Organic & Biomolecular Chemistry

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2014, **12**, 4347

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

Pedireddi Niharika, Bokka Venkat Ramulu and Gedu Satyanarayana*

Received 4th March 2014,
Accepted 24th April 2014

DOI: 10.1039/c4ob00490f

www.rsc.org/obc

Lewis acid ($FeCl_3$) 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.

Introduction

Coumarins are widely prevalent in nature, and show a broad range of biological activities[1] such as anti-inflammatory, anti-aging, 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 antagonist[7] 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 **3** [11] and **4** [11] (Fig. 1), obtained from *Aloe vera*[2,12] and *Gnetum cleistostachyum*,[1,13] respectively, show anti-inflammatory and anti-oxidant activities.[14] They are also notably known for their ability to protect low-density lipoproteins from oxidative attack[15] and recent studies have also revealed their ability to control the chronic heart and colon-rectal cancer.

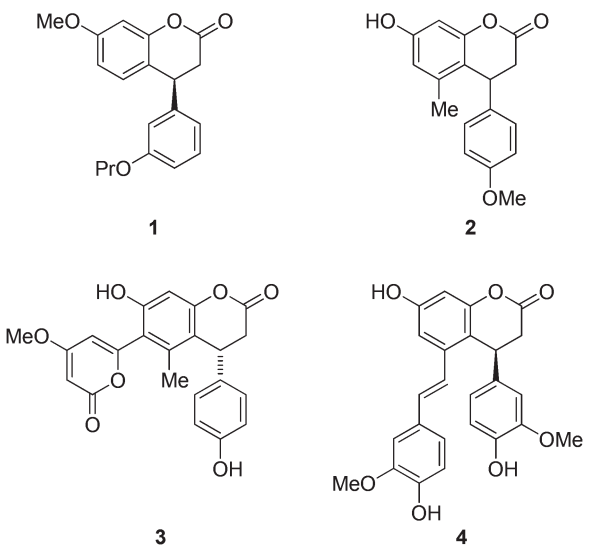


Fig. 1 Examples of unnatural and natural dihydrocoumarins of biological relevance.

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]

Department of Chemistry, Indian Institute of Technology (IIT) Hyderabad, Ordnance Factory Estate Campus, Yeddumailaram – 502 205, Medak District, Andhra Pradesh, India. E-mail: gvsatya@iith.ac.in; Fax: +91 (40) 2301 6032

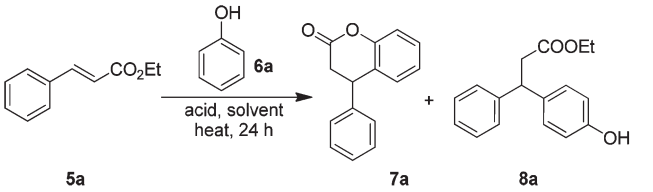
†Electronic supplementary information (ESI) available: ^{1}H-NMR data of the known compounds and the copies of ^{1}H and ^{13}C-NMR spectra are provided. See DOI: 10.1039/c4ob00490f

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 ($FeCl_3$) 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 ($FeCl_3$), 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 self-aromatization 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 ($FeCl_3$) 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 *para*-attack 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 $FeCl_3$ 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 temperature 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).

Table 1 Screening conditions for synthesis of dihydrocoumarin **7a** under Lewis acidic conditions



5a **7a** **8a**

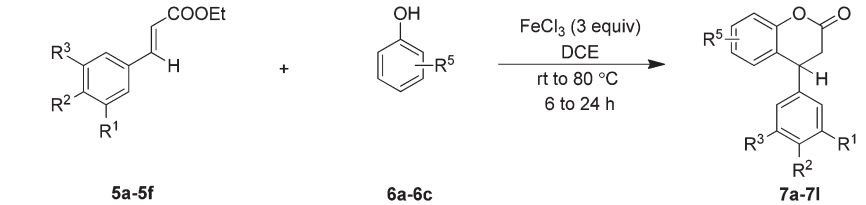
Entry[a]	Lewis acid	Solvent (mL)	Temp (°C)	Yield[b] (%) 7a	8a
1[c]	$FeCl_3$ (10 mol%)	DCE (2)	80	0	0
2	$FeCl_3$ (20 mol%)	DCE (2)	80	0	10
3	$FeCl_3$ (60 mol%)	DCE (2)	80	0	30
4	**$FeCl_3$ (3 equiv.)**	**DCE (2)**	**80**	**60**	**20**
5	$FeCl_3$ (5 equiv.)	DCE (2)	80	55	0
6	$FeCl_3$ (3 equiv.)	DCM (2)	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.

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,

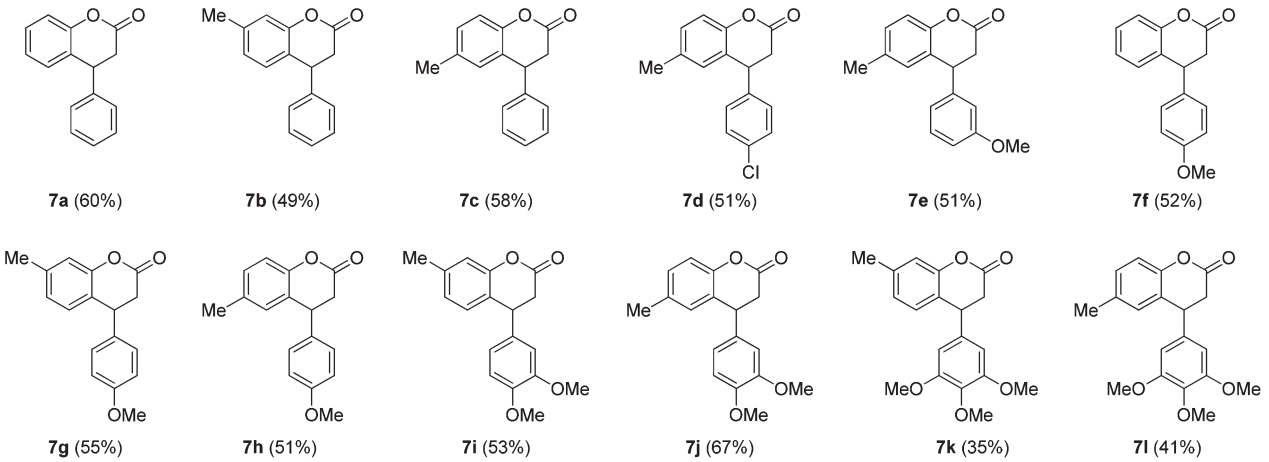
Table 2 Lewis acid ($FeCl_3$) mediated synthesis of dihydrocoumarins **7a–7l** starting from cinnamates **5a–5f**[a,b,c,d]



5a-5f
5a; R^1 = H, R^2 = H, R^3 = H
5b; R^1 = H, R^2 = Cl, R^3 = H
5c; R^1 = H, R^2 = H, R^3 = OMe
5d; R^1 = H, R^2 = OMe, R^3 = H
5e; R^1 = H, R^2 = OMe, R^3 = OMe
5f; R^1 = OMe, R^2 = OMe, R^3 = OMe

6a-6c
6a; R^5 = H
6b; R^5 = 3-Me
6c; R^5 = 4-Me

7a-7l



[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).

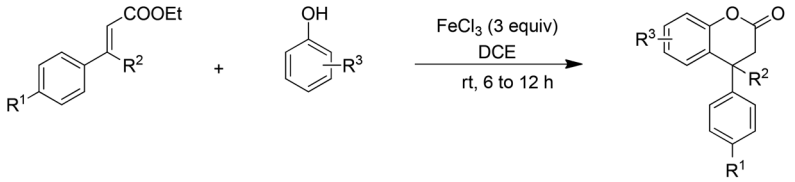
However, when attempting to apply the present method on β-methyl ethyl cinnamates **5k–5l**, it did not furnish the expected dihydrocoumarins, rather gave coumarins **10a–10c** (Table 4).

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 rearrangement/cleavage of either **X** or **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

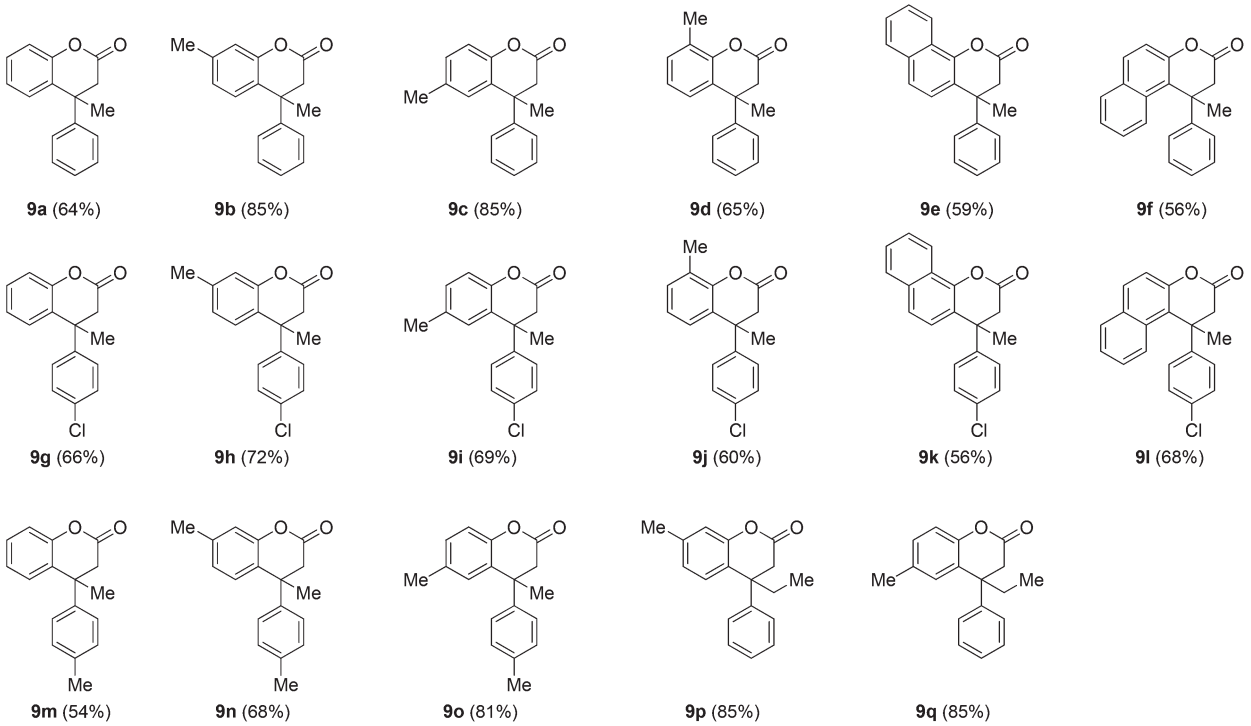
Table 3 Lewis acid ($FeCl_3$) mediated synthesis of dihydrocoumarins **9** starting from cinnamates **5**



5g-5j **6a-6f** **9a-9q**

5g; R^1 = H, R^2 = Me
5h; R^1 = Cl, R^2 = Me
5i; R^1 = Me, R^2 = Me
5j; R^1 = H, R^2 = Et

6a; R^3 = H
6b; R^3 = 3-Me
6c; R^3 = 4-Me
6d; R^3 = 2-Me
6e; 1-naphthol
6f; 2-naphthol



9a (64%) **9b** (85%) **9c** (85%) **9d** (65%) **9e** (59%) **9f** (56%)

9g (66%) **9h** (72%) **9i** (69%) **9j** (60%) **9k** (56%) **9l** (68%)

9m (54%) **9n** (68%) **9o** (81%) **9p** (85%) **9q** (85%)

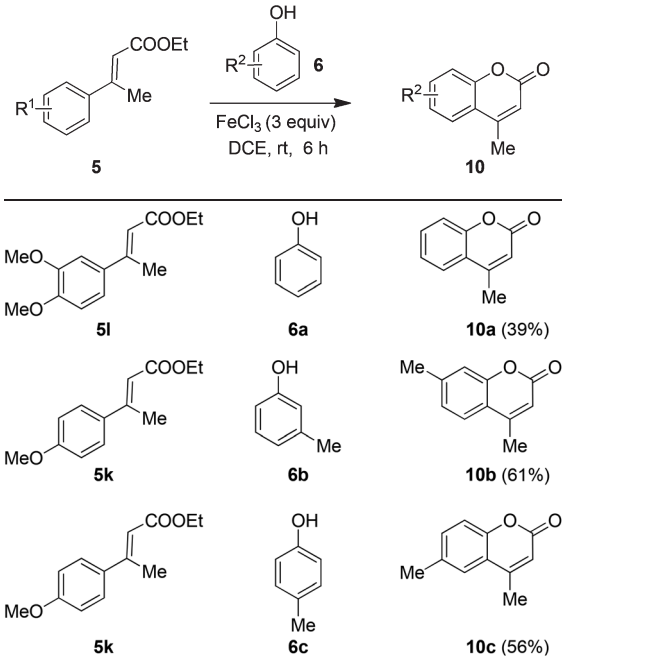
sufficient enough to compete with usual self-aromatization. Therefore, performing the reaction with 5 equiv. of the phenol **6a** led to the formation of the novel tetracyclic lactone **13a**, in 33% yield along with the aromatized product **14** (Table 5, entry 3). On the other hand, interestingly, 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 noteworthy 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.

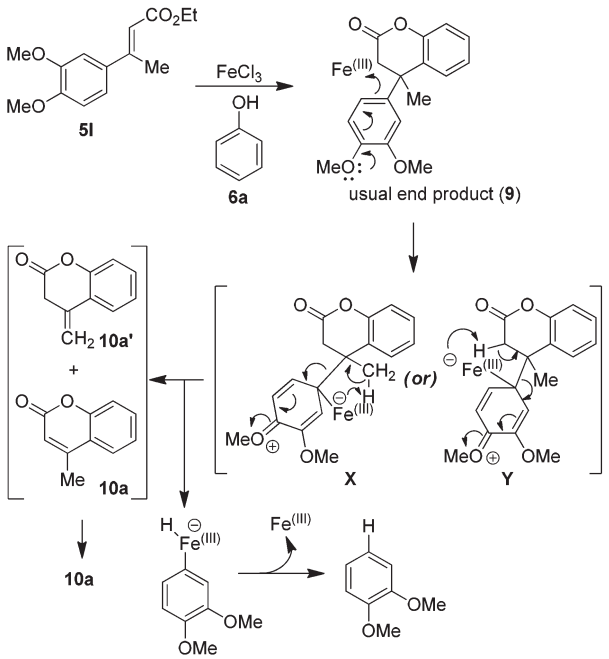
Among the screened conditions, conditions with either 5 or 10 equiv. of phenol **6a** in benzene (Table 5, entries 5 and 6) were found to be the best with respect to the formation of **13a**. Therefore, these conditions were used to generate different tetracyclic lactones **13**. Gratifyingly, the method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

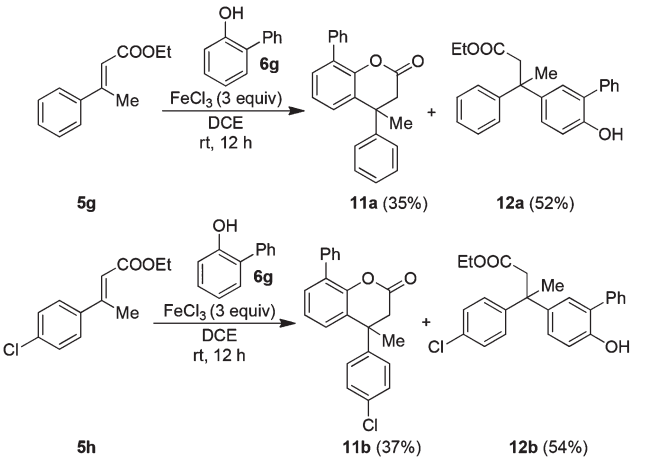
Table 4 Lewis acid ($FeCl_3$) mediated synthesis of coumarins **10** starting from cinnamates **5**





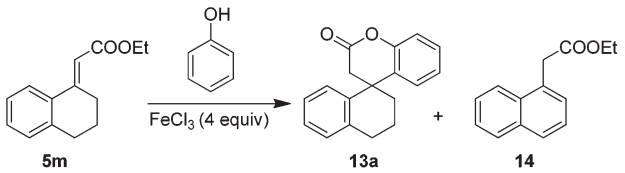
Scheme 1 Plausible mechanism for the formation of **10**.

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.



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

Table 5 Screening conditions for synthesis of spiro-dihydrocoumarins **13a** under Lewis acidic conditions



Entry[a]	$FeCl_3$ (equiv.)	Phenol (equiv.)	Solvent (mL)	Temp (°C)	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

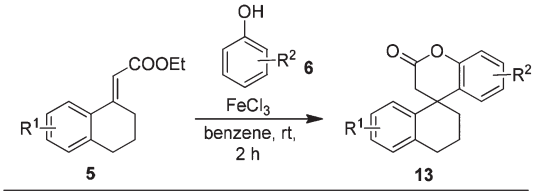
[a] All reactions were carried out on a 0.5 mmol scale of **5m**. [b] Isolated yields of chromatographically pure products.

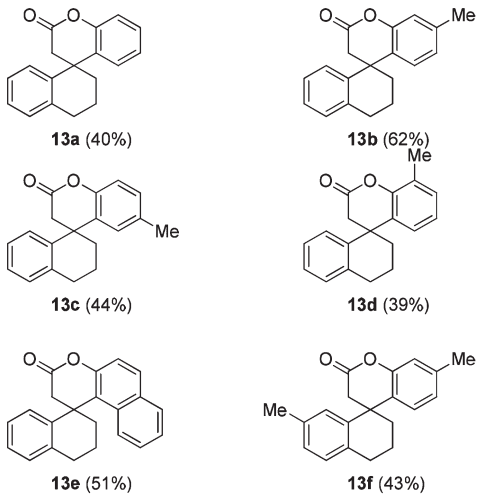
Experimental section

General

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (J in Hz) are reported in a standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ in ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH_2 and CH_3) 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 CH_2)

Table 6 Synthesis of spiro-dihydrocoumarins **13** from cinnamates **5**[a,b]





[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 ^{1}H-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 ^{1}H, ^{13}C 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 $FeCl_3$ 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 $FeCl_3$ (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 $NaHCO_3$ and extracted in ethyl acetate (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) 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 $FeCl_3$ (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 $NaHCO_3$ and extracted in ethyl acetate (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) 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 $FeCl_3$ (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_f(**5c**) = 0.83, R_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}. ^{1}H NMR ($CDCl_3$, 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, Ar*C*H$_2$CO), 3.77 (s, 3H, ArOCH$_3$), 3.03 (dd, 1H, J = 16.1 and 6.4 Hz, ArCHC*H*$_a$H$_b$CO), 2.98 (dd, 1H, J = 16.1 and 7.8 Hz, ArCHCH$_a$*H*$_b$CO), 2.25 (s, 3H, ArCH$_3$) ppm. ^{13}C NMR ($CDCl_3$, 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, ArOCH$_3$), 40.7 (d, Ar*C*HCH$_2$CO), 37.0 (t, *C*H$_2$CO), 20.7 (q, ArCH$_3$) 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 $FeCl_3$ (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_f(**5e**) = 0.75,

R_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}): ν_{max} = 2922, 2852, 1762, 1591, 1516, 1463, 1419, 1253, 1219, 1142, 1025, 817 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.93 (s, 1H, ArH), 6.89 (d, 1H, J = 8.3 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, ArC*H*CH_2CO), 3.85 (s, 3H, $ArOCH_3$), 3.81 (s, 3H, $ArOCH_3$), 3.03 (dd, 1H, J = 16.1 and 6.4 Hz, ArCHC*H*$_a$H$_b$CO), 2.96 (dd, 1H, J = 16.1 and 7.8 Hz, ArCHCH_a*H*$_b$CO), 2.34 (s, 3H, $ArCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.0 (s, O–C=O), 151.5 (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 × $ArOCH_3$), 40.0 (d, Ar*C*HCH_2CO), 37.3 (t, *C*H_2CO), 21.0 (q, $ArCH_3$) 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), *para*-cresol **6c** (81.0 mg, 0.75 mmol), anhydrous $FeCl_3$ (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_f(**5e**) = 0.75, R_f(**7j**) = 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}): ν_{max} = 2924, 2852, 1762, 1592, 1493, 1420, 1243, 1137, 1025, 813 cm^{-1}. ^1H NMR ($CDCl_3$, 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, ArC*H*CH_2CO), 3.85 (s, 3H, $ArOCH_3$), 3.82 (s, 3H, $ArOCH_3$), 3.03 (dd, 1H, J = 16.1 and 6.4 Hz, ArCHC*H*$_a$H$_b$CO), 2.96 (dd, 1H, J = 16.1 and 7.8 Hz, ArCHCH_a*H*$_b$CO), 2.25 (s, 3H, $ArCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 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 × $ArOCH_3$), 40.4 (d, Ar*C*HCH_2CO), 37.3 (t, *C*H_2CO), 20.7 (q, $ArCH_3$) 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 $FeCl_3$ (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_f(**5f**) = 0.80, R_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}): ν_{max} = 2923, 2852, 1767, 1508, 1461, 1235, 1126, 1008, 818 cm^{-1}. ^1H NMR ($CDCl_3$, 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, ArC*H*CH_2CO), 3.82 (s, 3H, $ArOCH_3$), 3.79 (s, 6H, 2 × $ArOCH_3$), 3.03 (dd, 1H, J = 16.1 and 6.4 Hz, ArCHC*H*$_a$H$_b$CO), 2.98 (dd, 1H, J = 16.1 and 7.8 Hz, ArCHCH$_a$*H*$_b$CO), 2.35 (s, 3H, $ArCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 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, $ArOCH_3$), 56.1 (q, 2C, 2 × $ArOCH_3$), 40.7 (d, Ar*C*HCH_2CO), 37.2 (t, *C*H_2CO), 21.1 (q, $ArCH_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{20}NaO_5]^+$ = $[M + Na]^+$: 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), *para*-cresol **6c** (81.0 mg, 0.75 mmol), anhydrous $FeCl_3$ (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_f(**5f**) = 0.80, R_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}): ν_{max} = 2921, 2850, 1764, 1591, 1460, 1243, 1124, 1006, 815 cm^{-1}. ^1H NMR ($CDCl_3$, 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, ArC*H*CH_2CO), 3.83 (s, 3H, $ArOCH_3$), 3.79 (s, 6H, 2 × $ArOCH_3$), 3.04 (dd, 1H, J = 16.1 and 6.3 Hz, ArCHC*H*$_a$H$_b$CO), 2.96 (dd, 1H, J = 16.1 and 7.8 Hz, ArCHCH$_a$*H*$_b$CO), 2.27 (s, 3H, $ArCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 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, $ArOCH_3$), 56.1 (q, 2C, 2 × $ArOCH_3$), 41.1 (d, Ar*C*HCH_2CO), 37.2 (t, *C*H_2CO), 20.7 (q, $ArCH_3$) 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 $FeCl_3$ (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_f(**5g**) = 0.60, R_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}): ν_{max} = 2922, 1774, 1586, 1487, 1448, 1283, 1202, 1135, 1051, 910, 758, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 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$_b$CO), 2.84 (d, 1H, J = 15.6 Hz, CH$_a$$H_b$CO), 1.76 [s, 3H, ArC($CH_2CO$)-C$H_3$] ppm. ^{13}C NMR ($CDCl_3$, 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, *C*H_2CO), 41.1

[s, Ar*C*(CH_2CO)CH_3], 27.5 [q, ArC(CH_2CO)*C*H_3] 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 $FeCl_3$ (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_f(**5g**) = 0.60, R_f(**9b**) = 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 ($CDCl_3$, 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, C$H_a$$H_b$CO), 2.80 (d, 1H, *J* = 15.6 Hz, CH_aH_bCO), 2.36 (s, 3H, $ArCH_3$), 1.72 [s, 3H, ArC(CH_2CO)CH_3] ppm. ^{13}C NMR ($CDCl_3$, 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, *C*H_2CO), 40.8 [s, Ar*C*(CH_2CO)CH_3], 27.6 [q, ArC(CH_2CO)*C*H_3], 21.0 (q, $ArCH_3$) 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 $FeCl_3$ (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_f(**5g**) = 0.60, R_f(**9c**) = 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}): ν_{max} = 2974, 2921, 1763, 1598, 1493, 1266, 1202, 1124, 1049, 913, 824, 732, 698 cm^{-1}. ^1H NMR ($CDCl_3$, 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, C$H_a$$H_b$CO), 2.80 (d, 1H, *J* = 15.6 Hz, CH_aH_bCO), 2.34 (s, 3H, $ArCH_3$), 1.73 [s, 3H, ArC(CH_2CO)CH_3] ppm. ^{13}C NMR ($CDCl_3$, 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, *C*H_2CO), 41.0 [s, Ar*C*(CH_2CO)CH_3], 27.5 [q, ArC(CH_2CO)-*C*H_3], 20.9 (q, $ArCH_3$) 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_f(**5g**) = 0.65, R_f(**9d**) = 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 ($CDCl_3$, 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, C$H_a$$H_b$CO), 2.81 (d, 1H, *J* = 15.6 Hz, CH_aH_bCO), 2.32 (s, 3H, $ArCH_3$), 1.73 [s, 3H, ArC-(CH_2CO)CH_3] ppm. ^{13}C NMR ($CDCl_3$, 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, *C*H_2CO), 41.1 [s, Ar*C*(CH_2CO)CH_3], 27.7 [q, ArC(CH_2CO)*C*H_3], 15.9 (q, $ArCH_3$) 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-2*H*-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 $FeCl_3$ (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_f(**5g**) = 0.60, R_f(**9e**) = 0.50 (petroleum ether–ethyl 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 ($CDCl_3$, 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, C$H_a$$H_b$CO), 2.93 (d, 1H, *J* = 15.6 Hz, CH_aH_bCO), 1.82 [s, 3H, ArC(CH_2CO)CH_3] ppm. ^{13}C NMR ($CDCl_3$, 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, *C*H_2CO), 41.4 [s, Ar*C*(CH_2CO)CH_3], 27.4 [q, ArC(CH_2CO)*C*H_3] 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 $FeCl_3$ (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}): ν_{max} = 2920, 2851, 1775, 1599, 1512, 1494, 1459, 1336, 1210, 1163, 1019, 982, 912, 814, 733, 701 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ =

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$_b$CO), 2.86 (d, 1H, J = 15.6 Hz, CH$_a$$H_b$CO), 1.94 [s, 3H, ArC(CH$_2$CO)C$H_3$] ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 166.5 (s, O–C=O), 149.9 (s, ArC), 147.0 (s, ArC), 131.9 (s, ArC), 130.4 (s, ArC), 130.1 (s, ArC), 129.0 (d, 2C, 2 × ArCH), 128.8 (d, ArCH), 127.0 (d, ArCH), 126.0 (d, 2C, 2 × ArCH), 125.9 (d, ArCH), 125.8 (d, ArCH), 124.4 (d, ArCH), 122.8 (s, ArC), 117.8 (d, ArCH), 48.0 (t, CH$_2$CO), 42.9 [s, ArC(CH$_2$CO)CH$_3$], 24.7 [q, ArC(CH$_2$CO)CH$_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 FeCl$_3$ (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(**5h**) = 0.60, R_f(**9g**) = 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}): ν_{max} = 2973, 2925, 1763, 1586, 1487, 1449, 1279, 1232, 1198, 1134, 1095, 1012, 910, 828, 756, 683 cm^{-1}. ^{1}H NMR (CDCl$_3$, 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$_b$CO), 2.82 (d, 1H, J = 15.6 Hz, CH$_a$$H_b$CO), 1.72 [s, 3H, ArC(CH$_2$CO)-C$H_3$] ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 167.2 (s, O–C=O), 151.1 (s, ArC), 142.5 (s, ArC), 133.1 (s, ArC), 130.2 (s, ArC), 129.0 (d, ArCH), 128.8 (d, 2C, 2 × ArCH), 127.6 (d, 2C, 2 × ArCH), 126.4 (d, ArCH), 124.8 (d, ArCH), 117.4 (d, ArCH), 43.6 (t, CH$_2$CO), 40.8 [s, ArC(CH$_2$CO)CH$_3$], 27.5 [q, ArC(CH$_2$CO)-CH$_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), *meta*-cresol **6b** (81.7 mg, 0.75 mmol), anhydrous FeCl$_3$ (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(**5h**) = 0.60, R_f(**9h**) = 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}. ^{1}H NMR (CDCl$_3$, 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$_b$CO), 2.79 (d, 1H, J = 15.6 Hz, CH$_a$$H_b$CO), 2.36 (s, 3H, ArCH$_3$), 1.69 [s, 3H, ArC(CH$_2$CO)C$H_3$] ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 167.4 (s, O–C=O), 151.0 (s, ArC), 142.8 (s, ArC), 139.4 (s, ArC), 133.0 (s, ArC), 128.8 (d, 2C, 2 × ArCH), 127.6 (d, 2C, 2 × ArCH), 127.1 (s, ArC), 126.1 (d, ArCH), 125.6 (d, ArCH), 117.8 (d, ArCH), 43.8 (t, CH$_2$CO), 40.6 [s, ArC(CH$_2$CO)CH$_3$], 27.6 [q, ArC(CH$_2$CO)CH$_3$], 21.0 (q, ArCH$_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{15}ClNaO_2]^+$ = $[M + Na]^+$: 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), *para*-cresol **6c** (81.7 mg, 0.75 mmol), anhydrous FeCl$_3$ (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(**5h**) = 0.60, R_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}. ^{1}H NMR (CDCl$_3$, 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$_b$CO), 2.80 (d, 1H, J = 15.6 Hz, CH$_a$$H_b$CO), 2.35 (s, 3H, ArCH$_3$), 1.72 [s, 3H, ArC(CH$_2$CO)C$H_3$] ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 167.4 (s, O–C=O), 149.1 (s, ArC), 142.6 (s, ArC), 134.5 (s, ArC), 133.1 (s, ArC), 129.8 (s, ArC), 129.5 (d, ArCH), 128.8 (d, 2C, 2 × ArCH), 127.7 (d, 2C, 2 × ArCH), 126.7 (d, ArCH), 117.2 (d, ArCH), 43.8 (t, CH$_2$CO), 40.8 [s, ArC(CH$_2$CO)CH$_3$], 27.5 [q, ArC-(CH$_2$CO)CH$_3$], 21.0 (q, ArCH$_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{15}ClNaO_2]^+$ = $[M + Na]^+$: 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), *ortho*-cresol **6d** (81.0 mg, 0.75 mmol), and anhydrous FeCl$_3$ (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 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 **9j** (85.8 mg, 60%) as a colorless viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2965, 2923, 1770, 1493, 1465, 1195, 1098, 1012, 828, 787, 754 cm^{-1}. ^{1}H NMR (CDCl$_3$, 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$_b$CO), 2.80 (d, 1H, J = 15.7 Hz, CH$_a$$H_b$CO), 2.31 (s, 3H, ArCH$_3$), 1.70 [s, 3H, ArC-(CH$_2$CO)C$H_3$] ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 167.3 (s, O–C=O), 149.4 (s, ArC), 142.7 (s, ArC), 133.0 (s, ArC), 130.5 (d, ArCH), 130.0 (s, ArC), 128.6 (d, 2C, 2 × ArCH), 127.7 (d, 2C, 2 × ArCH), 126.8 (s, ArC), 124.3 (d, ArCH), 123.9 (d, ArCH), 43.5 (t, CH$_2$CO), 40.9 [s, ArC(CH$_2$CO)CH$_3$], 27.7 [q, ArC(CH$_2$CO)CH$_3$], 15.9 (q, ArCH$_3$) 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 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_f(**5h**) = 0.60, R_f(**9k**) = 0.50

(petroleum ether–ethyl acetate 94 : 6, UV detection)]. Purification of the residue on a silica gel column (petroleum ether–ethyl 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}): ν_{max} = 2958, 2921, 2851, 1767, 1493, 1463, 1374, 1247, 1191, 1151, 1068, 1012, 816, 751, 699, 660 cm^{-1}. ^1H NMR ($CDCl_3$, 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$_b$CO), 2.94 (d, 1H, J = 15.6 Hz, CH$_a$$H_b$CO), 1.81 [s, 3H, ArC(CH$_2$CO)C$H_3$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.0 (s, O–C═O), 146.2 (s, ArC), 142.8 (s, ArC), 133.7 (s, ArC), 133.2 (s, ArC), 128.9 (d, 2C, 2 × ArCH), 127.8 (d, 2C, 2 × ArCH), 127.5 (d, ArCH), 127.0 (d, ArCH), 126.9 (d, ArCH), 124.5 (s, ArC), 124.5 (d, ArCH), 123.7 (s, ArC), 123.2 (d, ArCH), 121.6 (d, ArCH), 44.2 (t, CH$_2$CO), 41.1 [s, ArC(CH$_2$CO)CH$_3$], 27.4 [q, ArC(CH$_2$CO)CH$_3$] 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 (9l). GP-1 was carried out on the ester **5h** (112 mg, 0.5 mmol), β-naphthol **6f** (108.1 mg, 0.75 mmol), anhydrous $FeCl_3$ (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(**5h**) = 0.60, R_f(**9l**) = 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 ($CDCl_3$, 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$_b$CO), 2.84 (d, 1H, J = 15.6 Hz, CH$_a$$H_b$CO), 1.93 [s, 3H, ArC(CH$_2$CO)C$H_3$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.2 (s, O–C═O), 149.8 (s, ArC), 145.5 (s, ArC), 132.8 (s, ArC), 131.9 (s, ArC), 130.3 (d, ArCH), 130.1 (s, ArC), 129.2 (d, 2C, 2 × ArCH), 129.0 (d, ArCH), 127.4 (d, 2C, 2 × ArCH), 126.0 (d, ArCH), 125.7 (d, ArCH), 124.6 (d, ArCH), 122.0 (s, ArC), 117.8 (d, ArCH), 47.8 (t, CH$_2$CO), 42.6 [s, ArC(CH$_2$CO)CH$_3$], 24.7 [q, ArC(CH$_2$CO)CH$_3$] ppm. HR-MS (ESI+) m/z calculated 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 $FeCl_3$ (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}): ν_{max} = 2924, 1761, 1596, 1494, 1418, 1281, 1250, 1201, 1136, 1125, 1052, 915, 813 cm^{-1}. ^1H NMR ($CDCl_3$, 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(CH$_3$)CH_aH$_b$CO], 2.80 [d, 1H, J = 15.6 Hz, ArC(CH$_3$)CH$_a$$H_b$CO], 2.30 (s, 3H, ArCH$_3$), 1.72 [s, 3H, ArC(C$H_3$)CH$_2$CO] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.7 (s, O–C═O), 151.1 (s, ArC), 140.9 (s, ArC), 136.8 (s, ArC), 131.0 (s, ArC), 129.4 (d, 2C, 2 × ArCH), 128.6 (d, ArCH), 126.6 (d, ArCH), 126.0 (d, 2C, 2 × ArCH), 124.7 (d, ArCH), 117.3 (d, ArCH), 43.8 (t, CH$_2$CO), 40.8 [s, ArC(CH$_3$)CH$_2$CO], 27.5 [q, ArC(CH$_3$)CH$_2$CO], 20.8 (q, ArCH$_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{17}O_2]^+$ = $[M]^+$: 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), *meta*-cresol **6b** (81.0 mg, 0.75 mmol), anhydrous $FeCl_3$ (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(**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 ($CDCl_3$, 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$_b$CO], 2.78 [d, 1H, J = 15.6 Hz, ArC(CH$_3$)CH$_a$$H_b$CO], 2.36 (s, 3H, ArCH$_3$), 2.30 (s, 3H, ArCH$_3$), 1.70 [s, 3H, ArC(C$H_3$)CH$_2$CO] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.8 (s, O–C═O), 150.9 (s, ArC), 141.1 (s, ArC), 138.8 (s, ArC), 136.6 (s, ArC), 129.3 (d, 2C, 2 × ArCH), 127.8 (s, ArC), 126.2 (d, ArCH), 126.0 (d, 2C, 2 × ArCH), 125.3 (d, ArCH), 117.6 (d, ArCH), 43.9 (t, CH$_2$CO), 40.4 [s, ArC(CH$_3$)CH$_2$CO], 27.5 [q, ArC(CH$_3$)CH$_2$CO], 20.9 (q, ArCH$_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 289.1197.

4,6-Dimethyl-4-(4-methylphenyl)chroman-2-one (9o). GP-1 was carried out on the ester **5i** (97.0 mg, 0.5 mmol), *para*-cresol **6c** (81.0 mg, 0.75 mmol), anhydrous $FeCl_3$ (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(**9o**) = 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 **9o** (107.7 mg, 81%) as a yellow viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2921, 1763, 1594, 1493, 1416, 1279, 1199, 1134, 1123, 1051, 913, 814 cm^{-1}. ^1H NMR ($CDCl_3$, 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$_b$CO], 2.78 [d, 1H, J = 15.6 Hz, ArC(CH$_3$)CH$_a$$H_b$CO], 2.33 (s, 3H, ArCH$_3$), 2.30 (s, 3H, ArCH$_3$), 1.71 [s, 3H, ArC(C$H_3$)CH$_2$CO] ppm. ^{13}C NMR ($CDCl_3$, 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, Ar$C(CH_3)CH_2CO$], 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 $FeCl_3$ (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(**5j**) = 0.60, R_f(**9p**) = 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}): ν_{max} = 2970, 2924, 1762, 1623, 1577, 1446, 1412, 1208, 1192, 1161, 1150, 1061, 814, 759, 698 cm^{-1}. ^1H NMR ($CDCl_3$, 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$_b$CO), 2.81 (d, 1H, J = 15.6 Hz, CH$_a$$H_b$CO), 2.34 (s, 3H, Ar–$CH_3$), 2.25–2.00 (m, 2H, CH_2CH_3), 0.88 (t, 3H, J = 7.3 Hz, CH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.3 (s, O–C═O), 151.4 (s, ArC), 143.1 (s, ArC), 138.8 (s, ArC), 128.5 (d, 2C, 2 × ArCH), 126.8 (d, ArCH), 126.7 (d, ArCH), 126.6 (d, 2C, 2 × ArCH), 126.0 (s, ArC), 125.0 (d, ArCH), 117.9 (d, ArCH), 44.5 [s, Ar$C(CH_2CO)$Et], 39.8 (t, CH_2CO), 32.1 (t, CH_2CH_3), 20.9 (q, $ArCH_3$), 8.8 (q, CH_2CH_3), 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 $FeCl_3$ (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(**5j**) = 0.60, R_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}): ν_{max} = 2970, 2924, 1764, 1598, 1491, 1259, 1197, 1124, 1060, 922, 823, 734, 698 cm^{-1}. ^1H NMR ($CDCl_3$, 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$_b$CO), 2.81 (d, 1H, J = 15.6 Hz, CH$_a$$H_b$CO), 2.36 (s, 3H, Ar–$CH_3$), 2.21–2.02 (m, 2H, CH_2CH_3), 0.90 (t, 3H, J = 7.3 Hz, CH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.4 (s, O–C═O), 149.5 (s, ArC), 143.0 (s, ArC), 133.9 (s, ArC), 129.0 (d, ArCH), 128.8 (s, ArC), 128.6 (d, 2C, 2 × ArCH), 127.3 (d, ArCH), 126.9 (d, ArCH), 126.7 (d, 2C, 2 × ArCH), 117.2 (d, ArCH), 44.7 [s, Ar$C(CH_2CO)$-Et], 39.7 (t, CH_2CO), 32.1 (t, CH_2CH_3), 21.0 (q, Ar–CH_3), 8.8 (q, CH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}NaO_2]^+ = [M + Na]^+$: 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-phenylphenol **6g** (127.5 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 20 h [TLC control R_f(**5g**) = 0.60, R_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 ($CDCl_3$, 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$_b$CO), 2.86 (d, 1H, J = 15.6 Hz, CH$_a$$H_b$CO), 1.78 [s, 3H, ArC($CH_2CO$)$CH_3$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.2 (s, O–C═O), 148.0 (s, ArC), 144.0 (s, ArC), 136.6 (s, ArC), 131.5 (s, ArC), 130.8 (s, ArC), 130.4 (d, ArCH), 129.6 (d, 2C, 2 × ArCH), 128.8 (d, 2C, 2 × ArCH), 128.3 (d, 2C, 2 × ArCH), 127.6 (d, ArCH), 127.2 (d, ArCH), 126.3 (d, 2C, 2 × ArCH), 125.9 (s, ArCH), 124.6 (d, ArCH), 43.5 (t, CH_2CO), 41.4 [s, Ar$C(CH_2CO)CH_3$], 27.8 [q, ArC(CH_2CO)CH_3] 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 $FeCl_3$ (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_f(**5h**) = 0.60, R_f(**11b**) = 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 **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}): ν_{max} = 3342, 2922, 2852, 1770, 1680, 1640, 1454, 1426, 1256, 1198, 1120, 1068, 1023, 762, 699, 653 cm^{-1}. ^1H NMR ($CDCl_3$, 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$_b$CO), 2.85 (d, 1H, J = 15.6 Hz, CH$_a$$H_b$CO), 1.77 [s, 3H, ArC($CH_2CO$)$CH_3$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.2 (s, O–C═O), 147.9 (s, ArC), 143.9 (s, ArC), 136.5 (s, ArC), 131.5 (s, ArC), 130.5 (s, ArC), 130.3 (d, ArCH), 129.6 (d, 2C, 2 × ArCH), 128.7 (d, 2C, 2 × ArCH), 128.2 (d, 2C, 2 × ArCH), 127.5 (d, ArCH), 127.2 (d, ArCH), 126.2 (d, 2C, 2 × ArCH), 125.8 (d, ArCH), 124.5 (d, ArCH), 120.7 (s, ArC), 115.8 (s, ArC), 43.4 (t, CH_2CO), 41.4 [s, Ar$C(CH_2CO)CH_3$], 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 $FeCl_3$ (243.3 mg, 1.5 mmol) followed by addition of DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 12 h [TLC control R_f(**5g**) = 0.60, R_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}): ν_{max} = 3412, 2978, 2926, 1712, 1507, 1490, 1406, 1369, 1322, 1273, 1222, 1157, 1095, 1012, 829, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.50–7.40 (m, 3H, ArH), 7.36 (t, 1H, J = 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, OCH_2CH_3), 3.11 (s, 2H, CH_2COOEt), 1.86 [s, 3H, $ArC(CH_2CO)CH_3$], 0.97 (t, 3H, J = 7.3 Hz, OCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 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, OCH_2CH_3), 46.8 (t, CH_2COOEt), 45.0 (s, $ArCCH_2COOEt$), 28.5 [q, $ArC(CH_2COOEt)CH_3$], 13.9 (q, OCH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{24}H_{24}NaO_3]^+ = [M + Na]^+$: 383.1618; 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 $FeCl_3$ (243.3 mg, 1.5 mmol) followed by addition of DCE (2 mL). The resulting reaction mixture was stirred at room temperature for 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 ether–ethyl 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}): ν_{max} = 3429, 2978, 2922, 1712, 1507, 1490, 1464, 1406, 1369, 1273, 1222, 1157, 1095, 1012, 829, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 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, OCH_2CH_3), 3.07 (s, 2H, CH_2COOEt), 1.83 [s, 3H, $ArC(CH_2COOEt)CH_3$], 0.98 (t, 3H, J = 7.3 Hz, OCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 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, OCH_2CH_3), 46.6 (t, CH_2COOEt), 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(3*H*)-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 $FeCl_3$ (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_f(**5m**) = 0.73, R_f(**13a**) = 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}): ν_{max} = 2923, 2852, 1774, 1484, 1449, 1252, 1197, 1068, 920 cm^{-1}. ^1H NMR ($CDCl_3$, 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, $ArCH_2CH_2CH_2$), 1.95 (dd, 2H, J = 5.9 and 5.4 Hz, $ArCH_2CH_2CH_2$), 1.87–1.65 (m, 2H, $ArCH_2CH_2CH_2CH_2$) ppm. ^{13}C NMR ($CDCl_3$, 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, CH_2CO), 41.2 (s, $ArCCH_2CO$), 36.0 (t, CH_2), 30.0 (t, CH_2), 18.6 (t, CH_2) ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{17}O_2]^+ = [M + H]^+$: 265.1223; found 265.1216.

7-Methyl-3′,4′-dihydro-2′*H*-spiro[chromene-4,1′-naphthalen]-2(3*H*)-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 $FeCl_3$ (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_f(**5m**) = 0.75, R_f(**13b**) = 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 ($CDCl_3$, 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_aH_bCO), 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, $ArCH_3$), 1.92 (dd, 2H, J = 6.4 and 5.4 Hz, $ArCH_2CH_2CH_2$), 1.85–1.65 (m, 2H, $ArCH_2CH_2CH_2$) ppm. ^{13}C NMR ($CDCl_3$, 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, CH_2CO), 40.9 (s, $ArCCH_2CO$), 36.1 (t, CH_2), 30.0 (t, CH_2), 20.9 (q, $ArCH_3$), 18.6 (t, CH_2) 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(3*H*)-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 $FeCl_3$ (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(**5e**) = 0.73, R_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 ($CDCl_3$, 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, $ArCH_2CH_2CH_2$), 2.18 (s, 3H,

$ArCH_3$), 1.93 (dd, 2H, J = 5.9 and 5.4 Hz, $ArCH_2CH_2CH_2$), 1.87–1.65 (m, 2H, $ArCH_2CH_2CH_2$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 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, CH_2CO), 41.3 (s, $ArCCH_2CO$), 36.1 (t, CH_2), 30.0 (t, CH_2), 20.8 (q, $ArCH_3$), 18.7 (t, CH_2) 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(3*H*)-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 $FeCl_3$ (243 mg, 1.5 mmol) and benzene (2 mL). The resulting reaction mixture was stirred at room temperature for 2 h [TLC control R_f(**5e**) = 0.73, R_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 **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 ($CDCl_3$, 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, $ArCH_2CH_2CH_2$), 2.35 (s, 3H, $ArCH_3$), 2.05–1.90 (m, 2H, $ArCH_2CH_2CH_2$), 1.85–1.65 (m, 2H, $ArCH_2CH_2CH_2$) ppm. ^{13}C NMR ($CDCl_3$, 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, CH_2CO), 41.2 (s, $ArCCH_2CO$), 35.8 (t, CH_2), 30.0 (t, CH_2), 18.6 (t, CH_2), 15.9 (q, $ArCH_3$) 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(2*H*)-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 $FeCl_3$ (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_f(**5m**) = 0.73, R_f(**13e**) = 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}): ν_{max} = 2917, 2849, 1773, 1600, 1461, 1210, 1174, 1025, 812 cm^{-1}. ^1H NMR ($CDCl_3$, 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. ^{13}C NMR ($CDCl_3$, 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, CH_2CO), 42.4 (s, $ArCCH_2CO$), 33.4 (t, CH_2), 29.8 (t, CH_2), 18.8 (t, CH_2) 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(3*H*)-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 $FeCl_3$ (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 ($CDCl_3$, 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_aH_bCO), 2.91 (d, 1H, J = 15.6 Hz, CH_aH_bCO), 2.82 (dd, 2H, J = 5.9 and 5.4 Hz, $ArCH_2CH_2CH_2$), 2.32 (s, 3H, $ArCH_3$), 2.23 (s, 3H, $ArCH_3$), 1.89 (dd, 2H, J = 6.3 and 5.4 Hz, $ArCH_2CH_2CH_2$), 1.84–1.62 (m, 2H, $ArCH_2CH_2CH_2$) ppm. ^{13}C NMR ($CDCl_3$, 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, CH_2CO), 40.9 (s, $ArCCH_2CO$), 36.2 (t, CH_2), 29.6 (t, CH_2), 21.1 (q, $ArCH_3$), 20.9 (q, $ArCH_3$), 18.7 (t, CH_2) ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{21}O_2]^+$ = $[M + H]^+$: 293.1536; found 293.1525.

Acknowledgements

Financial support by the Council of Scientific and Industrial Research [(CSIR), 02(0018)/11/EMR-II], New Delhi is gratefully acknowledged. P.N thanks CSIR [(CSIR), 02(0018)/11/EMR-II] New Delhi for the financial support. B.V.R. thanks CSIR for the award of a fellowship.

Notes and references

1 (*a*) J. Staunton, in *Comprehensive Organic Chemistry*, ed. P. G. Sammes, Pergamon, Oxford, 1979, vol. 4, p. 651; (*b*) U. Matern, P. Lüer and D. Kreusch, in *Comprehensive Natural Products Chemistry*, ed. U. Sankawa, Pergamon, Oxford, 1999, vol. 1, p. 623.
2 X. Zhang, H. Wang, Y. Song, L. Nie, L. Wang, B. Liu, P. Shen and Y. Liua, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 949.
3 M. Takechi, Y. Tanaka, M. Takehara, G.-I. Nonaka and I. Nishioka, *Phytochemistry*, 1985, **24**, 2245.
4 M. Iinuma, T. Tanaka, M. Mizuno, T. Katsuzaki and H. Ogawa, *Chem. Pharm. Bull.*, 1989, **37**, 1813.

5 F. L. Hsu, G.-I. Nonaka and I. Nishioka, *Chem. Pharm. Bull.*, 1985, **33**, 3142.
6 (*a*) T. Yoshida, G. Ohbayashi, K. Ishihara, W. Ohwashi, K. Haba, Y. Okano, T. Shingu and T. Okuda, *Chem. Pharm. Bull.*, 1991, **39**, 2233; (*b*) T. Okuda, T. Hatano and K. Yakazi, *Chem. Pharm. Bull.*, 1983, **31**, 333; (*c*) R. Saijio, G.-I. Nonaka and I. Nishioka, *Chem. Pharm. Bull.*, 1989, **37**, 2063; (*d*) M. Iinuma, T. Tanaka and F. Asai, *Phytochemistry*, 1994, **36**, 941; (*e*) M. Iinuma, T. Tanaka, M. Mizuno, T. Katsuzaki and H. Ogawa, *Chem. Pharm. Bull.*, 1989, **37**, 1813; (*f*) F.-L. Hsu, G.-I. Nonaka and I. Nishioka, *Chem. Pharm. Bull.*, 1985, **33**, 3142; (*g*) G.-I. Nonaka, O. Kawahara and I. Nishioka, *Chem. Pharm. Bull.*, 1982, **30**, 4277.
7 M. A. McGuire, S. C. Shilcrat and E. Sorenson, *Tetrahedron Lett.*, 1999, **40**, 3293.
8 G. Chen, N. Tokunaga and T. Hayashi, *Org. Lett.*, 2005, **7**, 2285.
9 K. A. De Castro, J. Ko, D. Park, S. Park and H. Rhee, *Org. Process Res. Dev.*, 2007, **11**, 918.
10 (*a*) G. Speranza, A. Di Meo, S. Zanzola, G. Fontana and P. Mannito, *Synthesis*, 1997, 931; (*b*) M. Z. B. Bezerra, I. L. Machado, S. M. De Morais and R. Braz-Filho, *J. Braz. Chem. Soc.*, 1997, **8**, 229.
11 W. H. Santos and L. C. Silva-Filho, *Synthesis*, 2012, 3361.
12 X.-F. Zhang, L. Xie, Y. Liu, J.-F. Xiang, L. Li and Y.-L. Tang, *J. Mol. Struct.*, 2008, **888**, 145.
13 X.-M. Li, M. Lin, Y.-H. Wang and X. Liu, *Planta Med.*, 2004, **70**, 160.
14 (*a*) L. Dhooghe, S. Maregesi, I. Mincheva, D. Ferreira, J. P. J. Marais, F. Lemière, A. Matheeussen, P. Cos, L. Maes, A. Vlietinck, S. Apers and L. Pieters, *Phytochemistry*, 2010, **71**, 785; (*b*) J. Hokkanen, S. Mattila, L. Jaakola, A. M. Pirttila and A. Tolonen, *J. Agric. Food Chem.*, 2009, **57**, 9437; (*c*) N. Tabanca, R. S. Pawar, D. Ferreira, J. P. J. Marais, S. I. Khan, V. Joshi, D. E. Wedge and I. A. Khan, *Planta Med.*, 2007, **73**, 1107; (*d*) X.-F. Zhang, H.-M. Wang, Y.-L. Song, L.-H. Nie, L.-F. Wang, B. Liu, P. Shen and Y. Liu, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 949; (*e*) C.-S. Yao, M. Lin and L. Wang, *Chem. Pharm. Bull.*, 2006, **54**, 1053.
15 K. Vosmann, P. Wittkamp and N. Weber, *J. Agric. Food Chem.*, 2006, **54**, 2969 and references cited therein.
16 (*a*) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, John Wiley and Sons, New York, 1994; (*b*) M. A. McGuire, S. C. Shilcrat and E. Sorenson, *Tetrahedron Lett.*, 1999, **40**, 3293; (*c*) J. O. Park and S. W. Youn, *Org. Lett.*, 2010, **12**, 2258.
17 (*a*) C. Jia, T. Kitamura and Y. Fujiwara, *Acc. Chem. Res.*, 2001, **34**, 633; (*b*) V. Ritleng, C. Sirlin and M. Pfeffer, *Chem. Rev.*, 2002, **102**, 1731; (*c*) K. Li, L. N. Foresee and J. A. Tunge, *J. Org. Chem.*, 2005, **70**, 2881; (*d*) A. R. Jagdale and A. Sudalai, *Tetrahedron Lett.*, 2007, **48**, 4895; (*e*) S. Aoki, C. Amamoto, J. Oyamada and T. Kitamura, *Tetrahedron*, 2005, **61**, 9291.
18 (*a*) E. Fillion, A. M. Dumas, B. A. Kuropatwa, N. R. Malhotra and T. C. Sitler, *J. Org. Chem.*, 2006, **71**, 409; (*b*) C. E. Rodrigues-Santos and A. Echevarria, *Tetrahedron Lett.*, 2007, **48**, 4505; (*c*) S. Duan, R. Jana and J. A. Tunge, *J. Org. Chem.*, 2009, **74**, 4612.
19 (*a*) Y. Gu and K. Xue, *Tetrahedron Lett.*, 2010, **51**, 192; (*b*) A. Kumar, P. Kumar, V. D. Tripathi and S. Srivastava, *RSC Adv.*, 2012, **2**, 11641; (*c*) M. C. Laufer, H. Hausmann and W. F. Holderich, *J. Catal.*, 2003, **218**, 315; (*d*) E. Tang, W. Li, Z. Y. Gao and X. Gu, *Chin. Chem. Lett.*, 2012, **23**, 631; (*e*) D. P. Kamat, S. G. Tilve and V. P. Kamat, *Tetrahedron Lett.*, 2012, **53**, 4469; (*f*) C. R. Reddy, B. Srikanth, N. N. Rao and D.-S. Shin, *Tetrahedron*, 2008, **64**, 11666.
20 E. Fillion, A. M. Dumas, B. A. Kuropatwa, N. R. Malhotra and T. C. Sitler, *J. Org. Chem.*, 2006, **71**, 409.
21 (*a*) H. Poras, E. Stephan, G. Pourcelot and P. Cresson, *Chem. Ind.*, 1993, 206; (*b*) A. Patra and S. K. Misra, *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.*, 1990, **29**, 66; (*c*) A. I. Scott, P. A. Dodsox, F. McCapra and M. B. Meyers, *J. Am. Chem. Soc.*, 1963, **85**, 3702.
22 Z. Zhang, Y. Ma and Y. Zhao, *Synlett*, 2008, 1091.
23 B. V. Ramulu, A. G. K. Reddy and G. Satyanarayana, *Synlett*, 2013, 863.

