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Synthesis of 3-Alkylcoumarins from Salicylaldehydes and α,β-Unsaturated Aldehydes Utilizing Nucleophilic Carbenes: A New Umpoled Domino Reaction

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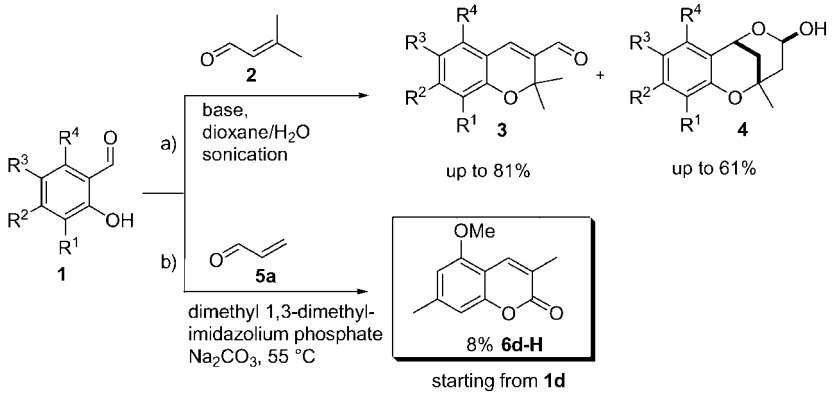
Starting from salicylaldehydes and α,β-unsaturated aldehydes, a new coumarin synthesis in ionic liquids is presented. The key feature is the generation of N-heterocyclic carbenes (NHC) and an Umpolung reaction.

During the last decade, N-heterocyclic carbenes (NHCs) have been successfully introduced as ligands for transition-metal catalysis[1] and recently NHCs have been effectively applied as organocatalysts[2] in a large number of chemical transformations, including transesterification/acylation,[3] benzoin[4] and Stetter[5] reactions. The generation of homoenolate equivalents, by NHC-catalyzed Umpolung of α,β-unsaturated aldehydes, was independently described by Glorius[6] and Bode[7] in the synthesis of γ-butyrolactones. Subsequently, this methodology has been extended towards the synthesis of β-lactones,[8] spiro γ-butyrolactones,[9] γ-lactams[10] and to redox esterification of α,β-unsaturated aldehydes.[11] Herein, we wish to report a novel synthesis of 3-substituted coumarins based on NHC-promoted Umpolung of α,β-unsaturated aldehydes followed by annulation with salicylaldehydes. Coumarins are naturally occurring benzopyran derivatives and have attracted intense interest in recent years because of their diverse pharmacological properties.[12] 3-Alkylcoumarins, which are important building blocks in organic synthesis, can in principle be prepared from carboxylic acids and salicylaldehydes by a modified Perkin reaction.[13] However, so far, this method has not been explored in detail leading to satisfying yields. In addition, a larger amount of acid anhydrides is required to give moderate yields.[14] This is in sharp contrast to the well-elaborated Knoevenagel condensation of malonates with salicylaldehydes leading to 3-substituted coumarins.



Scheme 1. Reaction path **a**: synthesis of 2,2-dimethyl-2*H*-chromene-3-carbaldehydes **3** and 9-methyl-8,12-dioxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6-trien-11-ols **4**.[15] Reaction path **b**: preliminary synthesis of coumarin **6d-H**.

Previously, we have reported that the base-catalyzed condensation of α,β-unsaturated carbonyl compound **2** with salicylaldehydes (2-hydroxybenzaldehydes) **1** yields different dihydrobenzopyrans **3** or **4** depending on the base used in

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the reaction.[15] The reactions, depicted in pathway **a**, Scheme 1, were performed in mixtures of dioxane and water. Upon screening for new conditions for the base-catalyzed condensation of salicylaldehydes with α,β-unsaturated aldehydes, we observed that a new product – a coumarin – was formed if the reactions were carried out in ionic liquids with 2-hydroxy-6-methoxy-4-methylbenzaldehyde (**1d**) and acrolein (**5a**) (pathway **b**, Scheme 1).

Although the coumarin **6d-H** – (Figure 1) being unequivocally characterized by X-ray crystallography – was obtained in low yield (8%), it was the only compound extractable from the reaction mixture by organic solvents, and the pure product could be obtained upon filtration through a pad of silica gel. Optimization of the reaction using 2-hydroxy-6-methoxy-4-methylbenzaldehyde (**1d**) and acrolein (**5a**) as model system was initiated by a quick run through commercially available ionic liquids (IL).[16] The screening of various ionic liquids showed that the nature of the imidazolium ion is of less importance for the formation of coumarins, whereas some dependency on the counterion was observed, i.e. when 1-ethyl-3-methylimidazolium thiocyanate was applied, a mixture of **6d-H** and **3d** was obtained. Ammonium-based ionic liquids did not provide coumarins, indicating that the formation of coumarins depends on the deprotonation of imidazolium ions leading to NHCs. Among the ionic liquids tested, dimethyl 1,3-dimethylimidazolium phosphate provided the highest yields, and was therefore used in further optimization of the reaction between 2-hydroxy-6-methoxy-4-methylbenzaldehyde (**1d**) and acrolein (**5a**). Next, a screening of bases was performed (Na_2CO_3, K_2CO_3, Cs_2CO_3, KOH, NEt_3, DMAP, DABCO, imidazole, sodium acetate, DBU, Hünig′s base), from which it was evident that the inorganic bases provided the highest yields of coumarin **6d-H**, with K_2CO_3 being the best base tested. Imidazole provided chromene **3d** in an 8% yield, whereas DMAP gave traces of both isomers **6d-H** and **3d**. Furthermore, we found that slow addition of acrolein and higher temperature (85 °C) improved the formation of coumarin **6d-H** to 53% (Table 2, Entry 4). Inspired by the work of Glorius[6] and Bode,[7] the coumarin synthesis was performed using catalytic amounts of carbene precursor and K_2CO_3 in toluene. These experiments were carried out in sealed reaction vessels at 70 °C and acrolein was added in one portion (Table 1).

Though the reaction displayed some catalytic character when 0.1 equiv. of dimethyl 1,3-dimethylimidazolium phosphate and of K_2CO_3 was applied (18% yield, Table 1, Entry 1), a considerably higher yield was obtained with stoichiometric amounts of carbene precursors (46% yield, Table 1, Entry 4). The latter result is comparable to the yield obtained using excess of carbene precursor (6.75 equiv.) and slow addition of acrolein at 85 °C, and thus both conditions were tested in the synthesis of coumarins **6** (Table 2).

The results depicted in Table 2 show that the highest yields were achieved with salicylaldehydes bearing substituents in the 6-position, thus shielding the aldehyde from unwanted interactions with the nucleophilic carbenes (Entries 2, 3, 4, 9 and 11, Table 2). Furthermore, a difference in yields obtained using either conditions **A** or **B** was observed which likewise seems to depend on the degree of shielding of the aromatic aldehyde. For salicylaldehyde derivatives without substituents in the 6-position, higher yields were obtained using stoichiometric amounts of carbene precursors (condition B, Entries 1 and 5, Table 2). However, in the case of 3-methoxy- (**1f**) and 4-methoxy-salicylaldehyde (**1g**), no significant difference in yield was observed using either condition **A** or **B**. The electron-deficient 4-nitrosalicylaldehyde only provided a trace of product (data not shown), most likely due to the decreased nucleophilicity of the corresponding phenolate. However, an alternative explanation might be that electron-poor benzaldehydes are more susceptible towards attacks from nucleophilic carbenes leading to non-extractable stable, zwitterionic by-products.

Next, the reactivity of α,β-unsaturated aldehydes was investigated. Coumarins were obtained from (*E*)-cinnamaldehyde (**5b**), (*E*)-2-methoxycinnamaldehyde (**5c**), (*E*)-4-

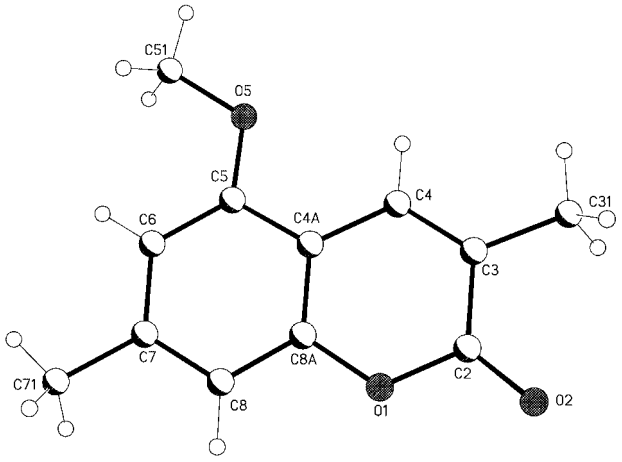
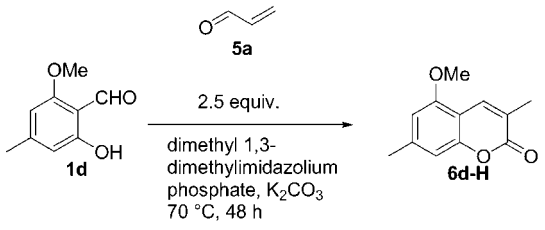


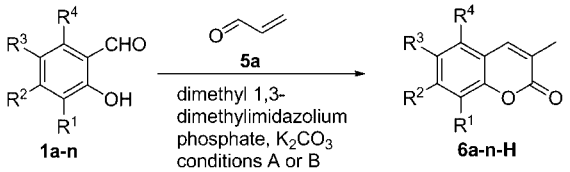
Figure 1. X-ray structure of **6d-H**.

Table 1. Reactions between **1d** and **5a** using catalytic and stoichiometric amounts of K_2CO_3 and dimethyl 1,3-dimethylimidazolium phosphate.



Entry	Equiv. K_2CO_3	Equiv. dimethyl 1,3-dimethyl-imidazolium phosphate	Isolated yield [%]
1	0.1	0.1	18
2	0.2	0.2	24
3	0.5	0.5	29
4	1.0	1.0	46
5	1.0	2.0	34

Table 2. Reactions of salicylaldehyde derivatives **1a**–**n** with acrolein.[a]



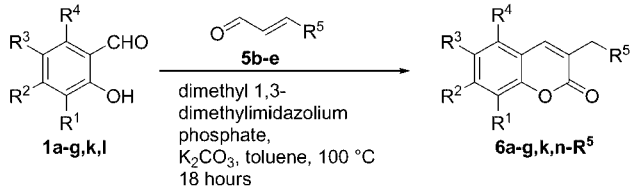
Entry	1	R^1	R^2	R^3	R^4	6	Condition A* yield [%][a]	Condition B** yield [%][a]
1	**1a**	H	H	H	H	**6a-H**	7	26
2	**1b**	H	H	H	OMe	**6b-H**	53	33
3	**1c**	Br	H	H	OMe	**6c-H**	42	29
4	**1d**	H	Me	H	OMe	**6d-H**	53	46
5	**1e**	H	H	OMe	H	**6e-H**	9	29
6	**1f**	H	OMe	H	H	**6f-H**	32	29
7	**1g**	OMe	H	H	H	**6g-H**	12	12
8	**1h**	H	H	I	H	**6h-H**	–	30
9	**1k**	H	H			**6k-H**	34	21
10	**1m**	OMe	H	Br	H	**6m-H**	–	37
11	**1n**	Me	H	H	*i*Pr	**6n-H**	57**	34

[a] Conditions: **A**) 1 equiv. of salicylicylaldehyde **1**, 6.75 equiv. of dimethyl 1,3-dimethylimidazolium phosphate, 1 equiv. of K_2CO_3 and 2.5 equiv. acrolein (**5a**) in 0.5 mL of toluene added over a period of 8 h, 85 °C, 2 d; **B**) biphasic system with toluene, 1 equiv. of salicylaldehyde, 1 equiv. of dimethyl 1,3-dimethylimidazolium phosphate and 1 equiv. of K_2CO_3, 2.5 equiv. of acrolein, 70 °C, 2 d. * Isolated yields. ** Analogous to condition A, but with 5 equiv. of acrolein.

methoxycinnamaldehyde (**5d**) and (2*E*,4*E*)-hexa-2,4-dienal (**5e**) (Table 3).

The general trends in the obtained yields from the reactions between salicylaldehyde derivatives **1a**–**g**,**k**,**n** and (*E*)-cinnamaldehyde are similar to those observed from reactions with acrolein. Salicylaldehydes with substitutions in the 6-position yielded the highest amounts of product, and again the best result was provided by salicylaldehyde **1n** (60%, Entry 9, Table 3). The methoxy groups of cinnamaldehydes (Entries 10 and 11, Table 3) did not influence the reactivity, in contrast to (*E*)-5-nitrocinnamaldehyde where no product formation was observed (data not shown). In addition, no products were isolated from crotonaldehyde and (*E*)-2-hexenal, but unexpectedly, (2*E*,4*E*)-hexa-2,4-di-

Table 3. Reaction of salicylaldehyde derivatives **1a**–**g**,**k**,**n** with (*E*)-cinnamaldehyde (**5b**, R^5 = Ph), (*E*)-2-methoxycinnamaldehyde (**5c**, R^5 = 2-MeO-Ph), (*E*)-4-methoxycinnamaldehyde (**5d**, R^5 = 4-MeO-Ph) and (2*E*,4*E*)-hexa-2,4-dienal (**5e**, R^5 = 2-butenyl).

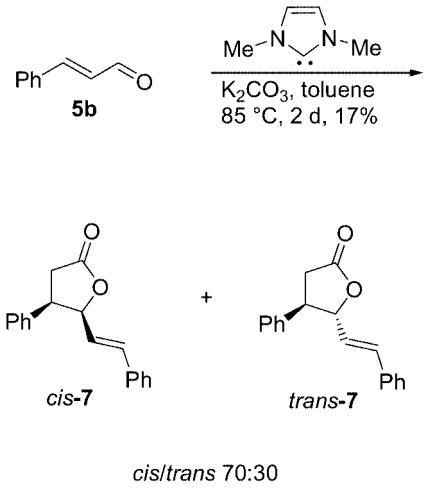


Entry	1	R^1	R^2	R^3	R^4	R^5	Product	Isolated yield [%]
1	**1a**	H	H	H	H	Ph	**6a-Ph**	18
2	**1b**	H	H	H	OMe	Ph	**6b-Ph**	35
3	**1c**	Br	H	H	OMe	Ph	**6c-Ph**	40
4	**1d**	H	Me	H	OMe	Ph	**6d-Ph**	42
5	**1e**	H	H	OMe	H	Ph	**6e-Ph**	27
6	**1f**	H	OMe	H	H	Ph	**6f-Ph**	11
7	**1g**	OMe	H	H	H	Ph	**6g-Ph**	29
8	**1k**	H	H		Ph	Ph	**6k-Ph**	39
9	**1n**	Me	H	H	*i*Pr	Ph	**6n-Ph**	60
10	**1d**	H	Me	H	OMe	2-MeO-C_6H_4	**6d-*o*-anisyl**	40
11	**1d**	H	Me	H	OMe	4- MeO-C_6H_4	**6d-*p*-anisyl**	42
12	**1d**	H	Me	H	OMe	2-butenyl	**6d-butenyl**	21[a]

[a] A mixture of *E*/*Z* isomers was isolated.

enal (**5e**) provided coumarin **6d-butenyl** in 21% yield as mixture of *E*/*Z* isomers (Entry 12, Table 3).

In the reactions with cinnamaldehydes, the formation of side products was observed. The side products were identified as *cis*/*trans* isomers of a γ-butyrolactone, *cis*-**7** and *trans*-**7**. In the absence of salicylaldehydes, without any optimization, the γ-butyrolactone was obtained in 17% yield, with the *cis* isomer as the major product formed (Scheme 2). This compliments the results reported by Glorius[6] and Bode.[7] However, in these cases only carbenes with bulky substituents led to the formation of lactones.



Scheme 2. Synthesis of γ-butyrolactones **7** from cinnamaldehyde in dimethyl 1,3-dimethylimidazolium phosphate and toluene.

In addition, we were pleased to find that the reaction time could be reduced when the reactions were performed under microwave irradiation.[17] As depicted in Table 4 the yields obtained from reactions between benzaldehyde **1a**,**b**,**d** and (*E*)-cinnamaldehyde (**5b**) either match or exceed the yields obtained above using a conventional oil bath as heat source.

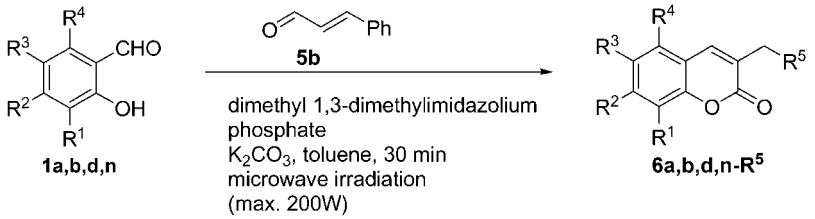
When the reaction between benzaldehyde **1d** and (*E*)-cinnamaldehyde (**5b**) was performed under microwave radiation with 1 equiv. of carbene precursor and 1 equiv. of potassium carbonate in toluene, **6b-Ph** was obtained in 43% yield after 30 min (Table 4, Entry 1). Furthermore, **6n-Ph** could be generated in 61% yield within 30 min, nearly the same amount as for the standard conditions. Under microwave irradiation an increase in the yields obtained from reactions between (*E*)-cinnamaldehyde (**5b**) and benzaldehydes **1a** or **1d** was observed. The coumarines **6b-Ph** and **6a-Ph** were formed in 50% and 36% yields, respectively.

A proposed mechanism for the formation of coumarins is outlined in Scheme 3.

The NHC **9**, generated upon deprotonation of imidazolium ion **8**, reacts with α,β-unsaturated aldehydes **5** resulting in homoenolate equivalent **11**. The protonation in the β position of **11** leading to tautomers **12** and **13** is consistent with previous reports[2a,7,18] suggesting that the use of weak bases, like K_2CO_3, results in protonation and not C–C bond formation. The salicylaldehyde **1a** reacts with the 2-substituted imidazolium **13** providing **15** that, through a condensation, yields the coumarin **6a**. A side reaction leads to the generation of propionate **14** by hydrolysis of the activated acid derivative **13**, and furthermore, the salicylaldehyde might also be incorporated in the imidazolium by attack of the carbene at the carbonyl function. The generation of polar, non-extractable compounds explains why only small amounts of starting materials were recovered in all reactions presented herein, with one exception, namely salicylaldehyde **1n**, where typically 20% could be recovered. Unfortunately, the formation of non-extractable compounds also prevents re-using the ionic liquids, which normally is an attractive feature of this class of solvents. When the reaction was performed in the presence of 5 vol.-% D_2O a mixture of deuterium-labeled **6b-Ph*** and non-labeled **6b-Ph** product (approx. 1:2) was achieved, but simultaneously the yield dropped to 5% (Scheme 1) probably due to hydrolysis of the activated acid derivatives **13**. Because double-deuterated material was not isolated, deprotonation-deuteration of the coumarin after its formation is quite unlikely. These features validate the proposed mechanism (Scheme 4).

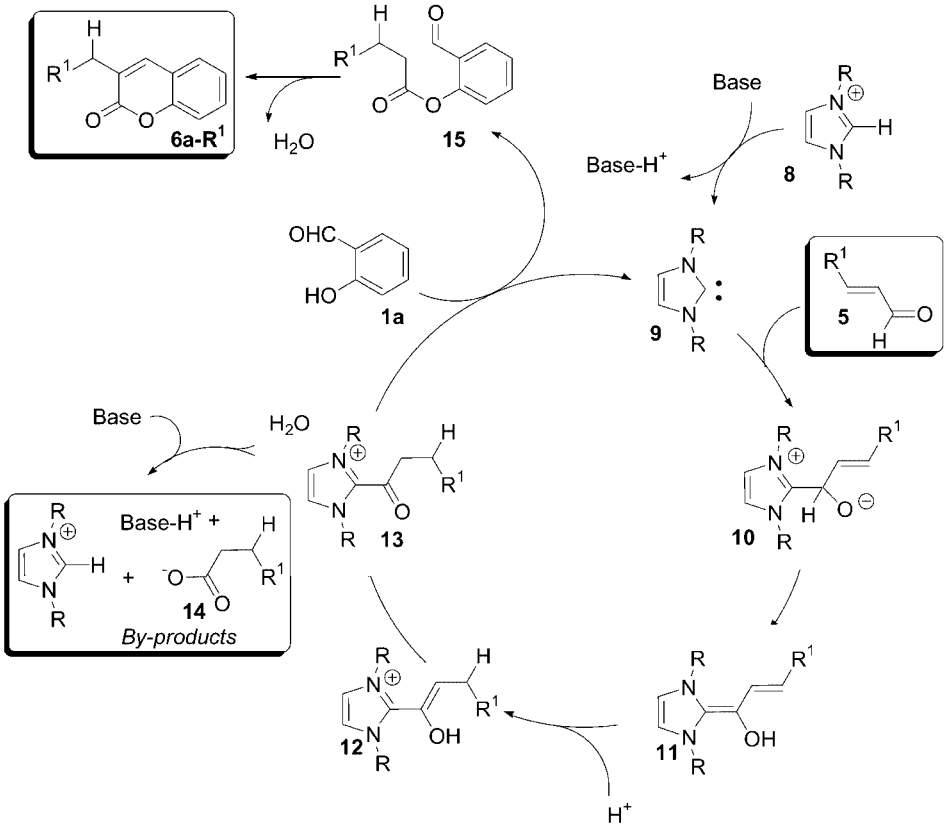
In conclusion, we have demonstrated a new domino reaction[19] from salicylaldehydes and α,β-unsaturated aldehydes

Table 4. Reactions between benzaldehydes **1a**,**b**,**d**,**n** and (*E*)-cinnamaldehyde performed under microwave irradiation.

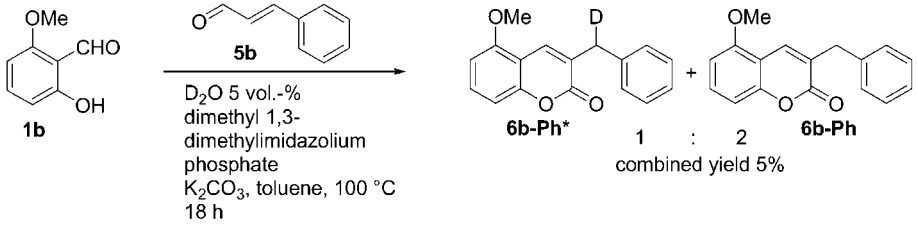


Entry	**1**	R^1	R^2	R^3	R^4	R^5	Product	Isolated yield [%][a]
1	**1a**	H	H	H	H	Ph	**6a-Ph**	36
2	**1b**	H	H	H	OMe	Ph	**6b-Ph**	50
4	**1d**	H	Me	H	OMe	Ph	**6d-Ph**	43
9	**1n**	Me	H	H	*i*Pr	Ph	**6n-Ph**	61

[a] Isolated yields after flash column chromatography.



Scheme 3. Mechanism for formation of coumarin **6a** from α,β-unsaturated aldehydes and salicylaldehydes via NHCs.



Scheme 4. Reaction between **1b** and **5b** in the presence of 5 vol.-% D_2O.

leading to the formation of coumarins. To the best of our knowledge this is the first example where NHC-generated homoenolate equivalents have been used in a direct synthesis of benzoannelated heterocycles. Although the presented reaction suffers from moderate yields, it tolerates a broad range of functionalities and provides coumarins from cheap and commercial available starting materials.

Experimental Section

General: Compounds were purchased from commercial sources and were used without further purification. Column chromatography was performed using Macherey–Nagel silica gel 60 (230–400 mesh) under flash conditions (EtOAc = ethyl acetate, Pent = *n*-pentane, cHex = cyclohexane). For thin-layer chromatography, aluminum foils layered with silica gel with fluorescence indicator (silica gel 60 F_{254}) produced by Merck were employed. Melting points were determined using a Laboratory Devices Inc. MelTemp II device and were corrected. ^1H and ^{13}C NMR spectra were recorded with a Bruker DP 300 (300 MHz/75 MHz) or Bruker DP 400 (400 MHz/100 MHz) instrument using $CDCl_3$ as the solvent and residual $CHCl_3/CDCl_3$ as shift reference: $\delta(CHCl_3)$ = 7.28 ppm, $\delta(CDCl_3)$ = 77.00 ppm. IR spectra were recorded with the Bruker FTIR device IFS 88. EI-MS and EI-HRMS spectra were recorded with a Finnigan MAT 90 instrument; elemental analyses were performed using a Heraeus CHN-O-Rapid device. X-ray crystallographic analyses were performed with a Nonius Kappa CCD or a STOE IPDS II diffractometer with Mo-K_α radiation.

Procedure A. 5-Methoxy-3,7-dimethylchromen-2-one (6d-H): Under argon, 0.200 g (1.20 mmol) of 2-hydroxy-6-methoxy-4-methylbenzaldehyde (**1d**) and 0.166 g (1.20 mmol) of K_2CO_3 were dissolved in 2.00 mL (2.47 g, 9.26 mmol) of dimethyl 1,3-dimethylimidazolium phosphate. The reaction mixture was heated to 85 °C, after which, 0.135 g (2.40 mmol) of acrolein (**5a**) in 0.5 mL of toluene was added over a period of 12 h using a syringe pump. After an additionally 36 h, the reaction mixture was cooled to room temp. and quenched with 10 mL of water. The product was extracted with 2×10 mL of EtOAc and 1×10 mL of CH_2Cl_2. The combined organic phases were dried with $MgSO_4$ and the solvent was removed under re-

duced pressure. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.130 g, 53%) as colourless solid.

Procedure B. 5-Methoxy-3,7-dimethylchromen-2-one (6d-H): Under argon, 0.100 g (0.602 mmol) of 2-hydroxy-6-methoxy-4-methylbenzaldehyde (**1d**), 0.0832 g (0.602 mmol) of K_2CO_3, 0.0844 g (1.51 mmol) of acrolein (**5a**) and 0.134 g (0.602 mmol) of dimethyl 1,3-dimethylimidazolium phosphate were suspended/dissolved in 2 mL of toluene. The reaction mixture was stirred at 70 °C for 24 h and cooled to room temp. The reaction was quenched by the addition of 10 mL of water. The product was extracted with 2 × 10 mL of EtOAc and 1 × 10 mL of CH_2Cl_2 The combined organic phases were dried with $MgSO_4$ and the solvent was removed under reduced pressure. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.057, g, 46%) as colourless solid.

Procedure C. 3-Benzyl-5-methoxy-7-methylchromen-2-one (6d-Ph): Under argon, 0.100 g (0.602 mmol) of 2-hydroxy-6-methoxy-4-methylbenzaldehyde (**1d**), 0.0832 g (0.602 mmol) of K_2CO_3, 0.199 g (1.51 mmol) of (*E*)-cinnamaldehyde and 0.134 g (0.602 mmol) of dimethyl 1,3-dimethylimidazolium phosphate were suspended/dissolved in 2 mL of toluene. The reaction mixture was stirred at 100 °C for 24 h and cooled to room temp. The reaction was quenched upon addition of 10 mL of water. The product was extracted with 2 × 10 mL of EtOAc and 1 × 10 mL of CH_2Cl_2. The combined organic phases were dried with $MgSO_4$ and the solvent was removed under reduced pressure. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.071 g, 42%) as colourless solid.

3-Methylchromen-2-one[20] (6a-H): Prepared according to procedure **B** from 0.200 g (1.64 mmol) of salicylaldehyde (**1a**), 0.227 g (1.64 mmol) of K_2CO_3, 0.230 g (4.10 mmol) of acrolein (**5a**) and 0.364 g (1.64 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.069 g, 26%) as colourless solid; m.p. 87–90 °C. R_f (cHex/EtOAc, 5:1) = 0.24. IR (KBr): $\tilde{\nu}$ = 1707 (s, ν C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.22 (d, ^4J = 1.3 Hz, 3 H, CH_3), 7.26 (dt, ^4J = 1.1 Hz, ^3J = 7.6 Hz, 1 H, C6-H), 7.31 (d, ^4J = 8.3 Hz, 1 H, C8-H), 7.40–7.50 (m, 2 H, C5-H, C7-H), 7.52 (qt, ^4J = 1.4 Hz, 1 H, C4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2 (+, CH_3), 116.5 (+, C-8), 119.6 (q, C-4a), 124.3 (+, C-6), 125.6 (q, C-3), 127.0 (+, C-5), 130.4 (+, C-7), 139.2 (+, C-4), 153.3 (q, C-8a), 162.3 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 160 (100) [M^+], 131 (64). HR-EIMS: calcd. 160.0524, found 160.0526.

5-Methoxy-3-methylchromen-2-one (6b-H): Prepared according to procedure **A** from 0.183 g (1.20 mmol) of 2-hydroxy-6-methoxybenzaldehyde (**1b**), 0.166 g (1.20 mmol) of K_2CO_3, 2.00 mL (2.47 g, 9.26 mmol) of dimethyl 1,3-dimethylimidazolium phosphate and 0.135 g (2.40 mmol) of acrolein (**5a**). Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.120 g, 53%) as colourless solid; m.p. 123–128 °C.R_f (cHex/EtOAc, 5:1) = 0.26. IR (KBr): $\tilde{\nu}$ = 1707 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.20 (d, ^4J = 1.3 Hz, 3 H, CH_3), 3.92 (s, 3 H, OCH_3), 6.69 (d, ^3J = 8.3 Hz, 1 H, C6-H), 6.90 (d, ^3J = 8.4 Hz, 1 H, C8-H), 7.35 (t, ^3J = 8.4 Hz, 1 H, C7-H), 7.88 (qt, ^4J = 1.3 Hz, 1 H, C4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.3 (+, CH_3), 56.0 (+, OCH_3), 105.0 (+, C-8), 108.9 (+, C-6), 110.2 (q, C-4a), 123.8 (q, C-3), 130.8 (+, C-7), 134.3 (+, C-4), 154.3 (q, C-8a), 155.5 (q, C-5), 162.3 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 190 (100) [M^+], 162 (20) [M^+ – CO], 147 (40). HR-EIMS: calcd. 190.0630, found 190.0634. $C_{10}H_8O_2$ (190 g/mol): calcd. C 69.46, H 5.30; found C 69.25, H 5.38.

8-Bromo-5-methoxy-3-methylchromen-2-one (6c-H): Prepared according to procedure **A** from 0.200 g (0.886 mmol) of 3-bromo-2-hydroxy-6-methoxybenzaldehyde (**1c**), 0.120 g (0.866 mmol) of K_2CO_3, 2.00 mL (2.47 g, 9.26 mmol) of dimethyl 1,3-dimethylimidazolium phosphate and 0.0971 g (1.73 mmol) of acrolein (**5a**). Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.099 g, 42%) as colourless solid; m.p. 171–173 °C. – R_f (cHex/EtOAc, 5:1) = 0.19. IR (KBr): $\tilde{\nu}$ = 1718 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.15 (d, ^4J = 1.4 Hz, 3 H, CH_3), 3.92 (s, 3 H, OCH_3), 6.61 (d, ^3J = 8.8 Hz, 1 H, C6-H), 7.56 (d, ^3J = 8.8 Hz, 1 H, C7-H), 7.84 (qt, ^4J = 1.4 Hz, 1 H, C4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.2 (+, CH_3), 56.2 (+, OCH_3), 100.6 (q, C-8), 106.2 (+, C-6), 111.4 (q, C-4a), 124.6 (q, C-3), 133.8 (+, C-4), 133.9 (+, C-7), 150.6 (q, C-5), 154.8 (q, C-8a), 161.2 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 268/270 (100/98, M^+), 225/227 (36/34) [M^+ – CO – CH_3]. HR-EIMS: calcd. 267.9735, found 267.9739. $C_{11}H_9BrO_3$ (268 g/mol): calcd. C 49.10, H 3.37; found C 48.74, H 3.49.

5-Methoxy-3,7-dimethylchromen-2-one (6d-H): Prepared according to procedure **B** from 0.100 g (0.602 mmol) of 2-hydroxy-6-methoxy-4-methylbenzaldehyde (**1d**), 0.0832 g (0.602 mmol) of K_2CO_3, 0.0844 g (1.51 mmol) of acrolein (**5a**) and 0.134 g (0.602 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 2 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.065 g, 53%) as colourless solid; m.p. 109–112 °C. R_f (cHex/EtOAc, 5:1) = 0.29. IR (KBr): $\tilde{\nu}$ = 1709 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.18 (d, ^4J = 1.1 Hz, 3 H, CH_3), 2.40 (s, 3 H, C7-CH_3), 3.90 (s, 3 H, OCH_3), 6.50 (s, 1 H, C6-H), 6.72 (s, 1 H, C8-H), 7.83 (qt, ^4J = 0.63 Hz, 1 H, C4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2 (+, CH_3), 22.3 (+, CH_3), 55.9 (+, OCH_3), 106.2 (+, C-8) 107.9 (q, C-4a), 109.1 (+, C-6), 122.4 (q, C-3), 134.4 (+, C-4), 142.1 (q, C-7), 154.3 (q, C-8a), 155.2 (q, C-5), 162.6 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 204 (100) [M^+], 176 (24) [M^+ – CO], 161 (36) [M^+ – CO – CH_3]. HR-EIMS: calcd. 204.0786, found 204.0791. $C_{12}H_{12}O_3$ (204 g/mol): calcd. C 70.57, H 5.92; found C 70.14, H 6.24.

6-Methoxy-3-methylchromen-2-one (6e-H):[21] Was prepared according to procedure **B** from 0.250 g (1.64 mmol) of 2-hydroxy-5-methoxybenzaldehyde (**1e**), 0.227 g (1.64 mmol) of K_2CO_3, 0.230 g (4.10 mmol) of acrolein (**5a**) and 0.364 g (1.64 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.091 g, 29%) as light yellow solid; m.p. 112–115 °C. – R_f (cHex/EtOAc, 5:1) = 0.20. IR (KBr): $\tilde{\nu}$ = 1708 (s, ν C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.20 (d, ^4J = 1.3 Hz, 3 H, CH_3), 3.83 (s, 3 H, CH_3), 6.84 (d, ^4J = 2.8 Hz, 1 H, C5-H), 7.03 (dd, ^4J = 3.0 Hz, ^3J = 9.1 Hz, 1 H, C7-H), 7.22 (d, ^3J = 9.1 Hz, 1 H, C8-H), 7.45 (s, 1 H, C4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.3 (+, CH_3), 55.8 (+, OCH_3), 109.4 (+, C-5), 117.4, (+, C-8), 118.0 (+, C-7), 120.0 (q, C-4a), 126.2 (q, C-3), 139.1 (+, C-4), 147.7 (q, C-8a), 156.0 (q, C-6), 162.4 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 190 (100) [M^+], 175 (20) [M^+ – CH_3], 147 (18) [M^+ – CO – CH_3]. HR-EIMS: calcd. 190.0630, found 190.0633. $C_{11}H_{10}O_3$ (190 g/mol): calcd. C 69.46, H 5.30; found C 69.27, H 5.44.

7-Methoxy-3-methylchromen-2-one (6f-H): Prepared according to procedure **A** from from 0.250 g (1.64 mmol) of 2-hydroxy-4-methoxybenzaldehyde (**1f**), 0.227 g (1.64 mmol) of K_2CO_3, 2.00 mL (2.47 g, 9.26 mmol) of dimethyl 1,3-dimethylimidazolium phos-

phate and 0.230 g (4.1 mmol) of acrolein (**5a**). Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.038 g, 12%) as colourless solid; m.p. 148–154 °C. – R_f (cHex/EtOAc, 5:1) = 0.23. IR (KBr): $\tilde{\nu}$ = 1704 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.10 (d, ^4J = 1.3 Hz, 3 H, CH_3), 3.84 (s, 3 H, OCH_3), 6.79 (d, ^4J = 2.4 Hz, 1 H, C8-H), 6.81 (dd, ^4J = 2.4 Hz, ^3J = 8.4 Hz, 1 H, C6-H), 7.29 (d, ^3J = 8.4 Hz, 1 H, C5-H), 7.44 (qt, ^4J = 1.1 Hz, 1 H, C4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.0 (+, CH_3), 55.7 (+, OCH_3), 100.6 (+, C-8), 112.3 (+, C-6), 113.2 (q, C-4a), 122.2 (q, C-5), 139.4 (+, C-4), 154.9 (q, C-8a), 161.8 (q, C-2), 162.6 (q, C-7) ppm. MS (EI): *m/z* (%) = 190 (100) [M^+], 162 (28) [M^+ – CO], 147 (48) [M^+ – CO – CH_3]. HR-EIMS: calcd. 190.0630, found 190.0631. $C_{10}H_8O_2$ (190 g/mol): calcd. C 69.46, H 5.30; found C 69.26, H 5.37.

8-Methoxy-3-methylchromen-2-one (6g-H):[22] Prepared according to procedure **A** from 0.250 g (1.64 mmol) of 2-hydroxy-3-methoxybenzaldehyde (**1g**), 0.227 g (1.64 mmol) of K_2CO_3, 2.00 mL (2.47 g, 9.26 mmol) of dimethyl 1,3-dimethylimidazolium phosphate and 0.230 g (4.1 mmol) of acrolein (**5a**). Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.099 g, 32%) as colourless solid; m.p. 80–82 °C. R_f (cHex/EtOAc, 5:1) = 0.19. IR (KBr): $\tilde{\nu}$ = 1714 (s, ν C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.21 (d, ^4J = 1.3 Hz, 3 H, CH_3), 3.95 (s, 3 H, OCH_3), 6.98 (dd, ^4J = 1.3 Hz, ^3J = 7.8 Hz, 1 H, C7-H), 7.01 (dd, ^4J = 1.1 Hz, ^3J = 8.2 Hz, 1 H, C5-H), 7.16 (dd, ^3J = 8.1 Hz, ^3J = 7.9 Hz, 1 H, C6-H), 7.48 (qt, ^4J = 1.3 Hz, 1 H, C4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.2 (+, CH_3), 56.2 (+, OCH_3), 112.5 (+, C-7), 118.5 (+, C-6), 120.3 (q, C-4a), 124.1 (+, C-5), 126.2 (q, C-3), 139.4 (+, C-4), 142.9 (q, C-8a), 147.1 (q, C-8), 161.7 (q, C-2) ppm. MS (EI): *m/z* (%) = 190 (100) [M^+], 162 (10) [M^+ – CO], 147 (10) [M^+ – CO – CH_3]. HR-EIMS: calcd. 190.0630, found 190.0633. $C_{10}H_8O_2$ (190 g/mol): calcd. C 69.46, H 5.30; found C 69.24, H 5.32.

6-Iodo-3-methylchromen-2-one (6h-H): Prepared according to procedure **B** from 0.215 g (1.64 mmol) of 2-hydroxy-5-iodobenzaldehyde (**1h**), 0.227 g (1.64 mmol) of K_2CO_3, 0.230 g (4.10 mmol) of acrolein (**5a**) and 0.364 g (1.64 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.075 g, 30%) as colourless solid; m.p. 158–162 °C. R_f (cHex/EtOAc, 5:1) = 0.34. IR (KBr): $\tilde{\nu}$ = 1723 (s, νC=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.22 (d, ^4J = 1.3 Hz, 3 H, CH_3), 7.07 (d, ^3J = 8.6 Hz, 1 H, C8-H), 7.41 (qt, ^4J = 0.9 Hz, 1 H, C4-H), 7.70–7.73 (m, 2 H, C5-H, C7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.3 (+, CH_3), 87.1 (q, C-6), 118.5 (+, C-8), 121.7 (q, C-4a), 127.1 (q, C-3), 135.4 (+, C-5), 137.7 (+, C-7), 139.0 (+, C-4), 152.4 (q, C-8a), 161.5 (q, C-2) ppm. MS (EI): *m/z* (%) = 286 (100) [M^+], 258 (16) [M^+ – CO]. HR-EIMS: calcd. 285.9491, found 285.9492. $C_{10}H_7IO_2$ (286 g/mol): calcd. C 41.99, H 2.47; found C 41.83, H 2.55.

2-Methylbenzo[f]chromen-3-one (6k-H):[23] Prepared according to procedure **A** from 0.292 g (1.64 mmol) of 2-hydroxynaphthalene-1-carbaldehyde (**1k**), 0.227 g (1.64 mmol) of K_2CO_3, 2.00 mL (2.47 g, 9.26 mmol) of dimethyl 1,3-dimethylimidazolium phosphate and 0.230 g (4.1 mmol) of acrolein (**5a**). Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.116 g, 34%) as colourless solid; m.p. 140–150 °C. R_f (cHex/EtOAc, 5:1) = 0.26. IR (KBr): $\tilde{\nu}$ = 1703 (s, νC=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.33 (d, ^4J = 1.3 Hz, 3 H, CH_3), 7.44 (d, ^3J = 8.9 Hz, 1 H, C10-H), 7.53–7.57 (m, 1 H, C_{Ar}-H), 7.64–7.68 (m, 1 H, C_{Ar}-H), 7.88–7.92 (m, 2 H, 2 × C_{Ar}-H), 8.22 (d, ^3J = 8.1 Hz, 1 H, C9-H), 8.28 (br. s, 1 H, C4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.6 (+, CH_3), 113.5 (q, C-4a), 116.9 (+, C-10), 121.5 (+, C-6), 125.1 (q, C-3), 125.8 (+, C-7), 127.9 (+, C-8), 128.7 (q, C-8a), 129.0 (+, C-5), 130.3 (q, C-4b), 131.7 (+, C-4), 135.1 (+, C-9), 152.6 (q, C-10), 162.3 (q, C-2) ppm. MS (EI): *m/z* (%) = 210 (16) [M^+], 182 (8) [M^+ – CO], 144 (100), 115 (28). HR-EIMS: calcd. 210.0681, found 210.0682. $C_{14}H_{10}IO_2$ (210 g/mol): calcd. C 79.98, H 4.79; found C 79.98, H 4.89.

6-Bromo-8-methoxy-3-methylchromen-2-one (6m-H): Prepared according to procedure **B** from 0.138 g (0.602 mmol) of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (**1m**), 0.0832 g (0.602 mmol) of K_2CO_3, 0.0844 g (1.51 mmol) of acrolein (**5a**) and 0.134 g (0.602 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 2.00 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.060 g, 37%) as colourless solid; m.p. 128–133 °C. R_f (cHex/EtOAc, 5:1) = 0.11. IR (KBr): $\tilde{\nu}$ = 1719 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.20 (d, ^4J = 1.4 Hz, 3 H, CH_3), 3.93 (s, 3 H, OCH_3), 7.07 (d, ^4J = 2.1 Hz, 1 H, C5-H), 7.10 (d, ^4J = 2.1 Hz, 1 H, C7-H), 7.37 (qt, ^4J = 1.3 Hz, 1 H, C4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.3 (+, CH_3), 56.5 (+, OCH_3), 115.6 (+, C-7), 116.5 (q, C-4a), 120.7 (+, C-5), 121.2 (q, C-6), 127.6 (q, C-3), 138.0 (+, C-4), 142.0 (q, C-8a), 147.7 (q, C-8), 161.0 (q, C-2) ppm. MS (EI): *m/z* (%) = 268/270 (100/98) [M^+]. HR-EIMS: calcd. 267.9735, found 267.9736. $C_{11}H_9BrO_3$ (269 g/mol): calcd. C 49.10, H 3.37; found C 48.91, H 3.48.

5-Isopropyl-3,8-dimethylchromen-2-one (6n-H): Prepared according to procedure **A** from 0.214 g (1.20 mmol) of 2-hydroxy-6-isopropyl-3-methylbenzaldehyde (**1n**), 0.166 g (1.20 mmol) of K_2CO_3, 2.00 mL (2.47 g, 9.26 mmol) of dimethyl 1,3-dimethylimidazolium phosphate and 0.336 g (6.0 mmol) of acrolein (**5a**). Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.147 g, 57%) as colourless solid; m.p. 102–104 °C. R_f (cHex/EtOAc, 5:1) = 0.40. IR (KBr): $\tilde{\nu}$ = 1719 (s, νC=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.29 (d, ^3J = 6.8 Hz, 6 H, 2 × CH_3), 2.25 (d, ^4J = 1.3 Hz, 3 H, CH_3), 2.41 (s, 3 H, C_{Ar}-CH_3), 3.36 (sept, ^3J = 6.8 Hz, 1 H, C_{aliph}-H), 7.08 (d, ^3J = 7.9 Hz, 1 H, C6-H), 7.27 (d, ^3J = 7.7 Hz, 1 H, C7-H), 7.82 (d, ^4J = 0.9 Hz, 1 H, C4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.5 (+, CH_3), 17.6 (+, CH_3), 23.7 (+, 2 × CH_3), 28.3 (+, CH), 116.8 (q, C-4), 120.1 (+, C-6), 123.3 (q, C-3), 124.5 (q, C-8), 131.8 (+, C-7), 136.0 (+, C-4), 143.2 (q, C-5), 152.1 (q, C-8a), 162.2 (q, C-2) ppm. MS (EI): *m/z* (%) = 216 (44) [M^+], 201 (100) [M^+ – CH_3]. HR-EIMS: calcd. 216.1150, found 216.1154. $C_{14}H_{16}O_2$ (216 g/mol): calcd. C 77.75, H 7.46; found C 77.71, H 7.36.

3-Benzylchromen-2-one (6a-Ph):[24] Prepared according to procedure **C** from 0.200 g (1.64 mmol) of salicylaldehyde (**1a**), 0.227 g (1.64 mmol) of K_2CO_3, 0.542 g (4.10 mmol) of (*E*)-cinnamaldehyde (**5b**) and 0.364 g (1.64 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, pent/Et_2O, 4:1 and then cHex/EtOAc, 5:1) yielded the title compound (0.069 g, 18%) as colourless solid; m.p. 110–113 °C. – R_f (cHex/EtOAc, 5:1) = 0.40. IR (KBr): $\tilde{\nu}$ = 1712 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 2 H, CH_2), 7.20–7.38 (m, 9 H), 7.44–7.48 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.6 (-, CH_2), 116.5 (+, C-8), 119.5 (q, C-4a), 124.3 (+), 126.9 (+), 127.4 (+), 128.8 (+, 2 × C_{benzyl}), 129.4 (+, 2 × C_{benzyl}), 129.5 (q, C-3), 130.8 (+), 137.7 (q), 139.3 (+, C4), 153.1 (q, C-8a), 161.7 (q, C-2) ppm. MS (EI): *m/z* (%) = 236 (100) [M^+], 207 (40), 131 (18). HR-EIMS: calcd.

236.0837, found 236.0835. $C_{16}H_{12}O_2$ (236 g/mol): calcd. C 81.34, H 5.12; found C 81.17, H 5.16.

3-Benzyl-5-methoxychromen-2-one (6b-Ph): Prepared according to procedure **C** from 0.250 g (1.64 mmol) of 2-hydroxy-6-methoxybenzaldehyde (**1b**), 0.227 g (1.64 mmol) of K_2CO_3, 0.542 g (4.10 mmol) of (*E*)-cinnamaldehyde (**5b**) and 0.364 g (1.64 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, pent/Et_2O, 4:1 and then cHex/EtOAc, 5:1) yielded the title compound (0.153 g, 35%) as colourless solid; m.p. 118–121 °C. R_f (cHex/EtOAc, 5:1) = 0.30. IR (KBr): $\tilde{\nu}$ = 1721 (s, νC=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.88 (s, 3 H, OCH_3), 3.89 (d, ^4J = 0.9 Hz, 2 H, CH_2), 6.67 (dd, ^4J = 0.6 Hz, ^3J = 8.3 Hz, 1 H, C6-H), 6.90 (d, ^3J = 8.3 Hz, 1 H, C8-H), 7.22–7.34 (m, 5 H, C_{Ar}-H), 7.38 (t, ^3J = 8.3 Hz, 1 H, C7-H), 7.78 (d, ^4J = 0.6 Hz, 1 H, C4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.8 (–, CH_2), 55.9 (+, OCH_3), 104.97 (+, C-8), 108.9 (+, C-6) ppm. 110.1 (q, C-4a), 126.7 (+), 127.2 (q, C-3), 128.7 (+, 2 × C_{benzyl}), 129.2 (+, 2 × C_{benzyl}), 131.3 (+), 134.5 (+), 138.2 (q), 154.2 (q, C-8a), 155.7 (q, C-5), 161.8 (q, C-2). MS (EI): *m*/*z* (%) = 266 (100) [M^+], 237 (16). HR-EIMS: calcd. 266.0943, found 266.0947. $C_{17}H_{14}O_3$ (266 g/mol): calcd. C 76.68, H 5.30; found C 76.14, H 5.33.

3-(Deuteriophenylmethyl)-5-methoxychromen-2-one (6b-Ph*): Prepared according to procedure **C** from 0.300 g (1.97 mmol) of 2-hydroxy-6-methoxybenzaldehyde (**1b**), 0.272 g (1.97 mmol) of K_2CO_3, 0.651 g (4.93 mmol) of (*E*)-cinnamaldehyde (**5b**), 0.438 g (1.97 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 6 mL of toluene and 300 μL D_2O. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, pent/Et_2O, 4:1 and then cHex/EtOAc, 5:1) yielded a 0.5:1 mixture, respectively, of the title compound **6b-Ph*** and non-deuterated product **6b-Ph** (0.025 g, 5%) as colourless solid; m.p. 114–117 °C. R_f (cHex/EtOAc, 5:1) = 0.33. IR (KBr): $\tilde{\nu}$ = 1723 (s, νC=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.88 (br. s, 5 H, CH_2/CHD, OCH_3), 6.67 (d, ^3J = 8.3 Hz, 1 H, C7-H), 6.90 (d, ^3J = 8.5 Hz, 1 H, C8-H), 7.22–7.40 (m, 6 H, C7-H, 5 × H_{benzyl}), 7.77 (s, 1 H, C4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.7 (–, ^1J = 19.7 Hz, C-D), 55.9 (+, OCH_3), 105.0 (+, C-8), 108.9 (+, C-6), 110.1 (q, C-4a), 126.7 (+), 127.2 (q, C-3), 128.7 (+, 2 × C_{benzyl}), 129.2 (+, 2 × C_{benzyl}), 131.3 (+, C-7), 134.5 (+, C-4), 138.2 (q), 154.2 (q, C-8a), 155.7 (q, C-5), 161.8 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 267 (7) [M^+**6b–Ph***], 266 (8) [M^+**6b–Ph**], 240 (12), 239 (15), 234 (16), 204 (16), 203 (100), 190 (20), 138 (20), 127 (28), 126 (40), 125 (20), 106 (20), 105 (22), 97 (10), 96 (14).

3-Benzyl-8-bromo-5-methoxychromen-2-one (6c-Ph): Prepared according to procedure **C** from 0.379 g (1.64 mmol) of 3-bromo-2-hydroxy-6-methoxybenzaldehyde (**1c**), 0.227 g (1.64 mmol) of K_2CO_3, 0.542 g (4.10 mmol) of (*E*)-cinnamaldehyde (**5b**) and 0.364 g (1.64 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, pent/Et_2O, 4:1 and then cHex/EtOAc, 5:1) yielded the title compound (0.225 g, 40%) as colourless solid; m.p. 154–159 °C. R_f (cHex/EtOAc, 5:1) = 0.24. IR (KBr): $\tilde{\nu}$ = 1716 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 3 H, OCH_3), 3.89 (s, 2 H, CH_2), 6.58 (d, ^3J = 8.8 Hz, 1 H, C6-H), 7.23–7.34 (m, 5 H, C_{Ar}-H), 7.56 (d, ^3J = 8.8 Hz, 1 H, C7-H), 7.72 (t, ^4J = 1.3 Hz, 1 H, C4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.7 (–, CH_2), 56.1 (+, OCH_3), 100.5 (q, C-8), 106.2 (C-6), 111.3 (q, C-4a), 126.8 (+), 128.1 (q, C-3), 128.8 (+, 2 × C_{benzyl}), 129.3 (+, 2 × C_{benzyl}), 134.1 (+), 134.2 (+), 137.9 (q), 150.5 (q, C-5), 155.1 (q, C-8a), 160.7 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 344/346 (100/98) [M^+], 315/317 (14/12), 165 (12). HR-EIMS: calcd. 344.0048, found 344.0043. $C_{17}H_{13}BrO_3$ (344 g/mol): calcd. C 59.15, H 3.80; found C 59.33, H 3.76.

3-Benzyl-5-methoxy-7-methylchromen-2-one (6d-Ph): Prepared according to procedure **C** from 0.100 g (0.602 mmol) of 2-hydroxy-6-methoxy-4-methylbenzaldehyde (**1d**), 0.0832 g (0.602 mmol) of K_2CO_3, 0.199 g (1.51 mmol) of (*E*)-cinnamaldehyde (**5b**) and 0.134 g (0.602 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 2 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, pent/Et_2O, 4:1 and then cHex/EtOAc, 5:1) yielded the title compound (0.071 g, 42%) as colourless solid; m.p. 122–125 °C. R_f (cHex/EtOAc, 5:1) = 0.33. IR (KBr): $\tilde{\nu}$ = 1709 (s, νC=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 3.87 (br. s, 2 H, CH_2), 6.48 (s, 1 H, C6-H), 6.72 (s, 1 H, C8-H), 7.21–7.35 (m, 5 H, C_{Ar}-H), 7.72 (br. s, 1 H, C4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.4 (+, CH_3), 36.8 (–, CH_2), 55.8 (+, CH_3), 106.2 (+, C-8), 107.8 (q, C-4a), 109.1 (+, C-6), 125.9 (q, C-3), 126.6 (+), 128.6 (+, 2 × C_{benzyl}), 129.2 (+, 2 × C_{benzyl}), 134.6 (+, C-4), 138.4 (q), 142.6 (q, C-7), 154.3 (q, C-8a), 155.4 (q, C-5), 162.1 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 280 (100) [M^+], 251 (16). HR-EIMS: calcd. 280.1099, found 280.1105. $C_{18}H_{16}O_3$ (280 g/mol): calcd. C 77.12, H 5.75; found C 77.11, H 5.628.

3-Benzyl-6-methoxychromen-2-one (6e-Ph): Prepared according to procedure **C** from 0.250 g (1.64 mmol) of 2-hydroxy-5-methoxybenzaldehyde (**1e**), 0.227 g (1.64 mmol) of K_2CO_3, 0.542 g (4.10 mmol) of (*E*)-cinnamaldehyde (**5b**) and 0.364 g (1.64 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, pent/Et_2O, 4:1 and then cHex/EtOAc, 5:1) yielded the title compound (0.117 g, 27%) as colourless solid; m.p. 125–130 °C. R_f (cHex/EtOAc, 5:1) = 0.40. IR (KBr): $\tilde{\nu}$ = 1708 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, OCH_3), 3.89 (br. s, 2 H, CH_2), 6.89 (d, ^4J = 2.9 Hz, 1 H, C5-H), 7.04 (dd, ^4J = 2.9 Hz, ^3J = 9.1 Hz, 1 H, C7-H), 7.21–7.38 (m, 7 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.6 (–, CH_2), 55.8 (+, CH_3), 109.5 (+, C-5), 117.5 (+, C-8), 118.6 (+, C-7), 119.8 (q, C-4a), 126.9 (+), 128.8 (+, 2 × C_{benzyl}), 129.5 (+, 2 × C_{benzyl}), 129.9 (q, C-3), 137.7 (q), 139.1 (+, C-4), 147.5 (q, C-8a), 156.0 (q, C-6), 161.9 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 266 (100) [M^+], 237 (20), 104 (56). HR-EIMS: calcd. 266.0943, found 266.0945. $C_{17}H_{14}O_3$ (266 g/mol): calcd. C 76.68, H 5.30; found C 76.56, H 5.43.

3-Benzyl-7-methoxychromen-2-one (6f-Ph):[25] Prepared according to procedure **C** from 0.250 g (1.64 mmol) of 2-hydroxy-4-methoxybenzaldehyde (**1f**), 0.227 g (1.64 mmol) of K_2CO_3, 0.542 g (4.10 mmol) of (*E*)-cinnamaldehyde (**5a**) and 0.364 g (1.64 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, pent/Et_2O, 4:1 and then cHex/EtOAc, 5:1) yielded the title compound (0.049 g, 11%) as colourless solid; m.p. 99–103 °C. R_f (cHex/EtOAc, 5:1) = 0.29. IR (KBr): $\tilde{\nu}$ = 1704 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, OCH_3), 3.84 (br. s, 2 H, CH_2), 6.78–6.80 (m, 2 H), 7.22–7.36 (m, 7 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.4 (–, CH_2), 55.8 (+, OCH_3), 100.5 (+, C-8), 112.4 (+, C-6), 113.1 (q, C-4a), 125.8 (q, C-3), 126.8 (+), 128.3 (+), 128.8 (+, 2 × C_{benzyl}), 129.4 (+, 2 × C_{benzyl}), 138.1 (q), 139.4 (+, C-4), 154.8 (q, C-8a), 162.1 (q), 162.1 (q) ppm. MS (EI): *m*/*z* (%) = 266 (100) [M^+], 237 (20). HR-EIMS: calcd. 266.0943, found 266.0948. $C_{17}H_{14}O_3$ (266 g/mol): calcd. C 76.68, H 5.30; found C 76.64, H 5.55.

3-Benzyl-8-methoxychromen-2-one (6g-Ph): Prepared according to procedure **C** from 0.250 g (1.64 mmol) of 2-hydroxy-3-methoxy-

benzaldehyde (**1g**), 0.227 g (1.64 mmol) of K_2CO_3, 0.542 g (4.10 mmol) of (*E*)-cinnamaldehyde (**5b**) and 0.364 g (1.64 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, pent/Et_2O, 4:1) yielded the title compound (0.127 g, 29%) as light yellow solid; m.p. 85–87 °C. R_f (cHex/EtOAc, 5:1) = 0.22. IR (KBr): $\tilde{\nu}$ = 1719 (s, νC=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.90 (br. s, 2 H, CH_2), 3.95 (s, 3 H, OCH_3), 6.92 (dd, ^4J = 1.3 Hz, ^3J = 7.7 Hz, 1 H, C7-H), 7.01 (dd, ^4J = 1.3 Hz, ^3J = 8.1 Hz, 1 H, C5-H), 7.13 (t, ^3J = 8.1 Hz, 1 H, C6-H), 7.23–7.37 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.5 (-, CH_2), 56.3 (+, OCH_3), 112.8 (+, C-7), 118.9 (+, C-6), 120.1 (q, C-4a), 124.1 (+, C-5), 126.8 (+), 128.8 (+, 2 × C_{benzyl}), 129.5 (+, 2 × C_{benzyl}), 129.8 (q, C-3), 137.7 (q), 139.4 (+, C-4), 142.8 (q, C-8a), 147.1 (q, C-8), 161.2 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 266 (100) [M^+], 237 (12). HR-EIMS: calcd. 266.0943, found 266.0946. $C_{17}H_{14}O_3$ (266 g/mol): calcd. C 76.68, H 5.30; found C 76.31, H 5.64.

2-Benzylbenzo[*f*]chromen-3-one (6k-Ph):[26] Prepared according to procedure **C** from 0.282 g (1.64 mmol) of 2-hydroxy-naphthalene-1-carbaldehyde (**1k**), 0.227 g (1.64 mmol) of K_2CO_3, 0.542 g (4.10 mmol) of (*E*)-cinnamaldehyde (**5b**) and 0.364 g (1.64 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, pent/Et_2O, 4:1 and then cHex/EtOAc, 5:1) yielded the title compound (0.183 g, 39%) as colourless solid; m.p. 158–161 °C. R_f (cHex/EtOAc, 5:1) = 0.27. IR (KBr): $\tilde{\nu}$ = 1714 (s, νC=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.01 (d, ^4J = 0.8 Hz, 2 H, CH_2), 7.28–7.41 (m, 5 H), 7.45 (d, ^3J = 9.1 Hz, 1 H, C10-H), 7.50–7.64 (m, 2 H), 7.88 (dd, ^4J = 1.1 Hz, ^3J = 8.1 Hz, 1 H), 7.92 (d, ^3J = 9.1 Hz, 1 H, C9-H), 8.05 (d, ^3J = 8.3 Hz, 1 H), 8.10 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.0 (-, CH_2), 113.4 (q, C-4a), 116.8 (+), 125.9 (+), 126.9 (+), 127.9 (+), 128.9 (+), 128.5 (q), 128.9 (+, 2 × C_{benzyl}), 129.0 (+), 129.4 (+, 2 × C_{benzyl}), 130.3 (q), 132.3 (+), 135.2 (+), 137.9 (q), 152.6 (q, C-10a), 161.8 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 286 (100) [M^+], 257 (28), 181 (16). HR-EIMS: calcd. 286.0994, found 286.0992.

3-Benzyl-5-isopropyl-8-methylchromen-2-one (6n-Ph): Prepared according to procedure **C** from 0.214 g (1.20 mmol) of 2-hydroxy-6-isopropyl-3-methylbenzaldehyde (**1n**), 0.166 g (1.20 mmol) of K_2CO_3, 0.396 g (3.00 mmol) of (*E*)-cinnamaldehyde (**5b**) and 0.267 g (1.20 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.211 g, 60%) as colourless solid; m.p. 83–86 °C. R_f (cHex/EtOAc, 5:1) = 0.41. IR (KBr): $\tilde{\nu}$ = 1718 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, ^3J = 6.9 Hz, 6 H, 2 × CH_3), 2.40 (s, 3 H, CH_3), 3.19 (sept, ^3J = 6.9 Hz, 1 H, C_{aliph}-H), 3.92 (br. s, 1 H, CH_2), 7.04 (d, ^3J = 7.8 Hz, 1 H, C6-H), 7.24–7.34 (m, 6 H, C7-H, 5 × C-H_{benzyl}), 7.63 (br. s, 1 H, C4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4 (+, CH_3), 23.5 (+, 2 × CH_3), 28.4 (+, CH), 36.9 (-, CH_2), 116.7 (q, C-4a), 120.1 (+, C-6), 123.4 (q, C-3), 126.8 (+), 128.0 (q, C-8), 128.7 (+, 2 × C_{benzyl}), 129.2 (+, 2 × C_{benzyl}), 132.1 (+), 136.3 (+, C-4), 138.2 (q), 143.5 (q, C-5), 152.0 (q, C-8a), 161.6 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 292 (100) [M^+], 277 (52) [$M^+ - OCH_3$]. HR-EIMS: calcd. 292.1463, found 292.1469. $C_{20}H_{20}O_2$ (292 g/mol): calcd. C 82.16, H 6.89; found C 81.94, H 7.01.

5-Methoxy-3-(2-methoxybenzyl)-7-methylchromen-2-one (6d-o-anisyl): Prepared according to procedure **C** from 0.200 g (1.20 mmol) of 2-hydroxy-6-methoxy-4-methylbenzaldehyde (**1d**), 0.166 g (1.20 mmol) of K_2CO_3, 0.487 g (3.00 mmol) of (*E*)-2-methoxycinnamaldehyde (**5c**) and 0.267 g (1.20 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.154 g, 42%) as colourless solid; m.p. 136–139 °C. R_f (cHex/EtOAc, 5:1) = 0.18. IR (KBr): $\tilde{\nu}$ = 1718 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 3.84 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 3.90 (br. s, 2 H, CH_2), 6.50 (s, 1 H, C6-H), 6.74 (s, 1 H, C8-H), 6.93 (d, ^3J = 7.9 Hz, 1 H, C-H_{benzyl}), 6.95 (dt, ^4J = 1.0 Hz, ^3J = 7.4 Hz, 1 H, C-H_{benzyl}), 7.26–7.30 (m, 2 H, 2 × C-H_{benzyl}), 7.67 (d, ^4J = 0.6 Hz, 1 H, C4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3 (+, CH_3), 30.9 (-, CH_2), 55.4 (+, OCH_3), 55.8 (+, OCH_3), 106.2 (+), 108.0 (q, C-4a), 109.1 (+), 110.6 (+), 120.6 (+), 125.2 (q), 126.6 (q), 128.1 (+), 131.0 (+), 134.3 (+), 142.2 (q, C-7), 154.1 (q, C-8a), 155.4 (q, C-OMe), 157.7 (q, C-OMe), 162.3 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 310 (100) [M^+], 279 (22) [$M^+ - OCH_3$], 203 (56). HR-EIMS: calcd. 310.1205, found 310.1207. $C_{19}H_{18}O_4$ (310 g/mol): calcd. C 73.53, H 5.85; found C 73.23, H 5.82.

5-Methoxy-3-(4-methoxybenzyl)-7-methylchromen-2-one (6d-p-anisyl): Prepared according to procedure **C** from 0.200 g (1.20 mmol) of 2-hydroxy-6-methoxy-4-methylbenzaldehyde (**1d**), 0.166 g (1.20 mmol) of K_2CO_3, 0.487 g (3.00 mmol) of (*E*)-4-methoxycinnamaldehyde (**5d**) and 0.267 g (1.20 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, cHex/EtOAc, 5:1) yielded the title compound (0.149 g, 40%) as colourless solid; m.p. 140–143 °C. R_f (cHex/EtOAc, 5:1) = 0.20. IR (KBr): $\tilde{\nu}$ = 1706 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 3.80 (br. s, 5 H, CH_2, OCH_3), 3.86 (s, 3 H, OCH_3), 6.48 (s, 1 H, C6-H), 6.71 (s, 1 H, C8-H), 6.85–6.88 (m, 2 H, 2 × C-H_{benzyl}), 7.20–7.24 (m, 2 H, 2 × C-H_{benzyl}), 7.69 (d, ^4J = 0.5 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.4 (+, CH_3), 35.9 (-, CH_2), 55.3 (+, OCH_3), 55.8 (+, OCH_3), 106.2 (+, C-8), 107.9 (q, C-4a), 109.1 (+, C-6), 114.1 (+, 2 × C_{benzyl}), 126.3 (q, C-3), 130.3 (+, 2 × C_{benzyl}), 130.4 (q, C_{benzyl}), 134.4 (+, C-4), 142.5 (q, C-7), 154.2 (q, C-8a), 155.4 (q, C-OMe), 158.3 (q, C-OMe), 162.1 (q, C-2) ppm. MS (EI): *m*/*z* (%) = 310 (76) [M^+], 296 (72), 134 (100). HR-EIMS: calcd. 310.1205, found 310.1206. $C_{19}H_{18}O_4$ (310 g/mol): calcd. C 73.53, H 5.85; found C 73.54, H 5.82.

3-(But-2-enyl)-5-methoxy-7-methylchromen-2-one (6d-butenyl): Prepared according to procedure **C** from 0.200 g (1.20 mmol) of 2-hydroxy-6-methoxy-4-methylbenzaldehyde (**1d**), 0.166 g (1.20 mmol) of K_2CO_3, 0.288 g (3.00 mmol) of (2*E*,4*E*)-hexa-2,4-dienal (**5e**) and 0.267 g (1.20 mmol) of dimethyl 1,3-dimethylimidazolium phosphate in 3 mL of toluene. Purification of the crude product by column chromatography (silica gel, 2.5 × 20 cm, pent/Et_2O, 4:1 and then cHex/EtOAc, 5:1) yielded a mixture of *E*/*Z* isomers of the title compound (0.063 g, 21%) as light yellow solid; m.p. 140–144 °C. R_f (cHex/EtOAc, 5:1) = 0.34. IR (KBr): $\tilde{\nu}$ = 1715 (s, νC=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.69–1.73 (m, 3 H, 2 × CH_3 *E*/*Z*), 2.40 (s, 3 H, C7-CH_3), 3.22, 3.29 (2 × d, ^3J = 4.4, ^3J = 7.2 Hz, 2 H, CH_2 *E*/*Z*), 3.89, 3.90 (2 × s, 3 H, CH_3, *E*/*Z*), 5.55–5.66, 5.70–5.77 (2 × m, 2 H, CH=CH *E*/*Z*), 6.50 (br. s, 1 H, C6-H), 6.72 (d, ^4J = 0.6 Hz, 1 H, C8-H), 7.79 (d, ^4J = 0.5 Hz, 1 H, C4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9, 18.0 (+, 2 × CH_3 *E*/*Z*), 22.4 (+, Ar-CH_3), 27.8, 33.6 (–, 2 × CH_2 *E*/*Z*), 55.9 (+, OCH_3), 106.2 (+, C-8), 107.9 (–, C-4a), 109.1, 109.2 (+, 2 × C-6 *E*/*Z*), 125.2, 125.58 (–, 2 × C-3 *E*/*Z*), 125.63, 126.7 (+, 2 × CH *E*/*Z*), 127.3, 128.4 (+, 2 × CH *E*/*Z*), 133.4, 133.8 (+, 2 × C-4 *E*/*Z*), 142.27, 142.29 (q, 2 × C-7 *E*/*Z*), 154.1, 154.2 (q, 2 × C8a *E*/*Z*), 155.4 (q, C-5), 162.1, 162.3 (q, 2 × C-2 *E*/*Z*) ppm. MS (EI): *m*/*z* (%) = 244 (100) [M^+], 229 (24) [$M^+ - CH_3$], 215 (18), 203 (52), 201 (18). HR-EIMS: calcd. 244.1099, found 244.1104.

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