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Lewis acid promoted dual bond formation: facile synthesis of dihydrocoumarins and spiro-tetracyclic dihydrocoumarins[†]

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Received 4th March 2014, Accepted 24th April 2014 DOI: 10.1039/c4ob00490f Lewis acid (FeCl₃) mediated dual bond (C–C and C–O) formation for synthesis of 3,4-dihydrocoumarins is presented. This method has successfully delivered a number of dihydrocoumarins containing dense functionalities on the aromatic ring. Significantly, the present method enabled achieving dihydrocoumarins with tertiary as well as quaternary carbon atoms at the benzylic position. Gratifyingly, the novel spiro-tetracyclic lactones have also been dextrously prepared using this process.

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Introduction

Coumarins are widely prevalent in nature, and show a broad range of biological activities¹ such as anti-inflammatory, antiaging, anti-oxidative and anti-cancer activities.² The coumarin derivatives, with the core carbon skeleton of 4-aryl-3,4-dihydrocoumarin, are present in several classes of plants (neoflavanoids) exhibiting some interesting biological activities such as antiherpetic activity,³ aldose reductase inhibition,⁴ protein kinase inhibition,⁵ and they are also important synthetic intermediates for pharmaceutical compounds. Some tannins possessing this dihydrocoumarin unit are known to have been used in the treatment of infections and diseases.⁶ Some of the synthetically prepared dihydrocoumarins have gained popularity for their biological advantages. For example, compound 1 is a key intermediate in the synthesis of an endothelin antagonist⁷ as well as the drug tolterodine,⁸ which is an antagonist formulated to treat overactive bladder (Fig. 1),9 whereas the dihydrocoumarin 2 acts as a bactericide with the in vitro activity against members of the Tripanosoma family (Fig. 1).¹⁰ Some of the naturally occurring dihydrocoumarins like 3¹¹ and 4¹¹ (Fig. 1), obtained from Aloe vera^{2,12} and Gnetum cleistostachyum,^{1,13} respectively, show anti-inflammatory and antioxidant activities.14 They are also notably known for their ability to protect low-density lipoproteins from oxidative attack¹⁵ and recent studies have also revealed their ability to control the chronic heart and colon-rectal cancer.



Owing to the diverse advantages of the aryl-dihydrocoumarins, development of various methodologies for their synthesis has received tremendous attention. There have been a reasonable number of reports on the synthesis of these dihydrocoumarins. A few to be mentioned include the transition-metal-mediated catalytic hydrogenation,¹⁶ protic acid induced hydroarylation of the cinnamic acids with phenols,¹⁷ Lewis acid mediated cyclization between highly activated phenols and arylonitriles,¹⁸ the use of oxidants on acids,¹⁹ synthesis from ionic liquids, solid state catalysts, the use of molecular iodine as a catalyst, 5-alkylidene Meldrum's acids,²⁰ Baeyer–Villiger oxidation of 1-indanones,²¹ and microwave assisted synthesis from phenols and cinnamoyl chloride in the presence of the montmorillonite K-10 catalyst.²²

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Paper

In this regard, we recently reported superacid mediated dual C-C bond formation, for the efficient synthesis of indanones.²³ Herein we report an efficient and practical method for the facile synthesis of the dihydrocoumarins promoted by a Lewis acid (FeCl₃) upon treatment of simple cinnamate esters with phenols. Notably, the approach has some significant advantages compared to those reported earlier. For example, the present method, using a Lewis acid (FeCl₃), describes the direct treatment of cinnamate esters with phenols. Particularly, the other striking facet is the facile formation of a stereogenic quaternary carbon atom at the benzylic position and to the best of our knowledge there is no report on dihydrocoumarins with a quaternary carbon atom in such mild acidic transformations. Significantly, this method is applicable to accomplish the novel spiro-tetracyclic lactones which are quite difficult to achieve starting from cyclohexanone derivatives, since selfaromatization is a serious problem either under strong acidic or basic conditions. Moreover, the present study is broadly applied to check the scope and limitations of the method by employing on different cinnamates with varying functionalities on the aromatic rings.

Results and discussion

To begin with, the required cinnamate esters 5 were prepared from the corresponding benzaldehydes/acetophenones using the standard Wittig-Horner-Wadsworth-Emmons reaction. In order to determine the best optimized reaction conditions, initially, the simple ethyl cinnamate 5a was chosen as the model to study the reaction with phenol under various conditions as described in Table 1. The initial trials with catalytic amounts of a Lewis acid (FeCl₃) did not facilitate the product 7a formation, rather furnished the Michael addition product 8a along with the recovery of the starting material (Table 1, entries 1 to 3). Though the precise mechanism cannot be given at this stage, the regioselective formation of the Michael addition product 8a, under catalytic loading of a Lewis acid would be explained due to selective activation of the enoate double bond by the Lewis acid that may facilitate the paraattack by the phenol. Gratifyingly, increasing the Lewis acid concentration (3 equiv.) at 80 °C in 1,2-dichloroethane resulted in the formation of lactone 7a in fair yields along with the Michael addition product 8a (Table 1, entry 4). An increase of FeCl₃ from 3 equiv. to 5 equiv. exclusively gave the final product 7a albeit in moderate yields (Table 1, entry 5). The use of dichloromethane as a solvent was found to be inferior (Table 1, entry 6), while in benzene it better facilitated 8a. The predominant formation of the cyclic product 7a, in a stoichiometric amount of the Lewis acid, may be justified based on simultaneous activation of the enoate double bond, the carbonyl group of the ester as well as the phenol by the Lewis acid that might facilitate the Michael addition/condensation to give the lactone product 7a. The use of $AlCl_3$ neither gave the lactone product nor allowed the recovery of the starting material (Table 1, entry 7). Also, it is concluded that the temp

	Lewis acid	Solvent (mL)	Temp (°C)	$\operatorname{Yield}^{b}(\%)$	
Entry ^a				7a	8a
1 ^{<i>c</i>}	$FeCl_3$ (10 mol%)	DCE (2)	80	0	0
2	$FeCl_3$ (20 mol%)	DCE (2)	80	0	10
3	$FeCl_3$ (60 mol%)	DCE (2)	80	0	30
4	$FeCl_3$ (3 equiv.)	DCE (2)	80	60	20
5	$FeCl_3$ (5 equiv.)	DCE (2)	80	55	0
6	$FeCl_3$ (3 equiv.)	DCM(2)	rt	20	0
7^d	$AlCl_3$ (3 equiv.)	DCE(2)	80	0	0
8	$FeCl_3$ (3 equiv.)	DCE (2)	rt	20	0
9	$FeCl_3$ (3 equiv.)	Benzene (2)	80	0	35
10^{c}	$AuCl_3$ (10 mol%)	DCE (2)	80	0	0
11^{c}	$Sc(OTf)_3$ (10 mol%)	DCE (2)	80	0	0
12^{c}	$Cu(OTf)_2$ (10 mol%)	DCE(2)	80	0	0
13	TfOH	DCE(2)	80	50	0

^{*a*} All reactions were carried out on a 0.5 mmol scale of **5a** and 1.5 equiv. of **6a**, in solvent DCE (2 mL). ^{*b*} Isolated yields of chromatographically pure products. ^{*c*} Only the starting material was recovered. ^{*d*} Neither the product (**7a**) nor the starting material was isolated.

erature played an important role, as when the reaction was conducted at ambient temperature, the reaction slowed down (Table 1, entry 8). The use of the other Lewis acid catalysts, like $Sc(OTf)_3$, $Cu(OTf)_2$ and $AuCl_3$, in the catalytic amounts was found to be futile and led to the starting material recovery (Table 1, entries 10 to 12). In the presence of a superacid (TfOH) also the product 7a was formed, however, in moderate yields (Table 1, entry 13).

Among all the screened conditions, conditions of entry 4 of Table 1 were found to be the best with regard to the formation of 7a. Therefore, to check the scope and generality of the method, these conditions were applied to different cinnamates **5a–5c** containing various functional groups on the aromatic rings with phenols **6a–6c**. Gratifyingly, the method was found amenable and gave dihydrocoumarins **7a–7e** containing a tertiary carbon atom, as summarized in Table 2. Disappointingly, in the case of electron rich cinnamate esters **5d–5f** it could not be amenable under standard conditions, however at the ambient temperature it furnished the clean lactone products **7f–7l** (Table 2).

Furthermore, to check the feasibility of the method, β -alkyl (methyl/ethyl) ethyl cinnamates **5g–5j** were explored. Interestingly, it was noted that the reaction is temperature and system dependent. For example, when β -methyl cinnamate ester **5g**, derived from the corresponding acetophenone, was treated with the phenol **6a** using the above optimized reaction conditions at 80 °C (Table 1, entry 4), it was not clean. However,

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^{*a*} All reactions were carried out on a 0.5 mmol scale of 5 and 1.5 equiv. of 6, in solvent DCE (2 mL). ^{*b*} Isolated yields of chromatographically pure products 7. ^{*c*} For compounds 7a–7e, the reaction was carried out at 80 °C for 24 h. ^{*d*} For compounds 7f–7l, the reaction was carried out at room temperature for 16 h.

the reaction was quite successful at room temperature and furnished the desired product **9a** (Table 3). This would be justified owing to the slightly increased reactivity of **5g** that may be due to the presence of the β -methyl substituent which would facilitate the polarization of the enoate double bond by the Lewis acid. After optimizing the reaction conditions for the ester **5g** at room temperature, the generality of the reaction was established by employing the reaction between β -alkyl cinnamate esters **5h**-**5j** and the phenols **6a**-**6f**. In general, the method was smooth and furnished the dihydrocoumarins **9b**-**9q** (Table 3).

However, when attempting to apply the present method on β -methyl ethyl cinnamates **5k–5l**, it did not furnish the expected dihydrocoumarins, rather gave coumarins **10a–10c** (Table 4).

This can be rationalized based on the more reactive nature of the electron rich aromatic ring derived from the cinnamates 5k-5l, with suitably positioned electron donating groups. Though, the precise reaction mechanism cannot be given at this stage, however their formation is believed to be *via* the formation of the usual dihydrocoumarin product **9** followed by ipso type of aromatic substitution through internal rearrange-

ment/cleavage of either \boldsymbol{X} or \boldsymbol{Y} intermediates, as shown in Scheme 1.

Furthermore, to study the regiochemical preference (*i.e.* the effect of the *ortho*-substituent on the Friedel–Crafts alkylation), 2-phenylphenol **6g** was used as an external phenol on the cinnamate esters **5g–5h**. However, the cyclized products **11a–11b** were formed, albeit, in poor yields, while the Michael addition adducts **12a–12b** were formed as the by-products, in moderate yields. This can be attributed to the steric crowding of 2-phenylphenol **6g** that prefers *para*-attack on the Michael acceptor ethyl cinnamates **5g–5h** (Scheme 2).

Upon accomplishing the dihydrocoumarins (7, 9 and 11) in a wide generality, we envisioned to use this method in a more applicable facet by performing the reaction with the cinnamate ester 5m obtained from the tetralone. Nevertheless, one could easily realize that such systems derived from six membered ketones would pose a serious problem of self-aromatization either under strong acidic or basic reaction conditions. As expected, the reaction of cinnamate ester 5m under standard conditions at 80 °C was unclear, whereas at room temperature, it gave only the self-aromatized product 14 (Table 5, entries 1 and 2). This made us to realize that the phenol is not

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sufficient enough to compete with usual self-aromatization. Therefore, performing the reaction with 5 equiv. of the phenol **6a** led to the formation of the novel tetracyclic lactone **13a**, in 33% yield along with the aromatized product **14** (Table 5, entry 3). On the other hand, interestingly, benzene was identified as the good solvent, hence it gave the product **13a**, albeit, in poor yield, even with 1.5 equiv. of phenol **6a** (Table 5, entry 4). Gratifyingly, with the increased amount of phenol **6a** (5 equiv.), the product **13a** was furnished in moderate yields along with the aromatized product **14** (Table 5, entry 5). However, a further increase of phenol **6a** quantity (10 equiv.) could not improve the yield of the product drastically (Table 5, entry 6). It is note-worthy that the amount of the Lewis acid is slightly increased to 4 equiv. from 3 equiv. wherever more amount of phenol has been used in order to maintain the reasonable reactivity to

promote the reaction, because phenol could also chelate with the Lewis acid and decrease its reactivity.

Among the screened conditions, conditions with either 5 or 10 equiv. of phenol **6a** in benzene (Table 5, entries 5 and 6) were found to be the best with respect to the formation of **13a**. Therefore, these conditions were used to generate different tetracyclic lactones **13**. Gratifyingly, the method conveniently furnished the novel tetracyclic lactones **13b–13f**, as summarized in Table 6.

Conclusions

In summary, we have developed a simple and practical method for the synthesis of dihydrocoumarins, a ubiquitous system

Table 4Lewis acid (FeCl3) mediated synthesis of coumarins10 starting from cinnamates 5



Scheme 1 Plausible mechanism for the formation of 10.

ÓMe

OMe

present in many natural products. It was also extended to synthesize the novel spiro-tetracyclic lactones. The strategy is efficient and successful for the synthesis of a number of analogues. Moreover, this method availed the creation of the quaternary centre.

`OMe

ÓMe



Scheme 2 Regioselective Michael addition of 2-phenylphenol 6g onto the cinnamate esters 5g-5h.

Table 5Screening conditions for synthesis of spiro-dihydrocoumarins13a under Lewis acidic conditions



Entry ^a	FeCl ₃ (equiv.)	Phenol (equiv.)	Solvent (mL)	Temp (°C)	$\operatorname{Yield}^{b}(\%)$	
					13a	14
1	3	1.5	DCE (2)	80	0	0
2	3	1.5	DCE (2)	rt	0	38
3	4	5	DCE (2)	rt	33	10
4	3	1.5	Benzene	rt	15	40
5	4	5	Benzene	rt	40	23
6	4	10	Benzene	rt	42	20

^{*a*} All reactions were carried out on a 0.5 mmol scale of **5m**. ^{*b*} Isolated yields of chromatographically pure products.

Experimental section

General

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ¹H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer at 295 K in CDCl₃; chemical shifts (δ ppm) and coupling constants (J in Hz) are reported in a standard fashion with reference to either internal standard tetramethylsilane (TMS) ($\delta_{\rm H} = 0.00$ ppm) or CHCl₃ ($\delta_{\rm H} = 7.25$ ppm). ¹³C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer at RT in CDCl₃; chemical shifts (δ in ppm) are reported relative to CHCl₃ [$\delta_{\rm C} =$ 77.00 ppm (central line of triplet)]. In the ¹³C NMR, the nature of carbons (C, CH, CH₂ and CH₃) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH₂)



^{*a*} All reactions were carried out on a 0.5 mmol scale of 5 and 5 equiv. of 6, in solvent benzene (2 mL). ^{*b*} Isolated yields of chromatographically pure products 13.

and q = quartet (for CH_3). In the ¹H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed from ¹H, ¹³C CPD and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF using a multimode source. All small scale dry reactions were carried out using the standard syringe-septum technique. Regarding the Horner-Wadsworth-Emmons reaction, TEPA from Avra Synthesis with a purity of 98%, NaH from Sigma-Aldrich (60% immersion in mineral oil), and benzaldehydes/acetophenones from Sisco Research Laboratories having 97-98% purity were used. Solvent THF was dried over sodium metal. Similarly, for cyclization reaction anhydrous FeCl3 from Merck Chemicals and phenols from Sisco Research Laboratories were used. DCE was dried over calcium hydride and used. Reactions were monitored by TLC on silica gel using a mixture of petroleum ether and ethyl acetate as eluents. Reactions were generally run under an argon or nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C was used. Acme's silica gel (60-120 mesh) was used for column chromatography (approximately 20 g per gram of crude material).

General procedure (GP-1) for cyclization

Into an oven dried Schlenk tube under a nitrogen atmosphere were added cinnamate ester 5 (88–133 mg, 0.5 mmol), phenol

6 (70–81 mg, 0.75 mmol) and anhydrous FeCl₃ (324.0 mg, 2 mmol) followed by DCE (2 mL). The resulting reaction mixture was stirred at 80 °C for **5a–5c** for 24 h (for other esters **5d–5j**, the reaction was carried out at room temperature, for 6 to 16 h). Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted in ethyl acetate (3 × 20 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Purification of the residue on a silica gel column using petroleum ether–ethyl acetate as the eluent furnished lactones 7 (35–67%) and **9** (54–90%) as viscous liquids/solids.

General procedure (GP-2) for spiro-cyclization

Into an oven dried Schlenk tube under a nitrogen atmosphere were added cinnamate ester 5 (88–133 mg, 0.5 mmol), phenol 6 (235–360 mg, 2.5 mmol) and anhydrous FeCl₃ (324.0 mg, 2 mmol) followed by benzene (2.5 mL). The resulting reaction mixture was stirred at rt for 2 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted in ethyl acetate (3×20 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Purification of the residue on a silica gel column using petroleum ether–ethyl acetate as the eluent furnished spiro-lactones 13 (39–62%) as viscous liquids/solids.

4-(3-Methoxyphenyl)-6-methylchroman-2-one (7e). GP-1 was carried out on the ester 5c (103 mg, 0.5 mmol), para-cresol 6c (81.0 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at 80 °C for 24 h [TLC control $R_{\rm f}(5c) = 0.83$, $R_{\rm f}(7e) = 0.66$ (petroleum ether-ethyl acetate 88:12, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 96:4 to 85:15 as the eluent) furnished the lactone 7e (66 mg, 51%) as a viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2924, 1765, 1511, 1493, 1462, 1245, 1199, 1179, 1145, 1033, 820 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.26 (dd, 1H, J = 7.8 and 7.8 Hz, ArH), 7.08 (dd, 1H, J = 8.3 and 2.0 Hz, ArH), 7.01 (d, 1H, J = 7.8 Hz, ArH), 6.81 (dd, 1H, J = 8.3 and 2.0 Hz, ArH), 6.79 (s, 1H, ArH), 6.73 (d, 1H, J = 7.8 Hz, ArH), 6.68 (dd, 1H, J = 2.0 and 2.0 Hz, ArH), 4.25 (dd, 1H, J = 7.8 and 6.4 Hz, ArCHCH2CO), 3.77 (s, 3H, ArOCH3), 3.03 (dd, 1H, J = 16.1 and 6.4 Hz, ArCHCH_aH_bCO), 2.98 (dd, 1H, J = 16.1and 7.8 Hz, ArCHCH_a H_b CO), 2.25 (s, 3H, ArCH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.8 (s, O-C=O), 160.0 (s, ArC), 149.6 (s, ArC), 142.1 (s, ArC), 134.3 (s, ArC), 130.1 (d, ArCH), 129.3 (d, ArCH), 128.6 (d, ArCH), 125.1 (s, ArC), 119.7 (d, ArCH), 116.8 (d, ArCH), 113.6 (d, ArCH), 112.5 (d, ArCH), 55.2 (q, ArOCH₃), 40.7 (d, ArCHCH₂CO), 37.0 (t, CH₂CO), 20.7 (q, ArCH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{16}NaO_3]^+$ = $[M + Na]^+$: 291.0992; found 291.0991.

4-(3,4-Dimethoxyphenyl)-7-methylchroman-2-one (7i). GP-1 was carried out on the ester **5e** (118.0 mg, 0.50 mmol), *meta*-cresol **6b** (81.0 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 16 h [TLC control $R_{\rm f}$ (**5e**) = 0.75,

 $R_{\rm f}(7i) = 0.50$ (petroleum ether-ethyl acetate 80:20, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 95:5 to 75:25 as the eluent) furnished the lactone 7i (79.0 mg, 53%) as a liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{\text{max}} = 2922, 2852, 1762, 1591,$ 1516, 1463, 1419, 1253, 1219, 1142, 1025, 817 cm⁻¹. ¹H NMR $(CDCl_3, 400 \text{ MHz}): \delta = 6.93 \text{ (s, 1H, ArH)}, 6.89 \text{ (d, 1H, } J = 8.3 \text{ Hz},$ ArH), 6.85 (d, 1H, J = 7.8 Hz, ArH), 6.81 (d, 1H, J = 7.8 Hz, ArH), 6.67 (dd, 1H, J = 8.3 and 1.9 Hz, ArH), 6.65 (d, 1H, J = 1.9 Hz, ArH), 4.23 (dd, 1H, J = 7.8 and 6.4 Hz, ArCHCH₂CO), 3.85 (s, 3H, ArOCH₃), 3.81 (s, 3H, ArOCH₃), 3.03 (dd, 1H, J = 16.1 and 6.4 Hz, ArCHCH_aH_bCO), 2.96 (dd, 1H, J = 16.1 and 7.8 Hz, ArCHCH_aH_bCO), 2.34 (s, 3H, ArCH₃) ppm. ¹³C NMR $(CDCl_3, 100 \text{ MHz}): \delta = 168.0 \text{ (s, O-C=O)}, 151.5 \text{ (s, ArC)}, 149.3$ (s, ArC), 148.4 (s, ArC), 139.0 (s, ArC), 132.9 (s, ArC), 127.9 (d, ArCH), 125.4 (d, ArCH), 122.9 (s, ArC), 119.7 (d, ArCH), 117.4 (d, ArCH), 111.5 (d, ArCH), 110.5 (d, ArCH), 55.9 (q, 2C, 2 × ArOCH₃), 40.0 (d, ArCHCH₂CO), 37.3 (t, CH₂CO), 21.0 (q, ArCH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}NaO_4]^+$ = $[M + Na]^+$: 321.1097; found 321.1098.

4-(3,4-Dimethoxyphenyl)-6-methylchroman-2-one (7j). GP-1 was carried out on the ester 5e (118.0 mg, 0.50 mmol), paracresol 6c (81.0 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 16 h [TLC control $R_{\rm f}(5e) = 0.75$, $R_{\rm f}(7i) = 0.57$ (petroleum ether-ethyl acetate 80:20, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 95:5 to 75:25 as the eluent) furnished the lactone 7j (99.8 mg, 67%) as a liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max} = 2924$, 2852, 1762, 1592, 1493, 1420, 1243, 1137, 1025, 813 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.07 (dd, 1H, J = 8.3 and 1.9 Hz, ArH), 7.00 (d, 1H, J = 8.3 Hz, ArH), 6.82 (d, 1H, J = 7.8 Hz, ArH), 6.78 (d, 1H, J = 1.9 Hz, ArH), 6.67 (dd, 1H, J = 7.8 and 1.9 Hz, ArH), 6.66 (s, 1H, ArH), 4.23 (dd, 1H, J = 7.8 and 6.4 Hz, ArCHCH₂CO), 3.85 (s, 3H, ArOCH₃), 3.82 (s, 3H, ArOCH₃), 3.03 (dd, 1H, J = 16.1 and 6.4 Hz, ArCHCH_aH_bCO), 2.96 (dd, 1H, J = 16.1 and 7.8 Hz, ArCHCH_aH_bCO), 2.25 (s, 3H, ArCH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 168.0 (s, O–C=O), 149.5 (s, ArC), 149.3 (s, ArC), 148.4 (s, ArC), 134.3 (s, ArC), 132.9 (s, ArC), 129.2 (d, ArCH), 128.5 (d, ArCH), 125.6 (s, ArC), 119.7 (d, ArCH), 116.8 (d, ArCH), 111.5 (d, ArCH), 110.5 (d, ArCH), 55.9 (q, 2C, 2 × ArOCH₃), 40.4 (d, ArCHCH₂CO), 37.3 (t, CH₂CO), 20.7 (q, ArCH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}NaO_4]^+$ = $[M + Na]^+$: 321.1097; found 321.1100.

7-Methyl-4-(3,4,5-trimethoxyphenyl)chroman-2-one (7k). GP-1 was carried out on the ester 5f (133.0 mg, 0.50 mmol), *meta*cresol 6b (81.0 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 16 h [TLC control $R_{\rm f}$ (5f) = 0.80, $R_{\rm f}$ (7k) = 0.55 (petroleum ether–ethyl acetate 85:15, UV detection)]. Purification of the residue on a silica gel column (petroleum ether–ethyl acetate 95:5 to 85:15 as the eluent) furnished the lactone 7k (57.4 mg, 35%) as a semi-solid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{\rm max}$ = 2923, 2852, 1767, 1508, 1461, 1235, 1126, 1008, 818 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 6.93 (s, 1H, ArH), 6.90 (d, 1H, J = 7.8 Hz, ArH), 6.88 (d, 1H, J = 7.8 Hz, ArH), 6.34 (s, 2H, ArH), 4.22 (dd, 1H, J = 7.8 and 6.4 Hz, ArCHCH₂CO), 3.82 (s, 3H, ArOCH₃), 3.79 (s, 6H, 2 × ArOCH₃), 3.03 (dd, 1H, J = 16.1 and 6.4 Hz, ArCHCH_aH_bCO), 2.98 (dd, 1H, J = 16.1 and 7.8 Hz, ArCHCH_aH_bCO), 2.35 (s, 3H, ArCH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.8 (s, O–C=O), 153.6 (s, 2C, 2 × ArC), 151.5 (s, ArC), 139.2 (s, ArC), 136.2 (s, ArC), 128.0 (d, ArCH), 125.4 (d, ArCH), 122.5 (s, ArC), 117.5 (d, ArCH), 104.5 (d, 2C, 2 × ArCH), 60.8 (q, ArOCH₃), 56.1 (q, 2C, 2 × ArOCH₃), 40.7 (d, ArCHCH₂CO), 37.2 (t, CH₂CO), 21.1 (q, ArCH₃) ppm. HR-MS (ESI+) m/z calculated for [C₁₉H₂₀NaO₅]⁺ = [M + Na]⁺: 351.1203; found 351.1206.

6-Methyl-4-(3,4,5-trimethoxyphenyl)chroman-2-one (7l). GP-1 was carried out on the ester 5f (133.0 mg, 0.50 mmol), paracresol 6c (81.0 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 16 h [TLC control $R_{\rm f}(5f) = 0.80$, $R_{\rm f}(7l) = 0.60$ (petroleum ether-ethyl acetate 85:15, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 95:5 to 80:15 as the eluent) furnished the lactone 7l (67.2 mg, 41%) as a liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{\rm max}$ = 2921, 2850, 1764, 1591, 1460, 1243, 1124, 1006, 815 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.08 (dd, 1H, J = 8.3 and 1.9 Hz, ArH), 7.01 (d, 1H, J = 8.3 Hz, ArH), 6.81 (d, 1H, J = 1.9 Hz, ArH), 6.34 (s, 2H, 2 × ArH), 4.21 (dd, 1H, J = 7.8 and 6.3 Hz, ArCHCH₂CO), 3.83 (s, 3H, ArOCH₃), 3.79 (s, 6H, $2 \times \text{ArOCH}_3$), 3.04 (dd, 1H, J = 16.1and 6.3 Hz, ArCHCH_aH_bCO), 2.96 (dd, 1H, J = 16.1 and 7.8 Hz, ArCHCH_aH_bCO), 2.27 (s, 3H, ArCH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.8 (s, O–C=O), 153.6 (s, 2C, 2 × ArC), 149.5 (s, ArC), 137.3 (s, ArC), 136.2 (s, ArC), 134.4 (s, ArC), 129.4 (d, ArCH), 128.6 (d, ArCH), 125.2 (s, ArC), 116.8 (s, ArC), 104.5 (d, 2C, 2 × ArCH), 60.8 (q, ArOCH₃), 56.1 (q, 2C, 2 × ArOCH₃), 41.1 (d, ArCHCH₂CO), 37.2 (t, CH₂CO), 20.7 (q, ArCH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{20}NaO_5]^+ = [M + Na]^+$: 351.1203; found 351.1204.

4-Methyl-4-phenylchroman-2-one (9a). GP-1 was carried out on the ester 5g (95.1 mg, 0.5 mmol), phenol 6a (69.8 mg, 0.75 mmol), and anhydrous FeCl₃ (243.3 mg, 1.5 mmol) followed by addition of DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5g) = 0.60, R_{\rm f}(9a) = 0.45$ (petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone 9a (76 mg, 64%) as a colorless viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max} = 2922$, 1774, 1586, 1487, 1448, 1283, 1202, 1135, 1051, 910, 758, 700 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.34 (dd, 1H, J = 7.8 and 1.5 Hz, ArH), 7.30 (dd, 2H, J = 7.8 and 1.5 Hz, ArH), 7.27-7.21 (m, 2H, ArH), 7.21-7.16 (m, 3H, ArH), 7.11 (dd, 1H, J = 8.3 and 1.5 Hz, ArH), 3.29 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.84 (d, 1H, J = 15.6 Hz, CH_a H_b CO), 1.76 [s, 3H, ArC(CH₂CO)- CH_3] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.4 (s, O-C=O), 151.2 (s, ArC), 143.9 (s, ArC), 130.8 (s, ArC), 128.7 (d, 3C, 3 × ArCH), 127.1 (d, ArCH), 126.6 (d, ArCH), 126.1 (d, 2C, 2 × ArCH), 124.7 (d, ArCH), 117.3 (d, ArCH), 43.7 (t, CH₂CO), 41.1

[s, Ar*C*(CH₂CO)CH₃], 27.5 [q, ArC(CH₂CO)*C*H₃] ppm. HR-MS (ESI+) m/z calculated for $[C_{16}H_{15}O_2]^+ = [M + H]^+$: 239.1067; found: 239.1067.

4,7-Dimethyl-4-phenylchroman-2-one (9b). GP-1 was carried out on the ester 5g (95.1 mg, 0.5 mmol), meta-cresol 6b (69.8 mg, 0.75 mmol), and anhydrous FeCl₃ (243.3 mg, 1.5 mmol) followed by addition of DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5{\rm g}) = 0.60, R_{\rm f}(9{\rm b}) = 0.45$ (petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone 9b (107.5 mg, 85%) as a colorless viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2972, 2926, 1763, 1623, 1578, 1445, 1413, 1215, 1199, 1164, 1150, 1047, 820, 764, 699 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.29 (ddd, 2H, J = 7.8, 7.3 and 1.9 Hz, ArH), 7.22 (t, 1H, J = 7.3 Hz, ArH), 7.17 (dd, 2H, J = 7.8 and 1.9 Hz, ArH), 7.11 (d, 1H, J = 7.8 Hz, ArH), 6.98 (dd, 1H, J = 7.8 and 1.0 Hz, ArH), 6.92 (d, 1H, J = 1.0 Hz, ArH), 3.26 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.80 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.36 (s, 3H, ArCH₃), 1.72 [s, 3H, ArC(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.7 (s, O-C=O), 151.0 (s, ArC), 144.1 (s, ArC), 139.0 (s, ArC), 128.6 (d, 2C, 2 × ArCH), 127.6 (s, ArC), 127.0 (d, ArCH), 126.3 (d, ArCH), 126.1 (d, 2C, 2 × ArCH), 125.4 (d, ArCH), 117.7 (d, ArCH), 43.9 (t, CH₂CO), 40.8 [s, ArC(CH₂CO)-CH₃], 27.6 [q, ArC(CH₂CO)CH₃], 21.0 (q, ArCH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{16}NaO_2]^+ = [M + Na]^+$: 275.1043; found 275.1048.

4,6-Dimethyl-4-phenylchroman-2-one (9c). GP-1 was carried on the ester 5g (95.1 mg, 0.5 mmol), para-cresol 6c (69.8 mg, 0.75 mmol), and anhydrous FeCl₃ (243.3 mg, 1.5 mmol) followed by addition of DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5{\rm g}) = 0.60, R_{\rm f}(9{\rm c}) = 0.45$ (petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone 9c (107.5 mg, 85%) as a colorless viscous liquid. IR (MIR-ATR, 4000-600 cm⁻¹): $\nu_{max} = 2974$, 2921, 1763, 1598, 1493, 1266, 1202, 1124, 1049, 913, 824, 732, 698 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.30 (ddd, 2H, J = 7.8, 7.3 and 2.0 Hz, ArH), 7.23 (t, 1H, J = 7.3 Hz, ArH), 7.18 (dd, 2H, J = 7.8 and 2.0 Hz, ArH), 7.11 (dd, 1H, J = 8.3 and 2.0 Hz, ArH), 7.02 (d, 1H, J = 2.0 Hz, ArH), 6.99 (d, 1H, J = 8.3 Hz, ArH), 3.25 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.80 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.34 (s, 3H, ArCH₃), 1.73 [s, 3H, ArC-(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.7 (s, O-C=O), 149.1 (s, ArC), 144.0 (s, ArC), 134.3 (s, ArC), 130.3 (s, ArC), 129.2 (d, ArCH), 128.6 (d, 2C, 2 × ArCH), 127.1 (d, ArCH), 126.9 (d, ArCH), 126.1 (d, 2C, 2 × ArCH), 117.0 (d, ArCH), 43.8 (t, CH₂CO), 41.0 [s, ArC(CH₂CO)CH₃], 27.5 [q, ArC(CH₂CO)- CH_3], 20.9 (q, ArCH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{16}NaO_2]^+ = [M + Na]^+: 275.1048;$ found 275.1042.

4,8-Dimethyl-4-phenylchroman-2-one (9d). GP-1 was carried out with the ester **5g** (95.1 mg, 0.5 mmol), *ortho*-cresol **6d** (81.0 mg, 0.75 mmol), and anhydrous FeCl_3 (243.3 mg, 1.5 mmol) followed by addition of DCE (2 mL). The resulting

reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5{\rm g}) = 0.65$, $R_{\rm f}(9{\rm d}) = 0.50$ (petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column chromatography (petroleum ether-ethyl acetate 98:2 to 94:6 as the eluent) furnished the lactone 9d (81.9 mg, 65%) as colorless viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2967, 2921, 1765, 1463, 1445, 1266, 1192, 1101, 915, 751, 699 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.29 (ddd, 2H, J = 8.8, 7.3 and 1.5 Hz, ArH), 7.23 (dd, 1H, J = 8.3 and 1.5 Hz, ArH), 7.21-7.15 (m, 3H, ArH), 7.07 (d, 2H, J = 4.9 Hz, ArH), 3.28 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.81 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.32 (s, 3H, ArCH₃), 1.73 [s, 3H, ArC-(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.7 (s, O-C=O), 149.4 (s, ArC), 144.0 (s, ArC), 130.5 (s, ArC), 130.2 (d, ArCH), 128.6 (d, 3C, 3 × ArCH), 127.1 (d, ArCH), 126.6 (s, ArC), 126.1 (d, 2C, 2 × ArCH), 124.1 (d, ArCH), 43.6 (t, CH₂CO), 41.1 [s, ArC(CH₂CO)CH₃], 27.7 [q, ArC(CH₂CO)CH₃], 15.9 (q, ArCH₃) ppm. HR-MS m/z calculated for $[C_{17}H_{17}O_2]^+ = [M + H]^+$: 253.1223; found: 253.1210.

4-Methyl-4-phenyl-3,4-dihydro-2H-benzo[h]chromen-2-one (9e). GP-1 was carried out on the ester 5g (95.1 mg, 0.5 mmol), 1-naphthol 6e (108.0 mg, 0.75 mmol), and anhydrous FeCl₃ (243.3 mg, 1.5 mmol) followed by addition of DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5\mathbf{g}) = 0.60, R_{\rm f}(9\mathbf{e}) = 0.50$ (petroleum etherethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 98:2 to 94:6 as the eluent) furnished the lactone 9e (84.9 mg, 59%) as a white solid, recrystallized the solid with dichloromethane/ hexane, m. p. 144–146 °C. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2970, 2928, 1769, 1494, 1468, 1190, 1150, 1068, 816, 750, 700, 625 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 8.29 (dd, 1H, J = 8.8, and 2.0 Hz, ArH), 7.84 (dd, 1H, J = 7.3 and 2.0 Hz, ArH), 7.64 (d, 1H, J = 8.8 Hz, ArH), 7.59–7.51 (m, 2H, ArH), 7.34–7.18 (m, 6H, ArH), 3.34 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.93 (d, 1H, J = 15.6 Hz, CH_aH_bCO , 1.82 [s, 3H, $ArC(CH_2CO)CH_3$] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.3 (s, O-C=O), 146.1 (s, ArC), 144.2 (s, ArC), 133.6 (s, ArC), 128.7 (d, 2C, 2 × ArCH), 127.4 (d, ArCH), 127.2 (d, ArCH), 126.8 (d, ArCH), 126.7 (d, ArCH), 126.3 (d, 2C, 2 × ArCH), 125.1 (s, ArC), 124.2 (d, ArCH), 123.7 (s, ArC), 123.6 (d, ArCH), 121.5 (d, ArCH), 44.2 (t, CH₂CO), 41.4 [s, ArC(CH₂CO)CH₃], 27.4 [q, ArC(CH₂CO)CH₃] ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{17}O_2]^+ = [M + H]^+$: 289.1223; found 289.1221.

1-Methyl-1-phenyl-1,2-dihydro-3*H***-benzo**[*f*]**chromen-3-one** (**9f**). GP-1 was carried out on the ester **5g** (95.1 mg, 0.5 mmol), β-naphthol **6f** (108.1 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_f(5g) = 0.65$, $R_f(9f) = 0.50$ (petroleum ether–ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether–ethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone **9f** (81 mg, 56%) as a colorless viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max} = 2920$, 2851, 1775, 1599, 1512, 1494, 1459, 1336, 1210, 1163, 1019, 982, 912, 814, 733, 701 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): $\delta =$ 7.79 (dd, 2H, J = 8.8 and 7.3 Hz, ArH), 7.40–7.19 (m, 7H, ArH), 7.13 (d, 1H, J = 8.3 Hz, ArH), 7.08 (ddd, 1H, J = 8.8, 7.8 and 1.4 Hz, ArH), 3.07 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.86 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 1.94 [s, 3H, ArC(CH_2CO) CH_3] ppm. ¹³C NMR ($CDCl_3$, 100 MHz): δ = 166.5 (s, O–C=O), 149.9 (s, ArC), 147.0 (s, ArC), 131.9 (s, ArC), 130.4 (s, ArC), 130.1 (s, ArC), 129.0 (d, 2C, 2 × ArCH), 128.8 (d, ArCH), 127.0 (d, ArCH), 126.0 (d, 2C, 2 × ArCH), 125.9 (d, ArCH), 125.8 (d, ArCH), 124.4 (d, ArCH), 122.8 (s, ArC), 117.8 (d, ArCH), 48.0 (t, CH_2CO), 42.9 [s, $ArC(CH_2CO)CH_3$], 24.7 [q, $ArC(CH_2CO)CH_3$] ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{16}NaO_2]^+ = [M + Na]^+$: 311.1048; found 311.1042.

4-(4-Chlorophenyl)-4-methylchroman-2-one (9g). GP-1 was carried out on the ester 5h (112 mg, 0.5 mmol), phenol 6a (69.8 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5{\rm h}) = 0.60, R_{\rm f}(9{\rm g}) =$ 0.35 (petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone 9g (90 mg, 66%) as a colorless viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{\text{max}} = 2973$, 2925, 1763, 1586, 1487, 1449, 1279, 1232, 1198, 1134, 1095, 1012, 910, 828, 756, 683 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.32 (ddd, 1H, J = 8.3, 7.3 and 2.0 Hz, ArH), 7.25 (d, 2H, J = 8.3 Hz, ArH), 7.22 (dd, 1H, J = 7.8 and 2.0 Hz, ArH), 7.18 (ddd, 1H, J = 8.3, 7.8 and 2.0 Hz, ArH), 7.10 (dd, 1H, J = 7.3 and 2.0 Hz, ArH), 7.09 (d, 2H, J = 8.3 Hz, ArH), 3.22 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.82 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 1.72 [s, 3H, ArC(CH₂CO)- CH_3] ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 167.2$ (s, O-C=O), 151.1 (s, ArC), 142.5 (s, ArC), 133.1 (s, ArC), 130.2 (s, ArC), 129.0 (d, ArCH), 128.8 (d, 2C, 2 × ArCH), 127.6 (d, 2C, 2 × ArCH), 126.4 (d, ArCH), 124.8 (d, ArCH), 117.4 (d, ArCH), 43.6 (t, CH₂CO), 40.8 [s, ArC(CH₂CO)CH₃], 27.5 [q, ArC(CH₂CO)- CH_3 ppm. HR-MS (ESI+) m/z calculated for $[C_{16}H_{13}ClNaO_2]^+$ = $[M + Na]^+$: 295.0502; found 295.0500.

4-(4-Chlorophenyl)-4,7-dimethylchroman-2-one (9h). GP-1 was carried out on the ester 5h (112 mg, 0.5 mmol), metacresol 6b (81.7 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5{\rm h}) = 0.60$, $R_{\rm f}(9{\rm h}) = 0.40$ (petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone 9h (103 mg, 72%) as a colorless viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2964, 2925, 1766, 1579, 1494, 1413, 1257, 1213, 1162, 1096, 1048, 1012, 820, 736 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.24 (d, 2H, J = 8.8 Hz, ArH), 7.09 (d, 2H, J = 8.8 Hz, ArH), 7.08 (d, 1H, J = 7.8 Hz, ArH), 6.98 (d, 1H, J = 7.8 Hz, ArH), 6.91 (s, 1H, ArH), 3.20 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.79 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.36 (s, 3H, ArCH₃), 1.69 [s, 3H, ArC(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.4 (s, O–C=O), 151.0 (s, ArC), 142.8 (s, ArC), 139.4 (s, ArC), 133.0 (s, ArC), 128.8 (d, 2C, 2 × ArCH), 127.6 (d, 2C, 2 × ArCH), 127.1 (s, ArC), 126.1 (d, ArCH), 125.6 (d, ArCH), 117.8 (d, ArCH), 43.8 (t, CH₂CO), 40.6

[s, Ar*C*(CH₂CO)CH₃], 27.6 [q, ArC(CH₂CO)*C*H₃], 21.0 (q, ArCH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{15}CINaO_2]^+ = [M + Na]^+$: 309.0658; found 309.0656.

4-(4-Chlorophenyl)-4,6-dimethylchroman-2-one (9i). GP-1 was carried out on the ester 5h (112 mg, 0.5 mmol), paracresol 6c (81.7 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5{\rm h}) = 0.60$, $R_{\rm f}(9i) = 0.45$ (petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone 9i (99 mg, 69%) as a colorless viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2972, 2924, 1761, 1592, 1491, 1413, 1278, 1199, 1124, 1095, 1012, 914, 824, 717, 671 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.26 (d, 2H, J = 8.8 Hz, ArH), 7.12 (dd, 1H, J = 8.3 and 1.4 Hz, ArH), 7.10 (d, 2H, J = 8.8 Hz, ArH), 7.01 (d, 1H, J = 1.4 Hz, ArH), 6.99 (d, 1H, J = 8.3 Hz, ArH), 3.20 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.80 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.35 (s, 3H, ArCH₃), 1.72 [s, 3H, ArC(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.4 (s, O-C=O), 149.1 (s, ArC), 142.6 (s, ArC), 134.5 (s, ArC), 133.1 (s, ArC), 129.8 (s, ArC), 129.5 (d, ArCH), 128.8 (d, 2C, 2 × ArCH), 127.7 (d, 2C, 2 × ArCH), 126.7 (d, ArCH), 117.2 (d, ArCH), 43.8 (t, CH₂CO), 40.8 [s, ArC(CH₂CO)CH₃], 27.5 [q, ArC- $(CH_2CO)CH_3$, 21.0 (q, ArCH₃) ppm. HR-MS (ESI+) m/zcalculated for $[C_{17}H_{15}CINaO_2]^+ = [M + Na]^+$: 309.0658; found 309.0650.

4-(4-Chlorophenyl)-4,8-dimethylchroman-2-one (9j). GP-1 was carried out on the ester 5h (112.3 mg, 0.5 mmol), orthocresol 6d (81.0 mg, 0.75 mmol), and anhydrous FeCl₃ (243.0 mg, 1.5 mmol) followed by addition of DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_f(5h) = 0.65$, $R_f(9j) = 0.56$ (petroleum etherethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone 9j (85.8 mg, 60%) as a colorless viscous liquid. IR (MIR-ATR, $4000-600 \text{ cm}^{-1}$): $\nu_{\rm max}$ = 2965, 2923, 1770, 1493, 1465, 1195, 1098, 1012, 828, 787, 754 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.26 (dd, 2H, J = 8.8, and 2.4 Hz, ArH), 7.18 (dd, 1H, J = 7.3 and 2.4 Hz, ArH), 7.10 (dd, 2H, J = 8.8 and 2.4 Hz, ArH), 7.06 (dd, 2H, J = 8.8 and 2.4 Hz, ArH), 3.22 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.80 (d, 1H, J = 15.7 Hz, CH_aH_bCO), 2.31 (s, 3H, ArCH₃), 1.70 [s, 3H, ArC-(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.3 (s, O-C=O), 149.4 (s, ArC), 142.7 (s, ArC), 133.0 (s, ArC), 130.5 (d, ArCH), 130.0 (s, ArC), 128.6 (d, 2C, 2 × ArCH), 127.7 (d, 2C, 2 × ArCH), 126.8 (s, ArC), 124.3 (d, ArCH), 123.9 (d, ArCH), 43.5 (t, CH₂CO), 40.9 [s, ArC(CH₂CO)CH₃], 27.7 [q, ArC(CH₂CO)CH₃], 15.9 (q, ArCH₃) ppm. HR-MS (APCI+) m/z calculated for $[C_{17}H_{16}ClO_2]^+ = [M + H]^+: 287.0833;$ found: 287.0824.

4-(4-Chlorophenyl)-4-methyl-3,4-dihydro-2*H***-benzo[***h***]chromen-2-one (9k).** GP-1 was carried out on the ester **5h** (112.3 mg, 0.5 mmol), 1-naphthol **6e** (108.0 mg, 0.75 mmol), and anhydrous FeCl₃ (243.3 mg, 1.5 mmol) followed by addition of DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}({\bf 5h}) = 0.60, R_{\rm f}({\bf 9k}) = 0.50$

(petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum etherethyl acetate 96:2 to 94:6 as the eluent) furnished the lactone 9k (77.8 mg, 56%) as a white solid, and the solid was recrystallized with dichloromethane/hexane, m. p. 152-154 °C. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{\text{max}} = 2958$, 2921, 2851, 1767, 1493, 1463, 1374, 1247, 1191, 1151, 1068, 1012, 816, 751, 699, 660 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 8.28 (dd, 1H, J = 6.8 and 2.4 Hz, ArH), 7.84 (dd, 1H, J = 6.8 and 2.4 Hz, ArH), 7.66 (d, 1H, J = 8.8 Hz, ArH), 7.60-7.52 (m, 2H, ArH), 7.25 (dd, 3H, J = 8.8 and 2.0 Hz, ArH), 7.15 (dd, 2H, J = 8.8 and 2.0 Hz, ArH), 3.29 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.94 (d, 1H, J = 15.6 Hz, CH_a H_b CO), 1.81 [s, 3H, ArC(CH₂CO)C H_3] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.0 (s, O-C=O), 146.2 (s, ArC), 142.8 (s, ArC), 133.7 (s, ArC), 133.2 (s, ArC), 128.9 (d, 2C, 2 × ArCH), 127.8 (d, 2C, 2 × ArCH), 127.5 (d, ArCH), 127.0 (d, ArCH), 126.9 (d, ArCH), 124.5 (s, ArC), 124.5 (d, ArCH), 123.7 (s, ArC), 123.2 (d, ArCH), 121.6 (d, ArCH), 44.2 (t, CH2CO), 41.1 [s, ArC-(CH₂CO)CH₃], 27.4 [q, ArC(CH₂CO)CH₃] ppm. HR-MS (APCI+) m/z calculated for $[C_{20}H_{16}O_2Cl]^+ = [M + H]^+$: 323.0833; found: 323.0822.

1-(4-Chlorophenyl)-1-methyl-1,2-dihydro-3*H*-benzo[*f*]chromen-3-one (91). GP-1 was carried out on the ester 5h (112 mg, 0.5 mmol), β-naphthol 6f (108.1 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5{\rm h}) = 0.60, R_{\rm f}(9{\rm l}) = 0.50$ (petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone 9l (110 mg, 68%) as a colorless viscous liquid. IR (MIR-ATR, 4000-600 cm⁻¹): ν_{max} = 2964, 2925, 1777, 1600, 1513, 1492, 1458, 1336, 1212, 1096, 1012, 913, 814, 748 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.80 (dd, 2H, J = 8.8 and 7.3 Hz, ArH), 7.36-7.30 (m, 2H, ArH), 7.28 (d, 2H, J = 8.3 Hz, ArH), 7.20 (d, 2H, J = 8.3 Hz, ArH), 7.14 (ddd, 1H, J = 8.8, 8.8 and 1.5 Hz, ArH), 7.11 (d, 1H, J = 8.8 Hz, ArH), 3.00 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.84 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 1.93 [s, 3H, $ArC(CH_2CO)CH_3$] ppm. ¹³C NMR $(CDCl_3, 100 \text{ MHz}): \delta = 166.2 \text{ (s, O-C=O)}, 149.8 \text{ (s, ArC)}, 145.5$ (s, ArC), 132.8 (s, ArC), 131.9 (s, ArC), 130.3 (d, ArCH), 130.1 (s, ArC), 129.2 (d, 2C, 2 × ArCH), 129.0 (d, ArCH), 127.4 (d, 2C, 2 × ArCH), 126.0 (d, ArCH), 125.7 (d, ArCH), 124.6 (d, ArCH), 122.0 (s, ArC), 117.8 (d, ArCH), 47.8 (t, CH₂CO), 42.6 [s, ArC(CH₂CO)-CH₃], 24.7 [q, ArC(CH₂CO)CH₃] ppm. HR-MS (ESI+) m/zcalculated for $[C_{20}H_{15}ClNaO_2]^+ = [M + Na]^+$: 345.0658; found 345.0655.

4-Methyl-4-(4-methylphenyl)chroman-2-one (9m). GP-1 was carried out on the ester **5i** (97.0 mg, 0.50 mmol), phenol **6a** (70.5 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_f(5i) = 0.70$, $R_f(9m) = 0.50$ (petroleum ether–ethyl acetate 95 : 5, UV detection)]. Purification of the residue on a silica gel column (petroleum ether–ethyl acetate 100 : 0 to 94 : 6 as the eluent) furnished the lactone **9m** (68.1 mg, 54%) as a liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max} = 2924$, 1761, 1596, 1494, 1418, 1281,

1250, 1201, 1136, 1125, 1052, 915, 813 cm^{-1.} ¹H NMR (CDCl₃, 400 MHz): δ = 7.31 (ddd, 1H, *J* = 7.8, 7.8 and 1.5 Hz, ArH), 7.21 (dd, 1H, *J* = 7.8 and 1.5 Hz, ArH), 7.16 (ddd, 1H, *J* = 7.8, 7.8 and 1.5 Hz, ArH), 7.13–7.07 (m, 3H, ArH), 7.05 (d, 2H, *J* = 8.3 Hz, ArH), 3.26 [d, 1H, *J* = 15.6 Hz, ArC(CH₃)CH_aH_bCO], 2.80 [d, 1H, *J* = 15.6 Hz, ArC(CH₃)CH_aH_bCO], 2.30 (s, 3H, ArCH₃), 1.72 [s, 3H, ArC(CH₃)CH₂CO] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.7 (s, O–C=O), 151.1 (s, ArC), 140.9 (s, ArC), 136.8 (s, ArC), 131.0 (s, ArC), 129.4 (d, 2C, 2 × ArCH), 128.6 (d, ArCH), 126.6 (d, ArCH), 126.0 (d, 2C, 2 × ArCH), 124.7 (d, ArCH), 117.3 (d, ArCH), 43.8 (t, CH₂CO), 40.8 [s, ArC(CH₃)CH₂CO], CH₂CO], 27.5 [q, ArC(CH₃)CH₂CO], 20.8 (q, ArCH₃) ppm. HR-MS (ESI+) *m*/*z* calculated for [C₁₇H₁₇O₂]⁺ = [M]⁺: 253.1223; found 253.1223.

4,7-Dimethyl-4-(4-methylphenyl)chroman-2-one (9n). GP-1 was carried out on the ester 5i (97.0 mg, 0.50 mmol), metacresol 6b (81.0 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5i) = 0.70$, $R_{\rm f}(9n) = 0.50$ (petroleum ether-ethyl acetate 95:5, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 100:0 to 94:6 as the eluent) furnished the lactone 9n (90.4 mg, 68%) as a yellow viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2922, 1766, 1578, 1506, 1449, 1414, 1253, 1200, 1164, 1124, 1048, 815 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.11 (d, 1H, *J* = 7.8 Hz, ArH), 7.10 (d, 2H, J = 8.3 Hz, ArH), 7.05 (d, 2H, J = 8.3 Hz, ArH), 6.98 (d, 1H, J = 7.8 Hz, ArH), 6.91 (s, 1H, ArH), 3.24 [d, 1H, J = 15.6 Hz, $ArC(CH_3)CH_aH_bCO]$, 2.78 [d, 1H, J = 15.6 Hz, $ArC(CH_3)$ -CH_aH_bCO], 2.36 (s, 3H, ArCH₃), 2.30 (s, 3H, ArCH₃), 1.70 [s, 3H, ArC(CH₃)CH₂CO] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.8 (s, O-C=O), 150.9 (s, ArC), 141.1 (s, ArC), 138.8 (s, ArC), 136.6 (s, ArC), 129.3 (d, 2C, 2 × ArCH), 127.8 (s, ArC), 126.2 (d, ArCH), 126.0 (d, 2C, 2 × ArCH), 125.3 (d, ArCH), 117.6 (d, ArCH), 43.9 (t, CH₂CO), 40.4 [s, ArC(CH₃)CH₂CO], 27.5 [q, ArC (CH₃)CH₂CO], 20.9 (q, ArCH₃), 20.8 (q, ArCH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}NaO_2]^+ = [M + Na]^+$: 289.1199; found 289.1197.

4,6-Dimethyl-4-(4-methylphenyl)chroman-2-one (90). GP-1 was carried out on the ester 5i (97.0 mg, 0.5 mmol), paracresol 6c (81.0 mg, 0.75 mmol), anhydrous FeCl3 (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5i) = 0.70$, $R_{\rm f}(90) = 0.48$ (petroleum ether-ethyl acetate 95:5, UV detection)]. Purification of the residue on a silica gel column chromatography (petroleum ether-ethyl acetate 100:0 to 94:6 as the eluent) furnished the lactone 90 (107.7 mg, 81%) as a yellow viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max} =$ 2921, 1763, 1594, 1493, 1416, 1279, 1199, 1134, 1123, 1051, 913, 814 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.15–7.08 (m, 3H, ArH), 7.06 (d, 2H, J = 8.3 Hz, ArH), 7.01 (d, 1H, J = 1.5 Hz, ArH), 6.98 (d, 1H, J = 8.3 Hz, ArH), 3.33 [d, 1H, J = 15.6 Hz, ArC- $(CH_3)CH_aH_bCO]$, 2.78 [d, 1H, J = 15.6 Hz, ArC(CH₃)CH_aH_bCO], 2.33 (s, 3H, ArCH₃), 2.30 (s, 3H, ArCH₃), 1.71 [s, 3H, ArC(CH₃)-CH₂CO] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.9 (s, O-C=O), 149.1 (s, ArC), 141.0 (s, ArC), 136.7 (s, ArC), 134.2 (s,

ArC), 130.6 (s, ArC), 129.3 (d, 2C, 2 × ArCH), 129.1 (d, ArCH), 126.9 (d, ArCH), 126.0 (d, 2C, 2 × ArCH), 117.0 (d, ArCH), 43.9 (t, CH_2CO), 40.7 [s, $ArC(CH_3)CH_2CO$], 27.5 [q, $ArC(CH_3)-CH_2CO$], 20.9 (q, $ArCH_3$), 20.8 (q, $ArCH_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}NaO_2]^+ = [M + Na]^+$: 289.1199; found 289.1199.

4-Ethyl-7-methyl-4-phenylchroman-2-one (9p). GP-1 was carried out on the ester 5j (95.1 mg, 0.5 mmol), meta-cresol 6b (69.8 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5\mathbf{j}) = 0.60, R_{\rm f}(9\mathbf{p}) =$ 0.45 (petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone 9p (107.5 mg, 85%) as a colorless viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{\text{max}} = 2970$, 2924, 1762, 1623, 1577, 1446, 1412, 1208, 1192, 1161, 1150, 1061, 814, 759, 698 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.27 (dd, 2H, J = 7.3 and 7.3 Hz, ArH), 7.22-7.10 (m, 4H, ArH), 6.99 (dd, 1H, J = 7.8 and 1.0 Hz, ArH), 6.88 (d, 1H, J = 1.0 Hz, ArH), 3.25 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.81 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.34 (s, 3H, Ar-CH₃), 2.25-2.00 (m, 2H, CH₂CH₃), 0.88 (t, 3H, J = 7.3 Hz, CH₂CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 168.3 (s, O-C=O), 151.4 (s, ArC), 143.1 (s, ArC), 138.8 (s, ArC), 128.5 (d, 2C, 2 × ArCH), 126.8 (d, ArCH), 126.7 (d, ArCH), 126.6 (d, 2C, 2 × ArCH), 126.0 (s, ArC), 125.0 (d, ArCH), 117.9 (d, ArCH), 44.5 [s, ArC(CH₂CO)Et], 39.8 (t, CH₂CO), 32.1 (t, CH₂CH₃), 20.9 (q, ArCH₃), 8.8 (q, CH₂CH₃), ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}NaO_2]^+ = [M + Na]^+$: 289.1199; found 289.1200.

4-Ethyl-6-methyl-4-phenylchroman-2-one (9q). GP-1 was carried out on the ester 5j (95.1 mg, 0.5 mmol), para-cresol 6c (69.8 mg, 0.75 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5j) = 0.60, R_{\rm f}(9q) =$ 0.45 (petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone 9q (107.5 mg, 85%) as a colorless viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{\text{max}} = 2970$, 2924, 1764, 1598, 1491, 1259, 1197, 1124, 1060, 922, 823, 734, 698 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.29 (dd, 2H, J = 7.8 and 7.3 Hz, ArH), 7.23-7.14 (m, 3H, ArH), 7.12-7.05 (m, 2H, ArH), 6.96 (d, 1H, J = 8.8 Hz, ArH), 3.25 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.81 (d, 1H, J = 15.6 Hz, CH_a H_b CO), 2.36 (s, 3H, Ar-CH₃), 2.21-2.02 (m, 2H, CH_2CH_3), 0.90 (t, 3H, J = 7.3 Hz, CH_2CH_3) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 168.4 (s, O–C=O), 149.5 (s, ArC), 143.0 (s, ArC), 133.9 (s, ArC), 129.0 (d, ArCH), 128.8 (s, ArC), 128.6 (d, 2C, 2 × ArCH), 127.3 (d, ArCH), 126.9 (d, ArCH), 126.7 (d, 2C, 2 × ArCH), 117.2 (d, ArCH), 44.7 [s, $ArC(CH_2CO)$ -Et], 39.7 (t, CH₂CO), 32.1 (t, CH₂CH₃), 21.0 (q, Ar-CH₃), 8.8 (q, (CH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}NaO_2]^{\dagger}$ $= [M + Na]^+$: 289.1199; found 289.1198.

4-Methyl-4,8-diphenylchroman-2-one (11a). GP-1 was carried out on the ester 5g (95.1 mg, 0.5 mmol), 2-phenyl-phenol 6g (127.5 mg, 0.75 mmol), and anhydrous FeCl₃ (243.3 mg, 1.5 mmol) followed by addition of DCE (2 mL). The

resulting reaction mixture was stirred at room temperature for 20 h [TLC control $R_{\rm f}(5g) = 0.60, R_{\rm f}(11a) = 0.50$ (petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone 11a (54.9 mg, 35%) as a colorless viscous liquid. IR (MIR-ATR, 4000-600 cm⁻¹): ν_{max} = 3342, 2922, 2852, 1770, 1680, 1640, 1454, 1426, 1256, 1198, 1120, 1068, 1023, 762, 699, 653 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.52 (dd, 2H, J = 8.3 and 1.5 Hz, ArH), 7.42 (dd, 2H, J = 7.8 and 7.3 Hz, ArH), 7.37 (dd, 2H, J = 6.4 and 2.4 Hz, ArH), 7.32 (dd, 2H, J = 7.8 and 1.5 Hz, ArH), 7.24 (ddd, 5H, J = 7.8, 6.4 and 1.5 Hz, ArH), 3.32 (d, 1H, J = 15.6 Hz, CH_aH_bCO , 2.86 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 1.78 [s, 3H, ArC(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.2 (s, O-C=O), 148.0 (s, ArC), 144.0 (s, ArC), 136.6 (s, ArC), 131.5 (s, ArC), 130.8 (s, ArC), 130.4 (d, ArCH), 129.6 (d, 2C, 2 × ArCH), 128.8 (d, 2C, 2 × ArCH), 128.3 (d, 2C, 2 × ArCH), 127.6 (d, ArCH), 127.2 (d, ArCH), 126.3 (d, 2C, 2 × ArCH), 125.9 (s, ArCH), 124.6 (d, ArCH), 43.5 (t, CH₂CO), 41.4 [s, ArC(CH₂CO)CH₃], 27.8 [q, ArC(CH₂CO)CH₃] ppm. HR-MS (APCI+) m/z calculated for $[C_{22}H_{19}O_2]^+ = [M + H]^+$: 315.1380; found: 315.1372.

4-(4-Chlorophenyl)-4-methyl-8-phenylchroman-2-one (11b). GP-1 was carried out on the ester 5h (112.3 mg, 0.5 mmol), 2-phenylphenol 6g (127.5 mg, 0.75 mmol), and anhydrous FeCl₃ (243.3 mg, 1.5 mmol) followed by addition of DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 6 h [TLC control $R_{\rm f}(5h) = 0.60, R_{\rm f}(11b) = 0.50$ (petroleum ether-ethyl acetate 94:6, UV detection)]. Purification of the residue on a silica gel column (petroleum etherethyl acetate 96:4 to 94:6 as the eluent) furnished the lactone 11b (64.5 mg, 37%) as a white solid, and the solid was recrystallized with dichloromethane/hexane, m. p. 172-174 °C. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{\text{max}} = 3342$, 2922, 2852, 1770, 1680, 1640, 1454, 1426, 1256, 1198, 1120, 1068, 1023, 762, 699, 653 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.50 (ddd, 2H, J = 9.8, 8.8 and 1.5 Hz, ArH), 7.41 (dd, 2H, J = 7.3 and 1.5 Hz, ArH), 7.36 (dd, 2H, J = 6.4 and 2.9 Hz, ArH), 7.31 (dd, 2H, J = 7.8 and 1.5 Hz, ArH), 7.22 (dd, 5H, J = 8.3 and 2.0 Hz, ArH), 3.31 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.85 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 1.77 [s, 3H, ArC(CH_2CO) CH_3] ppm. ¹³C NMR $(CDCl_3, 100 \text{ MHz}): \delta = 167.2 \text{ (s, O-C=O)}, 147.9 \text{ (s, ArC)}, 143.9$ (s, ArC), 136.5 (s, ArC), 131.5 (s, ArC), 130.5 (s, ArC), 130.3 (d, ArCH), 129.6 (d, 2C, 2 × ArCH), 128.7 (d, 2C, 2 × ArCH), 128.2 (d, 2C, 2 × ArCH), 127.5 (d, ArCH), 127.2 (d, ArCH), 126.2 (d, 2C, 2 × ArCH), 125.8 (d, ArCH), 124.5 (d, ArCH), 120.7 (s, ArC), 115.8 (s, ArC), 43.4 (t, CH₂CO), 41.4 [s, ArC(CH₂CO)CH₃], 27.5 $[q, ArC(CH_2CO)CH_3]$ ppm.

Ethyl 3-(6-hydroxy-1,1'-biphenyl-3-yl)-3-phenylbutanoate (12a). GP-1 was carried out on the ester 5g (95.1 mg, 0.5 mmol), 2-phenylphenol 6g (127.6 mg, 0.75 mmol), and anhydrous FeCl₃ (243.3 mg, 1.5 mmol) followed by addition of DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 12 h [TLC control $R_{\rm f}(5g) = 0.60$, $R_{\rm f}(12a) = 0.30$ (petroleum ether–ethyl acetate 92:8, UV detection)]. Purification of the residue on a silica gel column (petroleum ether–

ethyl acetate 96:4 to 94:6 as the eluent) furnished the Michael addition ester 12a (94.0 mg, 52%) as a colorless viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max} = 3412$, 2978, 2926, 1712, 1507, 1490, 1406, 1369, 1322, 1273, 1222, 1157, 1095, 1012, 829, 700 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.50-7.40 (m, 3H, ArH), 7.36 (t, 1H, I = 7.3 Hz, ArH), 7.30-7.13 (m, 6H, ArH), 7.08 (d, 1H, J = 2.4 Hz, ArH), 7.04 (dd, 1H, J = 8.3 and 2.4 Hz, ArH), 6.86 (d, 1H, J = 8.3 Hz, ArH), 5.28 (s, 1H, ArOH), 3.88 (q, 2H, J = 7.3 Hz, OCH₂CH₃), 3.11 (s, 2H, CH_2COOEt), 1.86 [s, 3H, ArC(CH₂CO)CH₃], 0.97 (t, 3H, J = 7.3 Hz, OCH₂CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 171.4 (s, O-C=O), 150.6 (s, ArC), 148.5 (s, ArC), 140.5 (s, ArC), 137.4 (s, ArC), 129.1 (d, 2C, 2 × ArCH), 129.0 (d, 2C, 2 × ArCH), 128.9 (d, ArCH), 128.0 (d, ArCH), 127.9 (d, 2C, 2 × ArCH), 127.7 (d, ArCH), 127.4 (s, ArC), 127.0 (d, 2C, 2 × ArCH), 126.0 (d, ArCH), 115.3 (d, ArCH), 60.0 (t, OCH₂CH₃), 46.8 (t, CH₂COOEt), 45.0 (s, ArCCH₂COOEt), 28.5 [q, ArC(CH₂COOEt)CH₃], 13.9 (q, OCH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{24}H_{24}NaO_3]^+ = [M + Na]^+: 383.1618; \text{ found } 383.1620.$

Ethyl 3-(4-chlorophenyl)-3-(6-hydroxy-1,1'-biphenyl-3-yl)butanoate (12b). GP-1 was carried on the ester 5h (112 mg, 0.5 mmol), 2-phenyl phenol 6g (127.6 mg, 0.75 mmol), and anhydrous FeCl₃ (243.3 mg, 1.5 mmol) followed by addition of DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 12 h [TLC control $R_f(5h) = 0.60$, $R_f(12b) = 0.30$ (petroleum ether-ethyl acetate 92:8, UV detection)]. Purification of the residue on a silica gel column (petroleum etherethyl acetate 96:4 to 94:6 as the eluent) furnished the Michael addition ester 12b (80.0 mg, 54%) as a colorless viscous liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max} = 3429$, 2978, 2922, 1712, 1507, 1490, 1464, 1406, 1369, 1273, 1222, 1157, 1095, 1012, 829, 700 cm $^{-1}$. ¹H NMR (CDCl₃, 400 MHz): δ = 7.52-7.30 (m, 5H, ArH), 7.22 (d, 2H, J = 8.8 Hz, ArH), 7.15 (d, 2H, J = 8.8 Hz, ArH), 7.03 (d, 1H, J = 2.4 Hz, ArH), 7.00 (dd, 1H, J = 8.8 and 2.4 Hz, ArH), 6.84 (d, 1H, J = 8.8 Hz, ArH), 5.38 (br. s, 1H, ArOH), 3.88 (q, 2H, J = 7.3 Hz, OCH₂CH₃), 3.07 (s, 2H, CH_2COOEt), 1.83 [s, 3H, ArC(CH_2COOEt) CH_3], 0.98 (t, 3H, J = 7.3 Hz, OCH₂CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 171.2 (s, O-C=O), 150.8 (s, ArC), 146.9 (s, ArC), 140.1 (s, ArC), 137.2 (s, ArC), 131.8 (s, ArC), 129.1 (d, 2C, 2 × ArCH), 129.0 (d, 2C, 2 × ArCH), 128.8 (d, ArCH), 128.5 (d, 2C, 2 × ArCH), 128.1 (d, 2C, 2 × ArCH), 127.8 (d, 2C, ArCH), 127.6 (s, ArC), 115.5 (d, ArCH), 60.2 (t, OCH₂CH₃), 46.6 (t, CH₂COOEt), 44.7 [s, ArC- $(CH_2COOEt)CH_3$], 28.5 [q, ArC $(CH_2COOEt)CH_3$], 13.9 (q, OCH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{24}H_{23}ClNaO_3]^+ = [M + Na]^+: 417.1228; found 417.1229.$

3',4'-Dihydro-2'H-spiro[chromene-4,1'-naphthalen]-2(3H)-one (13a). GP-2 was carried out on the ester 5m (108.0 mg, 0.50 mmol), phenol 6a (235.0 mg, 2.5 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and benzene (2 mL). The resulting reaction mixture was stirred at room temperature for 2 h [TLC control $R_{\rm f}(5{\rm m}) = 0.73$, $R_{\rm f}(13{\rm a}) = 0.56$ (petroleum ether-ethyl acetate 95:05, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 97:3 to 95:5 as the eluent) furnished the spiro-lactone 13a (52.8 mg, 40%) as a liquid. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max} = 2923$, 2852,

1774, 1484, 1449, 1252, 1197, 1068, 920 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.30–7.12 (m, 4H, ArH), 7.10 (dd, 1H, J = 8.3 and 1.0 Hz, ArH), 7.05 (d, 1H, J = 7.8 Hz, ArH), 6.98 (ddd, 1H, J = 7.8, 7.3 and 1.5 Hz, ArH), 6.64 (dd, 1H, J = 7.8 and 1.5 Hz, ArH), 3.20 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.95 (d, 1H, J = 15.6 Hz, CH_aH_bCO , 2.88 (dd, 2H, J = 7.8 and 5.4 Hz, ArCH₂CH₂CH₂), 1.95 (dd, 2H, J = 5.9 and 5.4 Hz, ArCH₂CH₂CH₂), 1.87–1.65 (m, 2H, ArCH₂CH₂CH₂) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.8 (s, O-C=O), 150.8 (s, ArC), 138.4 (s, ArC), 137.9 (s, ArC), 132.4 (s, ArC), 129.6 (d, ArCH), 128.6 (d, ArCH), 128.3 (d, ArCH), 128.1 (d, ArCH), 127.1 (d, ArCH), 126.5 (d, ArCH), 124.3 (d, ArCH), 117.0 (d, ArCH), 43.4 (t, CH₂CO), 41.2 (s, ArCCH₂CO), 36.0 (t, CH₂), 30.0 (t, CH₂), 18.6 (t, CH₂) ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{17}O_2]^{\dagger}$ $= [M + H]^+$: 265.1223; found 265.1216.

7-Methyl-3',4'-dihydro-2'H-spiro[chromene-4,1'-naphthalen]-2(3H)-one (13b). GP-2 was carried out on the ester 5m (108.0 mg, 0.50 mmol), meta-cresol 6b (270.0 mg, 2.5 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and benzene (2 mL). The resulting reaction mixture was stirred at room temperature for 2 h [TLC control $R_{\rm f}(5{\rm m}) = 0.75$, $R_{\rm f}(13{\rm b}) = 0.55$ (petroleum ether-ethyl acetate 95:5, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 97:3 to 95:5 as the eluent) furnished the lactone 13b (86.2 mg, 62%) as a liquid. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2920, 2851, 1769, 1578, 1490, 1448, 1163, 1065, 759 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.25–7.09 (m, 3H, ArH), 7.05 (d, 1H, J = 7.8 Hz, ArH), 6.91 (d, 1H, J = 1.0 Hz, ArH), 6.80 (dd, 1H, J = 7.8 and 1.0 Hz, ArH), 6.52 (d, 1H, J = 7.8 Hz, ArH), 3.17 (d, 1H, J = 15.6 Hz, $CH_{a}H_{b}CO$, 2.93 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.87 (dd, 2H, J = 7.8 and 5.4 Hz, $ArCH_2CH_2CH_2$), 2.32 (s, 3H, ArCH₃), 1.92 (dd, 2H, J = 6.4 and 5.4 Hz, ArCH₂CH₂CH₂), 1.85–1.65 (m, 2H, ArCH₂CH₂CH₂) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 168.0 (s, O-C=O), 150.7 (s, ArC), 138.5 (s, ArC), 138.4 (s, ArC), 138.1 (s, ArC), 129.5 (d, ArCH), 129.3 (s, ArC), 128.3 (d, ArCH), 128.1 (d, ArCH), 127.0 (d, ArCH), 126.4 (d, ArCH), 125.0 (d, ArCH), 117.4 (d, ArCH), 43.5 (t, CH₂CO), 40.9 (s, ArCCH₂CO), 36.1 (t, CH₂), 30.0 (t, CH₂), 20.9 (q, ArCH₃), 18.6 (t, CH₂) ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{19}O_2]^+ = [M + H]^+$: 279.1380; found 279.1371.

6-Methyl-3',4'-dihydro-2'H-spiro[chromene-4,1'-naphthalen]-2(3H)-one (13c). GP-2 was carried out on the ester 5m (108.0 mg, 0.50 mmol), para-cresol 6c (270.0 mg, 2.5 mmol), anhydrous FeCl₃ (243.0 mg, 1.5 mmol) and benzene (2 mL). The resulting reaction mixture was stirred at room temperature for 2 h [TLC control $R_{\rm f}(5e) = 0.73$, $R_{\rm f}(7j) = 0.58$ (petroleum ether-ethyl acetate 95:5, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 97:3 to 95:5 as the eluent) furnished the lactone 13c (61.2 mg, 44%) as a liquid. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2921, 2851, 1766, 1578, 1446, 1202, 1162, 962, 729 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.25–7.10 (m, 3H, ArH), 7.05 (d, 1H, J = 7.3 Hz, ArH), 7.03 (dd, 1H, J = 8.3 and 1.5 Hz, ArH), 6.98 (d, 1H, *J* = 8.3 Hz, ArH), 6.43 (d, 1H, *J* = 1.5 Hz, ArH), 3.15 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.92 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.91–2.80 (m, 2H, ArCH₂CH₂CH₂), 2.18 (s, 3H,

ArCH₃), 1.93 (dd, 2H, J = 5.9 and 5.4 Hz, ArCH₂CH₂CH₂CH₂), 1.87–1.65 (m, 2H, ArCH₂CH₂CH₂) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 167.9$ (s, O–C=O), 148.9 (s, ArC), 138.4 (s, ArC), 138.1 (s, ArC), 133.9 (s, ArC), 132.1 (s, ArC), 129.6 (d, ArCH), 128.8 (d, ArCH), 128.7 (d, ArCH), 128.2 (d, ArCH), 127.0 (d, ArCH), 126.5 (d, ArCH), 116.8 (d, ArCH), 43.6 (t, CH₂CO), 41.3 (s, ArCCH₂CO), 36.1 (t, CH₂), 30.0 (t, CH₂), 20.8 (q, ArCH₃), 18.7 (t, CH₂) ppm. HR-MS (ESI+) *m*/*z* calculated for $[C_{19}H_{19}O_2]^+$ = $[M + H]^+$: 279.1380; found 279.1369.

8-Methyl-3',4'-dihydro-2'H-spiro[chromene-4,1'-naphthalen]-2(3H)-one (13d). GP-2 was carried out on the ester 5m (108.0 mg, 0.50 mmol), ortho-cresol 6d (270.0 mg, 2.5 mmol), anhydrous FeCl₃ (243 mg, 1.5 mmol) and benzene (2 mL). The resulting reaction mixture was stirred at room temperature for 2 h [TLC control $R_{\rm f}(5e) = 0.73$, $R_{\rm f}(7i) = 0.58$ (petroleum etherethyl acetate 95:5, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 97:3 to 95:5 as the eluent) furnished the lactone 13d (54.2 mg, 39%) as a liquid. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2921, 2851, 1773, 1462, 1243, 1192, 1085, 920 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.25–7.12 (m, 3H, ArH), 7.08 (d, 1H, J = 7.3 Hz, ArH), 7.05 (d, 1H, J = 7.8 Hz, ArH), 6.87 (dd, 1H, J = 7.8 and 7.3 Hz, ArH), 6.45 (d, 1H, J = 7.8 Hz, ArH), 3.20 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.92 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.87 (dd, 2H, J = 7.3 and 5.9 Hz, ArCH₂CH₂CH₂), 2.35 (s, 3H, ArCH₃), 2.05-1.90 (m, 2H, ArCH₂CH₂CH₂), 1.85-1.65 (m, 2H, ArCH₂CH₂CH₂) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 167.9 (s, O-C=O), 149.1 (s, ArC), 138.4 (s, ArC), 138.2 (s, ArC), 132.2 (s, ArC), 129.8 (d, ArCH), 129.6 (d, ArCH), 128.1 (d, ArCH), 127.0 (d, ArCH), 126.4 (d, ArCH), 126.2 (1s and 1d, 2C, ArC and ArCH), 123.6 (d, ArCH), 43.3 (t, CH₂CO), 41.2 (s, ArCCH₂CO), 35.8 (t, CH₂), 30.0 (t, CH₂), 18.6 (t, CH₂), 15.9 (q, ArCH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{19}O_2]^+ = [M + H]^+$: 279.1380; found 279.1362.

3',4',7,10-Tetrahydro-2'H-spiro[benzo[f]chromene-1,1'-naphthalen]-3(2H)-one (13e). GP-2 was carried out on the ester 5m (108.0 mg, 0.50 mmol), phenol 6f (360.0 mg, 2.5 mmol), anhydrous FeCl₃ (243.3 mg, 1.5 mmol) and benzene (2 mL). The resulting reaction mixture was stirred at room temperature for 2 h [TLC control $R_{\rm f}(5{\rm m}) = 0.73$, $R_{\rm f}(13{\rm e}) = 0.55$ (petroleum ether-ethyl acetate 95:5, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 97:3 to 95:5 as the eluent) furnished the lactone 13e (80.7 mg, 51%) as a liquid. IR (MIR-ATR, 4000–600 cm $^{-1}$): $\nu_{\rm max}$ = 2917, 2849, 1773, 1600, 1461, 1210, 1174, 1025, 812 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): *δ* = 7.79 (d, 1H, *J* = 9.3 Hz, ArH), 7.78 (d, 1H, J = 8.3 Hz, ArH), 7.28 (ddd, 1H, J = 8.3, 7.8 and 1.5 Hz, ArH), 7.27 (d, 1H, J = 9.3 Hz, ArH), 7.22 (d, 1H, J = 7.8 Hz, ArH), 7.15 (ddd, 1H, J = 7.8, 7.8 and 1.5 Hz, ArH), 7.08 (ddd, 1H, J = 8.8, 8.3 and 1.5 Hz, ArH), 7.05 (d, 1H, J = 8.8 Hz, ArH), 6.95 (dd, 1H, J = 8.3 and 7.8 Hz, ArH), 6.77 (d, 1H, J = 7.8 Hz, ArH), 3.31 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 3.13–2.92 (m, 2H, $ArCH_2CH_2CH_2$, 2.98 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.35–2.20 (m, 1H, CH_aH_b), 2.16–1.90 (m, 3H, CH_aH_b and CH_2) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 166.7 (s, O-C=O), 150.1 (s, ArC), 141.8 (s, ArC), 136.0 (s, ArC), 132.1 (s, ArC), 130.1 (d, ArCH),

130.0 (s, ArC), 129.5 (d, ArCH), 128.9 (d, ArCH), 128.3 (d, ArCH), 126.9 (d, ArCH), 126.7 (d, ArCH), 125.8 (d, ArCH), 125.6 (d, ArCH), 124.3 (d, ArCH), 123.5 (s, ArC), 117.7 (d, ArCH), 44.5 (t, CH₂CO), 42.4 (s, ArCCH₂CO), 33.4 (t, CH₂), 29.8 (t, CH₂), 18.8 (t, CH₂) ppm. HR-MS (ESI+) *m/z* calculated for $[C_{22}H_{19}O_2]^+ = [M + H]^+$: 315.1380; found 315.1369.

7,7'-Dimethyl-3',4'-dihydro-2'H-spiro[chromene-4,1'-naphthalen]-2(3H)-one (13f). GP-2 was carried out on the ester 5n (115.0 mg, 0.50 mmol), meta-cresol 6b (270.0 mg, 2.5 mmol), anhydrous FeCl₃ (243.0 mg, 1.5 mmol) and benzene (2 mL). The resulting reaction mixture was stirred at room temperature for 2 h [TLC control $R_f(5n) = 0.73$, $R_f(13f) = 0.55$ (petroleum ether-ethyl acetate 95:5, UV detection)]. Purification of the residue on a silica gel column (petroleum ether-ethyl acetate 97:3 to 95:5 as the eluent) furnished the lactone 13f (62.8 mg, 43%) as a liquid. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2924, 2853, 1773, 1621, 1503, 1452, 1416, 1212, 1167, 963, 814 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.07 (d, 1H, J = 7.8 Hz, ArH), 7.01 (dd, 1H, J = 7.8 and 1.0 Hz, ArH), 6.91 (d, 1H, J = 1.0 Hz, ArH), 6.85 (s, 1H, ArH), 6.80 (d, 1H, J = 7.8 Hz, ArH), 6.52 (d, 1H, J = 7.8 Hz, ArH), 3.18 (d, 1H, J = 15.6 Hz, $CH_{a}H_{b}CO$, 2.91 (d, 1H, J = 15.6 Hz, $CH_{a}H_{b}CO$), 2.82 (dd, 2H, J = 5.9 and 5.4 Hz, ArCH₂CH₂CH₂), 2.32 (s, 3H, ArCH₃), 2.23 (s, 3H, ArCH₃), 1.89 (dd, 2H, J = 6.3 and 5.4 Hz, ArCH₂CH₂CH₂CH₂), 1.84–1.62 (m, 2H, ArCH₂CH₂CH₂) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 168.1 (s, O-C=O), 150.7 (s, ArC), 138.5 (s, ArC), 137.8 (s, ArC), 135.9 (s, ArC), 135.3 (s, ArC), 129.5 (s, ArC), 129.4 (d, ArCH), 128.4 (d, ArCH), 128.3 (d, ArCH), 128.0 (d, ArCH), 125.0 (d, ArCH), 117.3 (d, ArCH), 43.5 (t, CH₂CO), 40.9 (s, ArCCH₂CO), 36.2 (t, CH₂), 29.6 (t, CH₂), 21.1 (q, ArCH₃), 20.9 (q, ArCH₃), 18.7 (t, CH₂) ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{21}O_2]^+ = [M + H]^+$: 293.1536; found 293.1525.

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