 141.3, 137.9, 134.4, 127.3, 123.3, 121.2, 120.3, 117.6, 114.5, 110.1, 100.0, 64.2, 60.8, 60.5, 55.9, 55.7, 30.7, 29.8, 19.1, 13.7; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{27}H_{31}O_8$ 483.2013; Found 483.2016.

Butyl

(E)-3-(4,5-dimethoxy-2-((7-methoxy-4-oxo-4H-chromen-3-yl)methyl)phenyl)acrylate (3s).

Orange solid; yield: 325 mg (72%); R_f = 0.37 (EtOAc/hexanes = 1:2); mp 138-140 °C; IR (KBr) $\nu_{\max}$ 2924, 1730, 1631, 1440, 1166 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.14 (d, J = 9.0 Hz, 1H), 7.87 (d, J = 15.6 Hz, 1H), 7.23 (s, 1H), 7.09 (s, 1H), 6.94 (dd, J = 9.0, 2.4 Hz, 1H), 6.83 (s, 1H), 6.75 (d, J = 2.4 Hz, 1H), 6.26 (d, J = 15.6 Hz, 1H), 4.15 (t, J = 6.6 Hz,

2H), 3.90 (s, 6H), 3.88 (s, 2H), 3.87 (s, 3H), 1.64-1.61 (m, 2H), 1.39-1.36 (m, 2H), 0.90 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.7, 167.1, 164.0, 158.1, 152.9, 151.0, 148.1, 141.1, 131.4, 127.3, 125.7, 123.9, 117.6, 117.5, 114.5, 113.6, 108.7, 100.0, 64.4, 56.0, 55.9, 30.7, 29.7, 19.2, 13.7; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{26}\text{H}_{29}\text{O}_7$ 453.1908; Found 453.1909.

Ethyl

(E)-3-(4,5-dimethoxy-2-((7-methoxy-4-oxo-4*H*-chromen-3-yl)methyl)phenyl)acrylate (*3t*).

Yellow solid; yield: 326 mg (77%); $R_f = 0.42$ (EtOAc/hexanes = 1:2); mp 135-137 °C; IR (KBr) ν_{max} 2935, 1624, 1514, 1440, 1270, 1230 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3): δ 8.10 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 16.2$ Hz, 1H), 7.23 (s, 1H), 6.93 (dd, $J = 8.0, 2.4$ Hz, 1H), 6.81 (s, 1H), 6.72 (d, $J = 2.4$ Hz, 1H), 6.25 (d, $J = 16.2$ Hz, 1H), 4.18 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 3.87 (s, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 1.25 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.6, 166.9, 163.9, 158.1, 152.8, 151.0, 148.1, 141.1, 131.4, 127.2, 125.6, 123.8, 117.6, 117.5, 114.5, 113.5, 108.7, 99.9, 60.4, 55.9, 55.9, 55.7, 29.6, 28.4, 14.2; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{O}_7$ 425.1595; Found 425.1590.

Methyl

(E)-3-(6-((6-(benzyloxy)-4-oxo-4*H*-chromen-3-yl)methyl)-2,3,4-trimethoxyphenyl)acrylate (*3u*). White solid; yield: 371 mg (72%); $R_f = 0.42$ (EtOAc/hexanes = 1:4); mp 150-152 °C;

IR (KBr) $\nu_{\max}$ 2936, 1712, 1636, 1482, 1390, 1129, 1044 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.74 (d, $J = 15.6$ Hz, 1H), 7.68 (d, $J = 3.0$ Hz, 1H), 7.45-7.29 (m, 8H), 6.68 (s, 1H), 6.60 (d, $J = 15.6$ Hz, 1H), 5.13 (s, 2H), 3.90 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.1, 168.2, 156.0, 154.4, 153.9, 153.3, 151.4, 141.3, 138.2, 136.2, 134.4, 128.7, 128.2, 127.7, 124.2, 124.1, 122.7, 120.9, 120.4, 119.6, 110.0, 106.1, 70.6, 60.9, 60.5, 56.0, 51.6, 29.9; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{30}\text{H}_{29}\text{O}_8$ 517.1857; Found 517.1848.

Ethyl

(E)-3-(6-((6-(benzyloxy)-4-oxo-4H-chromen-3-yl)methyl)-2,3,4-trimethoxyphenyl)acrylate

(3v). White solid; yield: 392 mg (74%); $R_f = 0.45$ (EtOAc/hexanes = 1:4); mp 125-127 $^\circ\text{C}$;

IR (KBr) $\nu_{\max}$ 2934, 1707, 1638, 1482, 1128 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 16.2$ Hz, 1H), 7.67 (d, $J = 3.0$ Hz, 1H), 7.44-7.43 (m, 3H), 7.38 (t, $J = 7.2$ Hz, 2H), 7.33-7.29 (m, 3H), 6.69 (s, 1H), 6.58 (d, $J = 16.2$ Hz, 1H), 5.13 (s, 2H), 4.19 (q, $J = 7.2$ Hz, 2H), 3.90 (s, 2H), 3.85 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H), 1.26 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.0, 167.8, 155.9, 154.3, 153.9, 153.3, 151.3, 141.3, 137.9, 136.2, 134.4, 128.6, 128.2, 127.6, 124.2, 122.7, 121.3, 120.4, 119.6, 110.0, 106.1, 70.6, 60.9, 60.5, 60.3, 56.0, 29.9, 14.3; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{31}\text{H}_{31}\text{O}_8$ 531.2013; Found 531.2013.

Butyl

(E)-3-(6-((6-(benzyloxy)-4-oxo-4H-chromen-3-yl)methyl)-2,3,4-trimethoxyphenyl)acrylate

(3w). White solid; yield: 424 mg (76%); R_f = 0.35 (EtOAc/hexanes = 1:4); mp 92-94 °C;

IR (KBr) $\nu_{\max}$ 2916, 1708, 1638, 1482, 1128 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.72 (d, J = 15.6 Hz, 1H), 7.68 (d, J = 3.0 Hz, 1H), 7.45-7.42 (m, 2H), 7.38 (t, J = 7.2 Hz, 2H), 7.34-7.29 (m, 4H), 6.69 (s, 1H), 6.59 (d, J = 15.6 Hz, 1H), 5.13 (s, 2H), 4.13 (t, J = 6.6 Hz, 2H), 3.90 (s, 2H), 3.85 (s, 6H), 3.84 (s, 3H), 1.62-1.59 (m, 2H), 1.41-1.34 (m, 2H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.1, 167.9, 156.0, 154.4, 153.9, 153.3, 151.4, 141.3, 137.9, 136.3, 134.4, 128.7, 128.2, 127.7, 124.2, 124.1, 122.7, 121.3, 120.4, 119.6, 110.1, 106.1, 70.6, 64.3, 60.9, 60.5, 56.0, 30.9, 30.0, 19.2, 13.7; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{33}\text{H}_{35}\text{O}_8$ 559.2326; Found 559.2331.

Butyl

(E)-3-(2-((6-(benzyloxy)-4-oxo-4H-chromen-3-yl)methyl)-4,5-dimethoxyphenyl)acrylate

(3x). Yellow solid; yield: 385 mg (73%); R_f = 0.57 (EtOAc/hexanes = 1:2); mp 130-132 °C; IR (KBr) $\nu_{\max}$ 2923, 1727, 1482, 1168 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.88 (d, J = 15.6 Hz, 1H), 7.68 (d, J = 3.0 Hz, 1H), 7.41 (d, J = 7.2 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.34-7.28 (m, 4H), 7.10 (s, 1H), 6.83 (s, 1H), 6.27 (d, J = 15.6 Hz, 1H), 5.13 (s, 2H), 4.15 (t, J = 6.6 Hz, 2H), 3.92 (s, 2H), 3.89 (s, 3H), 3.87 (s, 3H), 1.65-1.60 (m, 2H), 1.38-1.34 (m, 2H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.1, 167.1, 155.9, 153.2, 151.4, 151.0, 148.2, 141.1, 136.3, 131.4, 128.7, 128.2, 127.7, 125.7, 124.2, 124.1,

123.2, 119.6, 117.7, 113.6, 108.8, 106.1, 70.6, 64.4, 56.0, 30.7, 28.7, 19.2, 13.7; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{32}H_{33}O_7$ 529.2221; Found 529.2227.

Methyl

(*E*)-3-(2,3,4-trimethoxy-6-((8-oxo-8*H*-[1,3]dioxolo[4,5-*g*]chromen-7-yl)methyl)phenyl)acrylate (3y). Yellow solid; yield: 345 mg (76%); R_f = 0.42 (EtOAc/hexanes = 1:2); mp 109-112 °C; IR (KBr) $\nu_{\max}$ 3446, 2923, 1643, 1464, 1256, 1169, 1129, 1035 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.72 (d, J = 16.2 Hz, 1H), 7.53 (s, 1H), 7.33 (s, 1H), 6.78 (s, 1H), 6.67 (s, 1H), 6.59 (d, J = 16.2 Hz, 1H), 6.07 (s, 2H), 3.88 (s, 2H), 3.85 (s, 6H), 3.84 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.2, 168.2, 154.4, 153.8, 153.7, 152.6, 152.6, 146.1, 141.3, 138.1, 134.4, 122.8, 120.8, 120.3, 118.6, 109.9, 102.3, 102.3, 97.8, 60.8, 60.5, 55.9, 51.5, 29.6; HRMS (ESI-quadrupole) m/z : $[M + 1]^+$ calcd for $C_{24}H_{23}O_9$ 455.1342; Found 455.1346.

Butyl

(*E*)-3-(2,3,4-trimethoxy-6-((8-oxo-8*H*-[1,3]dioxolo[4,5-*g*]chromen-7-yl)methyl)phenyl)acrylate (3z). White solid; yield: 357 mg (72%); R_f = 0.35 (EtOAc/hexanes = 1:4); mp 139-141 °C; IR (KBr) $\nu_{\max}$ 3419, 2923, 1705, 1644, 1464, 1256, 1035 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.69 (d, J = 16.2 Hz, 1H), 7.50 (s, 1H), 7.33 (s, 1H), 6.75 (s, 1H), 6.67 (s, 1H), 6.58 (d, J = 16.2 Hz, 1H), 6.05 (s, 2H), 4.12 (t, J = 6.6 Hz, 2H), 3.86 (s, 2H), 3.84 (s, 6H), 3.83 (s, 3H), 1.61-1.58 (m, 2H), 1.39-1.32 (m, 2H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C

NMR (150 MHz, CDCl₃) δ 176.2, 167.9, 154.4, 153.9, 153.7, 152.7, 152.6, 152.6, 146.1, 141.3, 137.9, 134.4, 122.8, 121.3, 120.4, 118.6, 110.0, 102.4, 102.3, 97.8, 64.2, 60.9, 60.8, 56.0, 30.7, 22.6, 19.1, 13.7; HRMS (ESI-quadrupole) m/z : [M + 1]⁺ calcd for C₂₇H₂₉O₉ 497.1806; Found 497.1798.

Ethyl

(E)-3-(6-((6-methyl-4-oxo-4H-chromen-3-yl)methyl)benzo[d][1,3]dioxol-5-yl)acrylate

(3aa). White solid; yield: 298 mg (76%); R_f = 0.40 (EtOAc/hexanes = 1:4); mp 175-177 °C; IR (KBr) $\nu_{\max}$ 2922, 2853, 1705, 1644, 1616, 1484, 1257, 1174, 1037 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.99 (d, J = 1.2 Hz, 1H), 7.87 (d, J = 15.6 Hz, 1H), 7.43 (dd, J = 8.4, 1.2 Hz, 1H), 7.38 (t, J = 1.2 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.06 (s, 1H), 6.78 (s, 1H), 6.21 (d, J = 15.6 Hz, 1H), 5.96 (s, 2H), 4.19 (q, J = 7.2 Hz, 2H), 3.88 (s, 2H), 2.43 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 177.3, 167.0, 154.7, 153.3, 149.6, 147.2, 141.0, 135.0, 134.8, 132.9, 127.1, 125.2, 123.5, 123.3, 118.1, 117.8, 110.8, 105.9, 101.5, 60.4, 28.9, 20.9, 14.3; HRMS (ESI-quadrupole) m/z : [M + 1]⁺ calcd for C₂₃H₂₁O₆ 393.1333; Found 393.1333.

Ethyl

(E)-3-(6-((6-chloro-4-oxo-4H-chromen-3-yl)methyl)benzo[d][1,3]dioxol-5-yl)acrylate

(3ab). White solid; yield: 305 mg (74%); R_f = 0.38 (EtOAc/hexanes = 1:4); mp 169-170 °C; IR (KBr) $\nu_{\max}$ 2981, 2903, 1705, 1647, 1484, 1465, 1259, 1176 cm⁻¹; ¹H NMR (600

MHz, CDCl₃) δ 8.17 (d, J = 2.4 Hz, 1H), 7.84 (d, J = 15.6 Hz, 1H), 7.56 (dd, J = 9.0, 3.0 Hz, 1H), 7.39 (s, 1H), 7.33 (d, J = 9.0 Hz, 1H), 7.05 (s, 1H), 6.77 (s, 1H), 6.21 (d, J = 15.6 Hz, 1H), 5.96 (s, 2H), 4.19 (q, J = 7.2 Hz, 2H), 3.87 (s, 2H), 1.27 (t, J = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 176.5, 166.9, 154.7, 153.5, 148.6, 147.3, 140.8, 133.8, 132.3, 130.9, 127.0, 125.3, 124.5, 123.9, 119.8, 118.2, 110.7, 105.9, 101.6, 60.5, 28.8, 14.3; HRMS (ESI-quadrupole) m/z : [M + 1]⁺ calcd for C₂₂H₁₈ClO₆ 413.2664; Found 413.2662.

Ethyl (E)-3-(6-((4-oxo-4H-chromen-3-yl)methyl)benzo[d][1,3]dioxol-5-yl)acrylate

(3ac). White solid; yield: 264 mg (70%); R_f = 0.27 (EtOAc/hexanes = 1:4); mp 170-172 °C; IR (KBr) $\nu_{\max}$ 2980, 2903, 1705, 1641, 1503, 1484, 1256, 1176 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.21 (dd, J = 7.8, 1.2 Hz, 1H), 7.86 (d, J = 15.6 Hz, 1H), 7.61 (dt, J = 9.0, 1.2 Hz, 1H), 7.40-7.35 (m, 3H), 7.05 (s, 1H), 6.78 (s, 1H), 6.20 (d, J = 15.6 Hz, 1H), 5.95 (s, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.87 (s, 2H), 1.26 (t, J = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 177.2, 166.9, 156.3, 153.3, 153.3, 149.6, 147.2, 140.9, 133.5, 132.7, 127.0, 125.9, 125.0, 123.7, 123.6, 118.0, 110.7, 105.9, 101.5, 60.4, 28.9, 14.2; HRMS (ESI-quadrupole) m/z : [M + 1]⁺ calcd for C₂₂H₁₉O₆ 379.1176; Found 379.1172.

Ethyl

(E)-3-(6-((7-methyl-4-oxo-4H-chromen-3-yl)methyl)benzo[d][1,3]dioxol-5-yl)acrylate

(3ad). White solid; yield: 302 mg (77%); R_f = 0.32 (EtOAc/hexanes = 1:4); mp 178-180 °C; IR (KBr) $\nu_{\max}$ 2923, 1708, 1629, 1451, 1307, 1255 cm⁻¹; ¹H NMR (600 MHz, CDCl₃)

δ 8.09 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 15.6 Hz, 1H), 7.35 (t, J = 1.2 Hz, 1H), 7.19-7.17 (m, 2H), 7.06 (s, 1H), 6.78 (s, 1H), 6.21 (d, J = 15.6 Hz, 1H), 5.96 (s, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.87 (s, 2H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.2, 166.9, 156.5, 153.1, 153.1, 149.6, 147.2, 144.9, 141.0, 132.9, 127.1, 126.6, 125.7, 123.6, 121.4, 118.1, 117.7, 110.7, 105.9, 101.5, 60.4, 28.9, 21.8, 14.3; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{23}\text{H}_{21}\text{O}_6$ 393.1333; Found 393.1332.

Ethyl

(*E*)-3-(6-((7-methoxy-4-oxo-4H-chromen-3-yl)methyl)benzo[d][1,3]dioxol-5-yl)acrylate

(3ae). White solid; yield: 294 mg (72%); R_f = 0.32 (EtOAc/hexanes = 1:4); mp 165-167 °C; IR (KBr) ν_{max} 2923, 1705, 1638, 1610, 1483, 1440, 1257 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.11 (d, J = 9.0 Hz, 1H), 7.86 (d, J = 15.6 Hz, 1H), 7.32 (s, 1H), 7.05 (s, 1H), 6.94 (dd, J = 8.4, 2.4 Hz, 1H), 6.78 (s, 1H), 6.75 (d, J = 2.4 Hz, 1H), 6.20 (d, J = 15.6 Hz, 1H), 5.96 (s, 2H), 4.19 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 3.87 (s, 2H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.6, 167.0, 164.0, 158.1, 152.9, 149.6, 147.2, 141.0, 132.9, 127.3, 127.0, 123.6, 118.0, 117.6, 114.5, 110.8, 105.9, 101.5, 100.0, 60.4, 55.8, 28.8, 14.3; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{23}\text{H}_{21}\text{O}_7$ 409.1282; Found 409.1286.

Ethyl

(*E*)-3-(6-((8-oxo-8H-[1,3]dioxolo[4,5-g]chromen-7-yl)methyl)benzo[d][1,3]dioxol-5-yl)a

crylate (3af). Yellow solid; yield: 291 mg (69%); $R_f = 0.42$ (EtOAc/hexanes = 1:2); mp 215-216 °C; IR (KBr) $\nu_{\max}$ 2921, 2852, 1698, 1641, 1462, 1255 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.85 (d, $J = 15.6$ Hz, 1H), 7.51 (s, 1H), 7.30 (t, $J = 1.2$ Hz, 1H), 7.05 (s, 1H), 6.77 (s, 1H), 6.20 (d, $J = 15.6$ Hz, 1H), 6.06 (s, 2H), 5.96 (s, 2H), 4.19 (q, $J = 7.2$ Hz, 2H), 3.85 (s, 2H), 1.27 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.2, 167.0, 153.8, 152.7, 152.6, 152.6, 149.6, 147.2, 146.1, 141.0, 132.9, 127.1, 123.0, 118.7, 118.0, 110.7, 105.9, 102.3, 101.5, 97.8, 60.5, 29.7, 14.3; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{23}\text{H}_{19}\text{O}_8$ 423.1074; Found 423.1076.

Butyl

(E)-3-(6-((5-methoxy-4-oxo-4H-chromen-3-yl)methyl)benzo[d][1,3]dioxol-5-yl)acrylate (3ag). White solid; yield: 353 mg (81%); $R_f = 0.20$ (EtOAc/hexanes = 1:2); mp 139-141 °C; IR (KBr) $\nu_{\max}$ 2924, 1705, 1647, 1475, 1259 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.83 (d, $J = 15.6$ Hz, 1H), 7.47 (t, $J = 8.4$ Hz, 1H), 7.02 (s, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 6.78 (s, 1H), 6.74 (d, $J = 8.4$ Hz, 1H), 6.18 (d, $J = 15.6$ Hz, 1H), 5.92 (s, 2H), 4.11 (t, $J = 7.2$ Hz, 2H), 3.93 (s, 3H), 3.79 (s, 2H), 1.61-1.57 (m, 2H), 1.36-1.31 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 176.8, 167.0, 159.9, 158.4, 151.3, 149.5, 147.0, 141.0, 133.5, 133.0, 126.9, 124.7, 117.9, 114.3, 110.9, 110.0, 106.0, 105.7, 101.4, 64.3, 56.3, 30.6, 28.9, 19.1, 13.6; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{25}\text{H}_{25}\text{O}_7$ 437.1595; Found 437.1591.

(E)-3-(4,5-Dimethoxy-2-(3-oxobut-1-en-1-yl)benzyl)-7-methyl-4H-chromen-4-one

(3ah). Yellow solid; yield: 280 mg (74%); R_f = 0.22 (EtOAc/hexanes = 1:3); mp 196-198 °C; IR (KBr) $\nu_{\max}$ 2923, 2853, 1639, 1513, 1254, 1166 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.10 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 16.2 Hz, 1H), 7.30 (s, 1H), 7.19 (d, J = 8.4 Hz, 1H), 7.17 (s, 1H), 7.10 (s, 1H), 6.80 (s, 1H), 6.51 (d, J = 16.2 Hz, 1H), 3.93 (s, 2H), 3.89 (s, 3), 3.88 (s, 3H), 2.45 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 198.6, 177.0, 156.5, 153.4, 151.3, 148.2, 145.0, 140.3, 132.1, 127.0, 126.7, 125.6, 125.6, 123.9, 121.3, 117.8, 113.6, 108.9, 56.0, 56.0, 28.3, 27.1, 21.8; HRMS (ESI-quadrupole) m/z : $[\text{M} + 1]^+$ calcd for $\text{C}_{23}\text{H}_{23}\text{O}_5$ 379.1540; Found 379.1540.

ASSOCIATED CONTENT

Supporting information

^1H NMR and ^{13}C NMR spectra of compounds **2a-2am**, **3a-3ah** and crystal data (CIF) for **3d**. The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX

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Notes

The authors declare no competing financial interest.

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