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Catalyst- and Additive-Free Decarboxylative C-4 Phosphorylation of Coumarin-3-Carboxylic Acids at Ambient Conditions

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ABSTRACT: A catalyst- and additive-free practical and green synthetic strategy for decarboxylative C-4 phosphorylation of coumarin-3-carboxylic acids, for the first time, has been accomplished to access a series of substituted 4-(diarylphosphoryl)chroman-2-ones at ambient conditions. The developed protocol is successfully applied to large-scale synthesis.

KEYWORDS: coumarin-3-carboxylic acids; decarboxylative C-4 phosphorylation; catalyst- and additive-free; ambient conditions; gram-scale synthetic application

Introduction

Coumarins, an important class of *O*-heterocycles, are already well-established to form the basic structural motif for a plethora of therapeutically promising organic scaffolds of both natural and synthetic origins, finding immense applications in treating multifaceted disease manifestations.[1] Coumarin derivatives are also used as additives in foods and cosmetics,[2] fragrances and perfumes,[3] and agrochemicals,[4] Also, such molecules find extensive applications as fluorescence sensors,[5] optical brighteners,[6] and molecular photonic devices.[7] 3,4-Dihydrcoumarin, *i.e.* chroman-2-one is a sub-class of this group and this interesting structural motif is also potentially found both in natural and their synthetic analogs exhibiting a wide range of biological profiles including antioxidant, cytotoxic, anticancer, immunomodulatory, anti-platelet aggregation, estrogenic, antibacterial and antileishmanial activity.[8] On the other hand, phosphorus-functionalized organic molecules have also found useful applications in the areas of industrial, agricultural, materials, and medicinal chemistry owing to their noteworthy biological and physical properties.[9] The imposition of a phosphoryl group on to diverse kinds of organic skeletons thus remains a valid and active exercise in chemical research.[10] As part of these research endeavors, a good deal of work on the combination of these two units, *i.e.* a coumarin system and a phosphoryl group, so as to open a route to a new class of organophosphorus compounds, has been reported in the recent past.[10b,c, 11] However, all these literature reports basically deal with the phosphorylation at C-3 position of a coumarin nucleus, and were implemented under varying reaction conditions, mostly non-ecofriendly.[11] An extensive literature survey revealed just two earlier reports on the direct C-4 phosphorylation of coumarins to access C-4 phosphorylated chroman-2-ones.[12] In 2012, Lenker *et al*.[12a] for the first-time reported the microwave-assisted synthesis of only two such derivatives. Later on, in 2017 Hong and co-investigators[12b] developed a visible-light-induced photocatalytic synthetic protocol for phosphorylated chroman-2-ones; however, their method is non-regioselective and furnished 3,4-bis(diphenylphosphoryl)-2*H*-chromen-2-ones. **Scheme 1a** overviews these earlier reports along with their merits and demerits.

Based on this background and as part of our research endeavors in developing green synthetic protocols for biologically relevant compounds,[13] we targeted this interesting research problem and envisioned that coumarin-3-carboxylic acid might be a suitable substrate, which would afford the targeted scaffold regioselectively *via* decarboxylative C-4 phosphorylation. To our delight, we now wish to report herein, for the first time, a regioselective decarboxylative C-4 phosphorylation strategy for coumarin-3-carboxylic acids without the aid of any catalyst or additive under ambient conditions (**Scheme 1b**). The key advantages of this newly developed method are the clean reaction profile, use of no catalyst or additive, DMSO as reaction medium, mild reaction conditions at room temperature, energy-efficiency, no need of column chromatographic purification, high atom-economy, and low E-factor, excellent regioselectivity, good to excellent yields, and large-scale synthetic applicability.

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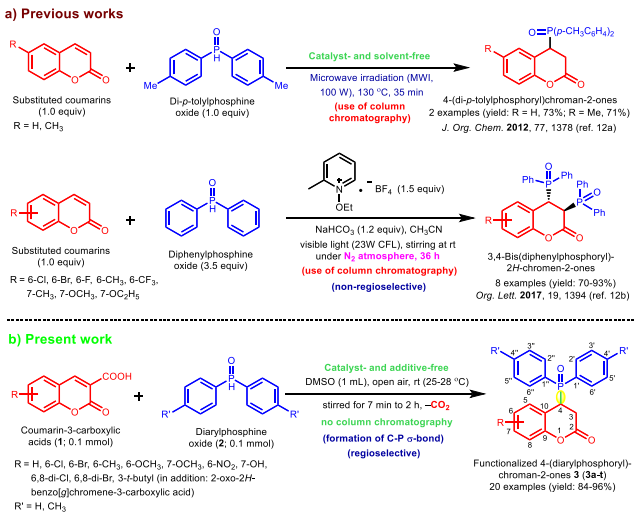
Scheme 1. Direct phosphorylation of coumarin-3-carboxylic acids

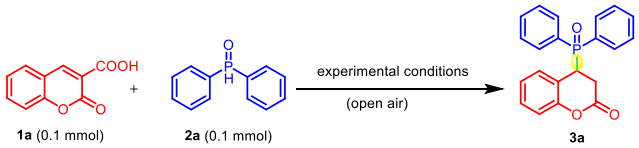


Results and Discussion

To optimize the best-suited reaction conditions, we first performed a series of trial reactions between coumarin-3-carboxylic acid (**1a**; 0.1 mmol) and diphenylphosphine oxide (**2a**; 0.1 mmol), as our model reaction, in the absence or presence of various solvents (*viz*. water, dichloromethane, acetonitrile, 1,4-dioxane, ethanol, and dimethyl sulfoxide) in open-air either at room or elevated temperature (Table 1, entries 1-8). Dimethyl sulfoxide (DMSO) came out as the best solvent for this conversion, just at ambient conditions, in terms of yield and time. We thus achieved the best result for our model reaction in preparing the desired product, 4-(diphenylphosphoryl)chroman-2-one (**3a**), in 92% yield at 10 min (Table 1, entry 7) upon stirring the reactants dissolved in 1 mL of DMSO in the open-air at room temperature (25-28 °C) without any additive and/or catalyst. Compound **3a** was characterized based on detailed spectroscopic (^{1}H NMR, ^{13}C NMR, DEPT-135, ^{31}P NMR, and HRMS) studies. The overall results are summarized in Table 1.

It seemed that ethanol (Table 1, entry 6), yielding 83% of **3a** in 30 min under identical reaction conditions, may also be a competitive solvent for this conversion, and to explore this issue, we carried out a set of two more reactions with coumarin-3-carboxylic acids (**1f**/**1i**) substituted with electron-donating and electron-withdrawing groups, separately in DMSO and ethanol, using the identical reaction conditions, and compared the results (Table 2). These experimental results, as summarized in Table 2, clearly demonstrated that DMSO is the most suitable solvent for the conversion for various substrates in terms of reaction-times and yields of the products (**3f**/**3i**).

Table 1. Optimization of reaction conditions

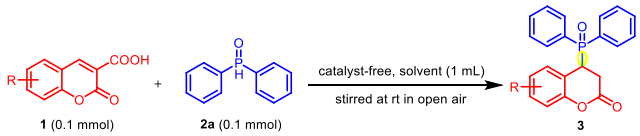


Entry	Solvent (1 mL)	Catalyst	Condition	Time (min)	Yield (%)[a,b]
1	no solvent	–	rt	60	–
2	H_2O	–	rt	60	66
3	CH_2Cl_2	–	rt	240	72
4	CH_3CN	–	rt	30	78
5	1,4-dioxane	–	rt	30	80
6	EtOH	–	rt	30	83
7	**DMSO**	**–**	**rt**	**10**	**92**
8	DMSO	–	80 °C	10	89

[a]Reaction conditions: coumarin-3-carboxylic acid (**1a**; 0.1 mmol) was stirred with diphenylphosphine oxide (**2a**; 0.1 mmol) in the absence or presence of solvent(s) without any additive either at room temperature (25-28 °C) or heating; [b]Isolated yields.

Table 2

Selection of solvent



Entry	R	Solvent	Product	Time (min)	Yield (%)[a,b]
1	H	DMSO	**3a**	10	92
2	H	EtOH	**3a**	30	83
3	7-OCH_3	DMSO	**3f**	15	71
4	7-OCH_3	EtOH	**3f**	90	42
5	6-NO_2	DMSO	**3i**	7	76
6	6-NO_2	EtOH	**3i**	60	43

[a]Reaction conditions: a coumarin-3-carboxylic acid (**1a**/**1f**/**1i**; 0.1 mmol) was stirred with diphenylphosphine oxide (**2a**; 0.1 mmol) dissolved in 1 mL of DMSO/EtOH in the absence any catalyst at room temperature (25-28 °C); [b]Isolated yields.

To check the feasibility as well as the effectiveness of this newly developed protocol, we then carried out a set of three similar reactions with 6-methylcoumarin-3-carboxylic acid (**1b**), 6-*tert*-butylcoumarin-3-carboxylic acid (**1c**) and 7-hydroxycoumarin-3-carboxylic acid (**1d**) using the optimized reaction conditions; all the three reactions took place efficiently, furnishing the expected products, *viz*. 4-(diphenylphosphoryl)-6-methylchroman-2-one (**3b**), 6-(*tert*-butyl)-4-(diphenylphosphoryl)chroman-2-one (**3c**) and 4-(diphenylphosphoryl)-7-hydroxychroman-2-one (**3d**), in 91%, 94% and 96% yields, respectively, at 35, 10 and 20 min. Encouraged with this satisfactory experimental outcomes, we then planned to extend the substrate scope, and accordingly, another set of seven more reactions with diversely substituted coumarin-3-carboxylic acids (**1e**–**1k**; containing methoxy, bromo, chloro, nitro, di-bromo and di-chloro groups) were performed under identical reaction conditions. All these reactions underwent smoothly, thereby affording the desired 4-(diphenylphosphoryl)chroman-2-one derivatives **3e**–**3k** with good to excellent yields ranging from 84-96% just at 7-15 min. To our delight, 3-oxo-3*H*-benzo[*f*]chromene-2-carboxylic acid (**1l**) also took part in the reaction giving rise to the desired phosphorylated product, 1-(diphenylphosphoryl)-1,2-dihydro-3*H*-benzo[*f*]chromen-3-one (**3l**) with 95% yield after 10 min.

We then tried to extend the scope of >P(O)H reagent and accordingly, we carried out a set of two reactions between di-

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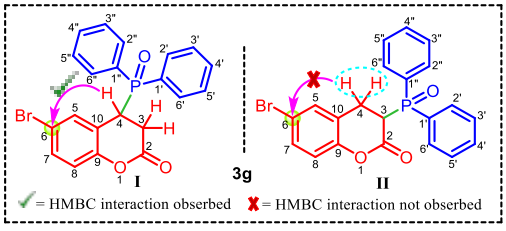
p-toylphosphine oxide **2b**, a variant of >P(O)H reagent, and unsubstituted coumarin-3-carboxylic acid **1a** and with 6-methylcoumarin-3-carboxylic acid **1b**, under the identical reaction conditions. Both the reactions took place smoothly giving the desired and known compounds, 4-(di-*p*-tolylphosphoryl)chroman-2-one (**3m**) and 4-(di-*p*-tolylphosphoryl)-6-methylchroman-2-one (**3n**), respectively, in 90% and 92% yields at 1 h; the physical and spectral data of both the products are in close agreement with those reported in literature.[12a] To our delight, we were also successful in synthesizing another set of six functionalized phosphorylated chroman-2-one derivatives **3o**–**3t** with good to excellent yields ranging from 87-94% within 1-2 h upon the reaction of the phosphorus reagent **2b** with the diversely substituted coumarin-3-carboxylic acids (**1d**, **1f-h**, **1j**, and **1k**) under identical reaction conditions. The overall results are shown in Table 3.

However, $(EtO)_3P$, $(PhO)_2P(O)H$ and $(MeO)_2P(O)H$ were found not to take part in the reaction – possibly, because the P-H hydrogen in case of the latter two reagents [$(PhO)_2P(O)H$ and $(MeO)_2P(O)H$] is reluctant to undergo tautomerization required for initiating decarboxylation of the coumaric acid substrate. No decarboxylation occurred upon the addition of either of the three P-reagents with coumaric acid dissolved in DMSO, and hence, there was no reaction at all.

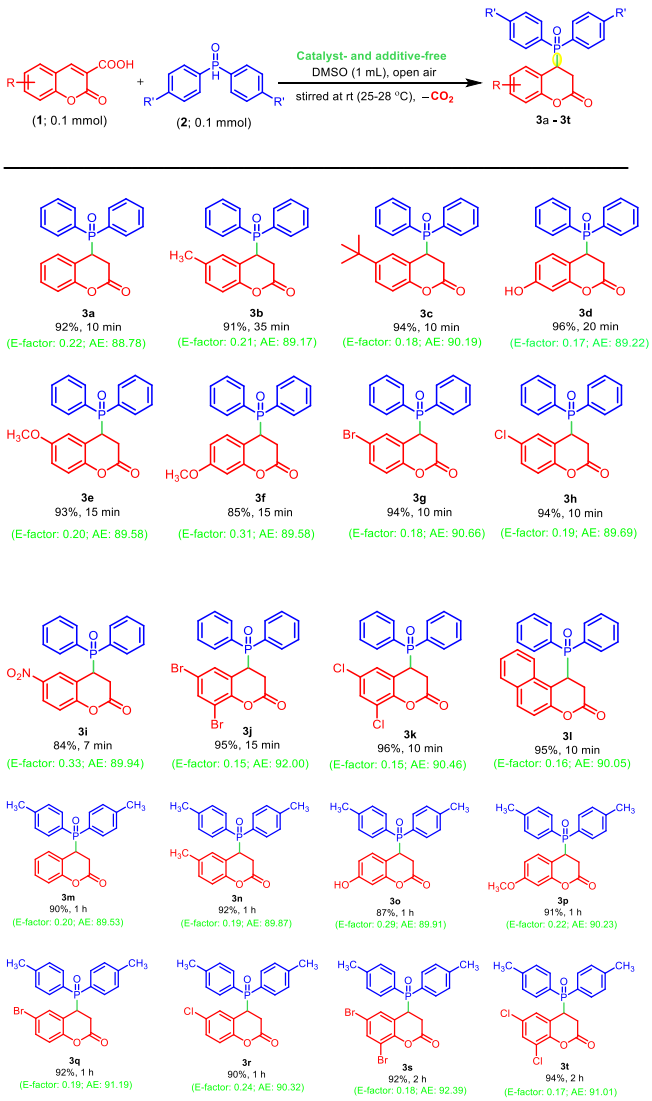
The synthesized compounds **3a**–**3t** were isolated pure just upon filtration, followed by drying in the open-air; no tedious chromatographic purification was required. All the products, except **3m** and **3n**, are new and were fully characterized based on their detailed spectral studies including ^{1}H NMR, ^{13}C NMR, DEPT-135, ^{31}P NMR, and HRMS. In support of the phosphorylation taking place at C-4 of the coumarin moiety, we further studied 2D-NMR, particularly the HMQC (^{1}H-^{13}C heteronuclear multiple quantum coherence) and HMBC (^{1}H-^{13}C heteronuclear multiple bond correlation) spectral analysis for a representative compound **3g** (see Supporting Information) – the key HMBC interaction between the multiplet proton signal for H-4 at δ_H 4.64-4.60 (-C*H*P-) and carbon-13 signal for C-6 at δ_C 120.48 confirmed the structure **I** for compound **3g**, while another possible structure **II** was discarded as no such interaction was observed between either H_a of -CH_2CO- at δ_H 3.18-3.11(m, merged with DMSO-d_6 water peak) or H_b of -CH_2CO- at δ_H 2.57-2.52 (m) and the C-6 at δ_C 120.48, as depicted in Figure 1.

Figure 1. The key HMBC interaction in compound 3g



To evaluate the greenness of this newly developed method, we herein calculated (see Supporting Information) two important green parameters,[14] *i.e.* E-factor (g/g), and atom economy (AE) for all the synthesized compounds (**3a**–**3t**). The calculated E-factors and atom economy are found to be in the range of 0.33-0.15, and 88.78-92.39%, respectively, which are indicative of the considerable greenness of this present method; the respective E-factor and atom economy for each entry is shown in Table 3.

Table 3. Synthesis of substituted 4-(diarylphosphoryl)-chroman-2-ones (3)[a,b]



[a]Reaction conditions: a coumarin-3-carboxylic acid (**1**; 0.1 mmol) was stirred in open air with diarylphosphine oxide (**2**; 0.1 mmol) dissolved in 1 mL of DMSO in the absence any catalyst at room temperature (25-28 °C); [b]Isolated yields.

Herein we propose a possible mechanism for this catalyst- and additive-free C-4 phosphorylation of substituted coumarin-3-carboxylic acids (**1**) with diarylphosphine oxide (**2**) in DMSO at ambient conditions, leading to the synthesis of a new series of substituted 4-(diarylphosphoryl)chroman-2-ones (**3**) (**Scheme 2**). Coumaric acid **1** first gets associated with the phosphorus substrate **2** in the reaction mixture through hydrogen bonding between the carboxylic acidic proton and the oxygen atom of Ar_2P=O (**2**), thereby facilitating tautomeric conversion of **2** to **2′**. This less stable P(III) form **2′**, which thus generated from the P(V) form **2** *via* tautomerization in solution phase (DMSO),[15] then takes part in a nucleophilic attack at C-4 of coumarin nucleus through phosphorus (C-P σ-bond formation)[16] to give an adduct **4** (non-isolable) that in turn affords the desired product **3** through a rapid tautomerization, followed

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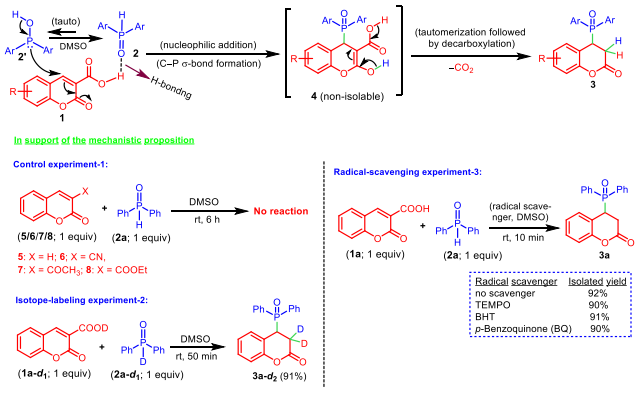
by decarboxylation (expulsion of CO_2 was detected during the gram-scale experiment) process[17]. To validate the role of the carboxylic acid group within the coumarin moiety, we performed a set of control experiments (**Scheme 2**, control experient-1) with unsubstituted coumarin **5** and coumarins substituted with other groups at the 3-position (*viz.* 3-cyanocoumarin **6**, 3-acetylcoumarin **7** and ethyl coumarin-3-carboxylate **8**), and in all these cases no reaction occurred under the optimized conditions. These observations support our presumption that the coumarin nucleus must bear a C_3-COOH group that plays a crucial role in initiating the reaction through hydrogen bonding.

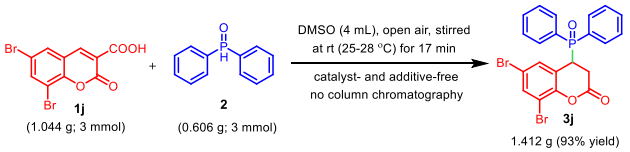
It is thus evident from the mechanistic pathway that during the reaction, C-3 of coumarin-3-carboxylic acids (**1**) becomes saturated by adopting two hydrogen atoms, one from its -COOH group and another from the $Ar_2P(O)H$, not from the water used during work-up. In support of this proposition, we performed an isotope (deuterium)-labeling experiment (**Scheme 2**, isotope-labeling experiment 2): deuterated coumarin-3-carboxylic acid-*d* (**1a-*d*$_1$**; see Supporting Information) upon reaction with diphenylphosphine oxide-*d* (**2a-*d*$_1$**)[18] furnished 4-(diphenylphosphoryl)chroman-2-one-3,3-d_2 (**3a-*d*$_2$**) solely in similar yield (91%) compared to the normal entry (Table 3, entry 1, **3a**) but with a somewhat elongated time (50 min), as usually expected for deuterated-substrates. The deuterated product **3a-*d*$_2$** was characterized based on ^{1}H-NMR and HRMS (experimental and Supporting Information). That this C-4 phosphorylation reaction follows an ionic path was furthermore documented by performing radical-scavenging experiments (experiment-3 as shown in **Scheme 2**) where none of the radical scavengers (*viz.* TEMP, BHT, *p*-benzoquinone) used could inhibit the reaction at all (see Supporting Information). The overall mechanistic aspects are shown in **Scheme 2**.

Scheme 2. Proposed mechanism of decarboxylative C-4 phosphorylation of coumarin-3-carboxylic acids



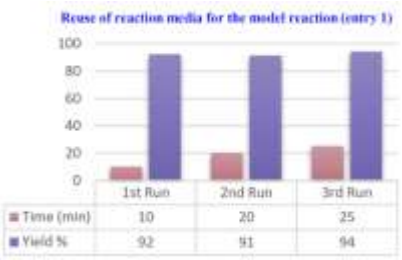
We checked the effectiveness of this catalyst- and additive-free protocol for a somewhat scaled-up (on the gram scale; 3 mmol scale; 30-fold enhancement) experiment with one representative entry (Table 3; entry 10); the large-scale reaction afforded the target product, 6,8-dibromo-4-(diphenylphosphoryl)chroman-2-one (**3j**), in 93% yield within 17 min (**Scheme 3**). It has been revealed that the large-scale reaction is almost similar to 0.1 mmol scale entry (Table 3, entry 10) in terms of respective yield and time.

Scheme 3. Representative gram-scale experiment (30-fold enhancement)



Besides, the reaction media containing the residual reactants, solvent (DMSO), and certain portions of the product obtained upon filtration of the reaction mixture after the completion of the reaction, followed by removal of added water (during processing) on boiling at 110 °C for 1 h, was successfully reused up to the third run in the case of a representative entry (Table 3, entry 1), *viz*. reaction between coumarin-3-carboxylic acid and diphenylphosphine oxide. The desired product **3a** was isolated in 92, 91 and 94% yields, respectively, almost similar to that from the first run, but the time frame was found to be elongated from 10 min (1st run) to 25 min (3rd run), thereby indicating in a gradual decrease in the efficiency of the reused solvent over further uses. The results are graphically represented in Figure 2.

Figure 2. Reusability of reaction media (Table 3, entry 1)



Conclusions

In conclusion, we have accomplished a catalyst- and additive-free practical and green synthetic method to access a new series of 4-(diarylphosphoryl)chroman-2-ones *via* decarboxylative C-4 phosphorylation of coumarin-3-carboxylic acids just under ambient conditions. This is the first report on C-4 phosphorylation of coumarin derivatives by decarboxylation under green conditions. The use of no catalyst or additive, green and reusable reaction media, clean reaction profile, mild reaction conditions at room temperature, energy-efficiency, no column chromatography, thereby avoiding the use of toxic organic solvents, excellent regioselectivity, good to excellent yields within a short reaction time-frame, large-scale synthetic applicability, and high atom-economy and low E-factor are the notable features of this present protocol.

Experimental Section

General information. All chemicals (analytical grade) except starting coumarin-3-carboxylic acids were purchased from reputed companies and used without further purification. All the starting coumarin-3-carboxylic acids (**1a-1l**) used in this present study were synthesized as per the previous report from our laboratory.[1e] ^{1}H-, ^{13}C-, ^{31}P-NMR spectra were collected at

400, 100 and 162 MHz, respectively, on a Bruker DRX spectrometer using $CDCl_3$ and DMSO-d_6 as solvents. Chemical shifts were reported in δ (ppm), relative to the internal standard, TMS. The signals observed are described as s (singlet), d (doublet), t (triplet), and m (multiplet). Coupling constants are reported as *J* value in Hz. Mass spectrometry was obtained using a Bruker maXis Impact (Q-TOF) high-resolution mass spectrometer. Elemental analyses were performed with a Perkin Elmer 2400 Series II elemental analyzer instrument. The melting point was recorded on a Chemiline CL-725 melting point apparatus and is uncorrected. Thin Layer Chromatography (TLC) was performed using silica gel 60 F254 (Merck) plates.

General procedure for the synthesis of functionalized 4-(diarylphosphoryl)chroman-2-ones (3)

Coumarin-3-carboxylic acids (**1**; 0.10 mmol) and diarylphosphine oxide (**2**; 0.10 mmol) were carefully weighed into an oven-dried open glass-vessel equipped with a magnetic stirrer bar. Then dimethylsulfoxide (DMSO) (1.0 mL) was added to the mixture, and stirred in the open-air under ambient conditions for a stipulated time-frame (7 min to 2 h), with occasional TLC monitoring to judge the progress of the reaction. On completion of the reaction, 2 mL of water was added to the resulting mixture and shaken for a while when the product precipitated out and allowed to settle, and then filtered off using ordinary filter paper. Upon drying in the open-air, the desired products, 4-(diarylphosphoryl)chroman-2-ones **3** (**3a**–**3t**), were obtained as pure. The structures of the isolated products were confirmed by elemental analyses and detailed spectral studies including ^{1}H-NMR, ^{13}C-NMR, DEPT-135, ^{31}P-NMR, and HRMS (2D-NMR for one representative entry, **3g**).

The physical and spectroscopic data of all the compounds **3** (**3a** – **3t** and **3a-*d*$_2$**) are given below*:*

4-(Diphenylphosphoryl)chroman-2-one (3a). Bright white amorphous solid; yield: 92% (32 mg; 0.1 mmol scale); Mp = 270 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.84 (m, 2H, Ar-H), 7.66-7.62 (m, 1H, Ar-H), 7.60-7.54 (m, 5H, Ar-H), 7.46-7.42 (m, 2H, Ar-H), 7.27-7.24 (m, 1H, Ar-H), 7.05-7.03 (m, 1H, Ar-H), 6.90-6.86 (m, 1H, Ar-H), 6.65-6.62 (m, 1H, Ar-H), 3.96-3.91 (m, 1H, -C*H*P), 3.25-3.19 (m, 1H, H$_a$ of -C*H*$_2$CO-), 3.08-2.95 (m, 1H, H$_b$ of -C*H*$_2$CO-) ppm. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.02-7.97 (m, 2H, Ar-H), 7.75-7.69 (m, 2H, Ar-H), 7.68-7.60 (m, 3H, Ar-H), 7.58-7.54 (m, 1H, Ar-H), 7.49-7.45 (m, 2H, Ar-H), 7.24-7.21 (m, 1H, Ar-H), 7.06-7.04 (m, 1H, Ar-H), 6.85-6.81 (m, 1H, Ar-H), 6.64-6.62 (m, 1H, Ar-H), 4.65 (t, *J* = 6.8 Hz, 1H, -C*H*P), 2.56-2.53 (m, 1H, H$_b$ of -C*H*$_2$CO-) ppm (*signal for H$_a$ proton of -CH$_2$CO- is merged with DMSO-d$_6$ water peak*). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.08 (d, J_{CP} = 4 Hz, lactone *C*O), 152.53 (d, J^3_{CP} = 4 Hz), 132.28 (d, J_{CP} = 15 Hz), 131.07 (2C), 130.99 (2C), 130.96 (d, J^1_{CP} = 93 Hz), 130.92, 130.65 (d, J^1_{CP} = 97 Hz), 129.50 (d, J_{CP} = 4 Hz), 129.15 (d, J_{CP} = 12 Hz, 2C), 128.90, 128.54 (d, J_{CP} = 12 Hz, 2C), 123.49, 117.99 (d, J_{CP} = 6 Hz), 116.82, 35.25 (J^1_{CP} = 65 Hz, *C*HP), 28.43 (*C*H$_2$CO) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.21 ppm. HRMS: *m/z* 349.0994 [M + H]$^+$ calcd for $C_{21}H_{17}O_3PH$, found: *m/z* 349.0988; *m/z* 387.0552 [M + K]$^+$ calcd for $C_{21}H_{17}O_3PK$, found: *m/z* 387.0548.

4-(Diphenylphosphoryl)-6-methylchroman-2-one (3b). White amorphous solid; yield: 91% (33 mg; 0.1 mmol scale); Mp = 269 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.03-7.98 (m, 2H, Ar-H), 7.69-7.61 (m, 5H, Ar-H), 7.59-7.55 (m, 1H, Ar-H), 7.49-7.46 (m, 2H, Ar-H), 7.03-7.01 (m, 1H, Ar-H), 6.94-6.92 (m, 1H, Ar-H), 6.33 (br s, 1H, Ar-H), 4.54-4.50 (m, 1H, -C*H*P), 2.56-2.52 (m, 1H, H$_b$ of -C*H*$_2$CO-), 1.94 (s, 3H, Ar-C*H*$_3$) ppm (*signal for H$_a$ proton of -CH$_2$CO- is merged with DMSO-d$_6$ water peak*). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.04 (lactone *C*O), 150.40 (d, J^3_{CP} = 4 Hz), 132.21 (d, J_{CP} = 2 Hz), 132.17 (dd, J_{CP} = 26, 3 and 2 Hz), 130.74 (d, J^1_{CP} = 94 Hz), 131.09 (2C), 131.02 (J_{CP} = 2 Hz, 2C), 130.95 (2C), 130.68 (d, J^1_{CP} = 97 Hz), 129.96 (d, J_{CP} = 4 Hz), 129.06 (d, J_{CP} = 10 Hz, 2C), 128.31 (d, J_{CP} = 12 Hz, 2C), 117.43 (d, J_{CP} = 6 Hz), 116.33 (d, J_{CP} = 2 Hz), 35.41 (d, J^1_{CP} = 64 Hz, *C*HP), 28.40 (*C*H$_2$CO), 19.95 (Ar-*C*H$_3$) ppm. ^{31}P NMR (162 MHz, DMSO-d_6): δ 32.35 ppm. HRMS: *m/z* 363.1150 [M + H]$^+$ calcd for $C_{22}H_{19}O_3PH$, found: *m/z* 363.1150; *m/z* 385.0970 [M + Na]$^+$ calcd for $C_{21}H_{19}O_3PNa$; found: *m/z* 385.0981.

6-(*tert*-Butyl)-4-(diphenylphosphoryl)chroman-2-one (3c). White amorphous solid; yield: 94% (38 mg; 0.1 mmol scale); Mp = 272 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.87 (m, 2H, Ar-H), 7.64-7.60 (m, 1H, Ar-H), 7.58-7.51 (m, 5H, Ar-H), 7.43-7.38 (m, 2H, Ar-H), 7.25-7.22 (m, 1H, Ar-H), 6.97-6.95 (m, 1H, Ar-H), 6.49-6.48 (m, 1H, Ar-H), 3.89-3.84 (m, 1H, -C*H*P), 3.22-3.15 (m, 1H, H$_a$ of -C*H*$_2$CO-), 3.07-2.93 (m, 1H, H$_b$ of -C*H*$_2$CO-), 1.01 (s, 9H, (C*H*$_3$)$_3$C) ppm. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.56-8.01 (m, 2H, Ar-H), 7.72-7.63 (m, 5H, Ar-H), 7.56-7.52 (m, 1H, Ar-H), 7.48-7.44 (m, 2H, Ar-H), 7.24-7.20 (m, 1H, Ar-H), 6.96 (d, 1H, *J* = 8.4 Hz, Ar-H), 6.58-6.57 (m, 1H, Ar-H), 4.58 (t, 1H, *J* = 6.8 Hz, -C*H*P), 2.56-2.52 (m, 1H, H$_b$ of -C*H*$_2$CO-), 0.94 (s, 9H, (C*H*$_3$)$_3$C) ppm (*signal for H$_a$ proton of -CH$_2$CO- is merged with DMSO-d$_6$ water peak*). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.16 (lactone *C*O), 150.29 (d, J^3_{CP} = 4 Hz), 145.63 (d, J_{CP} = 2 Hz), 132.14 (d, J_{CP} = 36 Hz), 131.16 (2C), 131.06 (J_{CP} = 3 Hz, 2C), 130.85 (d, J^1_{CP} = 91 Hz), 130.81 (d, J^1_{CP} = 98 Hz), 130.95 (2C), 129.13 (d, J_{CP} = 10 Hz, 2C), 128.41 (d, J_{CP} = 12 Hz), 126.6 (d, J_{CP} = 4 Hz), 125.61 (d, J_{CP} = 2 Hz), 116.74 (d, J_{CP} = 6 Hz), 116.08 (d, J_{CP} = 3 Hz), 35.63 (d, J^1_{CP} = 66 Hz, *C*HP), 33.76 (*C*(CH$_3$)$_3$), 30.81 (C(*C*H$_3$)$_3$, 3C), 28.36 (*C*H$_2$CO) ppm. ^{31}P NMR (162 MHz, DMSO-d_6): δ 32.55 ppm. HRMS: *m/z* 405.1620 [M + H]$^+$ calcd for $C_{25}H_{25}O_3PH$, found: *m/z* 405.1616; *m/z* 427.1439 [M + Na]$^+$ calcd for $C_{25}H_{25}O_3PNa$, found: *m/z* 427.1215; *m/z* 443.1178 [M + K]$^+$ calcd for $C_{25}H_{25}O_3PK$, found: *m/z* 443.1166.

4-(Diphenylphosphoryl)-7-hydroxychroman-2-one (3d). White amorphous powder; yield: 96% (35 mg; 0.1 mmol scale); Mp = 255 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (br s, 1H, -OH), 7.87-7.82 (m, 2H, Ar-H), 7.67-7.61 (m, 3H, Ar-H), 7.59-7.55 (m, 3H, Ar-H), 7.51-7.46 (m, 2H, Ar-H), 6.50 (br s, 1H, Ar-H), 6.43-6.38 (m, 2H, Ar-H), 3.87-3.83 (m, 1H, -C*H*P), 3.04-3.01 (m, 1H, H$_a$ of -C*H*$_2$CO-), 2.98-2.96 (m, 1H, H$_b$ of -C*H*$_2$CO-) ppm. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.75 (br s, 1H, -OH), 7.99-7.94 (m, 2H, Ar-H), 7.74-7.69 (m, 2H, Ar-H), 7.66-7.58 (m, 3H, Ar-H), 7.57-7.53 (m, 1H, Ar-H), 7.49-7.45 (m, 2H, Ar-H), 6.42-6.39 (m, 2H, Ar-H), 6.22 (dd, 1H, *J* = 8.4, 2.4, 2.0 Hz, Ar-H), 4.48 (t, 1H, *J* = 6.4 Hz, -C*H*P), 3.29-3.19 (m, 1H, H$_a$ of -C*H*$_2$CO-), 2.54-2.53 (m, 1H, H$_b$ of -C*H*$_2$CO-) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.09 (lactone *C*O, d, J^3_{CP} = 2 Hz), 157.82 (d, J^5_{CP} = 3 Hz), 153.19 (d, J^3_{CP} = 4 Hz), 132.08 (d, J_{CP} = 15 Hz), 131.27 (d, J^1_{CP} = 85 Hz), 131.04 (2C), 130.94 (2C), 130.93 (d, J^1_{CP} = 97 Hz), 130.84 (2C), 129.98 (d, J_{CP} = 4 Hz, 2C), 129.02 (d, J_{CP} = 11 Hz), 128.43 (d, J_{CP} = 12 Hz), 110.82 (d, J_{CP} = 3 Hz), 107.56 (d, J_{CP}

= 6 Hz), 103.56, 34.48 (d, J^1_{CP} = 66 Hz, *C*HP), 28.68 (*C*H_2CO) ppm. ^{31}P NMR (162 MHz, DMSO-d_6): δ 32.01 ppm. HRMS: *m/z* 365.0943 [M + H]$^+$ calcd for $C_{21}H_{17}O_4PH$, found: *m/z* 365.0941; *m/z* 387.0762 [M + Na]$^+$ calcd for $C_{21}H_{17}O_4PNa$, found: *m/z* 387.0766.

4-(Diphenylphosphoryl)-6-methoxychroman-2-one (3e). White amorphous solid; yield: 93% (35 mg; 0.1 mmol scale); Mp = 281 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86-7.81 (m, 2H, Ar-H), 7.63-7.51 (m, 6H, Ar-H), 7.45-7.40 (m, 2H, Ar-H), 6.56-6.55 (m, 1H, Ar-H), 6.51-6.48 (m, 1H, Ar-H), 6.43-6.40 (m, 1H, Ar-H), 3.88-3.79 (m, 1H, -C*H*P), 3.76 (s, 3H, Ar-OC*H*$_3$), 3.20-3.13 (m, 1H, H_a of -CH_2CO-), 3.03-2.89 (m, 1H, H_b of -CH_2CO-) ppm. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.03-7.98 (m, 2H, Ar-H), 7.75-7.70 (m, 2H, Ar-H), 7.67-7.61 (m, 3H, Ar-H), 7.59-7.55 (m, 1H, Ar-H), 7.51-7.47 (m, 2H, Ar-H), 6.99-6.97 (m, 1H, Ar-H), 6.79-6.76 (m, 1H, Ar-H), 6.14-6.13 (m, 1H, Ar-H), 4.59-4.55 (m, 1H, -C*H*P), 3.36 (s, 3H, Ar-OC*H*$_3$), 2.55-2.53 (m, 1H, H_b of -CH_2CO-) ppm (*signal for H_a proton of -CH_2CO- is merged with DMSO-d_6 water peak*). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.06 (d, J^3_{CP} = 3 Hz, lactone *C*O), 159.58, 154.64 (d, J^3_{CP} = 3 Hz), 132.31 (d, J_{CP} = 2 Hz), 132.08 (d, J_{CP} = 2 Hz), 131.09 (d, J_{CP} = 9 Hz, 2C), 130.94 (d, J_{CP} = 9 Hz, 2C), 130.82 (d, J^1_{CP} = 93 Hz), 130.72 (d, J^1_{CP} = 97 Hz), 129.09 (J_{CP} = 10 Hz, 2C), 128.46 (J_{CP} = 11 Hz, 2C), 118.58 (J_{CP} = 6 Hz), 117.45, 114.73, 113.85 (J_{CP} = 5 Hz), 55.09 (Ar-O*C*H$_3$), 35.59 (d, J^1_{CP} = 65 Hz, *C*HP), 28.21 (*C*H_2) ppm. ^{31}P NMR (162 MHz, DMSO-d_6): δ 32.20 ppm. HRMS: *m/z* 378.1021 [M]$^+$ calcd for $C_{22}H_{19}O_4P$, found: *m/z* 378.0150.

4-(Diphenylphosphoryl)-7-methoxychroman-2-one (3f). White amorphous solid; yield: 85% (32 mg; 0.1 mmol scale); Mp = 251 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88-7.83 (m, 2H, Ar-H), 7.64-7.53 (m, 6H, Ar-H), 7.46-7.41 (m, 2H, Ar-H), 6.94-6.92 (m, 1H, Ar-H), 6.79-6.75 (m, 1H, Ar-H), 6.06-6.05 (m, 1H, Ar-H), 3.89-3.84 (m, 1H, -C*H*P), 3.45 (s, 3H, Ar-OC*H*$_3$), 3.23-3.16 (m, 1H, H_a of -CH_2CO-), 3.04-2.89 (m, 1H, H_b of -CH_2CO-) ppm. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.00-7.95 (m, 2H, Ar-H), 7.76-7.71 (m, 2H, Ar-H), 7.65-7.59 (m, 3H, Ar-H), 7.55-7.53 (m, 1H, Ar-H), 7.49-7.45 (m, 2H, Ar-H), 6.66 (d, 1H, *J* = 2.4 Hz, Ar-H), 6.54-6.52 (m, 1H, Ar-H), 6.44-6.41 (m, 1H, Ar-H), 4.58-4.54 (m, 1H, -C*H*P), 3.69 (s, 3H, Ar-OC*H*$_3$), 3.33-3.23 (m, 1H, H_a of -CH_2CO-), 2.55-2.52 (m, 1H, H_b of -CH_2CO-) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.97 (lactone *C*O, d, J_{CP} = 3 Hz), 159.60 (d, J^5_{CP} = 2 Hz), 153.36 (d, J^3_{CP} = 5 Hz), 132.14 (dd, J_{CP} = 11 and 2 Hz), 131.14 (d, J^1_{CP} = 92 Hz), 131.02, 130.92 (2C), 130.82 (2C), 130.82 (d, J^1_{CP} = 97 Hz), 129.97 (d, J_{CP} = 3 Hz), 129.04 (d, J_{CP} = 10 Hz, 2C), 128.48 (d, J_{CP} = 11 Hz, 2C), 109.74 (d, J_{CP} = 3 Hz), 109.40 (d, J_{CP} = 6 Hz), 102.25, 55.43 (Ar-O*C*H$_3$), 34.49 (d, J^1_{CP} = 66 Hz, *C*HP), 28.57 (d, J^2_{CP} = 2 Hz, *C*H_2CO) ppm. ^{31}P NMR (162 MHz, DMSO-d_6): δ 32.05 ppm. HRMS: *m/z* 401.0919 [M + Na]$^+$ calcd for $C_{22}H_{19}O_4PNa$; Found: *m/z* 401.0927.

6-Bromo-4-(diphenylphosphoryl)chroman-2-one (3g). White amorphous solid; yield: 94% (40 mg; 0.1 mmol scale); Mp = 289 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.85 (m, 2H, Ar-H), 7.67-7.63 (m, 1H, Ar-H), 7.60-7.53 (m, 5H, Ar-H), 7.48-7.43 (m, 2H, Ar-H), 7.36-7.33 (m, 1H, Ar-H), 6.93-6.91 (m, 1H, Ar-H), 6.61-6.60 (m, 1H, Ar-H), 3.83-3.78 (m, 1H, -C*H*P), 3.18-3.11 (m, 1H, H_a of -CH_2CO-), 3.04-2.90 (m, 1H, H_b of -CH_2CO-) ppm. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.02-7.97 (m, 2H, Ar-H), 7.71-7.63 (m, 5H, Ar-H), 7.61-7.57 (m, 1H, Ar-H), 7.52-7.48 (m, 2H, Ar-H), 7.41-7.38 (m, 1H, Ar-H), 7.04 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.72-6.71 (m, 1H, Ar-H), 4.64-4.60 (m, 1H, -C*H*P), 2.57-2.52 (m, 1H, H_b of -CH_2CO-) ppm (*signal for H_a proton of -CH_2CO- is merged with DMSO-d_6 water peak*). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.40 (lactone *C*O), 151.72 (d, J^3_{CP} = 7 Hz), 132.48, 132.16 (dd, J_{CP} = 26, 4 and 2 Hz), 131.39 (d, J_{CP} = 2 Hz), 131.02 (2C), 130.94 (2C), 130.23 (d, J_{CP} = 94 Hz), 130.17 (d, J_{CP} = 97 Hz), 129.16 (d, J_{CP} = 11 Hz, 2C), 128.47 (d, J_{CP} = 12 Hz, 2C), 120.48 (d, J_{CP} = 6 Hz), 118.79 (d, J_{CP} = 3 Hz, 2C), 114.88 (d, J_{CP} = 2 Hz), 35.39 (d, J^1_{CP} = 65 Hz, *C*HP), 27.94 (*C*H_2CO) ppm. 2D-NMR: Selected HMQC interactions at δ 3.18-3.11 (m, H_a of -CH_2CO-, merged with DMSO-d_6 water peak) *vs* δ 27.94 (*C*H_2CO), δ 2.57-2.52 (m, H_b of -CH_2CO-) *vs* δ 27.94 (*C*H_2CO), δ 4.64-4.60 (-C*H*P-) *vs* δ 35.39 (*C*HP); HMBC interaction (selected) at δ 4.64-4.60 (-C*H*P-) *vs* δ 120.48 (C-6). ^{31}P NMR (162 MHz, DMSO-d_6): δ 32.63 ppm. HRMS: *m/z* 427.0099 [M + H]$^+$ calcd for $C_{21}H_{16}BrO_3PH$; found: *m/z* 427.0097; *m/z* 448.9918 [M + Na]$^+$ calcd for $C_{21}H_{16}BrO_3PNa$; found: *m/z* 448.9882.

6-Chloro-4-(diphenylphosphoryl)chroman-2-one (3h). White amorphous solid; yield: 94% (36 mg; 0.1 mmol scale); Mp = 283 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.84 (m, 2H, Ar-H), 7.66-7.63 (m, 1H, Ar-H), 7.59-7.54 (m, 5H, Ar-H), 7.48-7.42 (m, 2H, Ar-H), 7.21-7.18 (m, 1H, Ar-H), 6.98-6.96 (m, 1H, Ar-H), 6.49-6.48 (m, 1H, Ar-H), 3.85-3.80 (m, 1H, -C*H*P), 3.18-3.11 (m, 1H, H_a of -CH_2CO-), 3.04-2.90 (m, 1H, H_b of -CH_2CO-) ppm. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.02-7.97 (m, 2H, Ar-H), 7.69-7.59 (m, 6H, Ar-H), 7.49 (br s, 2H, Ar-H), 7.29-7.27 (m, 1H, Ar-H), 7.10-7.08 (m, 1H, Ar-H), 6.59 (br s, 1H, Ar-H), 4.64-4.61 (m, 1H, -C*H*P), 2.57-2.54 (m, 1H, H_b of -CH_2CO-) ppm (*signal for H_a proton of -CH_2CO- is merged with DMSO-d_6 water peak*). ^{13}C NMR (100 MHz, DMSO-d_6): δ= 165.45 (lactone *C*O), 155.65, 132.67, 132.48, 132.31, 131.19 (J_{CP} = 8 Hz), 131.02 (2C), 130.94 (2C), 130.69 (J_{CP} = 8 Hz), 129.22 (2C), 129.09 (J_{CP} = 5 Hz, 2C), 128.51 (J_{CP} = 10 Hz, 2C), 118.44, 102.03 (J_{CP} = 54 Hz), 35.42 (d, J^1_{CP} = 64 Hz, *C*HP), 27.94 (*C*H_2CO) ppm. ^{31}P NMR (162 MHz, DMSO-d_6): δ 32.56 ppm. HRMS: *m/z* 383.0604 [M + H]$^+$ calcd for $C_{21}H_{16}ClO_3PH$, found: *m/z* 383.0617; *m/z* 405.0423 [M + Na]$^+$ calcd for $C_{21}H_{16}ClO_3PNa$; found: *m/z* 405.0437; *m/z* 421.0163 [M + K]$^+$ calcd for $C_{21}H_{16}ClO_3PNK$; found: *m/z* 421.0175.

4-(Diphenylphosphoryl)-6-nitrochroman-2-one (3i). Pale yellow amorphous solid; yield: 84% (33 mg; 0.1 mmol scale); Mp = 288 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.12-8.09 (m, 1H, Ar-H), 8.06-8.01 (m, 2H, Ar-H), 7.71-7.65 (m, 4H, Ar-H), 7.57-7.53 (m, 2H, Ar-H), 7.48-7.45 (m, 3H, Ar-H), 7.33-7.31 (m, 1H, Ar-H), 4.85-4.81 (m, 1H, -C*H*P), 2.64-2.58 (m, 1H, H_b of -CH_2CO-) ppm (*signal for H_a proton of -CH_2CO- is merged with DMSO-d_6 water peak*). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.76 (lactone *C*O), 157.12, 142.53 (d, J_{CP} = 19 Hz), 132.53 (d, J_{CP} = 23 Hz), 131.08, 130.98 (2C), 130.88, 129.76 (d, J^1_{CP} = 104 Hz), 129.23 (J_{CP} = 11 Hz, 2C), 129.73 (d, J_{CP} = 97 Hz), 128.91, 128.53 (J_{CP} = 12 Hz, 2C), 125.16 (d, J_{CP} = 5 Hz), 124.54, 119.61 (d, J_{CP} = 6 Hz), 117.93 (J_{CP} = 1 Hz), 35.52 (d, J^1_{CP} = 64 Hz, *C*HP), 27.62 (*C*H_2CO) ppm. ^{31}P NMR (162 MHz, DMSO-d_6): δ 33.10 ppm. HRMS: *m/z* 416.0664 [M + Na]$^+$ calcd for $C_{21}H_{16}NO_5PNa$; found: *m/z* 416.0759.

6,8-Dibromo-4-(diphenylphosphoryl)chroman-2-one (3j). White amorphous solid; yield: 95% (48 mg; 0.1 mmol scale); Mp = 239-341 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.83 (m, 2H, Ar-H), 7.68-7.64 (m, 1H, Ar-H), 7.62-7.58 (m, 4H, Ar-H), 7.56-7.53 (m, 2H, Ar-H), 7.49-7.47 (m, 2H, Ar-H), 6.55-

6.54 (m, 1H, Ar-H), 3.84-3.79 (m, 1H, -C*H*P), 3.17-3.11 (m, 1H, H_a of -CH_2CO-), 3.04-2.90 (m, 1H, H_b of -CH_2CO-) ppm. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.03-7.97 (m, 2H, Ar-H), 7.78-7.77 (m, 1H, Ar-H), 7.70-7.66 (m, 5H, Ar-H), 7.59-7.58 (m, 1H, Ar-H), 7.53-7.48 (m, 2H, Ar-H), 6.71-6.70 (m, 1H, Ar-H), 4.69-4.66 (m, 1H, -C*H*P), 2.57-2.53 (m, 1H, H_b of -CH_2CO-) ppm (*signal for H_a proton of -CH_2CO- is merged with DMSO-d_6 water peak*). ^{13}CNMR (100 MHz, DMSO-d_6): δ = 164.69 (d, J^3_{CP} = 3 Hz, lactone *C*O), 148.75 (d, J^3_{CP} = 4 Hz), 133.89 (d, J_{CP} = 3 Hz), 132.58, 132.40 (d, J_{CP} = 2 Hz), 131.55 (d, J_{CP} = 5 Hz), 131.03 (d, J_{CP} = 3 Hz, 2C), 130.93 (2C), 129.88 (d, J^1_{CP} = 93 Hz), 129.82 (d, J^1_{CP} = 98 Hz), 129.20 (d, J_{CP} = 12 Hz, 2C), 128.52 (d, J_{CP} = 12 Hz, 2C), 122.09 (d, J_{CP} = 5 Hz), 114.95 (d, J_{CP} = 4 Hz), 110.85 (d, J^3_{CP} = 3 Hz), 35.90 (d, J^1_{CP} = 64 Hz, *C*HP), 27.79 (d, J^3_{CP} = 2 Hz, *C*H_2CO) ppm. ^{31}P NMR (162 MHz, DMSO-d_6): δ 32.98 ppm. HRMS: *m/z* 526.9023 [M + Na]$^+$ calcd for $C_{21}H_{15}Br_2O_3PNa$, found: *m/z* 526.9013 [M + Na]$^+$, 528.8996 [M + 2 + Na]+ and 530.8978 [M + 4 + Na]$^+$.

6,8-Dichloro-4-(diphenylphosphoryl)chroman-2-one (3k). White amorphous solid; yield: 96% (40 mg; 0.1 mmol scale); Mp = 274 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.84 (m, 2H, Ar-H), 7.68-7.64 (m, 1H, Ar-H), 7.62-7.55 (m, 5H, Ar-H), 7.49-7.45 (m, 2H, Ar-H), 7.32-7.31 (m, 1H, Ar-H), 6.39-6.38 (m, 1H, Ar-H), 3.86-3.81 (m, 1H, -C*H*P), 3.18-3.11 (m, 1H, H_a of -CH_2CO-), 3.04-2.91 (m, 1H, H_b of -CH_2CO-) ppm. ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.02-7.98 (m, 2H, Ar-H), 7.72-7.65 (m, 5H, Ar-H), 7.59-7.57 (m, 2H, Ar-H), 7.53-7.48 (m, 2H, Ar-H), 6.57-6.56 (m, 1H, Ar-H), 4.70 (t, 1H, *J* = 6.8 Hz, -C*H*P), 2.59-2.54 (m, 1H, H_b of -CH_2CO-) ppm (*signal for H_a proton of -CH_2CO- is merged with DMSO-d_6 water peak*). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.56 (lactone *C*O), 147.30 (d, J^3_{CP} = 4 Hz), 132.49 (d, J_{CP} = 17 Hz), 131.01 (2C), 130.93 (2C), 129.88 (d, J^1_{CP} = 94 Hz), 129.83 (d, J^1_{CP} = 98 Hz), 129.52, 129.20 (d, J_{CP} = 12 Hz, 2C), 128.54 (d, J_{CP} = 12 Hz, 2C), 128.56 (d, J_{CP} = 3 Hz), 128.00 (d, J_{CP} = 4 Hz), 126.97 (d, J_{CP} = 2 Hz), 121.84 (d, J_{CP} = 5 Hz), 121.38, 35.91 (d, J^1_{CP} = 63 Hz, *C*HP), 27.70 (*C*H_2CO) ppm. ^{31}P NMR (162 MHz, DMSO-d_6): δ 32.76 ppm. HRMS: *m/z* 417.0214 [M + H]$^+$ calcd for $C_{21}H_{15}Cl_2O_3PH$, found: *m/z* 417.0219; *m/z* 439.0034 [M + Na]$^+$ calcd for $C_{21}H_{15}Cl_2O_3PNa$; found: *m/z* 439.0046.

1-(Diphenylphosphoryl)-1*H*-benzo[*f*]chromen-3(2*H*)-one (3l). White amorphous solid; yield: 95% (38 mg; 0.1 mmol scale); Mp = 270 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.19-8.15 (m, 2H, Ar-H), 7.89 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.78-7.68 (m, 4H, Ar-H), 7.48 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.32 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.27-7.18 (m, 4H, Ar-H), 7.09-7.05 (m, 2H, Ar-H), 7.03-6.99 (m, 1H, Ar-H), 5.10-5.08 (m, 1H, -C*H*P), 2.73-2.67 (m,1H, H_b of -CH_2CO-) ppm (*signal for H_a proton of -CH_2CO- is merged with DMSO-d_6 water peak*). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.19 (J^3_{CP} = 2 Hz, lactone *C*O), 150.70 (J^3_{CP} = 6 Hz), 132.55, 131.83, 131.58 (J^3_{CP} = 9 Hz), 130.99 (J^3_{CP} = 9 Hz), 130.78 (J^3_{CP} = 97 Hz), 130.76 (J^3_{CP} = 101 Hz), 130.69 (J^3_{CP} = 3 Hz), 129.95, 129.80 (J_{CP} = 2 Hz), 129.14 (J_{CP} = 11 Hz, 2C), 127.94 (2C), 127.83 (2C), 125.84, 124.41, 123.86, 122.14, 117.32 (J_{CP} = 2 Hz), 111.57 (J_{CP} = 7 Hz), 32.76 (J^1_{CP} = 64 Hz, *C*HP), 29.26 (*C*H_2CO) ppm. ^{31}P NMR (162 MHz, DMSO-d_6): δ 32.66 ppm. HRMS: *m/z* 399.1150 [M + H]$^+$ calcd for $C_{25}H_{19}O_3PH$, found: *m/z* 399.1142; *m/z* 421.0970 [M + Na]$^+$ calcd for $C_{25}H_{19}O_3PNa$; found: *m/z* 421.1083.

4-(Di-*p*-tolylphosphoryl)chroman-2-one (3m).[12a] White amorphous powder; yield: 90% (34 mg; 0.1 mmol scale); Mp = 265-268 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71-7.66 (m, 2H, Ar-H), 7.43-7.38 (m, 2H, Ar-H), 7.33-7.31 (m, 2H, Ar-H), 7.23-7.19 (m, 3H, Ar-H), 7.00-6.98 (m, 1H, Ar-H), 6.89-6.86 (m, 1H, Ar-H), 6.85-6.65 (m, 1H, Ar-H), 3.91-3.85 (m, 1H, -C*H*P), 3.24-3.17 (m, 1H, H_a of -CH_2CO-), 3.02-2.89 (m, 1H, H_b of -CH_2CO-), 2.42 (s, 3H, Ar-CH_3), 2.38 (s, 3H, Ar-CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.06 (d, J^3_{CP} = 3 Hz, lactone *C*O), 152.45 (d, J^3_{CP} = 5 Hz), 142.27, 142.03 (d, J_{CP} = 3 Hz), 130.98 (d, J_{CP} = 10 Hz), 130.93 (2C), 130.88 (d, J_{CP} = 10 Hz), 129.62 (d, J_{CP} = 11 Hz, 2C), 129.50 (d, J_{CP} = 4 Hz), 129.03 (d, J_{CP} = 12 Hz, 2C), 128.71 (d, J_{CP} = 2 Hz), 127.94 (d, J_{CP} = 96 Hz), 127.60 (d, J_{CP} = 100 Hz), 123.44, 118.22 (J_{CP} = 6 Hz), 116.72 (J_{CP} = 3 Hz), 35.34 (J^1_{CP} = 65 Hz, *C*HP), 28.43 (*C*H_2CO), 21.08 (Ar-*C*H_3, 2C) ppm. ^{31}P NMR (162 MHz, DMSO-d_6): δ 32.50 ppm. Elemental analysis: calcd (%) for $C_{23}H_{21}O_3P$: C, 73.40; H, 5.62; Found: C, 73.48; H, 5.69.

4-(di-*p*-tolylphosphoryl)-6-methylchroman-2-one (3n).[12a] White amorphous solid; yield: 92% (36 mg; 0.1 mmol scale); Mp = 274-276 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71-7.66 (m, 2H, Ar-H), 7.42-7.37 (m, 2H, Ar-H), 7.33-7.31 (m, 2H, Ar-H), 7.22-7.19 (m, 2H, Ar-H), 7.02-7.00 (m, 1H, Ar-H), 6.88-6.86 (m, 1H, Ar-H), 6.37 (br s, 1H, Ar-H), 3.82-3.77 (m, 1H, -C*H*P), 3.20-3.14 (m, 1H, H_a of -CH_2CO-), 3.00-2.87 (m, 1H, H_b of -CH_2CO-), 2.42 (s, 3H, Ar-CH_3), 2.83 (s, 3H, Ar-CH_3), 2.07 (s, 3H, Ar-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.05 (d, J^3_{CP} = 3 Hz, lactone *C*O), 150.49 (d, J^3_{CP} = 5 Hz), 143.21 (d, J_{CP} = 3 Hz, 2C), 133.49 (d, J_{CP} = 3 Hz), 131.94 (d, J_{CP} = 9 Hz, 2C), 131.71 (J_{CP} = 8 Hz, 2C), 130.14 (d, J_{CP} = 4 Hz), 129.83, 129.72 (d, J_{CP} = 12 Hz, 2C), 129.27 (d, J_{CP} = 12 Hz, 2C), 126.45 (d, J^1_{CP} = 99 Hz), 125.58 (d, J^1_{CP} = 100 Hz), 117.23 (d, J_{CP} = 2 Hz), 116.95 (d, J_{CP} = 4 Hz), 38.08 (d, J^1_{CP} = 65 Hz, *C*HP), 28.93 (*C*H_2CO), 21.76 (2C, Ar-*C*H_3), 20.64 (Ar-CH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.75 ppm. Elemental analysis: calcd (%) for $C_{24}H_{23}O_3P$: C, 73.83; H, 5.94; Found: C, 73.91; H, 5.98.

4-(Di-*p*-tolylphosphoryl)-7-hydroxychroman-2-one (3o). White amorphous powder; yield: 87% (34 mg; 0.1 mmol scale); Mp = 278-279 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.67 (m, 2H, Ar-H), 7.52-7.48 (m, 2H, Ar-H), 7.36-7.34 (m, 2H, Ar-H), 7.29-7.27 (m, 2H, Ar-H), 6.49-6.48 (m, 1H, Ar-H), 6.46-6.39 (m, 2H, Ar-H), 3.81-3.77 (m, 1H, -C*H*P), 3.01-2.99 (m, 1H, H_a of -CH_2CO-), 2.95-2.93 (m, 1H, H_b of -CH_2CO-), 2.43 (s, 3H, Ar-CH_3), 2.41 (s, 3H, Ar-CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.27 (lactone *C*O, d, J^3_{CP} = 3 Hz), 157.77, 153.19 (d, J^3_{CP} = 4 Hz), 142.20 (d, J_{CP} = 2 Hz), 141.97 (d, J_{CP} = 4 Hz), 131.05 (d, J_{CP} = 10 Hz, 2C), 130.90 (d, J_{CP} = 8 Hz, 2C), 130.10 (d, J_{CP} = 2 Hz), 129.64 (d, J_{CP} = 11 Hz, 2C), 129.07 (d, J_{CP} = 12 Hz, 2C), 128.26 (d, J^1_{CP} = 93 Hz), 127.90 (d, J^1_{CP} = 98 Hz), 110.89, 107.83, 103.57, 34.56 (d, J^1_{CP} = 64 Hz, *C*HP), 28.73 (*C*H_2CO), 21.15 (2C, Ar-*C*H_3) ppm. ^{31}P NMR (162 MHz, DMSO-d_6): δ 29.19 ppm. Elemental analysis: calcd (%) for $C_{23}H_{21}O_4P$: C, 70.40; H, 5.39; Found: C, 70.51; H, 5.42.

4-(Di-*p*-tolylphosphoryl)-7-methoxychroman-2-one (3p). White amorphous solid; yield: 91% (37 mg; 0.1 mmol scale); Mp = 237-238 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70-7.65 (m, 2H, Ar-H), 7.45-7.40 (m, 2H, Ar-H), 7.33-7.30 (m, 2H, Ar-H), 7.23-7.20 (m, 2H, Ar-H), 6.55-6.53 (m, 2H, Ar-H), 6.45-6.42 (m, 1H, Ar-H), 3.85-3.79 (m, 1H, -C*H*P), 3.76 (s, 3H, Ar-OCH_3), 3.21-3.14 (m, 1H, H_a of -CH_2CO-), 3.00-2.86 (m, 1H, H_b of -CH_2CO-), 2.42 (s, 3H, Ar-CH_3), 2.39 (s, 3H, Ar-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.81 (d, J^3_{CP} = 2 Hz, lactone *C*O), 160.39 (d, J^5_{CP} = 3 Hz), 153.48 (d, J^3_{CP} = 4 Hz),

143.18, 131.91 (d, J^2_{CP} = 9 Hz, 2C), 131.62 (d, J^2_{CP} = 9 Hz, 2C), 130.40 (d, J_{CP} = 4 Hz, 2C), 129.77 (d, J_{CP} = 12 Hz, 2C), 129.39 (d, J_{CP} = 13 Hz, 2C), 126.65 (d, J^1_{CP} = 116 Hz), 125.66 (d, J^1_{CP} = 117 Hz), 110.58 (d, J_{CP} = 3 Hz), 108.99 (d, J_{CP} = 4 Hz), 102.75 (d, J_{CP} = 2 Hz), 55.62 (Ar-O*C*H$_3$), 37.16 (d, J^1_{CP} = 67 Hz, *C*HP), 29.01 (*C*H$_2$CO), 21.79 (Ar-*C*H$_3$, 2C) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.66 ppm. Elemental analysis: calcd (%) for $C_{24}H_{23}O_4P$: C, 70.93; H, 5.70; Found: C, 70.99; H, 5.78.

6-Bromo-4-(di-*p*-tolylphosphoryl)chroman-2-one (3q). White amorphous solid; yield: 92% (42 mg; 0.1 mmol scale); Mp = 285-286 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.75-7.69 (m, 2H, Ar-H), 7.42-7.30 (m, 5H, Ar-H), 7.24-7.22 (m, 2H, Ar-H), 6.88 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.59 (br s, 1H, Ar-H), 3.80-3.76 (m, 1H, -C*H*P), 3.16-3.09 (m, 1H, H$_a$ of -C*H*$_2$CO-), 3.01-2.87 (m, 1H, H$_b$ of -C*H*$_2$CO-), 2.44 (s, 3H, Ar-C*H*$_3$), 2.39 (s, 3H, Ar-C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 165.08 (lactone *C*O), 151.74 (d, J^3_{CP} = 5 Hz), 143.59, 132.34 (d, J_{CP} = 3 Hz), 132.13 (d, J_{CP} = 2 Hz), 131.72 (d, J_{CP} = 8 Hz, 2C), 131.64 (d, J_{CP} = 8 Hz, 2C), 129.96 (d, J_{CP} = 12 Hz, 2C), 129.49 (d, J_{CP} = 13 Hz, 2C), 125.89 (d, J^1_{CP} = 99 Hz), 125.39 (d, J^1_{CP} = 102 Hz), 119.66 (d, J_{CP} =5 Hz), 119.21 (2C), 116.32, (d, J_{CP} =5 Hz), 38.15 (d, J^1_{CP} = 64 Hz, *C*HP), 28.60 (*C*H$_2$CO), 21.78 (2C, Ar-CH$_3$) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.98 ppm. Elemental analysis: calcd (%) for $C_{23}H_{20}BrO_3P$: C, 60.68; H, 4.43; Found: C, 60.74; H, 4.46.

6-Chloro-4-(di-*p*-tolylphosphoryl)chroman-2-one (3r). White amorphous solid; yield: 90% (37 mg; 0.1 mmol scale); Mp = 287-288 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.74-7.69 (m, 2H, Ar-H), 7.44-7.34 (m, 4H, Ar-H), 7.26-7.22 (m, 2H, Ar-H), 7.19-7.16 (m, 1H, Ar-H), 6.94 (d, 1H, *J* = 8.8 Hz, Ar-H), 6.51-6.49 (m, 1H, Ar-H), 3.81-3.77 (m, 1H, -C*H*P), 3.17-3.10 (m, 1H, H$_a$ of -C*H*$_2$CO-), 3.01-2.87 (m, 1H, H$_b$ of -C*H*$_2$CO-), 2.44 (s, 3H, Ar-C*H*$_3$), 2.39 (s, 3H, Ar-C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 165.18 (d, *J* = 2 Hz, lactone *C*O), 151.19 (d, J^3_{CP} = 4 Hz), 143.57 (d, *J* = 2 Hz, 2C), 131.72 (d, J_{CP} = 9 Hz, 2C), 131.63 (d, J_{CP} = 9 Hz, 2C), 129.95 (d, J_{CP} = 12 Hz, 2C), 129.50 (d, J_{CP} = 12 Hz, 2C), 129.37 (d, J_{CP} = 4 Hz), 129.24 (d, J_{CP} = 3 Hz), 128.94 (d, J_{CP} = 5 Hz), 125.94 (d, J^1_{CP} = 99 Hz), 125.36 (d, J^1_{CP} = 100 Hz), 119.27 (d, J_{CP} = 5 Hz), 118.87 (d, J_{CP} = 4 Hz), 38.08 (d, J^1_{CP} = 64 Hz, *C*HP), 28.60 (d, J^2_{CP} = 2 Hz, *C*H$_2$CO), 21.78 (2C, Ar-CH$_3$) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ 26.88 ppm. Elemental analysis: calcd (%) for $C_{23}H_{20}ClO_3P$: C, 67.24; H, 4.91; Found: C, 67.31; H, 4.99.

6,8-Dibromo-4-(di-*p*-tolylphosphoryl)chroman-2-one (3s).

White amorphous solid; yield: 92% (49 mg; 0.1 mmol scale); Mp = 277-278 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.73-7.68 (m, 2H, Ar-H), 7.59-7.58 (m, 1H, Ar-H), 7.43-7.31 (m, 2H, Ar-H), 7.38-7.35 (m, 3H, Ar-H), 7.24-7.23 (m, 1H, Ar-H), 6.54-6.53 (m, 1H, Ar-H), 3.80-3.76 (m, 1H, -C*H*P), 3.16-3.09 (m, 1H, H$_a$ of -C*H*$_2$CO-), 3.01-2.88 (m, 1H, H$_b$ of -C*H*$_2$CO-), 2.44 (s, 3H, Ar-C*H*$_3$), 2.41 (s, 3H, Ar-C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 163.97 (d, J_{CP} = 3 Hz, lactone *C*O), 148.93 (d, J^3_{CP} = 3 Hz), 143.79 (d, J^3_{CP} = 3 Hz), 135.25 (d, J_{CP} = 3 Hz, 2C), 131.72 (d, J_{CP} = 10 Hz, 2C), 131.63 (d, J_{CP} = 9 Hz, 2C), 131.43 (d, J_{CP} = 5 Hz), 130.05 (d, J_{CP} = 12 Hz, 2C), 129.58 (d, J_{CP} = 12 Hz, 2C), 125.50 (d, J^1_{CP} = 100 Hz), 125.07 (d, J^1_{CP} = 101 Hz), 121.09 (d, J_{CP} =5 Hz), 116.13 (d, J_{CP} = 2 Hz), 112.21 (d, J_{CP} = 3 Hz), 38.66 (d, J^1_{CP} = 64 Hz, *C*HP), 28.60 (*C*H$_2$CO), 21.80 (2C, Ar-CH$_3$) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ 32.18 ppm. Elemental analysis: calcd (%) for $C_{23}H_{19}Br_2O_3P$: C, 51.71; H, 3.59; Found: C, 51.79; H, 3.61.

6,8-Dichloro-4-(di-*p*-tolylphosphoryl)chroman-2-one (3t).

White amorphous solid; yield: 94% (42 mg; 0.1 mmol scale); Mp = 281-282 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.73-7.69 (m, 2H, Ar-H), 7.45-7.40 (m, 2H, Ar-H), 7.37-7.35 (m, 3H, Ar-H), 7.30-7.29 (m, 1H, Ar-H), 7.25-7.24 (m, 1H, Ar-H), 6.41-6.40 (m, 1H, Ar-H), 3.83-3.78 (m, 1H, -C*H*P), 3.18-3.11 (m, 1H, H$_a$ of -C*H*$_2$CO-), 3.01-2.88 (m, 1H, H$_b$ of -C*H*$_2$CO-), 2.44 (s, 3H, Ar-C*H*$_3$), 2.41 (s, 3H, Ar-C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 163.94 (d, J_{CP} = 3 Hz, lactone *C*O), 143.78 (d, J^3_{CP} = 2 Hz, 2C), 131.71 (d, J_{CP} = 9 Hz, 2C), 131.62 (d, J_{CP} = 9 Hz, 2C), 130.33 (d, J_{CP} = 2 Hz), 130.04 (d, J_{CP} = 12 Hz, 2C), 129.70, 129.60 (d, J_{CP} = 12 Hz, 2C), 128.70 (d, J_{CP} = 4 Hz), 127.77 (d, J_{CP} = 3 Hz), 125.61 (d, J^1_{CP} = 98 Hz), 125.13 (d, J^1_{CP} = 102 Hz), 123.41 (d, J_{CP} = 4 Hz), 120.79 (d, J_{CP} = 4 Hz), 38.58 (d, J^1_{CP} = 64 Hz, *C*HP), 28.53 (*C*H$_2$CO), 21.80 (2C, Ar-CH$_3$) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.92 ppm. Elemental analysis: calcd (%) for $C_{23}H_{19}Cl_2O_3P$: C, 62.04; H, 4.30; Found: C, 62.11; H, 4.32.

4-(Diphenylphosphoryl)chroman-2-one-3,3-*d*$_2$ (3a-*d*$_2$). White amorphous solid; yield: 89% (31 mg; 0.1 mmol scale); Mp = 280 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 8.02-7.97 (m, 2H, Ar-H), 7.75-7.69 (m, 2H, Ar-H), 7.67-7.61 (m, 3H, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.49-7.45 (m, 2H, Ar-H), 7.25-7.21 (m, 1H, Ar-H), 7.05 (d, 1H, *J* = 8.0 Hz, Ar-H), 6.83 (t, 1H, *J* = 7.6 and 7.2 Hz, Ar-H), 6.63 (d, 1H, *J* = 7.6 Hz, Ar-H), 4.63 (t, 1H, *J* = 6.4 Hz, -C*H*P) ppm. HRMS: *m/z* 351.1119 [M + H]$^+$ calcd for $C_{21}H_{15}D_2O_3PH$, found: *m/z* 351.0903; *m/z* 373.0939 [M + Na]$^+$ calcd for $C_{21}H_{15}D_2O_3PNa$; found: *m/z* 373.0689.

ASSOCIATED CONTENT

Supporting Information

Scanned copies of ^{1}H-NMR, ^{13}C-NMR, DEPT-135, ^{31}P-NMR and HMRS spectra for the synthesized 4-(diarylphosphoryl)chroman-2-one **3** (**3a** – **3t** and **3a-*d*$_2$**) including 2D-NMR (HMQC and HMBC) for compound **3g**, synthetic procedures and ^{1}H-NMR spectra for deuterated diphenylphosphine oxide-*d* (**2a-*d*$_1$**) and couramin-3-carboxylic acid-*d* (**1a-*d*$_1$**), and calculations for atom economy (AE) and E-factors for all the reactions are documented (PDF).

FAIR data, including the primary NMR FID files, for compounds **3a**-**3t** (ZIP)

Notes

The author declares no competing financial interest.

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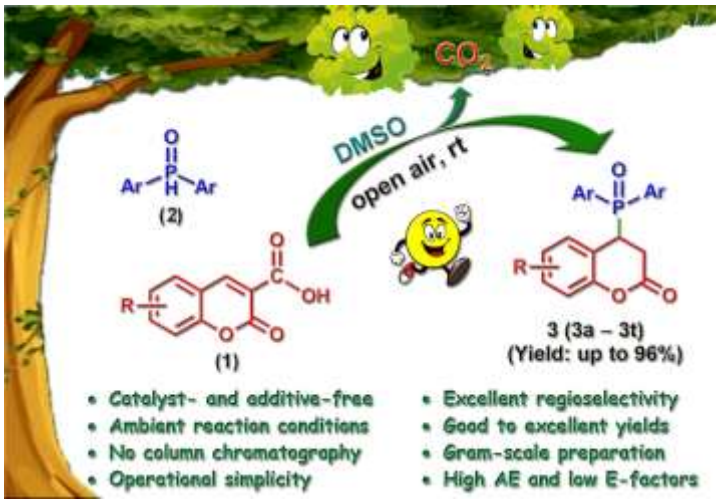
TOC Graphic



Exploration of a green and efficient strategy for decarboxylative and regioselective C-4 phosphorylation of coumarin-3-carboxylic acids