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Trifluoromethanesulfonic acid mediated Friedel–Crafts reaction of (*E*)-3-aryl-2-(diethoxyphosphoryl)acrylic acids with electron-rich hydroxyarenes. A convenient approach to α-methylene-δ-valerolactones

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Abstract—The synthesis of *trans*-3-diethoxyphosphoryl-4-aryl-3,4-dihydrocoumarins from electron-rich hydroxyarenes and (*E*)-3-aryl-2-(diethoxyphosphoryl)acrylic acids has been achieved by using CF_3SO_3H as a catalyst. The products could be easily transformed to the corresponding α-methylene-δ-valerolactones by means of the Horner–Wadsworth–Emmons reaction.

1. Introduction

The 3,4-dihydrocoumarine system is widely distributed in nature and some derivatives have been shown to exhibit pharmacological activity. The 4-aryl-3,4-dihydrocoumarins are a structural group of naturally occurring neoflavonoids.[1–3]

The most common method for the synthesis of 4-aryl-3,4-dihydrocoumarins involves Michael type reaction of electron-rich hydroxyarenes with cinnamic acids or their derivatives.[1–14] The vast majority of the previous investigations demonstrate that CF_3COOH is one of the most useful catalysts for this type of transformation.[8–10] The reaction is proposed to take place via a sequence involving initial protonation of cinnamic acid followed by electrophilic substitution of hydroxyarene by an in situ generated carbocationic intermediate and finally spontaneous lactonization of the resulting δ-hydroxyacid.[9] Unfortunately, this method is limited to the reaction of cinnamic acids bearing electron-donating groups on the aromatic ring. Thus, there is a hope that design of a new catalyst would increase the availability of functionalized 4-aryl-3,4-dihydrocoumarins.

Recently, we have developed a new, general route for the synthesis of (*E*)-3-aryl-2-(diethoxyphosphoryl)acrylic acids **1**.[15] Likewise, we have been involved in the chemistry of α-diethoxyphosphoryl-δ-valerolactones and we have reported both the efficient synthesis of α-methylene-δ-valerolactones derived from the corresponding α-diethoxyphosphoryl-δ-valerolactones[16] as well as their enantioselective synthesis.[17–19]

We envisioned the conjugate addition of electron-rich hydroxyarenes to the acids **1** as a way to access 4-aryl-3-diethoxyphosphoryl-3,4-dihydrocoumarins **3**. In this paper we describe the first synthesis of the dihydrocoumarins based on CF_3SO_3H promoted Friedel–Crafts reaction of the electron-rich hydroxyarenes **2** with the acids **1**. Importantly, we demonstrate that this strategy is well suited for the preparation of 4-aryl-3-diethoxyphosphoryl-3,4-dihydrocoumarins **3** from the acids **1** bearing electron-withdrawing substituents on the aromatic ring. Moreover, we demonstrate that the resulting α-diethoxyphosphoryl-δ-valerolactones **3** can be easily converted into the corresponding α-methylene-δ-valerolactones **4**, thus providing a new approach to functionalized 4-aryl-3,4-dihydrocoumarins.

2. Results and discussion

In the course of our previous studies we have reported that electron-rich hydroxyarenes undergo self-catalytic Michael reaction with dicyclohexylammonium 2-(diethoxyphosphoryl)acrylate to provide dicyclohexylammonium 2-diethoxyphosphoryl-3-(2-hydroxyaryl)propionates.[20] Our initial attempts to develop self-catalytic addition of electron-rich hydroxyarenes to the dicyclohexylammonium salts of the acids **1** under previously optimized conditions were

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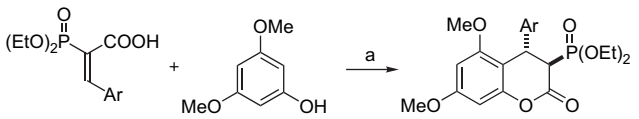
unsuccessful. In all cases the unreacted starting materials were recovered. The problem was eventually solved by modifying the reaction conditions.

We began our studies by reacting 3,5-dimethoxyphenol (**2a**) with (*E*)-2-diethoxyphosphoryl-3-(3,4,5-trimethoxyphenyl)-acrylic acid (**1a**) (Scheme 1) in CH_2Cl_2 in the presence of CF_3COOH (30 equiv) at room temperature (Table 1, entry 1). The reaction showed complete consumption after 18 days. Careful analysis of ^1H and ^{13}C NMR data revealed that it was fully regioselective with *C*-addition giving the lactone **3a** in 75% yield as a single diastereoisomer. The relative stereochemistry of the stereogenic centers C-3 and C-4 in the lactone **3a** was assigned to be *trans* on the basis of ^1H and ^{13}C NMR data. The values of coupling constants $^3J_{H3H4}$=0.8 Hz, $^3J_{PH4}$=15.5 Hz, $^3J_{PC5}$=0 Hz, and $^3J_{PCipso}$=16.9 Hz observed are characteristic for the *trans*-configuration.[21]



1a-e **2a** **3a-e**

Scheme 1. Reagents and conditions: (a) 3,5-dimethoxyphenol (1.1 equiv), catalyst (2 or 30 equiv), CH_2Cl_2, rt.

It was expected that replacement of CF_3COOH with a stronger Brønsted acid might facilitate the formation of a carbocation and favor the Friedel–Crafts reaction–lactonization sequence. Indeed, we found that CH_3SO_3H (2 equiv) smoothly promoted the addition of phenol **2a** (1.1 equiv) to the acid **1a** in CH_2Cl_2 at room temperature affording *trans*-lactone **3a** in 85% yield after 8 days (Table 1, entry 2).

This protocol was successfully extended to other (*E*)-3-aryl-2-(diethoxyphosphoryl)acrylic acids **1b–e** (Table 1, entries 3–6). Our studies showed that electronic effects of the aryl substituents had a profound impact on the reactivity of the substrates. Data presented in Table 1 show that a reasonable reaction rate is limited to acrylic acids **1b–c** bearing electron-donating substituent on the aromatic ring and heteroaromatic-substituted acid **1d**. In contrast, the reaction of phenol **1a** with (*E*)-2-diethoxyphosphoryl-3-(4-nitrophenyl)acrylic acid (**1e**) proceeded slowly and full conversion was achieved after 37 days! The long reaction time in this case is in agreement with the destabilizing effect that electron-withdrawing substituents on the aromatic ring exert on carbocations. In all cases, the corresponding products **3b–e** were obtained as the *trans* isomers exclusively, in high yields.

It is remarkable that the most significant improvement with respect to the reaction time was achieved by using CF_3SO_3H as a catalyst (Table 1, entries 7–11). Condensations of phenol **2a** (1.1 equiv) with acrylic acids **1a–d** performed in CH_2Cl_2 in the presence of CF_3SO_3H (2 equiv) at room temperature resulted in complete consumption of the starting materials within 1 day. Under the same reaction conditions, condensation of phenol **2a** with the acrylic acid **1e** was complete within 2 days. All reactions performed were completely regio- and diastereoselective and resulted in the formation of *trans*-lactones in high yields. From these results, CF_3SO_3H was seen as the optimal catalyst for the transformation of the acrylic acids **1** into 4-aryl-3-diethoxyphosphoryl-3,4-dihydrocoumarins **3** and was used throughout the study.

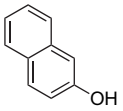
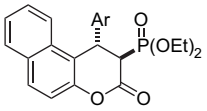
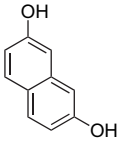
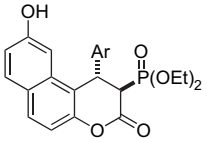
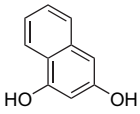
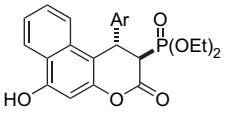
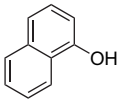
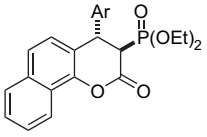
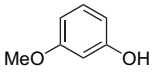
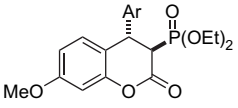
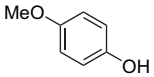
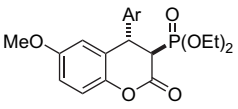
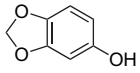
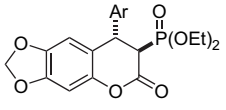
In the next stage of the research investigation into the reaction scope was carried out. A wide variety of hydroxyarenes have been evaluated under the optimal reaction conditions (1.1 equiv of hydroxyarene and 2 equiv of CF_3SO_3H, in CH_2Cl_2 at room temperature). As demonstrated in Table 2 the scope of this reaction could be extended to the use of 2-naphthol (**2b**), 2,7-dihydroxynaphthalene (**2c**), 1,3-dihydroxynaphthalene (**2d**), and 1-naphthol (**2e**). In all cases reactions proceeded in a completely regio- and diastereoselective manner leading to the formation of the corresponding *trans*-lactones **3f–p** within 1–2 days regardless the nature of the aryl substituent on the acrylic acid moiety. The structure of the *trans*-lactone **3n** derived from 1,3-dihydronaphthalene (**2d**) and (*E*)-3-(4-bromophenyl)-2-(diethoxyphosphoryl)acrylic acid (**1g**) was unambiguously confirmed by the single crystal X-ray analysis (Fig. 1). Details of the crystal structure determination were published elsewhere.[22]

The synthesis of dihydrocoumarins **3q–u** from phenols **2f–h** that are less electron-rich than 3,5-dimethoxyphenol (**2a**) was then explored (Scheme 2, Table 2). Generally these reactions required longer reaction times to achieve full conversion than 3,5-dimethoxyphenol (**2a**) or its naphthol counterparts. In the reactions of 3-methoxyphenol (**2f**) with the acids **1f** and **1g** catalyzed by CF_3SO_3H at room temperature full conversion was achieved after 5 and 17 days, respectively. The reaction of 4-methoxyphenol (**2g**) with the acid **1a** was complete after 6 days. In contrast, CF_3SO_3H catalyzed reactions were not applicable to the synthesis of

Table 1. 4-Aryl-3-diethoxyphosphoryl-3,4-dihydrocoumarins **3a–e** prepared

Entry	Acrylic acid **1** (Ar)	3,4-Dihydrocoumarin **3**	Time [days]	Yield [%]	Catalyst (equiv)
1	**1a** (3,4,5-$(CH_3O)_3$–C_6H_2–)	**3a**	18	75	CF_3COOH (30)
2	**1a** (3,4,5-$(CH_3O)_3$–C_6H_2–)	**3a**	8	85	CH_3SO_3H (2)
3	**1b** (2-CH_3O–C_6H_4–)	**3b**	8	85	CH_3SO_3H (2)
4	**1c** (4-CH_3–C_6H_4–)	**3c**	8	95	CH_3SO_3H (2)
5	**1d** (1-acetyl-1*H*-indol-3-yl)	**3d**	7	93	CH_3SO_3H (2)
6	**1e** (4-NO_2–C_6H_4–)	**3e**	37	86	CH_3SO_3H (2)
7	**1a** (3,4,5-$(CH_3O)_3$–C_6H_2–)	**3a**	1	82	CF_3SO_3H (2)
8	**1b** (2-CH_3O–C_6H_4–)	**3b**	1	86	CF_3SO_3H (2)
9	**1c** (4-CH_3–C_6H_4–)	**3c**	1	87	CF_3SO_3H (2)
10	**1d** (1-acetyl-1*H*-indol-3-yl)	**3d**	1	94	CF_3SO_3H (2)
11	**1e** (4-NO_2–C_6H_4–)	**3e**	2	89	CF_3SO_3H (2)

Table 2. 4-Aryl-3-diethoxyphosphoryl-3,4-dihydrocoumarins **3f–u** prepared

Entry	Hydroxyarene **2**	Acrylic acid **1** (Ar)	3,4-Dihydrocoumarin **3**	Time [days]	Yield [%]	Catalyst
						
1	**2b**	**1a** (3,4,5-$(CH_3O)_3$–C_6H_2–)	**3f**	1	79	CF_3SO_3H
2	**2b**	**1d** (1-acetyl-1*H*-indol-3-yl)	**3g**	1	74	CF_3SO_3H
3	**2b**	**1f** (4-CH_3O–C_6H_4–)	**3h**	1	86	CF_3SO_3H
4	**2b**	**1g** (4-Br–C_6H_4–)	**3i**	2	69	CF_3SO_3H
						
5	**2c**	**1a** (3,4,5-$(CH_3O)_3$–C_6H_2–)	**3j**	1	94	CF_3SO_3H
6	**2c**	**1f** (4-CH_3O–C_6H_4–)	**3k**	1	86	CF_3SO_3H
7	**2c**	**1g** (4-Br–C_6H_4–)	**3l**	1	75	CF_3SO_3H
						
8	**2d**	**1f** (4-CH_3O–C_6H_4–)	**3m**	1	90	CF_3SO_3H
9	**2d**	**1g** (4-Br–C_6H_4–)	**3n**	1	95	CF_3SO_3H
						
10	**2e**	**1f** (4-CH_3O–C_6H_4–)	**3o**	1	91	CF_3SO_3H
11	**2e**	**1g** (4-Br–C_6H_4–)	**3p**	1	66	CF_3SO_3H
						
12	**2f**	**1f** (4-CH_3O–C_6H_4–)	**3q**	5	78	CF_3SO_3H
13	**2f**	**1g** (4-Br–C_6H_4–)	**3r**	17	53	CF_3SO_3H
						
14	**2g**	**1a** (3,4,5-$(CH_3O)_3$–C_6H_2–)	**3s**	6	94	CF_3SO_3H
						
15	**2h**	**1f** (4-CH_3O–C_6H_4–)	**3t**	34	71	CH_3SO_3H
16	**2h**	**1g** (4-Br–C_6H_4–)	**3u**	58	73	CH_3SO_3H

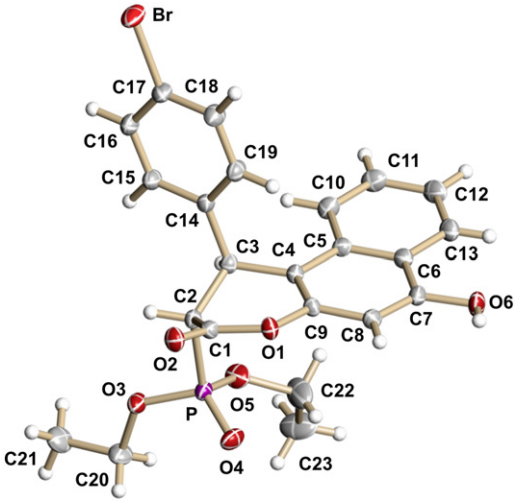
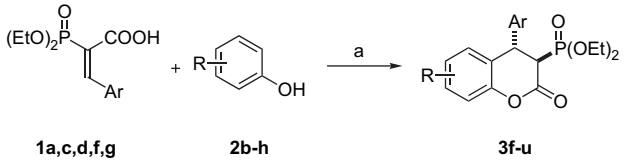


Figure 1. The crystal structure of *trans*-α-diethoxyphosphoryl-δ-valerolactone **3n** as published in Ref. 22. The C23 atom of the diethoxy substituent is disordered over two partially occupied positions. The picture shows site for which the occupation factor was 0.820(5). Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of an arbitrary radius.

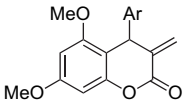
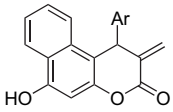
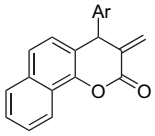
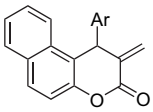
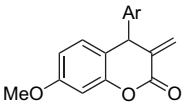
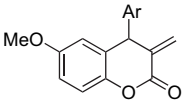
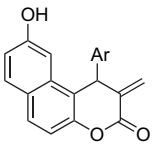
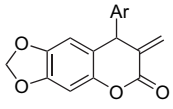
dihydrocoumarins **3t–u** from sesamol (**2h**). Reactions of sesamol (**2h**) with the acids **1f** and **1g** catalyzed by CF_3SO_3H were not chemoselective and provided mixtures of organophosphorus compounds. Both condensations could be effectively catalyzed by CH_3SO_3H, and complete conversion of starting materials was achieved after 34 and 58 days, respectively! As seen from the results phenols **2b–h** gave the corresponding products **3f–u** in high yield with complete regio- and *trans*-diastereoselectivity.



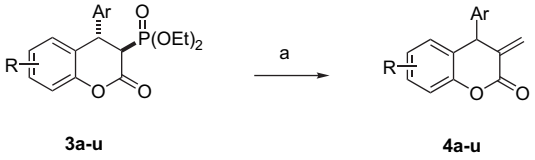
Scheme 2. Reagents and conditions: (a) hydroxyarene (1.1 equiv), catalyst (2 equiv), CH_2Cl_2, rt.

It is noteworthy that CF_3SO_3H promoted condensations of electron-rich hydroxyarenes **2a–g** with (*E*)-3-aryl-2-(diethoxyphosphoryl)acrylic acids **1a–g** provide a direct route to

Table 3. 4-Aryl-3-methylene-3,4-dihydrocoumarins **4a–u** prepared

Entry	Product **4**	Ar	Yield [%]	Entry	Product **4**	Ar	Yield [%]
							
1	**4a**	3,4,5-$(CH_3O)_3$–C_6H_2–	72	13	**4m**	4-CH_3O–C_6H_4–	60
2	**4b**	2-CH_3O–C_6H_4–	73	14	**4n**	4-Br–C_6H_4–	83
3	**4c**	4-CH_3–C_6H_4–	63				
4	**4d**	1-acetyl-1*H*-indol-3-yl	63	15	**4o**	4-CH_3O–C_6H_4–	75
5	**4e**	4-NO_2–C_6H_4–	70	16	**4p**	4-Br–C_6H_4–	89
							
6	**4f**	3,4,5-$(CH_3O)_3$–C_6H_2–	73	17	**4q**	4-CH_3O–C_6H_4–	78
7	**4g**	1-acetyl-1*H*-indol-3-yl	53	18	**4r**	4-Br–C_6H_4–	74
8	**4h**	4-CH_3O–C_6H_4–	79				
9	**4i**	4-Br–C_6H_4–	73	19	**4s**	3,4,5-$(CH_3O)_3$–C_6H_2–	64
							
10	**4j**	3,4,5-$(CH_3O)_3$–C_6H_2–	85	20	**4t**	4-CH_3O–C_6H_4–	78
11	**4k**	4-CH_3O–C_6H_4–	86	21	**4u**	4-Br–C_6H_4–	75
12	**4l**	4-Br–C_6H_4–	75				

a new, potentially useful class of α-diethoxyphosphoryl-δ-valerolactones. Transformation of α-diethoxyphosphoryl-δ-valerolactones **3a–u** into the corresponding α-methylene-δ-valerolactones **4a–u** seemed attractive to us (Scheme 3, Table 3). The Horner–Wadsworth–Emmons reaction of α-diethoxyphosphoryl-δ-valerolactones **3a–u** with an excess of paraformaldehyde performed in THF in the presence of potassium *tert*-butoxide afforded the corresponding α-methylene-δ-valerolactones **4a–u** in high yields. We found that THF used as a solvent gave much better results in terms of yield and purity of the products then the previously reported diethyl ether.[17]



Scheme 3. Reagents and conditions: (a) *t*-BuOK (1.2 equiv), THF, rt, 0.5 h; then HCHO (5 equiv), THF, rt, 1 h.

3. Conclusions

In summary, we have identified CF_3SO_3H as an efficient catalyst for Friedel–Crafts reaction of electron-rich hydroxyarenes with (*E*)-3-aryl-2-(diethoxyphosphoryl)acrylic acids **1**. The reaction features high efficiency of the catalyst regardless of electronic character of the aryl substituent on the acrylic acid moiety, high yield, and excellent regio- and diastereoselectivity providing a practical method for the synthesis of α-diethoxyphosphoryl-δ-valerolactones **3a–u**. The Horner–Wadsworth–Emmons olefination of these compounds with paraformaldehyde allowed the facile preparation of α-methylene-δ-valerolactones **4a–u**.

4. Experimental

4.1. General

NMR spectra were recorded on a Bruker DPX 250 instrument at 250.13 MHz for ^{1}H, 62.9 MHz for ^{13}C, and 101.3 MHz for ^{31}P NMR using tetramethylsilane as internal and 85% H_3PO_4 as external standard. The multiplicity of carbons was determined by DEPT experiments. IR spectra were measured on a Specord M80 (Zeiss) instrument. Elemental analyses were performed on a Perkin–Elmer PE 2400 analyzer. Melting points were determined in open capillaries and are uncorrected. Acrylic acids **1a–g** were prepared according to the literature procedure.[15] Spectral data of the acid **1d** have been reported elsewhere.[23] The synthesis and spectral data of **1a** and **1b** have not been previously reported.

4.1.1. (*E*)-2-(Diethoxyphosphoryl) 3-(3,4,5-trimethoxyphenyl)acrylic acid (1a). White solid (73% yield), mp 119–121 °C; IR (CCl_4): 1708, 1608, 1516, 1312, 1184, 1032, 964 cm^{-1}; ^{31}P NMR (acetone-d_6): 14.2; ^{1}H NMR (acetone-d_6): 1.32 (dt, 6H, $^3J_{HH}$=7.1 Hz, $^4J_{HH}$=0.6 Hz, 2×CH_3CH$_2$OP), 3.77 (s, 3H, CH_3OAr), 3.73 (s, 6H, 2×CH_3OAr), 4.08–4.20 (m, 4H, 2×CH$_3$CH_2OP), 6.99 (s, 2H, 2×CH_{Ar}), 7.42 (d, 1H, $^3J_{HP}$=24.5 Hz, C*H*Ar); ^{13}C NMR (acetone-d_6): 17.5 (d, $^3J_{CP}$=6.5 Hz, 2×), 57.5 (2×), 61.6, 64.1 (d, $^2J_{CP}$=5.0 Hz, 2×), 109.0 (2×), 126.4 (d, $^1J_{CP}$=176.4 Hz), 131.0 (d, $^3J_{CP}$=21.0 Hz), 142.2, 147.4 (d, $^2J_{CP}$=6.1 Hz), 155.3 (2×), 169.2 (d, $^2J_{CP}$=12.1 Hz). Anal. Calcd for $C_{16}H_{23}O_8P$: C, 51.34; H, 6.19. Found: C, 51.22; H, 6.13.

4.1.2. (*E*)-2-(Diethoxyphosphoryl)-3-(2-methoxyphenyl)-acrylic acid (1b). White solid (71% yield), mp 134–136 °C; IR (CCl_4): 1708, 1512, 1308, 1252, 1192, 1012, 976 cm^{-1}; ^{31}P NMR (acetone-d_6): 14.4; ^{1}H NMR (acetone-d_6): 1.32 (dt, 6H, $^3J_{HH}$=7.1 Hz, $^4J_{HH}$=0.6 Hz, 2×CH_3CH$_2$OP), 3.89 (s, 3H, CH_3OAr), 4.08–4.20 (m, 4H, 2×CH$_3$CH_2OP), 6.95 (ddd, 1H, $^3J_{HH}$=8.6, 7.6 Hz, $^4J_{HH}$=0.8 Hz, CH_{Ar}), 7.07 (dd, 1H, $^3J_{HH}$=7.6 Hz, $^4J_{HH}$=0.8 Hz, CH_{Ar}), 7.41 (ddd, 1H, $^3J_{HH}$=8.6, 7.7 Hz, $^4J_{HH}$=1.6 Hz, CH_{Ar}), 7.52 (dd, 1H, $^3J_{HH}$=7.7 Hz, $^4J_{HH}$=1.6 Hz, CH_{Ar}), 7.82 (d, 1H, $^3J_{HP}$=24.5 Hz, C*H*Ar); ^{13}C NMR (acetone-d_6): 17.5 (d, $^3J_{CP}$=6.3 Hz, 2×), 57.0, 64.1 (d, $^2J_{CP}$=5.1 Hz, 2×), 113.0, 122.2, 125.0 (d, $^3J_{CP}$=20.1 Hz), 127.3 (d, $^1J_{CP}$=177.6 Hz), 130.9, 133.7, 144.1 (d, $^2J_{CP}$=7.1 Hz), 159.7, 168.6 (d, $^2J_{CP}$=13.0 Hz). Anal. Calcd for $C_{14}H_{19}O_6P$: C, 53.50; H, 6.09. Found: C, 53.61; H, 6.18.

4.2. General procedure for the preparation of 4-aryl-3-diethoxyphosphoryl-3,4-dihydrocoumarins 3a–u

To a solution of a corresponding hydroxyarene **2** (2.2 mmol) in CH_2Cl_2 (15 mL) trifluoromethanesulfonic acid (600 mg, 4 mmol) or methanesulfonic acid (392 mg, 4 mmol) (for details see Table 1 or 2) and acrylic acid **1** (2 mmol) were added and a resulting mixture was left at room temperature for the appropriate period of time (shown in Table 1 or 2). The reaction progress was occasionally monitored with ^{31}P NMR. After the acrylic acid **1** was completely reacted, saturated $NaHCO_3$ solution was added (10 mL). The organic layer was separated, washed with water (2×10 mL) and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded a crude product, which was purified by column chromatography (eluent: ethyl acetate/hexane 2:1) or recrystallized from diethyl ether.

4.2.1. 3-Diethoxyphosphoryl-5,7-dimethoxy-4-(3,4,5-trimethoxyphenyl)chroman-2-one (3a). White solid (837 mg, 82% yield), mp 102–103 °C; R_f 0.12 (33% hexane/ethyl acetate); IR (CCl_4): 1760, 1628, 1596, 1248, 1200, 1128, 1096, 1048, 1024 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.5; ^{1}H NMR ($CDCl_3$): δ=1.05 (dt, 3H, $^3J_{HH}$=7.1 Hz, $^4J_{HH}$=0.3 Hz, CH_3CH$_2$OP), 1.34 (dt, 3H, $^3J_{HH}$=7.1 Hz, $^4J_{HH}$=0.3 Hz, CH_3CH$_2$OP), 3.53 (dd, 1H, $^2J_{HP}$=25.3 Hz, $^3J_{HH}$=0.8 Hz, PC*H*), 3.58–3.72 (m, 1H, CH$_3$CH_2OP), 3.77 (s, 9H, 3×CH_3OAr), 3.79 (s, 3H, CH_3OAr), 3.80–3.97 (m, 1H, CH$_3$CH_2OP), 3.82 (s, 3H, CH_3OAr), 4.07–4.21 (m, 2H, CH$_3$CH_2OP), 4.91 (dd, 1H, $^3J_{HP}$=15.5 Hz, $^3J_{HH}$=0.8 Hz, ArC*H*Ar), 6.28 (d, 1H, $^4J_{HH}$=2.3 Hz, CH_{Ar}), 6.32 (d, 1H, $^4J_{HH}$=2.3 Hz, CH_{Ar}), 6.33 (s, 2H, 2×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=15.8 (d, $^3J_{CP}$=6.0 Hz), 16.0 (d, $^3J_{CP}$=6.3 Hz), 36.4 (d, $^2J_{CP}$=3.6 Hz), 48.2 (d, $^1J_{CP}$=124.3 Hz), 55.3, 55.7, 55.8, 60.5, 63.0 (d, $^2J_{CP}$=6.8 Hz), 63.1 (d, $^2J_{CP}$=6.8 Hz), 93.3, 95.0, 103.4 (2×), 136.9, 137.2 (d, $^3J_{CP}$=16.9 Hz), 152.7, 153.3 (2×), 157.4, 157.5, 160.8, 163.3 (d, $^2J_{CP}$=5.7 Hz). Anal. Calcd for $C_{24}H_{31}O_{10}P$: C, 56.47; H, 6.12. Found: C, 56.55; H, 6.17.

4.2.2. 3-Diethoxyphosphoryl-5,7-dimethoxy-4-(2-methoxyphenyl)-chroman-2-one (3b). Pale-pink solid (775 mg, 86% yield), mp 188–190 °C; IR (CCl_4): 1756, 1628, 1592, 1256, 1240, 1208, 1144, 1148, 1020 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=19.5; ^1H NMR ($CDCl_3$): δ=1.10 (t, 3H, $^3J_{HH}$=7.1 Hz, C*H*$_3$CH$_2$OP), 1.31 (t, 3H, $^3J_{HH}$=7.1 Hz, C*H*$_3$CH$_2$OP), 3.60 (dd, 1H, $^2J_{HP}$=25.7 Hz, $^3J_{HH}$=1.0 Hz, PC*H*), 3.70 (s, 3H, C*H*$_3$OAr), 3.81 (s, 3H, C*H*$_3$OAr), 3.83 (s, 3H, C*H*$_3$OAr), 3.68–4.02 (m, 2H, CH$_3$C*H*$_2$OP), 4.08–4.18 (m, 2H, CH$_3$C*H*$_2$OP), 5.11 (dd, 1H, $^3J_{HP}$=16.9 Hz, $^3J_{HH}$=1.0 Hz, ArC*H*Ar), 6.24 (d, 1H, $^4J_{HH}$=2.3 Hz, C*H*$_{Ar}$), 6.30 (d, 1H, $^4J_{HH}$=2.3 Hz, C*H*$_{Ar}$), 6.76–6.88 (m, 3H, 3×C*H*$_{Ar}$), 7.16–7.22 (m, 1H, C*H*$_{Ar}$); ^{13}C NMR ($CDCl_3$): δ=15.9 (d, $^3J_{CP}$=6.4 Hz), 16.0 (d, $^3J_{CP}$=6.1 Hz), 32.6 (d, $^2J_{CP}$=3.3 Hz), 45.8 (d, $^1J_{CP}$=123.4 Hz), 54.7, 55.3, 55.6, 62.9 (d, $^2J_{CP}$=6.3 Hz), 63.0 (d, $^2J_{CP}$=5.7 Hz), 93.3, 94.8, 102.8, 110.5, 120.3, 128.3, 128.5, 128.8 (d, $^3J_{CP}$=15.5 Hz), 153.3, 156.5, 157.7, 160.6, 163.6 (d, $^2J_{CP}$=5.0 Hz). Anal. Calcd for $C_{22}H_{27}O_8P$: C, 58.66; H, 6.04. Found: C, 58.55; H, 6.16.

4.2.3. 3-Diethoxyphosphoryl-5,7-dimethoxy-4-(4-methylphenyl)chroman-2-one (3c). Pale-yellow oil (756 mg, 87% yield); R_f 0.25 (33% hexane/ethyl acetate); IR (film): 1764, 1628, 1596, 1260, 1208, 1136, 1080 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.6; ^1H NMR ($CDCl_3$): δ=1.06 (dt, 3H, $^3J_{HH}$=7.1 Hz, $^4J_{HP}$=0.6 Hz, C*H*$_3$CH$_2$OP), 1.34 (dt, 3H, $^3J_{HH}$=7.1 Hz, $^4J_{HP}$=0.6 Hz, C*H*$_3$CH$_2$OP), 2.27 (s, 3H, C*H*$_3$Ar), 3.45 (dd, 1H, $^2J_{HP}$=25.1 Hz, $^3J_{HH}$=1.0 Hz, PC*H*), 3.67–3.79 (m, 1H, CH$_3$C*H*$_2$OP), 3.73 (s, 3H, C*H*$_3$OAr), 3.80 (s, 3H, C*H*$_3$OAr), 3.86–3.97 (m, 1H, CH$_3$C*H*$_2$OP), 4.10–4.18 (m, 2H, CH$_3$C*H*$_2$OP), 4.93 (dd, 1H, $^3J_{HP}$=15.6 Hz, $^3J_{HH}$=1.0 Hz, ArC*H*Ar), 6.25 (d, 1H, $^4J_{HH}$=2.2 Hz, C*H*$_{Ar}$), 6.31 (d, 1H, $^4J_{HH}$=2.2 Hz, C*H*$_{Ar}$), 6.97–7.15 (m, 4H, 4×C*H*$_{Ar}$); ^{13}C NMR ($CDCl_3$): δ=15.8 (d, $^3J_{CP}$=6.3 Hz), 15.9 (d, $^3J_{CP}$=6.4 Hz), 20.7, 35.8 (d, $^2J_{CP}$=3.6 Hz), 48.3 (d, $^1J_{CP}$=124.1 Hz), 55.3, 55.7, 62.9 (d, $^2J_{CP}$=8.1 Hz), 63.1 (d, $^2J_{CP}$=7.3 Hz), 93.4, 95.0, 103.9, 126.3 (2×), 129.4 (2×), 136.8, 138.5 (d, $^3J_{CP}$=16.7 Hz), 152.7, 157.4, 160.7, 163.2 (d, $^2J_{CP}$=5.7 Hz). Anal. Calcd for $C_{22}H_{27}O_7P$: C, 60.82; H, 6.26. Found: C, 60.75; H, 6.19.

4.2.4. 4-(1-Acetyl-1*H*-indol-3-yl)-3-diethoxyphosphoryl-5,7-dimethoxychroman-2-one (3d). Pink solid (943 mg, 94% yield), mp 165–166 °C; IR (CCl_4): 1764, 1712, 1632, 1556, 1448, 1352, 1256, 1212, 1140, 1096, 1048 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.1; ^1H NMR ($CDCl_3$): δ=1.08 (dt, 3H, $^3J_{HH}$=6.7 Hz, $^4J_{HP}$=0.4 Hz, C*H*$_3$CH$_2$OP), 1.35 (dt, 3H, $^3J_{HH}$=7.0 Hz, $^4J_{HP}$=0.5 Hz, C*H*$_3$CH$_2$OP), 2.47 (s, 3H, C*H*$_3$C═O), 3.66–3.94 (m, 1H, CH$_3$C*H*$_2$OP), 3.71 (dd, 1H, $^2J_{HP}$=25.0 Hz, $^3J_{HH}$=1.0 Hz, PC*H*), 3.74 (s, 3H, C*H*$_3$OAr), 3.85 (s, 3H, C*H*$_3$OAr), 3.88–4.02 (m, 1H, CH$_3$C*H*$_2$OP), 4.12–4.23 (m, 2H, CH$_3$C*H*$_2$OP), 5.24 (dd, 1H, $^3J_{HP}$=12.5 Hz, $^3J_{HH}$=1.0 Hz, ArC*H*Ar), 6.32 (d, 1H, $^4J_{HH}$=2.3 Hz, C*H*$_{Ar}$), 6.36 (d, 1H, $^4J_{HH}$=2.3 Hz, C*H*$_{Ar}$), 6.75 (s, 1H, C*H*$_{Ar}$), 7.32–7.43 (m, 3H, 3×C*H*$_{Ar}$), 7.68–7.75 (m, 1H, C*H*$_{Ar}$), 8.41 (d, 1H, $^3J_{HH}$=7.8 Hz, C*H*$_{Ar}$); ^{13}C NMR ($CDCl_3$): δ=15.8 (d, $^3J_{CP}$=5.8 Hz), 16.0 (d, $^3J_{CP}$=6.3 Hz), 23.7, 27.6, 46.2 (d, $^1J_{CP}$=125.0 Hz), 55.4, 55.7, 63.1 (d, $^2J_{CP}$=7.0 Hz), 63.2 (d, $^2J_{CP}$=6.6 Hz), 93.5, 95.1, 102.3, 116.7, 118.3, 121.9, 122.6 (d, $^3J_{CP}$=17.7 Hz), 123.6, 125.5, 128.0, 136.2, 152.8, 157.3, 160.9, 162.9 (d, $^2J_{CP}$=4.7 Hz), 168.1. Anal. Calcd for $C_{25}H_{28}NO_8P$: C, 59.88; H, 5.63; N, 2.79. Found: C, 59.99; H, 5.71; N, 2.88.

4.2.5. 3-Diethoxyphosphoryl-5,7-dimethoxy-4-(4-nitrophenyl)chroman-2-one (3e). Pale-yellow oil (828 mg, 89% yield); R_f 0.21 (33% hexane/ethyl acetate); IR (film): 1756, 1632, 1592, 1520, 1348, 1256, 1212, 1156, 1100, 1048, 1016 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=17.7; ^1H NMR ($CDCl_3$): δ=1.07 (t, 3H, $^3J_{HH}$=7.0 Hz, C*H*$_3$CH$_2$OP), 1.42 (t, 3H, $^3J_{HH}$=7.1 Hz, C*H*$_3$CH$_2$OP), 3.50 (dd, 1H, $^2J_{HP}$=25.4 Hz, $^3J_{HH}$=0.8 Hz, PC*H*), 3.67–3.79 (m, 1H, CH$_3$C*H*$_2$OP), 3.75 (s, 3H, C*H*$_3$OAr), 3.82 (s, 3H, C*H*$_3$OAr), 3.90–4.00 (m, 1H, CH$_3$C*H*$_2$OP), 4.11–4.22 (m, 2H, CH$_3$C*H*$_2$OP), 5.08 (dd, 1H, $^3J_{HH}$=17.5, 0.8 Hz, ArC*H*Ar), 6.29 (d, 1H, $^4J_{HH}$=2.3 Hz, C*H*$_{Ar}$), 6.35 (d, 1H, $^4J_{HH}$=2.3 Hz, C*H*$_{Ar}$), 7.31 (d, 2H, $^3J_{HH}$=8.8 Hz, 2×C*H*$_{Ar}$), 8.13 (d, 2H, $^3J_{HH}$=8.8 Hz, 2×C*H*$_{Ar}$); ^{13}C NMR ($CDCl_3$): δ=15.8 (d, $^3J_{CP}$=6.1 Hz), 15.9 (d, $^3J_{CP}$=6.2 Hz), 36.1 (d, $^2J_{CP}$=3.6 Hz), 47.4 (d, $^1J_{CP}$=125.9 Hz), 55.4, 55.7, 63.3 (d, $^2J_{CP}$=6.8 Hz), 63.4 (d, $^2J_{CP}$=6.5 Hz), 93.6, 95.1, 102.1, 124.0 (2×), 127.6 (2×), 146.9, 148.8 (d, $^3J_{CP}$=17.0 Hz), 152.7, 157.3, 161.3, 162.5 (d, $^2J_{CP}$=6.0 Hz). Anal. Calcd for $C_{21}H_{24}NO_9P$: C, 54.20; H, 5.20; N, 3.01. Found: C, 54.27; H, 5.29; N, 3.08.

4.2.6. 2-Diethoxyphosphoryl-1-(3,4,5-trimethoxyphenyl)-1,2-dihydrobenzo[*f*]chromen-3-one (3f). White solid (791 mg, 79% yield), mp 140–141 °C; R_f 0.20 (33% hexane/ethyl acetate); IR (CCl_4): 1760, 1488, 1440, 1260, 1216, 1152, 1052, 1020 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.1; ^1H NMR ($CDCl_3$): δ=0.78 (dt, 3H, $^3J_{HH}$=7.3 Hz, $^4J_{HH}$=0.5 Hz, C*H*$_3$CH$_2$OP), 1.32 (dt, 3H, $^3J_{HH}$=7.0 Hz, $^4J_{HH}$=0.8 Hz, C*H*$_3$CH$_2$OP), 3.37–3.44 (m, 1H, CH$_3$C*H*$_2$OP), 3.63–3.84 (m, 2H, CH$_3$C*H*$_2$OP, PC*H*), 3.74 (s, 6H, 2×C*H*$_3$OAr), 3.77 (s, 3H, C*H*$_3$OAr), 4.09–4.21 (m, 2H, CH$_3$C*H*$_2$OP), 5.34 (d, 1H, $^3J_{HP}$=15.3 Hz, ArC*H*Ar), 6.37 (s, 2H, 2×C*H*$_{Ar}$), 7.35 (d, 1H, $^3J_{HH}$=9.0 Hz, C*H*$_{Ar}$), 7.41–7.60 (m, 2H, 2×C*H*$_{Ar}$), 7.79–7.98 (m, 3H, 3×C*H*$_{Ar}$); ^{13}C NMR ($CDCl_3$): δ=15.6 (d, $^3J_{CP}$=6.1 Hz), 16.0 (d, $^3J_{CP}$=6.2 Hz), 39.6 (d, $^2J_{CP}$=3.5 Hz), 48.6 (d, $^1J_{CP}$=124.2 Hz), 55.9 (2×), 60.5, 63.0 (d, $^2J_{CP}$=7.1 Hz), 63.3 (d, $^2J_{CP}$=6.7 Hz), 103.6 (2×), 115.2, 116.6, 122.9, 125.3, 127.6, 128.6, 130.1, 130.7, 131.0, 136.2 (d, $^3J_{CP}$=16.5 Hz), 137.4, 149.4, 153.7 (2×), 162.9 (d, $^2J_{CP}$=6.0 Hz). Anal. Calcd for $C_{26}H_{29}O_8P$: C, 62.40; H, 5.84. Found: C, 62.55; H, 5.89.

4.2.7. 1-(1-Acetyl-1*H*-indol-3-yl)-2-diethoxyphosphoryl-1,2-dihydrobenzo[*f*]chromen-3-one (3g). Yellow solid (727 mg, 74% yield), mp 166–168 °C; R_f 0.40 (33% hexane/ethyl acetate); IR (CCl_4): 1768, 1712, 1448, 1380, 1240, 1216, 1152, 1024 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=17.9; ^1H NMR ($CDCl_3$): δ=0.82 (dt, 3H, $^3J_{HH}$=7.0 Hz, $^4J_{HP}$=0.4 Hz, C*H*$_3$CH$_2$OP), 1.31 (dt, 3H, $^3J_{HH}$=7.1 Hz, $^4J_{HP}$=0.5 Hz, C*H*$_3$CH$_2$OP), 2.34 (s, 3H, C*H*$_3$C═O), 3.45–3.61 (m, 1H, CH$_3$C*H*$_2$OP), 3.70–3.82 (m, 1H, CH$_3$C*H*$_2$OP), 3.89 (dd, 1H, $^2J_{HP}$=25.1 Hz, $^3J_{HH}$=0.8 Hz, PC*H*), 4.08–4.23 (m, 2H, CH$_3$C*H*$_2$OP), 5.68 (dd, 1H, $^3J_{HP}$=14.3 Hz, $^3J_{HH}$=0.8 Hz, ArC*H*Ar), 6.63 (s, 1H, C*H*$_{Ar}$), 7.37 (d, 1H, $^3J_{HH}$=8.9 Hz, C*H*$_{Ar}$), 7.41–7.51 (m, 4H, 4×C*H*$_{Ar}$), 7.76–7.91 (m, 3H, 3×C*H*$_{Ar}$), 7.93 (d, 1H, $^3J_{HH}$=8.9 Hz, C*H*$_{Ar}$), 8.40–8.46 (m, 1H, C*H*$_{Ar}$); ^{13}C NMR ($CDCl_3$): δ=15.6 (d, $^3J_{CP}$=6.2 Hz), 16.0 (d, $^3J_{CP}$=6.2 Hz), 23.6, 30.6 (d, $^2J_{CP}$=2.7 Hz), 46.2 (d, $^1J_{CP}$=124.1 Hz), 63.1 (d, $^2J_{CP}$=7.0 Hz), 63.5 (d, $^2J_{CP}$=6.7 Hz), 114.2, 116.9, 117.0, 118.1, 121.5 (d, $^3J_{CP}$=17.0 Hz),

122.8, 122.9, 124.0, 125.4, 125.9, 127.8 (2×), 128.6, 130.3, 130.5, 131.0, 136.3, 149.3, 162.7 (d, $^2J_{CP}$=5.3 Hz), 168.11. Anal. Calcd for $C_{27}H_{26}NO_6P$: C, 65.98; H, 5.33; N, 2.85. Found: C, 65.90; H, 5.21; N, 2.68.

4.2.8. 2-Diethoxyphosphoryl-1-(4-methoxyphenyl)-1,2-dihydrobenzo[*f*]chromen-3-one (3h). Yellow oil (758 mg, 86% yield); R_f 0.23 (33% hexane/ethyl acetate); IR (film): 1772, 1608, 1512, 1454, 1440, 1392, 1304, 1268, 1152, 1040 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.2; ^{1}H NMR ($CDCl_3$): δ=0.80 (t, 3H, $^3J_{HH}$=7.0 Hz, C*H*$_3$CH$_2$OP), 1.30 (t, 3H, $^3J_{HH}$=7.1 Hz, C*H*$_3$CH$_2$OP), 3.38–3.48 (m, 1H, CH$_3$C*H*$_2$OP), 3.64–3.81 (m, 1H, CH$_3$C*H*$_2$OP), 3.66 (dd, 1H, $^2J_{HP}$=25.0 Hz, $^3J_{HH}$=1.0 Hz, PC*H*), 3.73 (s, 3H, C*H*$_3$OAr), 4.06–4.20 (m, 2H, CH$_3$C*H*$_2$OP), 5.36 (dd, 1H, $^3J_{HP}$=14.8 Hz, $^3J_{HH}$=1.0 Hz, ArC*H*Ar), 6.79 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×C*H*$_{Ar}$), 7.07 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×C*H*$_{Ar}$), 7.33 (d, 1H, $^3J_{HH}$=8.5 Hz, C*H*$_{Ar}$), 7.40–7.51 (m, 2H, 2×C*H*$_{Ar}$), 7.80–7.91 (m, 3H, 3×C*H*$_{Ar}$); ^{13}C NMR ($CDCl_3$): δ=15.6 (d, $^3J_{CP}$=6.1 Hz), 16.0 (d, $^3J_{CP}$=6.2 Hz), 38.5 (d, $^2J_{CP}$=3.7 Hz), 48.8 (d, $^1J_{CP}$=127.2 Hz), 55.0, 63.0 (d, $^2J_{CP}$=7.0 Hz), 63.2 (d, $^2J_{CP}$=7.0 Hz), 114.6 (2×), 115.6, 116.8, 123.0, 125.2, 127.5, 127.8 (2×), 128.5, 129.9, 130.7, 131.0, 132.5 (d, $^3J_{CP}$=16.6 Hz), 149.3, 158.9, 163.0 (d, $^2J_{CP}$=5.7 Hz). Anal. Calcd for $C_{24}H_{25}O_6P$: C, 65.45; H, 5.72. Found: C, 65.58; H, 5.86.

4.2.9. 1-(4-Bromophenyl)-2-diethoxyphosphoryl-1,2-dihydrobenzo[*f*]chromen-3-one (3i). White solid (675 mg, 69% yield), mp 133–134 °C; R_f 0.35 (33% hexane/ethyl acetate); IR (CCl_4): 1768, 1592, 1232, 1152, 1128, 1048 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=17.8; ^{1}H NMR ($CDCl_3$): δ=0.80 (dt, 3H, $^3J_{HH}$=7.0 Hz, $^4J_{HP}$=0.4 Hz, C*H*$_3$CH$_2$OP), 1.30 (dt, 3H, $^3J_{HH}$=7.1 Hz, $^4J_{HP}$=0.5 Hz, C*H*$_3$CH$_2$OP), 3.36–3.51 (m, 1H, CH$_3$C*H*$_2$OP), 3.64 (dd, 1H, $^2J_{HP}$=25.2 Hz, $^3J_{HH}$=1.0 Hz, PC*H*), 3.66–3.80 (m, 1H, CH$_3$C*H*$_2$OP), 4.02–4.21 (m, 2H, CH$_3$C*H*$_2$OP), 5.37 (dd, 1H, $^3J_{HP}$=15.3 Hz, $^3J_{HH}$=1.0 Hz, ArC*H*Ar), 7.04 (d, 2H, $^3J_{HH}$=8.4 Hz, 2×C*H*$_{Ar}$), 7.24–7.54 (m, 5H, 5×C*H*$_{Ar}$), 7.77–7.87 (m, 3H, 3×C*H*$_{Ar}$); ^{13}C NMR ($CDCl_3$): δ=15.6 (d, $^3J_{CP}$=6.3 Hz), 16.0 (d, $^3J_{CP}$=6.1 Hz), 38.7 (d, $^2J_{CP}$=3.1 Hz), 48.3 (d, $^1J_{CP}$=123.9 Hz), 63.0 (d, $^2J_{CP}$=6.9 Hz), 63.4 (d, $^2J_{CP}$=6.7 Hz), 114.6, 116.8, 121.6, 123.1, 125.3, 128.0, 128.4 (2×), 127.7, 130.3, 130.5, 131.0, 132.3 (2×), 139.5 (d, $^3J_{CP}$=16.7 Hz), 149.5, 162.6 (d, $^2J_{CP}$=5.7 Hz). Anal. Calcd for $C_{23}H_{22}BrO_5P$: C, 56.46; H, 4.53. Found: C, 56.38; H, 4.42.

4.2.10. 2-Diethoxyphosphoryl-9-hydroxy-1-(3,4,5-trimethoxyphenyl)-1,2-dihydrobenzo[*f*]chromen-3-one (3j). White solid (971 mg, 94% yield), mp 228–230 °C; IR (CCl_4): 1764, 1512, 1328, 1240, 1216, 1192, 1152, 1124, 1024 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.8; ^{1}H NMR ($CDCl_3$): δ=0.76 (dt, 3H, $^3J_{HH}$=7.1 Hz, $^4J_{HH}$=0.5 Hz, C*H*$_3$CH$_2$OP), 1.35 (dt, 3H, $^3J_{HH}$=7.1 Hz, $^4J_{HH}$=0.6 Hz, C*H*$_3$CH$_2$OP), 3.29–3.45 (m, 1H, CH$_3$C*H*$_2$OP), 3.64–3.74 (m, 1H, CH$_3$C*H*$_2$OP), 3.66 (s, 6H, 2×C*H*$_3$OAr), 3.68 (dd, 1H, $^2J_{HP}$=25.3 Hz, $^3J_{HH}$=0.8 Hz, PC*H*), 3.76 (s, 3H, C*H*$_3$OAr), 4.13–4.25 (m, 2H, CH$_3$C*H*$_2$OP), 5.24 (dd, 1H, $^3J_{HP}$=17.5 Hz, $^3J_{HH}$=0.8 Hz, ArC*H*Ar), 6.36 (s, 2H, 2×C*H*$_{Ar}$), 7.04 (dd, 1H, $^3J_{HH}$=8.8 Hz, $^4J_{HH}$=2.3 Hz, C*H*$_{Ar}$), 7.16 (d, 1H, $^3J_{HH}$=8.8 Hz, C*H*$_{Ar}$), 7.22 (d, 1H, $^4J_{HH}$=2.3 Hz, C*H*$_{Ar}$), 7.71 (d, 1H, $^3J_{HH}$=8.9 Hz, C*H*$_{Ar}$), 7.78 (d, 1H, $^3J_{HH}$=8.9 Hz, C*H*$_{Ar}$); ^{13}C NMR ($CDCl_3$): δ=15.6 (d, $^3J_{CP}$=5.2 Hz), 16.0 (d, $^3J_{CP}$=6.3 Hz), 39.6, 48.5 (d, $^1J_{CP}$=124.5 Hz), 55.9 (2×), 60.6, 63.7 (d, $^2J_{CP}$=6.9 Hz), 64.0 (d, $^2J_{CP}$=6.3 Hz), 103.8 (2×), 105.6, 113.4, 113.5, 117.6, 126.0, 130.0, 130.2, 132.7, 136.4 (d, $^3J_{CP}$=17.0 Hz), 137.4, 149.8, 153.7 (2×), 156.5, 162.2 (d, $^2J_{CP}$=5.5 Hz). Anal. Calcd for $C_{26}H_{29}O_9P$: C, 60.46; H, 5.66. Found: C, 60.58; H, 5.74.

4.2.11. 2-Diethoxyphosphoryl-9-hydroxy-1-(4-methoxyphenyl)-1,2-dihydrobenzo[*f*]chromen-3-one (3k). Yellow oil (785 mg, 86% yield); R_f 0.24 (33% hexane/ethyl acetate); IR (film): 1764, 1512, 1216, 1152, 1024 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=19.4; ^{1}H NMR ($CDCl_3$): δ=0.77 (t, 3H, $^3J_{HH}$=7.5 Hz, C*H*$_3$CH$_2$OP), 1.31 (t, 3H, $^3J_{HH}$=7.3 Hz, C*H*$_3$CH$_2$OP), 3.26–3.42 (m, 1H, CH$_3$C*H*$_2$OP), 3.65 (dd, 1H, $^2J_{HP}$=25.1 Hz, $^3J_{HH}$=0.8 Hz, PC*H*), 3.62–3.76 (m, 1H, CH$_3$C*H*$_2$OP), 3.67 (s, 3H, C*H*$_3$OAr), 4.11–4.23 (m, 2H, CH$_3$C*H*$_2$OP), 5.16 (dd, 1H, $^3J_{HP}$=15.2 Hz, $^3J_{HH}$=0.8 Hz, ArC*H*Ar), 6.72 (d, 2H, $^3J_{HH}$=10.0 Hz, 2×C*H*$_{Ar}$), 7.02–7.06 (m, 3H, 3×C*H*$_{Ar}$), 7.14 (d, 1H, $^3J_{HH}$=10.0 Hz, C*H*$_{Ar}$), 7.20 (d, 1H, $^4J_{HH}$=2.5 Hz, C*H*$_{Ar}$), 7.68 (d, 1H, $^3J_{HH}$=7.5 Hz, C*H*$_{Ar}$), 7.76 (d, 1H, $^3J_{HH}$=7.5 Hz, C*H*$_{Ar}$); ^{13}C NMR ($CDCl_3$): δ=15.6 (d, $^3J_{CP}$=6.0 Hz), 16.0 (d, $^3J_{CP}$=6.2 Hz), 38.4 (d, $^2J_{CP}$=2.5 Hz), 48.3 (d, $^1J_{CP}$=124.1 Hz), 55.0, 63.5 (d, $^2J_{CP}$=7.6 Hz), 63.8 (d, $^2J_{CP}$=7.4 Hz), 105.5, 113.6, 113.9, 114.5 (2×), 117.6, 126.0, 127.8 (2×), 129.7, 130.2, 132.3 (d, $^3J_{CP}$=14.5 Hz), 132.5, 149.7, 156.4, 159.0, 163.0 (d, $^2J_{CP}$=6.0 Hz). Anal. Calcd for $C_{24}H_{25}O_7P$: C, 63.16; H, 5.52. Found: C, 63.08; H, 5.44.

4.2.12. 1-(4-Bromophenyl)-2-diethoxyphosphoryl-9-hydroxy-1,2-dihydrobenzo[*f*]chromen-3-one (3l). White solid (758 mg, 75% yield), mp 227–228 °C; IR (CCl_4): 1760, 1472, 1244, 1216, 1200, 1152, 1024 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=19.0; ^{1}H NMR ($CDCl_3$): δ=0.76 (t, 3H, $^3J_{HH}$=7.0 Hz, C*H*$_3$CH$_2$OP), 1.36 (t, 3H, $^3J_{HH}$=7.0 Hz, C*H*$_3$CH$_2$OP), 3.27–3.43 (m, 1H, CH$_3$C*H*$_2$OP), 3.61–3.75 (m, 1H, CH$_3$C*H*$_2$OP), 3.66 (d, $^2J_{HP}$=24.6 Hz, PC*H*), 4.11–4.26 (m, 2H, CH$_3$C*H*$_2$OP), 5.28 (d, 1H, $^2J_{HP}$=15.6 Hz, ArC*H*Ar), 6.97 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×C*H*$_{Ar}$), 7.02 (dd, 1H, $^3J_{HH}$=8.8 Hz, $^4J_{HH}$=2.1 Hz, C*H*$_{Ar}$), 7.14 (d, 1H, $^3J_{HH}$=8.8 Hz, C*H*$_{Ar}$), 7.17 (d, 1H, $^4J_{HH}$=2.1 Hz, C*H*$_{Ar}$), 7.28 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×C*H*$_{Ar}$), 7.68 (d, 1H $^3J_{HH}$=8.8 Hz, C*H*$_{Ar}$), 7.78 (d, 1H, $^3J_{HH}$=8.8 Hz, C*H*$_{Ar}$), 8.28 (s, 1H, O*H*); ^{13}C NMR ($CDCl_3$): δ=15.6 (d, $^3J_{CP}$=6.3 Hz), 16.0 (d, $^3J_{CP}$=6.7 Hz), 38.7 (d, $^2J_{CP}$=3.4 Hz), 48.2 (d, $^1J_{CP}$=123.9 Hz), 63.8 (d, $^2J_{CP}$=7.7 Hz), 64.1 (d, $^2J_{CP}$=6.8 Hz), 105.4, 113.0, 113.6, 117.8, 121.7, 126.0, 128.6 (2×), 130.2, 130.3, 132.4 (2×), 132.4, 139.4 (d, $^3J_{CP}$=17.0 Hz), 149.9, 156.6, 162.6 (d, $^2J_{CP}$=6.3 Hz). Anal. Calcd for $C_{23}H_{22}BrO_6P$: C, 54.67; H, 4.39. Found: C, 54.58; H, 4.42.

4.2.13. 2-Diethoxyphosphoryl-6-hydroxy-1-(4-methoxyphenyl)-1,2-dihydrobenzo[*f*]chromen-3-one (3m). Pale-yellow solid (822 mg, 90% yield), mp 123–125 °C; R_f 0.29 (33% hexane/ethyl acetate); IR (CCl_4): 1764, 1592, 1512, 1248, 1224, 1152, 1128, 1112, 1048, 1024 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.7; ^{1}H NMR ($CDCl_3$): δ=1.14 (t, 3H, $^3J_{HH}$=7.0 Hz, C*H*$_3$CH$_2$OP), 1.29 (t, 3H, $^3J_{HH}$=7.3 Hz, C*H*$_3$CH$_2$OP), 3.72 (dd, 1H, $^2J_{HP}$=24.8 Hz, $^3J_{HH}$=0.8 Hz, PC*H*), 3.72 (s, 3H, C*H*$_3$OAr), 3.80–3.96 (m, 1H, CH$_3$C*H*$_2$OP), 3.97–4.16 (m, 3H, CH$_3$C*H*$_2$OP), 5.21 (dd, 1H, $^3J_{HP}$=15.0 Hz, $^3J_{HH}$=0.8 Hz, ArC*H*Ar), 6.77 (s, 1H, C*H*$_{Ar}$), 6.77 (d, 2H, $^3J_{HH}$=8.7 Hz, 2×C*H*$_{Ar}$), 7.05 (d, 2H,

$^3J_{HH}$=8.7 Hz, 2×CH_{Ar}), 7.27–7.44 (m, 2H, 2×CH_{Ar}), 7.69 (d, 1H, $^3J_{HH}$=8.1 Hz, CH_{Ar}), 8.11 (d, 1H, $^3J_{HH}$=8.1 Hz, CH_{Ar}), 8.61 (s, 1H, O*H*); ^{13}C NMR ($CDCl_3$): δ=15.9 (d, $^3J_{CP}$=5.8 Hz), 16.1 (d, $^3J_{CP}$=5.8 Hz), 38.2, 49.4 (d, $^1J_{CP}$=124.7 Hz), 55.1, 63.8 (d, $^2J_{CP}$=6.6 Hz), 64.0 (d, $^2J_{CP}$=6.6 Hz), 99.3, 106.0, 114.6 (2×), 122.5, 123.1, 123.2, 124.0, 127.9 (2×), 131.4, 132.9 (d, $^3J_{CP}$=16.9 Hz), 149.7, 154.8, 158.9, 163.4 (d, $^2J_{CP}$=5.7 Hz). Anal. Calcd for $C_{24}H_{25}O_7P$: C, 63.16; H, 5.52. Found: C, 63.05; H, 5.46.

4.2.14. 1-(4-Bromophenyl)-2-diethoxyphosphoryl-6-hydroxy-1,2-dihydrobenzo[*f*]chromen-3-one (3n). Pink solid (960 mg, 95% yield), mp 167–168 °C; R_f 0.25 (33% hexane/ethyl acetate); IR (CCl_4): 1772, 1592, 1224, 1156, 1124, 1048, 1012 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.2; ^{1}H NMR ($CDCl_3$): δ=1.17 (t, 3H, $^3J_{HH}$=7.1 Hz, CH_3CH$_2$OP), 1.27 (t, 3H, $^3J_{HH}$=7.0 Hz, CH_3CH$_2$OP), 3.70 (dd, $^2J_{HP}$=24.8 Hz, $^3J_{HH}$=0.9 Hz, PC*H*), 3.85–4.19 (m, 4H, CH$_3$CH_2-OP), 5.20 (dd, 1H, $^2J_{HP}$=14.9 Hz, $^3J_{HH}$=0.9 Hz, ArC*H*Ar), 6.74 (s, 1H, CH_{Ar}), 7.01 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×CH_{Ar}), 7.25–7.43 (m, 2H, 2×CH_{Ar}), 7.36 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×CH_{Ar}), 7.62 (d, 1H, $^3J_{HH}$=8.3 Hz, CH_{Ar}), 8.09 (d, 1H, $^3J_{HH}$=8.3 Hz, CH_{Ar}), 8.61 (s, 1H, O*H*); ^{13}C NMR ($CDCl_3$): δ=15.9 (d, $^3J_{CP}$=5.7 Hz), 16.1 (d, $^3J_{CP}$=6.1 Hz), 38.4 (d, $^2J_{CP}$=3.1 Hz), 49.0 (d, $^1J_{CP}$=125.7 Hz), 64.0 (d, $^2J_{CP}$=6.6 Hz), 64.2 (d, $^2J_{CP}$=5.0 Hz), 99.3, 105.0, 121.7, 122.3, 123.2, 123.2, 124.2, 128.2, 128.6 (2×), 131.3, 132.4 (2×), 139.9 (d, $^3J_{CP}$=16.4 Hz), 149.8, 153.4, 163.2 (d, $^2J_{CP}$=5.7 Hz). Anal. Calcd for $C_{23}H_{22}BrO_6P$: C, 54.67; H, 4.39. Found: C, 54.70; H, 4.48.

4.2.15. 2-Diethoxyphosphoryl-4-(4-methoxyphenyl)-3,4-dihydrobenzo[*h*]chromen-2-one (3o). Red oil (802 mg, 91% yield); R_f 0.27 (33% hexane/ethyl acetate); IR (film): 1764, 1608, 1512, 1376, 1256, 1228, 1212, 1180, 1168, 1136, 1092, 1024 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.3; ^{1}H NMR ($CDCl_3$): δ=0.62 (dt, 3H, $^3J_{HH}$=7.1 Hz, $^4J_{HP}$=0.5 Hz, CH_3CH$_2$OP), 1.31 (dt, 3H, $^3J_{HH}$=7.0 Hz, $^4J_{HP}$=0.6 Hz, CH_3CH$_2$OP), 3.28–3.45 (m, 1H, CH$_3$CH_2OP), 3.63–3.78 (m, 1H, CH$_3$CH_2OP), 3.65 (dd, 1H, $^2J_{HP}$=24.8 Hz, $^3J_{HH}$=1.0 Hz, PC*H*), 3.74 (s, 3H, CH_3OAr), 4.06–4.22 (m, 2H, CH$_3$CH_2OP), 4.88 (dd, 1H, $^3J_{HP}$=14.9 Hz, $^3J_{HH}$=1.0 Hz, ArC*H*Ar), 6.79 (d, 2H, $^3J_{HH}$=8.8 Hz, 2×CH_{Ar}), 7.04 (d, 2H, $^3J_{HH}$=8.8 Hz, 2×CH_{Ar}), 7.31 (d, 1H, $^3J_{HH}$=8.4 Hz, CH_{Ar}), 7.51–7.63 (m, 2H, 2×CH_{Ar}), 7.64 (d, 1H, $^3J_{HH}$=8.4 Hz, CH_{Ar}), 7.82–7.86 (m, 1H, CH_{Ar}), 8.30–8.33 (m, 1H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=15.4 (d, $^3J_{CP}$=6.3 Hz), 16.0 (d, $^3J_{CP}$=6.1 Hz), 41.9 (d, $^2J_{CP}$=3.1 Hz), 48.5 (d, $^1J_{CP}$=123.5 Hz), 55.0, 62.9 (d, $^2J_{CP}$=7.0 Hz), 63.2 (d, $^2J_{CP}$=6.6 Hz), 114.4 (2×), 117.4, 121.0, 123.3, 124.6, 125.7, 126.6, 126.7, 127.5, 127.8 (2×), 133.1 (d, $^3J_{CP}$=16.9 Hz), 133.6, 146.4, 158.9, 163.1 (d, $^2J_{CP}$=6.1 Hz). Anal. Calcd for $C_{24}H_{25}O_6P$: C, 65.45; H, 5.72. Found: C, 65.29; H, 5.66.

4.2.16. 4-(4-Bromophenyl)-2-diethoxyphosphoryl-3,4-dihydrobenzo[*h*]chromen-2-one (3p). Red oil (646 mg, 66% yield); R_f 0.32 (33% hexane/ethyl acetate); IR (film): 1764, 1256, 1216, 1136, 1088, 1024 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.2; ^{1}H NMR ($CDCl_3$): δ=0.61 (dt, 3H, $^3J_{HH}$=7.1 Hz, $^4J_{HP}$=0.6 Hz, CH_3CH$_2$OP), 1.32 (dt, 3H, $^3J_{HH}$=7.1 Hz, $^4J_{HP}$=0.6 Hz, CH_3CH$_2$OP), 3.28–3.45 (m, 1H, CH$_3$CH_2OP), 3.62–3.78 (m, 1H, CH$_3$CH_2OP), 3.63 (dd, 1H, $^2J_{HP}$=24.9 Hz, $^3J_{HH}$=1.1 Hz, PC*H*), 4.06–4.21 (m, 2H, CH$_3$CH_2OP), 4.88 (dd, 1H, $^3J_{HP}$=15.1 Hz, $^3J_{HH}$=1.1 Hz, ArC*H*Ar), 7.00 (d, 2H, $^3J_{HH}$=8.6 Hz, 2×CH_{Ar}), 7.28 (d, 1H, $^3J_{HH}$=8.4 Hz, CH_{Ar}), 7.40 (d, 2H, $^3J_{HH}$=8.6 Hz, 2×CH_{Ar}), 7.55–7.61 (m, 2H, 2×CH_{Ar}), 7.65 (d, 1H, $^3J_{HH}$=8.4 Hz, CH_{Ar}), 7.82–7.86 (m, 1H, CH_{Ar}), 8.29–8.34 (m, 1H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=15.4 (d, $^3J_{CP}$=6.3 Hz), 16.0 (d, $^3J_{CP}$=6.1 Hz), 42.2 (d, $^2J_{CP}$=2.9 Hz), 48.1 (d, $^1J_{CP}$=124.4 Hz), 63.0 (d, $^2J_{CP}$=7.0 Hz), 63.4 (d, $^2J_{CP}$=6.6 Hz), 116.4, 121.0, 121.7, 123.3, 124.8, 125.5, 126.8, 127.0, 127.5, 128.6 (2×), 132.3 (2×), 133.8, 140.1 (d, $^3J_{CP}$=16.9 Hz), 146.6, 162.8 (d, $^2J_{CP}$=6.2 Hz). Anal. Calcd for $C_{23}H_{22}BrO_5P$: C, 56.46; H, 4.53. Found: C, 56.60; H, 4.61.

4.2.17. 3-Diethoxyphosphoryl-7-methoxy-4-(4-methoxyphenyl)chroman-2-one (3q). Yellow oil (656 mg, 78% yield); R_f 0.23 (33% hexane/ethyl acetate); IR (film): 1768, 1624, 1588, 1508, 1440, 1320, 1256, 1156, 1032 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.4; ^{1}H NMR ($CDCl_3$): δ=1.00 (dt, 3H, $^3J_{HH}$=7.0 Hz, $^4J_{HP}$=0.4 Hz, CH_3CH$_2$OP), 1.33 (dt, 3H, $^3J_{HH}$=7.0 Hz, $^4J_{HP}$=0.4 Hz, CH_3CH$_2$OP), 3.53–3.68 (m, 1H, CH$_3$CH_2OP), 3.55 (dd, 1H, $^2J_{HP}$=25.0 Hz, $^3J_{HH}$=0.8 Hz, PC*H*), 3.74 (s, 3H, CH_3OAr), 3.78–3.93 (m, 1H, CH$_3$CH_2OP), 3.81 (s, 3H, CH_3OAr), 4.08–4.20 (m, 2H, CH$_3$CH_2OP), 4.70 (dd, 1H, $^3J_{HP}$=14.5 Hz, $^3J_{HH}$=0.8 Hz, ArC*H*Ar), 6.70 (d, 1H, $^4J_{HH}$=2.5 Hz, CH_{Ar}), 6.71 (dd, 1H, $^4J_{HH}$=2.5 Hz, $^3J_{HH}$=8.7 Hz, CH_{Ar}), 6.79 (d, 2H, $^3J_{HH}$=8.6 Hz, 2×CH_{Ar}), 6.98 (d, 2H, $^3J_{HH}$=8.6 Hz, 2×CH_{Ar}), 7.15 (d, $^3J_{HH}$=8.7 Hz, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=15.9 (d, $^3J_{CP}$=6.2 Hz), 16.1 (d, $^3J_{CP}$=6.1 Hz), 41.0 (d, $^2J_{CP}$=3.3 Hz), 48.7 (d, $^1J_{CP}$=123.9 Hz), 55.2, 55.5, 63.1 (d, $^2J_{CP}$=7.2 Hz), 63.2 (d, $^2J_{CP}$=6.3 Hz), 102.1, 111.2, 114.4 (2×), 114.7, 127.6 (2×), 129.6, 133.9 (d, $^3J_{CP}$=17.0 Hz), 152.3, 158.8, 160.2, 163.2 (d, $^2J_{CP}$=5.7 Hz). Anal. Calcd for $C_{21}H_{25}O_7P$: C, 60.00; H, 5.99. Found: C, 60.09; H, 6.04.

4.2.18. 4-(4-Bromophenyl)-3-diethoxyphosphoryl-7-methoxychroman-2-one (3r). Yellow oil (497 mg, 53% yield); R_f 0.27 (33% hexane/ethyl acetate); IR (film): 1764, 1628, 1508, 1260, 1144, 1120, 1104, 1012 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.0; ^{1}H NMR ($CDCl_3$): δ=1.00 (t, 3H, $^3J_{HH}$=7.1 Hz, CH_3CH$_2$OP), 1.33 (t, 3H, $^3J_{HH}$=6.8 Hz, CH_3CH$_2$OP), 3.53 (dd, 1H, $^2J_{HP}$=25.1 Hz, $^3J_{HH}$=1.0 Hz, PC*H*), 3.54–3.74 (m, 1H, CH$_3$CH_2OP), 3.82 (s, 3H, CH_3OAr), 3.83–3.86 (m, 1H, CH$_3$CH_2OP), 4.09–4.21 (m, 2H, CH$_3$CH_2OP), 4.71 (dd, 1H, $^3J_{HH}$=14.7, 1.0 Hz, ArC*H*Ar), 6.70 (d, 1H, $^4J_{HH}$=2.5 Hz, CH_{Ar}), 6.72 (dd, 1H, $^3J_{HH}$=8.1 Hz, $^4J_{HH}$=2.5 Hz, CH_{Ar}), 6.95 (d, 2H, $^3J_{HH}$=8.4 Hz, 2×CH_{Ar}), 7.13 (d, 1H, $^3J_{HH}$=8.1 Hz, CH_{Ar}), 7.40 (d, 2H, $^3J_{HH}$=8.4 Hz, 2×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=15.5 (d, $^3J_{CP}$=5.9 Hz), 15.7 (d, $^3J_{CP}$=6.1 Hz), 40.8, 47.8 (d, $^1J_{CP}$=124.2 Hz), 55.1, 62.8 (d, $^2J_{CP}$=9.2 Hz), 62.9 (d, $^2J_{CP}$=7.3 Hz), 101.8, 111.0, 113.3, 121.0, 128.0 (2×), 129.2, 131.8 (2×), 140.5 (d, $^3J_{CP}$=17.0 Hz), 152.0, 160.0, 162.3 (d, $^2J_{CP}$=5.7 Hz). Anal. Calcd for $C_{20}H_{22}BrO_6P$: C, 51.19; H, 4.73. Found: C, 51.16; H, 4.68.

4.2.19. 3-Diethoxyphosphoryl-6-methoxy-4-(3,4,5-trimethoxyphenyl)chroman-2-one (3s). Red oil (903 mg, 94% yield); R_f 0.10 (33% hexane/ethyl acetate); IR (CCl_4): 1760, 1588, 1456, 1328, 1260, 1040 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.2; ^{1}H NMR ($CDCl_3$): δ=0.98 (t, 3H, $^3J_{HH}$=7.5 Hz, CH_3CH$_2$OP), 1.35 (t, 3H, $^3J_{HH}$=7.2 Hz, CH_3CH$_2$OP), 3.51–3.70 (m, 1H, CH$_3$CH_2OP), 3.56 (dd, 1H, $^2J_{HP}$=24.0 Hz,

$^3J_{HH}$=1.2 Hz, PC*H*), 3.74–3.89 (m, 1H, CH_3CH_2OP), 3.77 (s, 6H, 2×CH_3OAr), 3.78 (s, 3H, CH_3OAr), 3.79 (s, 3H, CH_3OAr), 4.08–4.25 (m, 2H, CH_3CH_2OP), 4.68 (dd, 1H, $^3J_{HP}$=14.8 Hz, $^3J_{HH}$=1.2 Hz, ArC*H*Ar), 6.29 (s, 2H, 2×CH_{Ar}), 6.78 (d, 1H, $^4J_{HH}$=3.0 Hz, CH_{Ar}), 6.88 (dd, 1H, $^4J_{HH}$=3.0 Hz, $^3J_{HH}$=9.0 Hz, CH_{Ar}), 7.09 (d, 1H, $^3J_{HH}$=9.0 Hz, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=15.8 (d, $^3J_{CP}$=6.1 Hz), 16.0 (d, $^3J_{CP}$=6.3 Hz), 43.0 (d, $^2J_{CP}$=3.4 Hz), 48.2 (d, $^1J_{CP}$=123.7 Hz), 55.5, 56.0 (2×), 60.6, 63.0 (d, $^2J_{CP}$=7.0 Hz), 63.3 (d, $^2J_{CP}$=7.4 Hz), 103.6 (2×), 113.2, 114.9, 117.5, 123.0, 137.0 (d, $^3J_{CP}$=17.3 Hz), 137.3, 145.3, 153.6 (2×), 156.6, 163.2 (d, $^2J_{CP}$=5.7 Hz). Anal. Calcd for $C_{23}H_{29}O_9P$: C, 57.50; H, 6.08. Found: C, 57.39; H, 6.02.

4.2.20. 7-Diethoxyphosphoryl-8-(4-methoxyphenyl)-7,8-dihydro-[1,3]dioxolo[4,5-*g*]chromen-6-one (3t). Yellow oil (617 mg, 71% yield); R_f 0.25 (33% hexane/ethyl acetate); IR (film): 1756, 1608, 1444, 1392, 1024 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=18.3; ^{1}H NMR ($CDCl_3$): δ=1.08 (d, 3H, $^3J_{HH}$=7.1 Hz, CH_3CH_2OP), 1.34 (d, 3H, $^3J_{HH}$=7.1 Hz, CH_3CH_2OP), 3.51 (dd, 1H, $^2J_{HP}$=25.0 Hz, $^3J_{HH}$=1.0 Hz, PC*H*), 3.66–3.83 (m, 1H, CH_3CH_2OP), 3.75 (s, 3H, CH_3OAr), 3.80–4.02 (m, 1H, CH_3CH_2OP), 4.08–4.24 (m, 2H, CH_3CH_2OP), 4.61 (dd, 1H, $^3J_{HP}$=14.6 Hz, $^3J_{HH}$=1.0 Hz, ArC*H*Ar), 5.95 (d, 1H, $^2J_{HH}$=1.2 Hz, CH_2O_2), 5.97 (d, 1H, $^2J_{HH}$=1.2 Hz, CH_2O_2), 6.66 (s, 2H, 2×CH_{Ar}), 6.81 (d, 2H, $^3J_{HH}$=8.8 Hz, 2×CH_{Ar}), 7.00 (d, 2H, $^3J_{HH}$=8.8 Hz, 2×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=15.6 (d, $^3J_{CP}$=5.8 Hz), 15.7 (d, $^3J_{CP}$=6.2 Hz), 41.3, 47.9 (d, $^1J_{CP}$=123.6 Hz), 54.7, 62.8 (d, $^2J_{CP}$=6.2 Hz), 62.9 (d, $^2J_{CP}$=5.8 Hz), 98.2, 101.4, 107.3, 114.1 (2×), 114.5, 127.3 (2×), 133.1 (d, $^3J_{CP}$=16.9 Hz), 144.3, 145.6, 147.4, 158.6, 162.7 (d, $^2J_{CP}$=5.7 Hz). Anal. Calcd for $C_{21}H_{23}O_8P$: C, 58.07; H, 5.34. Found: C, 58.19; H, 5.41.

4.2.21. 8-(4-Bromophenyl)-7-diethoxyphosphoryl-7,8-dihydro-[1,3]dioxolo[4,5-*g*]chromen-6-one (3u). Pale-pink solid (706 mg, 73% yield), mp 188–190 °C; R_f 0.32 (33% hexane/ethyl acetate); IR (CCl_4): 1760, 1640, 1480, 1444, 1392, 1048 cm^{-1}; ^{31}P NMR ($CDCl_3$): δ=17.9; ^{1}H NMR ($CDCl_3$): δ=1.11 (dt, 3H, $^3J_{HH}$=7.0 Hz, $^4J_{HP}$=0.4 Hz, CH_3CH_2OP), 1.38 (dt, 3H, $^3J_{HH}$=7.0 Hz, $^4J_{HP}$=0.6 Hz, CH_3CH_2OP), 3.52 (dd, 1H, $^2J_{HP}$=25.1 Hz, $^3J_{HH}$=1.2 Hz, PC*H*), 3.66–3.85 (m, 1H, CH_3CH_2OP), 3.89–4.04 (m, 1H, CH_3CH_2OP), 4.12–4.27 (m, 2H, CH_3CH_2OP), 4.65 (dd, 1H, $^3J_{HP}$=14.8 Hz, $^3J_{HH}$=1.2 Hz, ArC*H*Ar), 6.00 (d, 1H, $^2J_{HH}$=1.3 Hz, CH_2O_2), 6.02 (d, 1H, $^2J_{HH}$=1.3 Hz, CH_2O_2), 6.67 (s, 1H, CH_{Ar}), 6.70 (s, 1H, CH_{Ar}), 6.99 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×CH_{Ar}), 7.45 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=15.0 (d, $^3J_{CP}$=6.8 Hz), 16.1 (d, $^3J_{CP}$=6.5 Hz), 41.8 (d, $^2J_{CP}$=3.5 Hz), 45.4 (d, $^1J_{CP}$=124.7 Hz), 63.2 (d, $^2J_{CP}$=7.5 Hz), 63.4 (d, $^2J_{CP}$=6.9 Hz), 98.8, 101.8, 107.6, 113.8, 121.6, 128.3 (2×), 132.2 (2×), 140.3 (d, $^3J_{CP}$=17.0 Hz), 144.8, 146.0, 148.0, 162.7 (d, $^2J_{CP}$=5.7 Hz). Anal. Calcd for $C_{20}H_{20}BrO_7P$: C, 49.71; H, 4.17. Found: C, 49.65; H, 4.10.

4.3. General procedure for the preparation of 4-aryl-3-methylene-3,4-dihydrocoumarins 4a–u

To a stirred solution of the corresponding α-diethoxyphosphoryl-δ-valerolactone **3** (1 mmol) in THF (10 mL) potassium *tert*-butoxide (134 mg, 1.2 mmol) was added and the resulting mixture was stirred at room temperature for 30 min. Then paraformaldehyde (150 mg, 5 mmol) was added in one portion. After 1 h the reaction mixture was quenched with brine (10 mL), THF was removed under reduced pressure and the water layer was extracted with CH_2Cl_2 (2×10 mL). The organic layer was dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography (eluent: ethyl acetate/hexane 3:1) or recrystallized from diethyl ether.

4.3.1. 5,7-Dimethoxy-3-methylene-4-(3,4,5-trimethoxyphenyl)chroman-2-one (4a). White solid (278 mg, 72% yield), mp 134–135 °C; R_f 0.64 (25% hexane/ethyl acetate); IR (CCl_4): 1752, 1624, 1592, 1464, 1420, 1128, 1104 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=3.77 (s, 6H, 2×CH_3OAr), 3.79 (s, 3H, CH_3OAr), 3.80 (s, 3H, CH_3OAr), 3.82 (s, 3H, CH_3OAr), 5.04 (s, 1H, ArC*H*Ar), 5.86 (s, 1H, H_2C=C), 6.30 (d, 1H, $^4J_{HH}$=2.3 Hz, CH_{Ar}), 6.32 (d, 1H, $^4J_{HH}$=2.3 Hz, CH_{Ar}), 6.34 (s, 2H, 2×CH_{Ar}), 6.35 (s, 1H, H_2C=C); ^{13}C NMR ($CDCl_3$): δ=42.3, 55.4, 55.7, 55.9 (2×), 60.6, 93.3, 98.0, 103.7 (2×), 105.8, 128.1, 136.5, 136.8, 136.9, 151.8, 153.2 (2×), 157.2, 160.7, 163.2. Anal. Calcd for $C_{21}H_{22}O_7$: C, 65.28; H, 5.74. Found: C, 65.39; H, 5.79.

4.3.2. 5,7-Dimethoxy-4-(2-methoxyphenyl)-3-methylenechroman-2-one (4b). White solid (238 mg, 73% yield), mp 144–146 °C; R_f 0.75 (25% hexane/ethyl acetate); IR (CCl_4): 1748, 1624, 1592, 1456, 1200, 1144, 1092, 1032 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=3.69 (s, 3H, CH_3OAr), 3.77 (s, 3H, CH_3OAr), 3.79 (s, 3H, CH_3OAr), 5.21 (s, 1H, ArC*H*Ar), 5.84 (s, 1H, H_2C=C), 6.19 (d, 1H, $^4J_{HH}$=2.3 Hz, CH_{Ar}), 6.29 (d, 1H, $^4J_{HH}$=2.3 Hz, CH_{Ar}), 6.34 (s, 1H, H_2C=C), 6.79–6.87 (m, 2H, 2×CH_{Ar}), 7.10–7.21 (m, 2H, 2×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=39.2, 54.6, 55.3, 55.5, 93.4, 93.7, 104.5, 110.9, 120.2, 128.1, 128.5, 128.9, 130.8, 135.7, 152.0, 156.5, 157.6, 160.3, 163.1. Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.56. Found: C, 69.80; H, 5.49.

4.3.3. 5,7-Dimethoxy-3-methylene-4-(4-methylphenyl)-chroman-2-one (4c). Yellow solid (196 mg, 63% yield), mp 117–118 °C; R_f 0.82 (25% hexane/ethyl acetate); IR (CCl_4): 1740, 1628, 1596, 1464, 1424, 1292, 1200, 1120, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=2.27 (s, 3H, CH_3Ar), 3.76 (s, 3H, CH_3OAr), 3.80 (s, 3H, CH_3OAr), 5.07 (s, 1H, ArC*H*Ar), 5.85 (s, 1H, H_2C=C), 6.27 (d, 1H, $^4J_{HH}$=2.3 Hz, CH_{Ar}), 6.29 (d, 1H, $^4J_{HH}$=2.3 Hz, CH_{Ar}), 6.34 (s, 1H, H_2C=C), 6.98–7.07 (m, 4H, 4×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=20.8, 41.9, 55.3, 55.6, 94.2, 95.3, 105.9, 126.7 (2×), 128.0, 129.6 (2×), 136.5, 136.8, 138.2, 151.7, 157.2, 160.6, 163.2. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.70; H, 5.97.

4.3.4. 4-(1-Acetyl-1*H*-indol-3-yl)-5,7-dimethoxy-3-methylenechroman-2-one (4d). Yellow oil (238 mg, 63% yield); R_f 0.73 (25% hexane/ethyl acetate); IR (film): 1716, 1620, 1608, 1596, 1504, 1448, 1380, 1344, 1328, 1216, 1140, 1104 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=2.53 (s, 3H, CH_3C=O), 3.80 (s, 3H, CH_3OAr), 3.86 (s, 3H, CH_3OAr), 5.38 (s, 1H, ArC*H*Ar), 6.04 (s, 1H, H_2C=C), 6.32–6.41 (m, 3H, 3×CH_{Ar}), 6.89 (s, 1H, H_2C=C), 7.30–7.43 (m, 2H, 2×CH_{Ar}), 7.66–7.70 (m, 1H, CH_{Ar}), 8.45 (d, 1H, $^3J_{HH}$=7.8 Hz, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=23.8, 34.0, 55.4, 55.7, 94.1, 95.2, 104.9, 116.7, 118.9, 122.2, 122.3, 123.5, 125.3, 128.0, 128.6, 135.3, 136.3, 151.9, 156.9, 160.8, 163.2, 168.4.

Anal. Calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71. Found: C, 69.89; H, 4.97; N, 3.63.

4.3.5. 5,7-Dimethoxy-3-methylene-4-(4-nitrophenyl)-chroman-2-one (4e). Pale-yellow oil (239 mg, 70% yield); R_f 0.65 (25% hexane/ethyl acetate); IR (film): 1760, 1624, 1592, 1528, 1344, 1144, 1104 cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.77 (s, 3H, CH_3OAr), 3.82 (s, 3H, CH_3OAr), 5.20 (s, 1H, ArCHAr), 5.94 (s, 1H, H_2C=C), 6.29 (d, 1H, $^4J_{HH}$=2.3 Hz, CH_{Ar}), 6.34 (d, 1H, $^4J_{HH}$=2.3 Hz, CH_{Ar}), 6.47 (s, 1H, H_2C=C), 7.30 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×CH_{Ar}), 8.12 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=42.0, 55.4, 55.7, 94.1, 95.2, 104.1, 123.9 (2×), 127.6 (2×), 130.1, 135.1, 146.8, 148.8, 151.7, 157.1, 161.2, 161.4. Anal. Calcd for $C_{18}H_{15}NO_6$: C, 63.34; H, 4.43; N, 4.10. Found: C, 63.46; H, 4.47; N, 4.23.

4.3.6. 2-Methylene-1-(3,4,5-trimethoxyphenyl)-1,2-dihydrobenzo[*f*]chromen-3-one (4f). White solid (275 mg, 73% yield), mp 125–126 °C; IR (CCl_4): 1736, 1584, 1508, 1216, 1132 cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.70 (s, 6H, 2×CH_3OAr), 3.77 (s, 3H, CH_3OAr), 5.45 (s, 1H, ArCHAr), 6.00 (s, 1H, H_2C=C), 6.34 (s, 2H, 2×CH_{Ar}), 6.43 (s, 1H, H_2C=C), 7.35 (d, 1H, $^3J_{HH}$=9.0 Hz, CH_{Ar}), 7.43–7.56 (m, 2H, 2×CH_{Ar}), 7.85–7.89 (m, 3H, 3×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=45.4, 55.9 (2×), 60.6, 103.8 (2×), 117.2, 117.3, 122.8, 125.2, 127.4, 128.5, 128.7, 130.0, 130.7, 131.0, 135.8, 136.6, 137.3, 148.4, 153.6 (2×), 162.8. Anal. Calcd for $C_{21}H_{16}O_3$: C, 73.39; H, 5.36. Found: C, 73.34; H, 5.22.

4.3.7. 1-(1-Acetyl-1*H*-indol-3-yl)-2-methylene-1,2-dihydrobenzo[*f*]chromen-3-one (4g). Yellow oil (195 mg, 53% yield); IR (film): 1708, 1448, 1380, 1328, 1216, 1124 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.35 (s, 3H, CH_3C=O), 5.77 (s, 1H, ArCHAr), 6.16 (s, 1H, H_2C=C), 6.43 (s, 1H, H_2C=C), 6.71 (s, 1H, CH_{Ar}), 7.35–7.50 (m, 5H, 5×CH_{Ar}), 7.74–7.80 (m, 2H, 2×CH_{Ar}), 7.87–7.92 (m, 2H, 2×CH_{Ar}), 8.40–8.44 (m, 1H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=23.8, 36.7, 116.8, 117.0, 117.4, 118.4, 121.1, 122.6, 122.8, 123.8, 125.5, 125.7, 127.6, 128.2, 128.6, 128.8, 130.2, 130.2, 131.1, 135.0, 137.0, 148.5, 162.7, 168.2. Anal. Calcd for $C_{24}H_{17}NO_3$: C, 78.46; H, 4.66; N, 3.81. Found: C, 78.33; H, 4.57; N, 3.70.

4.3.8. 1-(4-Methoxyphenyl)-2-methylene-1,2-dihydrobenzo[*f*]chromen-3-one (4h). Yellow oil (250 mg, 79% yield); R_f 0.85 (25% hexane/ethyl acetate); IR (film): 1760, 1512, 1256, 1220, 1124 cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.72 (s, 3H, CH_3OAr), 5.49 (s, 1H, ArCHAr), 5.98 (s, 1H, H_2C=C), 6.40 (s, 1H, H_2C=C), 6.89 (d, 2H, $^3J_{HH}$=8.7 Hz, 2×CH_{Ar}), 7.03 (d, 2H, $^3J_{HH}$=8.7 Hz, 2×CH_{Ar}), 7.33 (d, 1H, $^3J_{HH}$=8.9 Hz, CH_{Ar}), 7.44–7.52 (m, 2H, 2×CH_{Ar}), 7.80–7.88 (m, 3H, 3×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=44.3, 54.9, 114.3 (2×), 117.2, 117.5, 122.8, 125.1, 127.3, 127.7 (2×), 128.2, 128.6, 129.6, 130.6, 130.9, 132.1, 136.8, 148.2, 158.6, 162.8. Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.60; H, 5.01.

4.3.9. 1-(4-Bromophenyl)-2-methylene-1,2-dihydrobenzo[*f*]chromen-3-one (4i). Pale-yellow solid (267 mg, 73% yield), mp 112–114 °C; R_f 0.86 (25% hexane/ethyl acetate); IR (CCl_4): 1740, 1220, 1132 cm^{-1}; ^1H NMR ($CDCl_3$): δ=5.49 (s, 1H, ArCHAr), 6.03 (s, 1H, H_2C=C), 6.46 (s, 1H, H_2C=C), 7.00 (d, 2H, $^3J_{HH}$=7.5 Hz, 2×CH_{Ar}), 7.32–7.40 (m, 3H, 3×CH_{Ar}), 7.42–7.54 (m, 2H, 2×CH_{Ar}), 7.73–7.79 (m, 1H, CH_{Ar}), 7.88 (d, 2H, $^3J_{HH}$=7.5 Hz, 2×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=44.5, 116.5, 117.3, 121.3, 122.5, 125.3, 127.5, 128.4 (2×), 128.7, 129.2, 130.1, 130.4, 130.9, 132.0 (2×), 136.0, 139.2, 148.4, 162.3. Anal. Calcd for $C_{20}H_{13}BrO_2$: C, 65.77; H, 3.59. Found: C, 65.89; H, 3.67.

4.3.10. 9-Hydroxy-2-methylene-1-(3,4,5-trimethoxyphenyl)-1,2-dihydrobenzo[*f*]chromen-3-one (4j). White solid (333 mg, 85% yield), mp 170–172 °C; IR (CCl_4): 1728, 1228, 1128 cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.69 (s, 6H, 2×CH_3OAr), 3.78 (s, 3H, CH_3OAr), 5.29 (s, 1H, ArCHAr), 6.98 (s, 1H, H_2C=C), 6.32 (s, 2H, 2×CH_{Ar}), 6.40 (s, 1H, H_2C=C), 7.06 (dd, 1H, $^4J_{HH}$=2.5 Hz, $^3J_{HH}$=8.8 Hz, CH_{Ar}), 7.13 (d, 1H, $^4J_{HH}$=2.5 Hz, CH_{Ar}), 7.19 (d, 1H, $^3J_{HH}$=8.8 Hz, CH_{Ar}), 7.76 (d, 1H, $^3J_{HH}$=3.6 Hz, CH_{Ar}), 7.80 (d, 1H, $^3J_{HH}$=3.6 Hz, CH_{Ar}); ^{13}C NMR (acetone-*d*): δ=45.9, 56.4 (2×), 60.4, 105.2 (2×), 106.3, 114.8, 116.8, 118.4, 126.9, 128.9, 130.7, 131.4, 133.6, 137.8, 138.3, 138.6, 150.1, 154.8 (2×), 157.6, 163.2. Anal. Calcd for $C_{23}H_{20}O_6$: C, 70.40; H, 5.14. Found: C, 70.53; H, 5.24.

4.3.11. 9-Hydroxy-1-(4-methoxyphenyl)-2-methylene-1,2-dihydrobenzo[*f*]chromen-3-one (4k). Pale-yellow oil (286 mg, 86% yield); R_f 0.73 (25% hexane/ethyl acetate); IR (film): 1760, 1648, 1500, 1448, 1256, 1036 cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.72 (s, 3H, CH_3OAr), 5.31 (s, 1H, ArCHAr), 5.94 (s, 1H, H_2C=C), 6.37 (s, 1H, H_2C=C), 6.75 (d, 2H, $^3J_{HH}$=8.8 Hz, 2×CH_{Ar}), 7.00–7.15 (m, 4H, 4×CH_{Ar}), 7.17 (d, 1H, $^3J_{HH}$=8.9 Hz, CH_{Ar}), 7.74 (d, 1H, $^3J_{HH}$=3.0 Hz, CH_{Ar}), 7.77 (d, 1H, $^3J_{HH}$=3.0 Hz, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=44.4, 55.0, 105.6, 114.4 (2×), 114.4, 116.0, 117.2, 126.2, 127.7 (2×), 128.7, 129.5, 130.5, 132.1, 132.3, 136.7, 148.7, 155.4, 158.5, 163.9. Anal. Calcd for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 75.98; H, 4.94.

4.3.12. 1-(4-Bromophenyl)-9-hydroxy-2-methylene-1,2-dihydrobenzo[*f*]chromen-3-one (4l). Pale-yellow oil (316 mg, 83% yield); R_f 0.85 (25% hexane/ethyl acetate); IR (film): 1744, 1712, 1632, 1216, 1140 cm^{-1}; ^1H NMR ($CDCl_3$): δ=5.22 (s, 1H, ArCHAr), 5.99 (s, 1H, H_2C=C), 6.43 (s, 1H, H_2C=C), 6.96–7.08 (m, 4H, 4×CH_{Ar}), 7.17 (d, 1H, $^3J_{HH}$=9.0 Hz, CH_{Ar}), 7.74 (d, 2H, $^3J_{HH}$=8.7 Hz, 2×CH_{Ar}), 7.75–7.81 (m, 2H, 2×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=44.9, 105.4, 115.0, 115.2, 117.2, 121.6, 126.5, 128.6 (2×), 129.2, 130.1, 130.9, 132.3 (2×), 136.3, 139.1, 141.2, 149.3, 155.2, 162.9. Anal. Calcd for $C_{20}H_{13}BrO_3$: C, 63.01; H, 3.44. Found: C, 62.94; H, 3.36.

4.3.13. 6-Hydroxy-1-(4-methoxyphenyl)-2-methylene-1,2-dihydrobenzo[*f*]chromen-3-one (4m). Pale-yellow oil (199 mg, 60% yield); R_f 0.75 (25% hexane/ethyl acetate); IR (film): 1740, 1588, 1512, 1252, 1112, 1040 cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.71 (s, 3H, CH_3OAr), 5.40 (s, 1H, ArCHAr), 6.03 (s, 1H, H_2C=C), 6.42 (s, 1H, H_2C=C), 6.76 (d, 2H, $^3J_{HH}$=8.8 Hz, 2×CH_{Ar}), 6.93 (s, 1H, CH_{Ar}), 7.04 (d, 2H, $^3J_{HH}$=8.8 Hz, 2×CH_{Ar}), 7.39–7.50 (m, 2H, 2×CH_{Ar}), 7.72–7.76 (m, 1H, CH_{Ar}), 8.27–8.34 (m, 1H,

CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=44.1, 55.2, 100.0, 109.0, 114.4 (2×), 114.7, 115.5, 122.8, 123.0, 124.3, 127.9 (2×), 128.8, 131.6, 132.8, 137.2, 148.4, 153.7, 158.8, 164.1. Anal. Calcd for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 75.82; H, 4.77.

4.3.14. 1-(4-Bromophenyl)-6-hydroxy-2-methylene-1,2-dihydrobenzo[*f*]chromen-3-one (4n). Pale-yellow oil (316 mg, 83% yield); R_f 0.80 (25% hexane/ethyl acetate); IR (film): 1744, 1592, 1392, 1268, 1124 cm^{-1}; ^1H NMR ($CDCl_3$): δ=5.39 (s, 1H, ArC*H*Ar), 6.02 (s, 1H, H_2C=C), 6.45 (s, 1H, H_2C=C), 6.91 (s, 1H, CH_{Ar}), 7.00 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×CH_{Ar}), 7.35 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×CH_{Ar}), 7.40–7.49 (m, 2H, 2×CH_{Ar}), 7.62–7.68 (m, 1H, CH_{Ar}), 8.23–8.26 (m, 1H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=44.2, 99.8, 107.7, 121.7, 122.4, 123.1, 124.3, 128.0, 128.5 (2×), 129.3, 132.1 (2×), 132.4, 136.5, 139.9, 148.1, 154.2, 163.4, 171.7. Anal. Calcd for $C_{20}H_{13}BrO_3$: C, 63.01; H, 3.44. Found: C, 63.14; H, 3.51.

4.3.15. 4-(4-Methoxyphenyl)-3-methylene-3,4-dihydrobenzo[*h*]chromen-2-one (4o). Pale-yellow oil (237 mg, 75% yield); R_f 0.71 (25% hexane/ethyl acetate); IR (film): 1748, 1608, 1512, 1252, 1128, 1032 cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.77 (s, 3H, CH_3OAr), 5.03 (s, 1H, ArC*H*Ar), 5.79 (s, 1H, H_2C=C), 6.52 (s, 1H, H_2C=C), 6.84 (d, 2H, $^3J_{HH}$=8.8 Hz, 2×CH_{Ar}), 7.07 (d, 2H, $^3J_{HH}$=8.8 Hz, 2×CH_{Ar}), 7.14 (d, 1H, $^3J_{HH}$=8.5 Hz, CH_{Ar}), 7.50–7.62 (m, 3H, 3×CH_{Ar}), 7.80–7.84 (m, 1H, CH_{Ar}), 8.33–8.38 (m, 1H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=47.4, 55.1, 114.3 (2×), 119.3, 121.2, 123.6, 124.4, 125.4, 126.6, 126.7, 127.5, 128.8 (2×), 129.4, 133.0, 133.5, 136.9, 145.2, 158.8, 162.6. Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.82; H, 5.21.

4.3.16. 4-(4-Bromophenyl)-3-methylene-3,4-dihydrobenzo[*h*]chromen-2-one (4p). Pale-yellow oil (325 mg, 89% yield); R_f 0.73 (25% hexane/ethyl acetate); IR (film): 1740, 1544, 1488, 1272, 1128, 1072 cm^{-1}; ^1H NMR ($CDCl_3$): δ=5.04 (s, 1H, ArC*H*Ar), 5.81 (s, 1H, H_2C=C), 6.56 (s, 1H, H_2C=C), 7.04 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×CH_{Ar}), 7.11 (d, 1H, $^3J_{HH}$=8.5 Hz, CH_{Ar}), 7.44 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×CH_{Ar}), 7.52–7.64 (m, 3H, 3×CH_{Ar}), 7.81–7.85 (m, 1H, CH_{Ar}), 8.34–8.38 (m, 1H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=46.0, 116.6, 119.6, 119.9, 122.0, 123.0, 123.5, 125.2, 125.3, 125.9, 127.8 (2×), 128.5, 130.5 (2×), 132.0, 134.5, 138.4, 143.7, 160.6. Anal. Calcd for $C_{20}H_{13}BrO_2$: C, 65.77; H, 3.59. Found: C, 65.69; H, 3.47.

4.3.17. 7-Methoxy-4-(4-methoxyphenyl)-3-methylenechroman-2-one (4q). Pale-yellow oil (231 mg, 78% yield); R_f 0.77 (25% hexane/ethyl acetate); IR (film): 1748, 1612, 1508, 1252, 1156, 1120, 1032 cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.78 (s, 3H, CH_3OAr), 3.80 (s, 3H, CH_3OAr), 4.84 (s, 1H, ArC*H*Ar), 5.67 (s, 1H, H_2C=C), 6.42 (s, 1H, H_2C=C), 6.66 (dd, 1H, $^3J_{HH}$=7.3 Hz, $^4J_{HH}$=2.5 Hz, CH_{Ar}), 6.68 (d, 1H, $^4J_{HH}$=2.5 Hz, CH_{Ar}), 6.84 (d, 2H, $^3J_{HH}$=9.0 Hz, 2×CH_{Ar}), 6.95 (d, 1H, $^3J_{HH}$=7.3 Hz, CH_{Ar}), 7.03 (d, 2H, $^3J_{HH}$=9.0 Hz, 2×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=46.6, 55.2, 55.5, 102.4, 111.0, 114.3 (2×), 116.8, 128.9, 128.9 (2×), 129.2, 132.8, 137.2, 151.2, 158.8, 159.9, 163.0. Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 73.04; H, 5.55.

4.3.18. 4-(4-Bromophenyl)-7-methoxy-3-methylenechroman-2-one (4r). Pale-yellow oil (255 mg, 74% yield); R_f 0.81 (25% hexane/ethyl acetate); IR (film): 1744, 1624, 1508, 1488, 1272, 1196, 1156, 1032 cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.81 (s, 3H, CH_3OAr), 4.85 (s, 1H, ArC*H*Ar), 5.70 (s, 1H, H_2C=C), 6.46 (s, 1H, H_2C=C), 6.66–6.69 (m, 2H, 2×CH_{Ar}), 6.92–6.96 (m, 1H, CH_{Ar}), 7.00 (d, 2H, $^3J_{HH}$=8.4 Hz, 2×CH_{Ar}), 7.44 (d, 2H, $^3J_{HH}$=8.4 Hz, 2×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=46.7, 55.4, 102.5, 111.2, 115.7, 121.3, 129.1, 129.4 (2×), 129.6, 132.0 (2×), 136.2, 140.0, 151.2, 160.1, 162.5. Anal. Calcd for $C_{17}H_{13}BrO_3$: C, 59.15; H, 3.80. Found: C, 59.24; H, 3.88.

4.3.19. 6-Methoxy-3-methylene-4-(3,4,5-trimethoxyphenyl)chroman-2-one (4s). Yellow oil (228 mg, 64% yield); R_f 0.76 (25% hexane/ethyl acetate); IR (film): 1716, 1588, 1496, 1464, 1240, 1200, 1128 cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.75 (s, 3H, CH_3OAr), 3.78 (s, 6H, 2×CH_3OAr), 3.82 (s, 3H, CH_3OAr), 4.82 (s, 1H, ArC*H*Ar), 5.73 (s, 1H, H_2C=C), 6.34 (s, 2H, 2×CH_{Ar}), 6.45 (s, 1H, H_2C=C), 6.62 (d, 1H, $^4J_{HH}$=2.9 Hz, CH_{Ar}), 6.84 (dd, 1H, $^3J_{HH}$=8.9 Hz, $^4J_{HH}$=2.9 Hz, CH_{Ar}), 7.08 (d, 1H, $^3J_{HH}$=8.9 Hz, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=48.5, 55.5, 56.0 (2×), 60.7, 104.8 (2×), 113.4, 113.9, 117.9, 125.4, 129.2, 135.8, 136.4, 137.3, 144.4, 153.5 (2×), 156.3, 163.1. Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66. Found: C, 67.30; H, 5.58.

4.3.20. 8-(4-Methoxyphenyl)-7-methylene-7,8-dihydro-[1,3]dioxolo[4,5-*g*]chromen-6-one (4t). Yellow oil (242 mg, 78% yield); R_f 0.80 (25% hexane/ethyl acetate); IR (film): 1776, 1704, 1588, 1548, 1400, 1376, 1216, 1120 cm^{-1}; ^1H NMR ($CDCl_3$):δ=3.78 (s, 3H, CH_3OAr), 4.77 (s, 1H, ArC*H*Ar), 5.67 (s, 1H, H_2C=C), 5.95 (s, 2H, CH_2O_2), 6.42 (s, 1H, H_2C=C), 6.47 (s, 1H, CH_{Ar}), 6.65 (s, 1H, CH_{Ar}), 6.86 (d, 2H, $^3J_{HH}$=8.8 Hz, 2×CH_{Ar}), 7.04 (d, 1H, $^3J_{HH}$=8.8 Hz, 2×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=47.0, 55.1, 99.0, 101.6, 107.2, 114.3 (2×), 117.0, 128.7 (2×), 128.9, 132.5, 136.7, 144.4, 144.8, 147.4, 158.8, 162.9. Anal. Calcd for $C_{18}H_{14}O_5$: C, 69.67; H, 4.55. Found: C, 69.75; H, 4.62.

4.3.21. 8-(4-Bromophenyl)-7-methylene-7,8-dihydro-[1,3]dioxolo[4,5-*g*]chromen-6-one (4u). Yellow oil (273 mg, 76% yield); R_f 0.78 (25% hexane/ethyl acetate); IR (film): 1756, 1504, 1480, 1440, 1240, 1152 cm^{-1}; ^1H NMR ($CDCl_3$):δ=4.78 (s, 1H, ArC*H*Ar), 5.71 (s, 1H, H_2C=C), 5.97 (s, 2H, CH_2O_2), 6.45 (s, 2H, 2×CH_{Ar}), 6.65 (s, 1H, H_2C=C), 7.01 (d, 2H, $^3J_{HH}$=8.5 Hz, 2×CH_{Ar}), 7.45 (d, 1H, $^3J_{HH}$=8.5 Hz, 2×CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ=47.3, 99.1, 101.8, 107.1, 115.9, 121.5, 129.3 (2×), 129.6, 132.0 (2×), 135.9, 139.7, 144.6, 144.9, 147.7, 162.5. Anal. Calcd for $C_{17}H_{11}BrO_4$: C, 56.85; H, 3.09. Found: C, 56.77; H, 3.04.

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