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A novel route to substituted 3-methylidenechroman-2-ones and 3-methylchromen-2-ones

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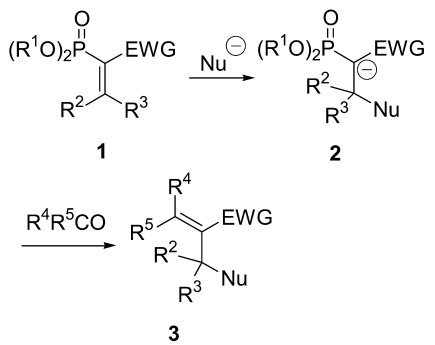
Abstract—3-Methylidenechroman-2-ones, or their rearrangement products 3-methylchromen-2-ones, were efficiently synthesized by Michael addition of various nucleophiles to 3-diethoxyphosphorylchromen-2-ones followed by Horner–Wadsworth–Emmons reaction of the adducts with formaldehyde. Relative configuration and conformation of the intermediate adducts were studied using NMR spectroscopy and semiempirical PM3 calculations.

1. Introduction

The synthetic utility of vinylphosphonates **1** containing electron-withdrowing groups in the α-position is well recognized.[1] For example they accept various nucleophiles to give adducts **2** which are excellent reagents for the olefination of carbonyl compounds to yield **3** (Scheme 1). Recently we employed this reaction sequence to synthesize a series of substituted 3-alkylidenedihydro-2-furanones.[2]

Now we present another example showing the potential of this methodology, this time in the synthesis of 3-methylidenechroman-2-ones **7** (3-methylidene-3,4-dihydrocoumarins) or their rearrangement products 3-methylchromen-2-ones **8**.



Scheme 1.

3-Methylidenechroman-2-ones belong to a biologically important class of α-methylidene γ- and δ-lactones.[3] So far, their synthesis has been accomplished by reductive amination of the 3-formylchroman-2-one,[4] elimination of a phenylselenyl residue from 3-phenylselenylmethylchroman-2-one[5] or employing the Claisen rearrangement of α-aryloxymethylacrylates followed by lactonization of the rearrangement product.[6–11] Also, intra- or intermolecular Horner–Wadsworth–Emmons reaction were used to synthesize 2,9*b*-dihydro-1*H*-cyclopenta[c]chromen-4-one[12] or various 3-arylidenechroman-2-ones respectively.[13]

2. Results and discussion

Details of our method are presented in Scheme 2.

The starting 3-diethoxyphosphorylchromen-2-ones **4a**,**b** are known and can be easily prepared by reaction of ethyl diethoxyphosphorylacetate with corresponding aromatic hydroxyaldehydes.[13] On the other hand, additions of nucleophiles to **4**, except 2-([1,3]dioxolan-2-yl)ethylmagnesium bromide,[12] have not been investigated so far. Therefore we decided to test the effectiveness of various nucleophiles **5** in this reaction. Additions of different Grignard reagents in the presence of CuI catalyst, as well as sodium salts of diethyl phosphite and nitromethane proceeded smoothly to give, after standard work up, the crude adducts **6** which were purified by column chromatography. As it turned out, the use of 3 to 5 fold excess of the Grignard reagent improved the yield significantly. Results are given in the Table 1. Unfortunately the sodium salt of diethyl malonate and enamines, generated in situ from carbonyl compound (acetone, cyclohexanone) and proline,

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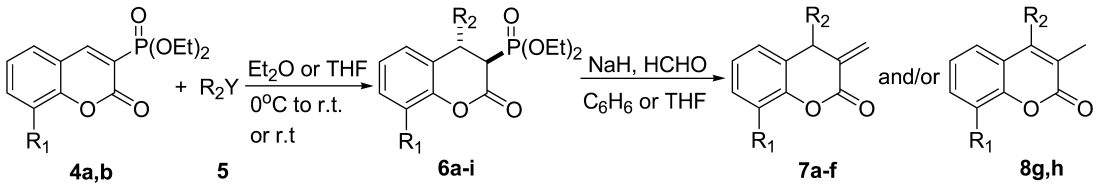

Scheme 2.

Table 1. Synthesis of the adducts **6**, 3-methylidenechroman-2-ones **7** and 3-methylchromen-2-ones **8**

Compound	R_1	R_2Y **5** (equivalents of nucleophile)	**6** Yield (%)[a]	**7** Yield (%)[a]	**8** Yield (%)[a]
a	H	MeMgI (3)	85[b]	71[c]	–
b	OMe	MeMgI (5)	73[b]	68[c]	–
c	H	*n*-BuMgBr (3)	82[b]	58[c]	–
d	OMe	*n*-BuMgBr (5)	91[b]	89[c]	–
e	H	CH_2=CHMgBr (3)	71[d]	55[e]	–
f	OMe	CH_2=CHMgBr (3)	75[d]	50[e]	–
g	H	$(EtO)_2P(O)Na$ (1)	73	–	63[c]
h	OMe	$(EtO)_2P(O)Na$ (1)	50	–	40[c]
i	H	O_2NCH_2Na (1.5)	58	–	–

[a] Yields of pure, isolated products based on **4** or **5**, respectively.
[b] Grignard reagent prepared from the corresponding alkyl halide and magnesium in Et_2O was used.
[c] Reaction was performed in refluxing benzene.
[d] Commercially available vinylmagnesium bromide, 1.0 M solution in THF was used (FLUKA®).
[e] Reaction was performed in THF at rt.

were ineffective as nucleophiles in the addition reactions and only starting materials were recovered. Adducts **6** were always formed as single diastereoisomers. Since, in this type of Michael additions, thermodynamic control is usually observed[2,14] we expected that *trans* isomers would be formed. Careful analysis of ^1H, ^{13}C and ^{31}P NMR spectra of the adducts **6** fully confirmed their structure and the anticipated stereochemistry. This analysis allowed us also to propose the preferred conformation of the dihydropyranone ring with phosphoryl and R_2 groups in *pseudo*-axial positions (Fig. 1). In particular, the $^3J_{H3-H4}$ coupling constants were very small (0.8–1.3 Hz), the $^3J_{P-C11}$ couplings were large (17.1–18.9 Hz), and there was an absence of $^3J_{P-C10}$ couplings. Dihedral angels estimated from these coupling constants, using Karplus equation, had values ~90°, ~150° or ~50° and ~90°, respectively. Characteristic coupling constants for **6a** were as follows: $^3J_{H3-H4}$=1.0 Hz, $^3J_{P-H4}$=12.0 Hz, $^3J_{P-C10}$=0.0 Hz and $^3J_{P-C11}$=18.6.

Interesting features present in the ^1H NMR spectra of all adducts **6**, were that protons of one of the ethoxy groups absorbed at an unexpectedly low frequency, e.g., in **6a**, the methyl protons of one of the ethoxy groups had a chemical shift 0.82 ppm as compared to 1.25 ppm for the other. To rationalize these observations, analysis was performed of the heat of formation dependence on the dihedral angle H3–C3–P–O (rotation around the P–C bond) for **6a**. Global energetic minimum has been identified using PM3 Hamiltonian[15] as implemented in Ampac 6.7.[16] The structure representing this minimum is shown on Figure 2. In this structure, the methyl and phosphoryl groups are in diaxial arrangement, with P–C3–C4-Me dihedral angle around 140°. This is in accord with the presented NMR data. Furthermore, H3–C3–P–O dihedral angle has value of 94°, which gives an almost exactly antiparallel array of P=O and C=O bonds and therefore minimizes interactions between these polar groups. In this arrangement one of the ethoxy groups is placed in the shielding area of the carbonyl bond and/or benzene ring. These results provide a plausible explanation of the observed low chemical shift of the methyl and methylene protons for one of the ethoxy groups in **6a**. We believe that this rationalization is valid also for the other adducts **6**.

Adducts **6a–i** were next employed in Horner–Wadsworth–Emmons olefination of formaldehyde. Best results were obtained using sodium hydride as a base and 3 equiv. of paraformaldehyde in refluxing benzene. In these conditions adducts **6** were transformed into the expected 3-methylidenechroman-2-ones **7** and/or into their rearrangement products 3-methylchromen-2-ones **8**. Only adduct **6i** gave

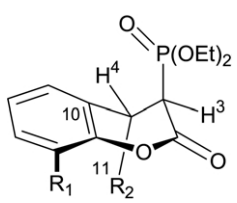

Figure 1. Preferred conformation of the dihydropyranone ring in adducts **6**.

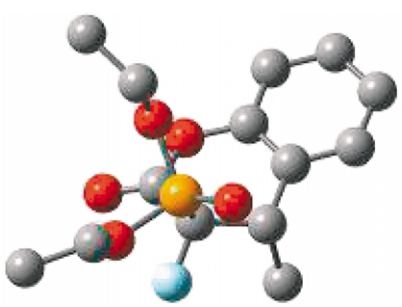

Figure 2. Structure representing global energetic minimum for adduct **6a**.

a complex mixture of products which were difficult to identify. Crude products were purified by column chromatography. Yields are shown in Table 1.

Olefinations performed with adducts **6a**–**d** yielded corresponding 3-methylidenechromanones **7a**–**d**, whereas these performed with adducts **6g**,**h** gave 3-methylchromenones **8g**,**h**, as the only products. On the other hand, reactions with adducts **6e** and **6f** were not chemoselective and mixtures of **7e/8e** and **7f/8f** in 3:7 and 7:3 ratios were obtained, respectively. However, we were pleased to observe that when reactions of **6e**,**f** were performed at room temperature, in THF as a solvent, almost no rearrangement took place and the yields were still good (Table 1). In these conditions adduct **6e** gave a mixture of **7e** and **8e** in 95:5 ratio. This mixture was easily separated by column chromatography to give pure **7e**. Reaction of **6f** gave chromanone **7f** and no detectable amounts of the rearrangement product. Structures of all chromanones **7** and chromenones **8** were unequivocally confirmed by their ^{1}H and ^{13}C NMR spectra.

3. Conclusions

In summary, we have shown that Michael addition of various nucleophiles to 3-diethoxyphosphorylchromen-2-ones **4a**,**b** combined with Horner–Wadsworth–Emmons reaction of the adducts **6** with formaldehyde is a convenient tool for the synthesis of 3-methylidenechroman-2-ones **7** or 3-methylchromen-2-ones **8**. The relative configuration and preferred conformation of the intermediate adducts **6** was also elucidated on the basis of ^{1}H and ^{13}C NMR spectra and semiempirical PM3 calculations.

4. Experimental

4.1. General

Organic solvents and reagents were purified by the appropriate standard procedures.[17] IR spectra were recorded on a Specord M80 spectrometer. ^{1}H NMR (250 MHz), ^{13}C NMR (62.9 MHz) and ^{31}P NMR (101 MHz) spectra were recorded on a Bruker DPX-250 spectrometer with TMS as an internal standard and 85% H_3PO_4 as an external standard, respectively. ^{31}P NMR spectra were recorded using broad band proton decoupling. Column chromatography was performed on FLUKA® silica gel 60 (230–400 mesh).

All Grigard reagents, but vinylmagnesium bromide, were prepared from corresponding alkyl halides and magnesium in Et_2O. Vinylmagnesium bromide was purchased from FLUKA®. 3-Diethoxyphosphorylchromen-2-ones **4a**,**b** were prepared using previously reported procedure.[13]

4.2. General procedure for the preparation of 3-diethoxyphosphorylchroman-2-ones 6a–f

To a solution of chromenone **4** (3.5 mmol) and a catalytic amount of CuI (0.034 g, 0.18 mmol) in Et_2O (20 mL), a solution of Grignard reagent (excesses are given in Table 1) was added dropwise, under argon atmosphere, at 0 °C. When the addition was completed the solution was warmed to room temperature and stirred for 2.5 h. After this time the reaction mixture was quenched with water (2 mL), acidified to pH~1.5 with 10% HCl solution and extracted with $CHCl_3$ (4×10 mL). The organic extracts were washed with water (10 mL) and dried over $MgSO_4$. Evaporation of the solvent gave crude product which was purified by column chromatography and/or by crystallization.

4.2.1. *trans*-3-Diethoxyphosphoryl-4-methylchroman-2-one (6a). Yield 0.89 g, 85%; white prisms (from EtOAc/hexane); mp 110–111 °C; ^{31}P NMR δ (ppm) 19.01; ^{1}H NMR δ (ppm) 0.82 (t, 3H, $^{3}J_{HH}$=7.3 Hz, C H_3CH_2O), 1.22 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 1.24 (d, 3H, $^{3}J_{HH}$=7.3 Hz, C H_3CH), 3.25 (dd, 1H, $^{2}J_{HP}$=25.0 Hz, $^{3}J_{HH}$=1.0 Hz, CHC H P), 3.38 (ddq, 1H, $^{2}J_{HH}$=10.0 Hz, $^{3}J_{HP}$=9.0 Hz, $^{3}J_{HH}$=7.0 Hz, CH_3C H HO), 3.61 (ddq, 1H, $^{3}J_{HP}$=12.0 Hz, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{HH}$=1.0 Hz, C H CHP), 3.70 (ddq, 1H, $^{2}J_{HH}$=10.0 Hz, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{HP}$=7.3 Hz, CH_3CH H O), 4.05 (dq, 2H, $^{3}J_{HP}$=8.0 Hz, $^{3}J_{HH}$=7.0 Hz, CH_3C H_2O), 6.95–7.22 (m, 4H, C_6H_4); $^{1}H\{^{31}P\}$ NMR δ (ppm) 0.82 (t, 3H, $^{3}J_{HH}$=7.3 Hz, C H_3CH_2O), 1.22 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 1.24 (d, 3H, $^{3}J_{HH}$=7.3 Hz, C H_3CH), 3.25 (d, 1H, $^{3}J_{HH}$=1.0 Hz, CHC H P), 3.38 (dq, 1H, $^{2}J_{HH}$=10.0 Hz, $^{3}J_{HH}$=7.0 Hz, CH_3C H HO), 3.61 (dq, 1H, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{HH}$=1.0 Hz, C H CHP), 3.70 (dq, 1H, $^{2}J_{HH}$=10.0 Hz, $^{3}J_{HH}$=7.3 Hz, CH_3CH H O), 4.05 (q, 2H, $^{3}J_{HH}$=7.0 Hz, CH_3C H_2O), 6.35–7.22 (m, 4H, C_6H_4); ^{13}C NMR δ (ppm) 15.86 (d, $^{3}J_{CP}$=6.2 Hz, C H_3CH_2OP), 16.21 (d, $^{3}J_{CP}$=6.3 Hz, C H_3CH_2OP), 23.68 (d, $^{3}J_{CP}$=18.6 Hz, C H_3CHCHP), 32.44 (d, $^{2}J_{CP}$=4.4 Hz, CH_3C HCHP), 47.23 (d, $^{1}J_{CP}$=127.8 Hz, CH_3CH C HP), 62.88 (d, $^{2}J_{CP}$=7.1 Hz, CH_3C H_2OP), 63.19 (d, $^{2}J_{CP}$=6.7 Hz, CH_3C H_2OP), 116.68 (s, C_6H_4), 124.95 (s, C_6H_4), 125.61 (s, C_6H_4), 127.84 (s, C_6H_4), 128.51 (s, C_6H_4), 150.89 (s, C_6H_4), 163.75 (d, $^{2}J_{CP}$=6.3 Hz, C=O); IR (cm^{-1}, film) 1772 (C=O), 1260 (P=O), 1028 (P–O). Anal. calcd for $C_{14}H_{19}O_5P$ (298.28) C, 56.38; H, 6.42; P, 10.38. Found C, 56.22; H, 6.48; P, 10.20.

4.2.2. *trans*-3-Diethoxyphosphoryl-8-methoxy-4-methylchroman-2-one (6b). Yield 0.84 g, 73%; light yellow prisms (from EtOAc/hexane); mp 107–108 °C; ^{31}P NMR δ (ppm) 18.53; ^{1}H NMR δ (ppm) 0.91 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 1.32 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 1.33 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH), 3.31 (dd, 1H, $^{2}J_{HP}$=25.0 Hz, $^{3}J_{HH}$=0.8 Hz, CHC H P), 3.46 (ddq, 1H, $^{2}J_{HH}$=10.0 Hz, $^{3}J_{HP}$=9.0 Hz, $^{3}J_{HH}$=7.0 Hz, CH_3CH H O), 3.54–3.67 (m, 1H, C H CHP), 3.79 (ddq, 1H, $^{2}J_{HH}$=10.0 Hz, $^{3}J_{HH}$=7.0 Hz, $^{3}J_{HP}$=7.0 Hz, CH_3C H HO), 3.89 (s, 3H, C H_3O), 4.12 (dq, 2H, $^{3}J_{HP}$=8.0 Hz, $^{3}J_{HH}$=7.0 Hz, CH_3C H_2O), 6.82–7.11 (m, 3H, C_6H_3); ^{13}C NMR δ (ppm) 15.49 (d, $^{3}J_{CP}$=6.4 Hz, C H_3CH_2OP), 15.92 (d, $^{3}J_{CP}$=6.3 Hz, C H_3CH_2OP), 23.10 (d, $^{3}J_{CP}$=18.6 Hz, C H_3CHCHP), 32.35 (d, $^{2}J_{CP}$=4.3 Hz, CH_3C HCHP), 46.78 (d, $^{1}J_{CP}$=128.0 Hz, CH_3CH C HP), 55.87 (s, C H_3O), 62.47 (d, $^{2}J_{CP}$=11.0 Hz, CH_3C H_2OP), 62.89 (d, $^{2}J_{CP}$=6.7 Hz, CH_3C H_2OP), 111.05 (s, C_6H_3), 119.02 (s, C_6H_3), 124.67 (s, C_6H_3), 126.36 (s, C_6H_3), 139.84 (s, C_6H_3), 147.15 (s, C_6H_3), 162.89 (d, $^{2}J_{CP}$=6.3 Hz, C=O); IR (cm^{-1}, film) 1756 (C=O), 1216 (P=O), 1068 (P–O). Anal. calcd for $C_{15}H_{21}O_6P$ (328.30) C, 54.88; H, 6.45; P, 9.43. Found C, 54.95; H, 6.58; P, 9.31.

4.2.3. *trans*-3-Diethoxyphosphoryl-4-butylchroman-2-one (6c). Yield 0.89 g, 82%; oil; (eluent EtOAc/hexane=9/

1); ^{31}P NMR δ (ppm) 19.31; ^{1}H NMR δ (ppm) 0.79 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C $H_3(CH_2)_2CH_2$), 0.82 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 1.19–1.32 (m, 4H, $CH_3(CH_2)_2CH_2$), 1.25 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 1.47–1.56 (m, 2H, $CH_3(CH_2)_2C$ H_2), 3.33 (dd, 1H, $^{2}J_{HP}$=24.5 Hz, $^{3}J_{HH}$=0.8 Hz, CHC *H* P), 3.36 (m, 1H, CH_3CH *H* O), 3.38 (m, 1H, C *H* CHP), 3.69 (ddq, 1H, $^{2}J_{HH}$=10.0 Hz, $^{3}J_{HH}$=7.0 Hz, $^{3}J_{HP}$=7.0 Hz, CH_3C *H* HO), 4.05 (dq, 2H, $^{3}J_{HP}$=8.0 Hz, $^{3}J_{HH}$=7.0 Hz, CH_3C H_2O), 6.95–7.21 (m, 4H, C_6H_4); ^{13}C NMR δ (ppm) 13.45 (s, *C* $H_3(CH_2)_2CH_2$), 15.48 (d, $^{3}J_{CP}$=6.1 Hz, *C* H_3CH_2OP), 15.80 (d, $^{3}J_{CP}$=6.2 Hz, *C* H_3CH_2OP), 21.94 (s, CH_3C $H_2CH_2CH_2$), 28.10 (s, CH_3CH_2C H_2CH_2), 36.32 (d, $^{3}J_{CP}$=17.1 Hz, $CH_3(CH_2)_2C$ H_2), 36.90 (d, $^{2}J_{CP}$=4.3 Hz, *C* HCHP), 45.36 (d, $^{1}J_{CP}$=127.9 Hz, CH *C* HP), 62.45 (d, $^{2}J_{CP}$=7.0 Hz, CH_3C H_2OP), 62.74 (d, $^{2}J_{CP}$=6.7 Hz, CH_3C H_2OP), 116.26 (s, C_6H_4), 123.98 (s, C_6H_4), 124.19 (s, C_6H_4), 128.14 (s, C_6H_4), 128.37 (s, C_6H_4), 150.75 (s, C_6H_4), 163.55 (d, $^{2}J_{CP}$=6.0 Hz, *C*=O); IR (cm^{-1}, film) 1768 (*C=O*), 1224 (*P=O*), 1020 (*P–O*). Anal. calcd for $C_{17}H_{25}O_5P$ (340.36) C, 59.99; H, 7.40; P, 9.10. Found C, 60.17; H, 7.32; P, 9.14.

4.2.4. *trans*-3-Diethoxyphosphoryl-8-methoxy-4-butylchroman-2-one (6d). Yield 1.18 g, 91%; oil; (eluent $CHCl_3$); ^{31}P NMR δ (ppm) 18.83; ^{1}H NMR δ (ppm) 0.86 (t, 3H, $^{3}J_{HH}$=6.8 Hz, C $H_3(CH_2)_2CH_2$), 0.91 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 1.25–1.39 (m, 4H, $CH_3(CH_2)_2$-CH_2), 1.32 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 1.51–1.62 (m, 2H, $CH_3(CH_2)_2C$ H_2), 3.37–3.44 (m, 1H, CH_3CH *H* O), 3.39 (dd, 1H, $^{2}J_{HP}$=25.5 Hz, $^{3}J_{HH}$=1.0 Hz, CHC *H* P), 3.44–3.53 (m, 1H, C *H* CHP), 3.79 (ddq, 1H, $^{2}J_{HH}$=10.0 Hz, $^{3}J_{HH}$=7.0 Hz, $^{3}J_{HP}$=7.0 Hz, CH_3C *H* HO), 3.89 (s, 3H, C H_3O), 4.12 (dq, 2H, $^{3}J_{HP}$=8.0 Hz, $^{3}J_{HH}$=7.0 Hz, CH_3C H_2O), 6.78–7.07 (m, 3H, C_6H_3); ^{13}C NMR δ (ppm) 13.60 (s, *C* $H_3(CH_2)_2CH_2$), 15.53 (d, $^{3}J_{CP}$=6.4 Hz, *C* H_3CH_2OP), 15.94 (d, $^{3}J_{CP}$=6.3 Hz, *C* H_3CH_2OP), 22.12 (s, CH_3C $H_2CH_2CH_2$), 28.32 (s, CH_3CH_2C H_2CH_2), 36.26 (d, $^{3}J_{CP}$=17.1 Hz, $CH_3(CH_2)_2C$ H_2), 37.23 (d, $^{2}J_{CP}$=4.3 Hz, *C* HCHP), 45.35 (d, $^{1}J_{CP}$=128.3 Hz, CH *C* HP), 55.88 (s, *C* H_3O), 62.64 (d, $^{2}J_{CP}$=7.0 Hz, CH_3C H_2OP), 62.93 (d, $^{2}J_{CP}$=6.7 Hz, CH_3C H_2OP), 111.08 (s, C_6H_3), 120.05 (s, C_6H_3), 124.31 (s, C_6H_3), 125.17 (s, C_6H_3), 140.11 (s, C_6H_3), 147.19 (s, C_6H_3), 163.21 (d, $^{2}J_{CP}$=5.7 Hz, *C*=O); IR (cm^{-1}, film) 1760 (*C=O*), 1216 (*P=O*), 1020 (*P–O*). Anal. calcd for $C_{18}H_{27}O_6P$ (370.39) C, 58.37; H, 7.35; P, 8.36. Found C, 58.19; H, 7.46; P, 8.33.

4.2.5. *trans*-3-Diethoxyphosphoryl-4-vinylchroman-2-one (6e). Yield 0.77 g, 71%; eluent $CHCl_3$/acetone 95/5, white prisms (from AcOEt/hexane); mp 64–68 °C; ^{31}P NMR δ (ppm) 18.66; ^{1}H NMR δ (ppm) 0.91 (t, 3H, $^{3}J_{HH}$=7.3 Hz, C H_3CH_2O), 1.34 (t, 3H, $^{3}J_{HH}$=7.3 Hz, CH_3CH *H* O), 3.49 (dd, 1H, $^{2}J_{HP}$=25.0 Hz, $^{3}J_{HH}$=1.3 Hz, CHC *H* P), 3.79 (qdd, 1H, $^{2}J_{HH}$=10.0 Hz, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{HP}$=7.3 Hz, CH_3C *H* HO), 4.14 (dq, 2H, $^{3}J_{HP}$=8.0 Hz, $^{3}J_{HH}$=7.3 Hz, CH_3C H_2O), 4.18–4.22 (m, 1H, C *H* CHP), 4.92 (dd, 1H, $^{3}J_{HH}$=17.0 Hz, $^{4}J_{HH}$=1.5 Hz, C *H* H=CH), 5.13 (dd, 1H, $^{3}J_{HH}$=10.3 Hz, $^{4}J_{HH}$=1.0 Hz, CH *H*=CH), 5.89 (2dd, 1H, $^{3}J_{HH}$=17.0 Hz, $^{3}J_{HH}$=10.3 Hz, $^{3}J_{HH}$=6.0 Hz, $^{3}J_{HH}$=6.0 Hz, CH_2=C *H*), 7.05–7.28 (m, 4H, C_6H_4); ^{13}C NMR δ (ppm) 15.50 (d, $^{3}J_{CP}$=6.1 Hz, *C* H_3CH_2OP), 15.82 (d, $^{3}J_{CP}$=6.3 Hz, *C* H_3CH_2OP), 40.07 (d, $^{2}J_{CP}$=3.5 Hz, *C* HCHP), 44.94 (d, $^{1}J_{CP}$=127.2 Hz, CH *C* HP), 62.67 (d, $^{2}J_{CP}$=7.0 Hz, CH_3C H_2OP), 62.97 (d, $^{2}J_{CP}$=6.7 Hz, CH_3C H_2OP), 116.25 (s, *C* H_2=CHCH), 116.32 (s, C_6H_4), 121.43 (s, C_6H_4), 124.63 (s, C_6H_4), 128.42 (s, C_6H_4), 128.69 (s, C_6H_4), 137.07 (d, $^{3}J_{CP}$=18.5 Hz, CH_2=*C* HCH), 151.00 (s, C_6H_4), 162.85 (d, $^{2}J_{CP}$=5.9 Hz, *C*=O); IR (cm^{-1}, film) 1768 (*C=O*), 1640 (*C=C*), 1256 (*P=O*), 1024 (*P–O*). Anal. calcd for $C_{15}H_{19}O_5P$ (310.29) C, 58.06; H, 6.17; P, 9.98. Found C, 58.17; H, 6.12; P, 9.73.

4.2.6. *trans*-3-Diethoxyphosphoryl-8-methoxy-4-vinylchroman-2-one (6f). Yield 0.89 g, 75%; eluent AcOEt, light yellow prisms (from AcOEt/hexane); mp 60–63 °C; ^{31}P NMR δ (ppm) 18.50; ^{1}H NMR δ (ppm) 0.92 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 1.33 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 3.44–3.49 (m, 1H, CH_3CH *H* O), 3.49 (dd, 1H, $^{2}J_{HP}$=24.8 Hz, $^{3}J_{HH}$=0.8 Hz, CHC *H* P), 3.79 (ddq, 1H, $^{2}J_{HH}$=10.0 Hz, $^{3}J_{HP}$=7.3 Hz, $^{3}J_{HH}$=7 Hz, CH_3C *H* HO), 3.89 (s, 3H, C H_3O), 4.13 (dq, 2H, $^{3}J_{HP}$=8.0 Hz, $^{3}J_{HH}$=7.0 Hz, CH_3CH *H* O), 4.17–4.21 (m, 1H, C *H* CHP), 4.92 (dd, 1H, $^{3}J_{HH}$=17.0 Hz, $^{4}J_{HH}$=1.5 Hz, C *H* H=CH), 5.13 (dd, 1H, $^{3}J_{HH}$=10.0 Hz, $^{4}J_{HH}$=0.8 Hz, CH *H*=CH), 5.88 (2dd, 1H, $^{3}J_{HH}$=17.0 Hz, $^{3}J_{HH}$=10.3 Hz, $^{3}J_{HH}$=6.0 Hz, $^{3}J_{HH}$=6.0 Hz, CH_2=C *H*), 6.82–7.10 (m, 3H, C_6H_3); ^{13}C NMR δ (ppm) 15.65 (d, $^{3}J_{CP}$=6.5 Hz, *C* H_3CH_2OP), 16.08 (d, $^{3}J_{CP}$=6.3 Hz, *C* H_3CH_2OP), 40.54 (d, $^{2}J_{CP}$=3.6 Hz, *C* HCHP), 45.05 (d, $^{1}J_{CP}$=127.4 Hz, CH *C* HP), 56.05 (s, *C* H_3O), 62.95 (d, $^{2}J_{CP}$=7.0 Hz, CH_3C H_2OP), 63.26 (d, $^{2}J_{CP}$=6.8 Hz, CH_3C H_2OP), 116.65 (s, *C* H_2=CHCH), 137.02 (d, $^{3}J_{CP}$=18.9 Hz, CH_2=*C* HCH), 111.61 (s, C_6H_3), 120.08 (s, C_6H_3), 122.77 (s, C_6H_3), 124.86 (s, C_6H_3), 140.54 (s, C_6H_3), 147.37 (s, C_6H_3), 162.67 (d, $^{2}J_{CP}$=5.7 Hz, *C*=O); IR (cm^{-1}, film) 1760 (*C=O*), 1680 (*C=C*), 1256 (*P=O*), 1020 (*P–O*). Anal. calcd for $C_{16}H_{21}O_6P$ (340.32) C, 56.47; H, 6.22; P, 9.10. Found C, 56.40; H, 6.13; P, 8.98.

4.3. General procedure for the preparation of 3,4-di-(diethoxyphosphoryl)-chroman-2-ones 6g,h

To a stirred solution of sodium diethylphosphite in THF (10 mL), generated from NaH (0.13 g, 5.40 mmol) and diethylphosphite (0.44 g, 3.20 mmol), a solution of chromenone **4** (3.20 mmol) in THF (10 mL) was added at room temperature, under argon atmosphere. The reaction mixture was stirred for 3 h and water (10 mL) was added. Extraction with CH_2Cl_2 (3×10 mL), drying ($MgSO_4$) and evaporation of the solvent gave a crude product which was purified by column chromatography (eluent $CHCl_3$/MeOH=98/2).

4.3.1. *trans*-3,4-Di-(diethoxyphosphoryl)chroman-2-one (6g). Yield 0.98 g, 73%; oil; ^{31}P NMR δ (ppm) 18.66 (d, $^{3}J_{PP}$=71.7 Hz, *P* CHCHP), 22.79 (d, $^{3}J_{PP}$=71.7 Hz, PCHCH *P*); ^{1}H NMR δ (ppm) 0.93 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 1.20 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 1.30 (t, 3H, $^{3}J_{HH}$=7.3 Hz, C H_3CH_2O), 1.33 (t, 3H, $^{3}J_{HH}$=7.0 Hz, C H_3CH_2O), 3.59–4.31 (m, 10H, CH_3C H_2O, PC *H* C *H* P), 7.03–7.39 (m, 4H, C_6H_4); ^{13}C NMR δ (ppm) 15.57 (d, $^{3}J_{CP}$=6.1 Hz, *C* H_3CH_2OP), 15.85 (d, $^{3}J_{CP}$=5.4 Hz, *C* H_3CH_2OP), 15.87 (d, $^{3}J_{CP}$=6.3 Hz, *C* H_3CH_2OP), 16.03 (d, $^{3}J_{CP}$=5.5 Hz, *C* H_3CH_2OP), 35.97 (dd, $^{1}J_{CP}$=141.1 Hz, $^{2}J_{CP}$=3.8 Hz, P *C* HCHP), 40.00 (dd, $^{1}J_{CP}$=126.1 Hz, $^{2}J_{CP}$=3.9 Hz, PCH *C* HP), 63.00 (d, $^{2}J_{CP}$=3.4 Hz, CH_3C

H_2OP), 63.11 (d, $^2J_{CP}$=3.4 Hz, CH_3C H_2OP), 63.26 (d, $^2J_{CP}$=7.2 Hz, CH_3C H_2OP), 63.48 (d, $^2J_{CP}$=6.7 Hz, CH_3C H_2OP), 115.21 (dd, $^3J_{CP}$=7.6 Hz, $^2J_{CP}$=1.3 Hz, C_6H_4), 116.47 (d, $^4J_{CP}$=3.2 Hz, C_6H_4), 124.58 (d, $^5J_{CP}$=3.2 Hz, C_6H_4), 129.31 (d, $^4J_{CP}$=4.4 Hz, C_6H_4), 129.76 (d, $^3J_{CP}$=5.0 Hz, C_6H_4), 151.46 (d, $^3J_{CP}$=5.0 Hz, C_6H_4), 161.87 (dd, $^3J_{CP}$=6.3 Hz, $^2J_{CP}$=1.9 Hz, C=O); IR (cm^{-1}, film) 1768 (C=O), 1200 (P=O), 1232 (P=O), 1016 (P–O), 1026 (P–O). Anal. calcd for $C_{17}H_{26}O_8P_2$ (420.34) C, 48.58; H, 6.23; P, 14.74. Found C, 48.66; H, 6.30; P, 14.87.

4.3.2. *trans*-3,4-Di-(diethoxyphosphoryl)-8-methoxychroman-2-one (6h). Yield 0.72 g, 50%; oil; ^{31}P NMR δ (ppm) 18.20 (d, $^3J_{PP}$=71.7 Hz, P CHCHP), 22.45 (d, $^3J_{PP}$=71.7 Hz, PCHCH P; ^{1}H NMR δ (ppm) 0.95 (t, 3H, $^3J_{HH}$=7.0 Hz, C H_3CH_2O), 1.22 (t, 3H, $^3J_{HH}$=7.1 Hz, C H_3CH_2O), 1.32 (t, 3H, $^3J_{HH}$=7.1 Hz, C H_3CH_2O), 1.33 (dt, 3H, $^3J_{HH}$=7.0 Hz, $^4J_{HP}$=0.6 Hz, C H_3CH_2O), 3.88 (s, 3H, C H_3O), 3.57–4.18 (m, 10H, CH_3C H_2O, PC H C H P), 6.90–7.14 (m, 3H, C_6H_3); ^{13}C NMR δ (ppm) 15.68 (d, $^3J_{CP}$=6.3 Hz, C H_3CH_2OP), 16.09 (2d, $^3J_{CP}$=5.9 Hz, C H_3CH_2OP), 16.27 (d, $^3J_{CP}$=5.5 Hz, C H_3CH_2OP), 36.36 (dd, $^1J_{CP}$=141.0 Hz, $^2J_{CP}$=3.8 Hz, P C HCHP), 40.02 (dd, $^1J_{CP}$=126.4 Hz, $^2J_{CP}$=4.0 Hz, PCH C HP), 56.13 (s, C H_3O), 63.18 (d, $^2J_{CP}$=2.2 Hz, CH_3C H_2OP), 63.29 (d, $^2J_{CP}$=2.3 Hz, CH_3C H_2OP), 63.45 (d, $^2J_{CP}$=7.2 Hz, CH_3C H_2OP), 63.67 (d, $^2J_{CP}$=6.8 Hz, CH_3C H_2OP), 112.15 (d, $^5J_{CP}$=3.8 Hz, C_6H_3), 116.49 (dd, $^3J_{CP}$=8.2 Hz, $^2J_{CP}$=1.9 Hz, C_6H_3), 121.39 (d, $^3J_{CP}$=5.0 Hz, C_6H_3), 124.64 (d, $^4J_{CP}$=3.2 Hz, C_6H_3), 141.15 (d, $^3J_{CP}$=6.3 Hz, C_6H_3), 147.41 (d, $^4J_{CP}$=3.8 Hz, C_6H_3), 161.59 (dd, $^3J_{CP}$=5.7 Hz, $^2J_{CP}$=1.9 Hz, C=O); IR (cm^{-1}, film) 1764 (C=O), 1200 (P=O), 1276 (P=O), 1044 (P–O), 1080 (P–O). Anal. calcd for $C_{18}H_{28}O_9P_2$ (450.37) C, 48.01; H, 6.27; P, 13.75. Found C, 48.12; H, 6.18; P, 13.65.

4.3.3. Preparation of *trans*-3-diethoxyphosphoryl-4-nitromethylchroman-2-one (6i). A solution of nitromethane (0.24 g, 3.91 mmol) in THF (5 mL) was added to a stirred suspension of NaH (0.11 g, 4.60 mmol) in THF (15 mL), under argon atmosphere, and the reaction mixture was stirred at 40 °C for 15 min. After this time, a solution of chromanone **4a** (1.00 g, 3.55 mmol) in THF (5 mL) was added dropwise and the reaction mixture was stirred at 50 °C for 2 h. After was cooled to rt, it was acidified to pH~1.5 with 1 N HCl solution. Extraction with $CHCl_3$ (4×15 mL), drying ($MgSO_4$) and evaporation of the solvent yielded a crude product which was purified by column chromatography (eluent, EtOAc) to give pure **6i** (0.71 g, 58%); oil; ^{31}P NMR δ (ppm) 16.99; ^{1}H NMR δ (ppm) 0.96 (t, 3H, $^3J_{HH}$=7.0 Hz, C H_3CH_2O), 1.33 (t, 3H, $^3J_{HH}$=7.5 Hz, C H_3CH_2O), 3.50–3.60 (m, 1H, CH_3CH H O), 3.56 (dd, 1H, $^2J_{HP}$=26.3 Hz, $^3J_{HH}$=1.0 Hz, CHC H P), 3.60–3.64 (m, 1H, C H CHP), 3.79 (ddq, 1H, $^2J_{HH}$=10.0 Hz, $^3J_{HH}$=7.0 Hz, $^3J_{HP}$=7.0 Hz, CH_3C H HO), 4.15 (dq, 2H, $^3J_{HP}$=8.0 Hz, $^3J_{HH}$=7.5 Hz, CH_3C H_2O), 4.52–4.55 (m, 2H, C H_2NO_2), 7.09–7.30 (m, 4H, C_6H_4); ^{13}C NMR δ (ppm) 15.73 (d, $^3J_{CP}$=6.1 Hz, C H_3CH_2OP), 16.01 (d, $^3J_{CP}$=6.2 Hz, C H_3CH_2OP), 35.80 (d, $^2J_{CP}$=2.7 Hz, C HCHP), 42.85 (d, $^1J_{CP}$=128.3 Hz, CH C HP), 63.36 (d, $^2J_{CP}$=7.1 Hz, CH_3C H_2OP), 63.72 (d, $^2J_{CP}$=6.7 Hz, CH_3C H_2OP), 78.13 (d, $^3J_{CP}$=19.0 Hz, NO_2C H_2CHCHP), 117.09 (s, C_6H_4), 118.22 (s, C_6H_4), 125.42 (s, C_6H_4), 128.68 (s, C_6H_4), 130.31 (s, C_6H_4), 151.36 (s, C_6H_4), 162.04 (d, $^2J_{CP}$=6.3 Hz, C=O); IR (cm^{-1}, film) 1764 (C=O), 1556 (N=O), 1256 (P=O), 1028 (P–O). Anal. calcd for $C_{14}H_{18}NO_7P$ (343.28) C, 48.99; H, 5.29; N, 4.08; P, 9.02. Found C, 49.08; H, 5.34; N, 3.89; P, 8.90.

4.4. General procedure for the preparation of 3-methylidenechroman-2-ones 7a–d and 3-methylchromen-2-ones 8g,h

A solution of 3-diethoxyphosphorylchromanone **6** (1.5 mmol) in benzene (5 mL) was added at room temperature to a suspension of NaH (0.04 g, 1.7 mmol) in benzene (10 mL) and the reaction mixture was stirred under argon atmosphere for 0.5 h. Then paraformaldehyde (0.13 g, 4.5 mmol) was added in one portion. The mixture was refluxed for 1 h, cooled to room temperature, and water (20 mL) was added. Extraction with benzene (2×15 mL), drying ($MgSO_4$) and evaporation of the solvent gave a crude product which was purified by column chromatography.

4.4.1. 3-Methylidene-4-methylchroman-2-one (7a). Yield 0.19 g, 71%, (lit.[10]); oil; (eluent $CHCl_3$/hexane=9/1); ^{1}H NMR δ (ppm) 1.44 (d, 3H, $^3J_{HH}$=7.0 Hz, C H_3CHC), 3.81 (qdd, 1H, $^3J_{HH}$=7.0 Hz, $^4J_{HH}$=2.0 Hz, $^4J_{HH}$=1.0 Hz, CH_3C H C), 5.75 (dd, 1H, $^4J_{HH}$=2.0 Hz, $^2J_{HH}$=1.0 Hz, C H H=CCH), 6.35 (t, 1H, $^4J_{HH}$=$^2J_{HH}$=1.0 Hz, CH H=CCH), 7.08–7.22 (m, 3H, C_6H_3); ^{13}C NMR δ (ppm) 22.67 (s, C H_3CH), 37.32 (s, CH_3C H), 117.12 (s, C_6H_4), 124.77 (s, C H_2=CCH), 126.77 (s, C_6H_4), 127.03 (s, C_6H_4), 127.12 (s, C_6H_4), 128.25 (s, C_6H_4), 138.01 (s, CH_2=C CH), 150.09 (s, C_6H_4), 163.52 (s, C=O); IR (cm^{-1}, film) 1756 (C=O), 1608 (C=C). Anal. calcd for $C_{11}H_{10}O_2$ (174.20) C, 75.84; H, 5.79. Found C, 75.69; H, 5.71.

4.4.2. 8-Methoxy-3-methylidene-4-methylchroman-2-one (7b). Yield 0.21 g, 68%; oil; (eluent $CHCl_3$/hexane); ^{1}H NMR δ (ppm) 1.42 (d, 3H, $^3J_{HH}$=7.3 Hz, C H_3CHC), 3.79 (qdd, 1H, $^3J_{HH}$=7.3 Hz, $^4J_{HH}$=1.0 Hz, $^4J_{HH}$=0.8 Hz, CH_3C H C), 3.89 (s, 3H, C H_3O), 5.74 (t, 1H, $^2J_{HH}$=$^4J_{HH}$=1.0 Hz, C H H=CCH), 6.34 (dd, 1H, $^2J_{HH}$=1.0 Hz, $^4J_{HH}$=0.8 Hz, CH H=CCH), 6.76–7.10 (m, 3H, C_6H_3); ^{13}C NMR δ (ppm) 21.71 (s, C H_3CH), 36.62 (s, CH_3C H), 55.04 (s, C H_3O), 109.91 (s, C_6H_3), 117.16 (s, C_6H_3), 123.75 (s, C_6H_3), 126.07 (s, C H_2=CCH), 127.17 (s, C_6H_3), 136.91 (s, C_6H_3), 138.31 (s, CH_2=C CH), 146.70 (s, C_6H_3), 161.95 (s, C=O); IR (cm^{-1}, film) 1756 (C=O), 1660 (C=C). Anal. calcd for $C_{12}H_{12}O_3$ (204.23) C, 70.58; H, 5.92. Found C, 70.67; H, 6.09.

4.4.3. 4-Butyl-3-methylidenechroman-2-one (7c). Yield 0.19 g, 58%; oil; (eluent $CHCl_3$/hexane=7/3); ^{1}H NMR δ (ppm) 0.87 (t, 3H, $^3J_{HH}$=6.8 Hz, C $H_3(CH_2)_2CH_2$), 1.25–1.37 (m, 4H, $CH_3(CH_2)_2CH_2$), 1.58–1.68 (m, 2H, $CH_3(CH_2)_2C$ H_2), 3.58 (td, 1H, $^3J_{HH}$=7.3 Hz, $^4J_{HH}$=1.0 Hz, $CH_3(CH_2)_3C$ H), 5.69 (dd, 1H, $^2J_{HH}$=1.3 Hz, $^4J_{HH}$=1.0 Hz, C H H=CCH), 6.36 (d, 1H, $^2J_{HH}$=1.3 Hz, CH H=CCH), 7.05–7.26 (m, 4H, C_6H_4); ^{13}C NMR δ (ppm) 13.79 (s, C $H_3(CH_2)_2CH_2$), 22.27 (s, CH_3C $H_2(CH_2)_2$), 28.16 (s, CH_3CH_2C H_2CH_2), 37.54 (s, $CH_3(CH_2)_2C$ H_2), 43.82 (s, CH_2=C C H), 128.05 (s, C H_2=CCH), 136.68 (s, CH_2=C CH), 117.06 (s, C_6H_4), 124.53 (s, C_6H_4), 126.40 (s, C_6H_4), 127.74 (s, C_6H_4), 128.14

(s, C_6H_4), 150.22 (s, C_6H_4), 163.64 (s, C=O); IR (cm^{-1}, film) 1752 (C=O), 1600 (C=C). Anal. calcd for $C_{14}H_{16}O_2$ (216.28) C, 77.75; H, 7.46. Found C, 77.92; H, 7.38.

4.4.4. 4-Butyl-8-methoxy-3-methylidenechroman-2-one (7d). Yield 0.33 g, 89%; oil; (eluent $CHCl_3$); ^{1}H NMR δ (ppm) 0.68 (t, 3H, $^3J_{HH}$=7.0 Hz, C $H_3(CH_2)_2CH_2$), 1.23–1.33 (m, 4H, $CH_3(CH_2)_2CH_2$), 1.59–1.65 (m, 2H, $CH_3(CH_2)_2C$ H_2), 3.56 (t, 1H, $^3J_{HH}$=7.3 Hz, $CH_3(CH_2)_3C$ H), 3.86 (s, 3H, C H_3O), 5.68 (d, 1H, $^2J_{HH}$=1.0 Hz, C H H=CCH), 6.35 (d, 1H, $^2J_{HH}$=1.0 Hz, CH H=CCH), 6.71–7.09 (m, 3H, C_6H_3); ^{13}C NMR δ (ppm) 13.75 (s, C $H_3(CH_2)_2CH_2$), 22.24 (s, CH_3C $H_2(CH_2)_2$), 28.15 (s, CH_3CH_2C H_2CH_2), 37.26 (s, $CH_3(CH_2)_2C$ H_2), 43.98 (s, CH_2=C C H), 55.93 (s, C H_3O), 127.88 (s, C H_2=CCH), 136.58 (s, CH_2=C CH), 10.78 (s, C_6H_3), 19.12 (s, C_6H_3), 124.47 (s, C_6H_3), 127.48 (s, C_6H_3), 139.42 (s, C_6H_3), 147.64 (s, C_6H_3), 163.01 (s, C=O); IR (cm^{-1}, film) 1748 (C=O), 1664 (C=C). Anal. calcd for $C_{15}H_{18}O_3$ (246.31) C, 73.15; H, 7.37. Found C, 73.11; H, 7.45.

4.4.5. 4-Diethoxyphosphoryl-3-methylchromen-2-one (8g). Yield 0.28 g, 63%; oil; (eluent AcOEt/hexane=9/1); ^{31}P NMR δ (ppm) 13.39; ^{1}H NMR δ (ppm) 1.28 (t, 6H, $^3J_{HH}$=7.0 Hz, $(CH_3CH_2O)_2$), 2.55 (d, 3H, $^4J_{HP}$=3.0 Hz, C H_3C=CP), 4.01–4.22 (m, 4H, $(CH_3C$ $H_2O)_2$), 7.12–8.44 (m, 4H, C_6H_4); ^{13}C NMR δ (ppm) 15.76 (2d, $^3J_{CP}$=6.2 Hz, C H_3CH_2OP), 16.09 (d, $^3J_{CP}$=6.4 Hz, C H_3C=CP), 40.35 (d, $^3J_{CP}$=3.7 Hz, PC=C C H_3), 62.95 (d, $^2J_{CP}$=7.1 Hz, CH_3C H_2OP), 63.28 (d, $^2J_{CP}$=6.7 Hz, CH_3C H_2OP), 116.58 (s, C_6H_4), 116.62 (s, C_6H_4), 124.88 (s, C_6H_4), 128.68 (s, C_6H_4), 128.92 (s, C_6H_4), 35.55 (d, $^1J_{CP}$=178.9 Hz, P C=CCH_3), 137.29 (d, $^2J_{CP}$=18.3 Hz, PC=C CH_3), 151.26 (s, C_6H_4), 163.23 (d, $^3J_{CP}$=5.7 Hz, C=O); IR (cm^{-1}, film) 1732 (C=O), 1624 (C=C), 1220 (P=O), 1024 (P–O). Anal. calcd for $C_{14}H_{17}O_5P$ (296.26) C, 56.76; H, 5.78; P, 10.45. Found C, 56.61; H, 5.83; P, 10.25.

4.4.6. 4-Diethoxyphosphoryl-8-methoxy-3-methylchromen-2-one (8h). Yield 0.20 g, 40%; oil; (eluent AcOEt/hexane=9/1); ^{31}P NMR δ (ppm) 13.12; ^{1}H NMR δ (ppm) 1.35 (t, 6H, $^3J_{HH}$=7.0 Hz, $(CH_3CH_2O)_2$), 2.63 (d, 3H, $^4J_{HP}$=3.0 Hz, C H_3C=CP), 3.96 (s, 3H, C H_3O), 4.11–4.29 (m, 4H, $(CH_3C$ $H_2O)_2$), 7.03–8.08 (m, 3H, C_6H_3); ^{13}C NMR δ (ppm) 15.29 (d, $^3J_{CP}$=6.4 Hz, $(C$ $H_3CH_2O)_2P$), 15.39 (d, $^3J_{CP}$=5.8 Hz, C H_3C=CP), 55.25 (s, C H_3O), 61.75 (d, $^2J_{CP}$=5.5 Hz, $(CH_3C$ $H_2O)_2P$), 134.88 (d, $^2J_{CP}$=9.5 Hz, PC=C CH_3), 135.70 (d, $^1J_{CP}$=173.3 Hz, P C=CCH_3), 111.56 (s, C_6H_3), 117.74 (d, $^2J_{CP}$=12.0 Hz, C_6H_3), 118.32 (s, C_6H_3), 122.73 (s, C_6H_3), 140.94 (d, $^3J_{CP}$=13.9 Hz, C_6H_3), 147.41 (d, $^4J_{CP}$=3.8 Hz, C_6H_3), 159.56 (d, $^3J_{CP}$=23.3 Hz, C=O); IR (cm^{-1}, film) 1724 (C=O), 1648 (C=C), 1212 (P=O), 1076 (P–O). Anal. calcd for $C_{15}H_{19}O_6P$ (326.29) C, 55.22; H, 5.87; P, 9.49. Found C, 55.40;, H, 5.73; P, 9.69.

4.5. General procedure for the preparation of 3-methylidenechroman-2-ones 7e,f

A solution of 3-diethoxyphosphorylchromanone **6** (1.5 mmol) in THF (5 mL) was added at room temperature to a suspension of NaH (0.04 g, 1.7 mmol) in THF (10 mL) and the reaction mixture was stirred under argon atmosphere for 0.5 h. Then paraformaldehyde (0.13 g, 4.5 mmol) was added in one portion. The mixture was stirred for 5 h and water (20 mL) was added. Extraction with $CHCl_3$ (2×15 mL), drying ($MgSO_4$) and evaporation of the solvent gave a crude product which was purified by column chromatography (eluent $CHCl_3$/hexane=9/1).

4.5.1. 3-Methylidene-4-vinylchroman-2-one (7e). Yield 0.15 g, 55%; oil; ^{1}H NMR δ (ppm) 4.32–4.39 (m, 1H, CH_2=CHC H), 5.10 (ddd, 1H, $^3J_{HH}$=17.0 Hz, $^2J_{HH}$=1.3 Hz, $^4J_{HH}$=1.0 Hz, CH H=CHCH), 5.29 (ddd, 1H, $^3J_{HH}$=10.0 Hz, $^2J_{HH}$=1.3 Hz, $^4J_{HH}$=1.0 Hz, C H H=CHCH), 5.76–5.90 (m, 1H, CH_2=C H CH), 5.82 (dd, 1H, $^2J_{HH}$=1.5 Hz, $^4J_{HH}$=1.0 Hz, CH H=CCH), 6.49 (dd, 1H, $^2J_{HH}$=1.5 Hz, $^4J_{HH}$=1.0 Hz, C H H=CCH), 7.06–7.32 (m, 4H, C_6H_4); ^{13}C NMR δ (ppm) 46.16 (s, CH_2=CH C H), 117.13 (s, C_6H_4), 117.94 (s, C H_2=CHCH), 123.40 (s, C_6H_4), 124.72 (s, C_6H_4), 127.85 (s, C_6H_4), 128.73 (s, C_6H_4), 129.23 (s, C H_2=CCH), 134.82 (s, CH_2=C CH), 136.80 (s, CH_2=C HCH), 150.33 (s, C_6H_4), 162.90 (s, C=O); IR (cm^{-1}, film) 1760 (C=O), 1608 (C=C), 1660 (C=C). Anal. calcd for $C_{12}H_{10}O_2$ (186.21) C, 77.40; H, 5.41. Found C, 77.58; H, 5.30.

4.5.2. 8-Methoxy-3-methylidene-4-vinylchroman-2-one (7f). Yield 0.19 g, 60%; oil; ^{1}H NMR δ (ppm) 3.89 (s, 3H, C H_3O), 4.31–4.37 (m, 1H, CH_2=CHC H), 5.10 (dt, 1H, $^3J_{HH}$=17.0 Hz, $^2J_{HH}$=$^4J_{HH}$=1.0 Hz, C H H=CHCH), 5.26 (dt, 1H, $^3J_{HH}$=10.0 Hz, $^2J_{HH}$=$^4J_{HH}$=1.0 Hz, CH H=CHCH), 5.79 (ddd, 1H, $^3J_{HH}$=17.0 Hz, $^3J_{HH}$=10.0 Hz, $^3J_{HH}$=6.5 Hz, CH_2=C H CH), 5.80 (dd, 1H, $^4J_{HH}$=1.5 Hz, $^2J_{HH}$=1.0 Hz, C H H=CCH), 6.48 (t, 1H, $^4J_{HH}$=$^2J_{HH}$=1.0 Hz, CH H=CCH), 6.76–7.08 (m, 3H, C_6H_3); ^{13}C NMR δ (ppm) 45.38 (s, CH_2=CH C H), 55.05 (s, C H_3O), 116.76 (s, C H_2=CHCH), 128.67 (s, C H_2=CCH), 133.71 (s, CH_2=C HCH), 135.74 (s, CH_2=C CH), 110.31 (s, C_6H_3), 118.13 (s, C_6H_3), 123.51 (s, C_6H_3), 123.68 (s, C_6H_3), 138.62 (s, C_6H_3), 146.72 (s, C_6H_3), 161.40 (s, C=O); IR (cm^{-1}, film) 1748 (C=O), 1616 (C=C), 1664 (C=C). Anal. calcd for $C_{13}H_{12}O_3$ (216.24) C, 72.21; H, 5.59. Found C, 72.27; H, 5.49.

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