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Synthesis of heterocyclic-fused benzopyrans *via* the Pd(II)-catalyzed C–H alkenylation/C–O cyclization of flavones and coumarins†

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An efficient and practical method for effecting a tandem C–H alkenylation/C–O cyclization has been achieved *via* the C–H functionalization of flavone derivatives. The synthetic utility of the one-pot sequence was demonstrated by obtaining convenient access to coumarin-annelated benzopyrans. The reaction scope for the transformation was found to be fairly broad, affording good yields of a wide range of flavone- or coumarin-fused benzopyran motifs, which are privileged structures in many biologically active compounds.

Introduction

Substantial advances have been made toward enhancing the efficiency of direct C–H bond activation in (hetero)arenes for the C–C and C–heteroatom bond forming reactions of high synthetic utility. C–H functionalization is advantageous in that it enables the construction of complicated target molecules in lesser reaction steps without pre-functionalizing the starting materials. The direct transition metal-catalyzed functionalization of C–H bonds in heterocycles is an extremely valuable process in the research field of synthetic applications and medicinal chemistry.[1] Since the discovery of the direct olefination of arenes by Fujiwara *et al.*,[2] impressive progress has been made toward improving the efficiency of oxidative C–H alkenylation of heterocycles as promising alternatives to the conventional approach.[3,4]

Flavone-fused benzopyran is an important structural motif in many naturally occurring products and has been shown to display a diverse range of biological activities (Fig. 1).[5] In this regard, the benzopyran motif continues to attract the attention of synthetic chemists.[6] In our ongoing studies toward the construction of scaffold focused chemical libraries, we were interested in developing an efficient and practical method for synthesizing a variety of heterocyclic-fused benzopyrans.

Driven by the need for a concise and general synthetic route to flavone- or coumarin-fused benzopyrans, we were particularly interested in exploring efficient approaches to these derivatives through a one-pot process. From the viewpoint of synthetic and environmental considerations, one-pot reactions are advantageous for conducting multistep reactions in one synthetic operation. These approaches ideally generate molecular complexity from relatively simple starting materials in a single reaction vessel, thereby minimizing undesired waste.[7] Over the course of developing efficient flavone synthetic methods, our group recently reported efficient and versatile methods for effecting the direct C–O cyclization of the phenolic hydroxyl group onto the C–H bond at the C3 position of flavone derivatives, permitting the construction of a variety of flavone-fused benzopyrans (Scheme 1a).[8] This finding prompted us to explore the feasibility of an expeditious synthetic approach to flavone-fused benzopyrans through a one-pot alkenylation/C–O cyclization sequence. C–H bond functionalization that involves the use of the innate nucleophilicity of chromones or coumarins could provide a useful strategy for cross-coupling reactions with high site selectivities.[9]

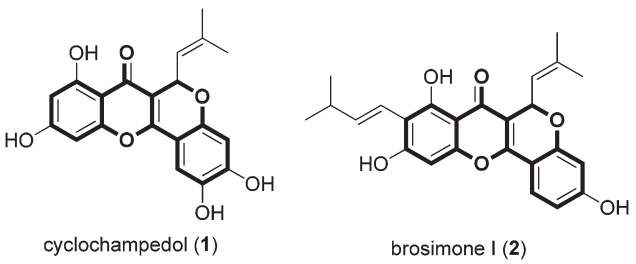

Fig. 1 Examples of biologically active compounds bearing a flavone-fused benzopyran motif.

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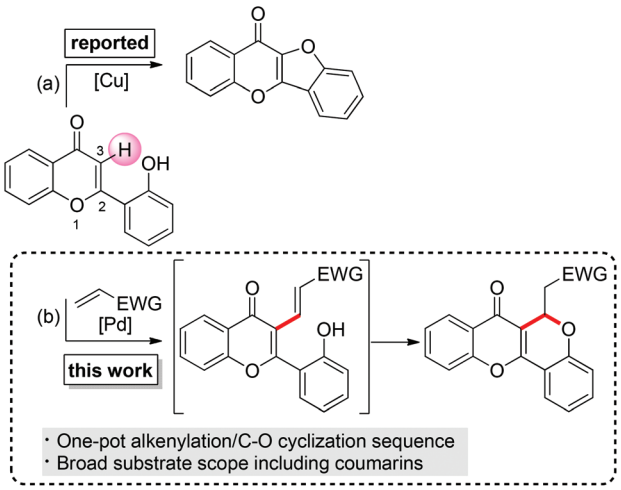
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ob00180j



Scheme 1 Proposed flavone-fused benzopyran synthesis by the C–H alkenylation/C–O cyclization.

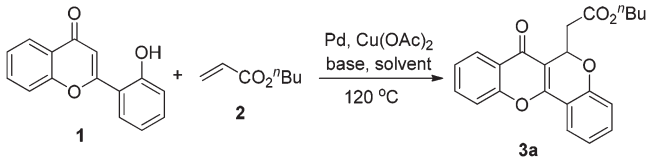
If the installed olefin contains an electron-withdrawing group, the cyclization reaction might take place, generating the desired product. In this context, we anticipated that the C3 alkenylated enolones generated *in situ* from a Pd(II)-catalyzed alkenylation reaction could undergo C–O cyclization by employing the phenolic hydroxyl group as a nucleophile to afford flavonoids bearing benzopyrans in an atom-economical approach (Scheme 1b). This strategy would present opportunities for the construction of flavone-fused benzopyrans which resemble the core structures of biologically active natural products (Fig. 1). Herein we report an efficient and practical C–H alkenylation/C–O cyclization process that is broadly applicable to the readily accessible flavone and coumarin systems[10] and enables the construction of heterocyclic-annelated benzopyrans.

Results and discussion

At the outset, the feasibility of this strategy was tested by investigating a one-pot alkenylation/C–O cyclization of 2-(2-hydroxyphenyl)-4*H*-chromen-4-one (**1**) with *n*-butyl acrylate (**2**) as model substrates; representative results of a catalyst screen for this conversion are listed in Table 1. The oxidizing agent was critical to the efficiency of this type of cross-coupling reaction as it facilitated the re-oxidation of Pd(0) to Pd(II). We therefore surveyed the capabilities of a variety of oxidizing agents, including Cu(II), Ag(II), $K_2S_2O_8$, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), MnO_2, (2,2,6,6-tetramethyl-piperidin-1-yl)oxy (TEMPO), and $PhCO_3{}^tBu$ (see the ESI† for additional data). We were pleased to observe that benzopyran **3a** was obtained under a catalytic system comprising both $Pd(OAc)_2$ and $Cu(OAc)_2$ in acetonitrile, albeit in a 10% yield (entry 1). Among the Cu species screened, $Cu(OAc)_2$ was found to be the most effective and economical oxidant for promoting the reaction oxidants (see the ESI† for additional data). Both the base and the solvent were found to fundamentally influence the efficiency of the reaction, in the presence of Cs_2CO_3 and *t*-BuOH as the optimal base and solvent, respectively. Among the palladium sources tested, $Pd(acac)_2$ displayed the best catalytic efficiency. In an effort to enhance the electrophilic character of the α,β-unsaturated ketone system and optimize the conjugate addition step, a series of Lewis acids was intensively screened. When the reaction was subjected to treatment with catalytic amounts of Al_2O_3 as a Lewis acid, an enhanced reactivity was obtained. Under the optimized reaction conditions (entry 12), the C–H alkenylation/C–O cyclization of **1** with *n*-butyl acrylate (**2**) proceeded to provide the best isolated yield, 74% (entry 12). Under the reaction conditions, only trace amounts (<5%) of the flavone-annelated benzofuran were observed from the direct intramolecular C–O cyclization.

With the optimized reaction conditions as shown for entry 12 (Table 1), we set up a series of experiments to investigate the substrate scope of both the alkene and the flavone substrates for the one-pot reaction (Table 2). The catalytic synthesis smoothly proceeded with substrates in the presence of a variety of functional groups. For example, alkene substrates were extended to a variety of alkenes conjugated with methyl ester, *tert*-butyl, *n*-butyl, methyl ketone, phenyl ketone, amide, or phosphonate groups to afford the desired products. The substrate scope of the flavones was subsequently examined, and a relatively broad range of functional groups (*e.g.*, alkyl, fluoro, chloro, and bromo) was found to be compatible with the reaction conditions. Encouraged by the successful results

Table 1 Optimization of the C–H alkenylation/C–O cyclization in a flavone substrate[a]

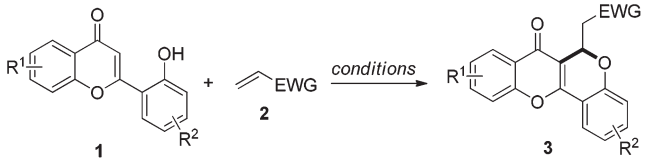


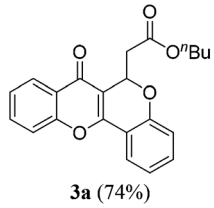
1 2 3a

Entry	Pd	Solvent	Base	Additive (0.2 equiv.)	Time (h)	Yield (%)
1	$Pd(OAc)_2$	MeCN	Na_2CO_3	—	24	10%
2	$Pd(OAc)_2$	MeCN	Ag_2CO_3	—	24	12%
3	$Pd(OAc)_2$	MeCN	Cs_2CO_3	—	24	27%
4	$Pd(OAc)_2$	MeCN	CsOPiv	—	24	26%
5	$Pd(OAc)_2$	1,4-Dioxane	Cs_2CO_3	—	12	48%
6	$Pd(OAc)_2$	DME	Cs_2CO_3	—	12	54%
7	$Pd(OAc)_2$	*t*-BuOH	Cs_2CO_3	—	12	56%
8	$Pd(acac)_2$	*t*-BuOH	Cs_2CO_3	—	4	63%
9	$Pd(acac)_2$	*t*-BuOH	Cs_2CO_3	$Zn(OTf)_2$	4	67%
10	$Pd(acac)_2$	*t*-BuOH	Cs_2CO_3	$Li(OTf)_2$	4	65%
11	$Pd(acac)_2$	*t*-BuOH	Cs_2CO_3	$Al(OTf)_3$	4	62%
12	**$Pd(acac)_2$**	***t*-BuOH**	**Cs_2CO_3**	**Al_2O_3**	**4**	**74%**

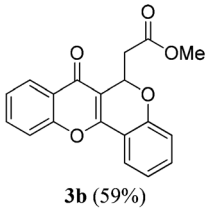
[a] Reactions were conducted with flavone, butyl acrylate (2 equiv.), Pd catalyst (0.2 equiv.), $Cu(OAc)_2$ (3 equiv.), and base (2 equiv.) in a solvent at 120 °C. MeCN = acetonitrile, Piv = pivaloyl, DME = dimethoxyethane, acac = acetoacetyl.

Table 2 Scope of the C–H alkenylation/C–O cyclization of flavones[a]

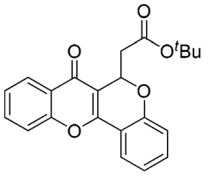




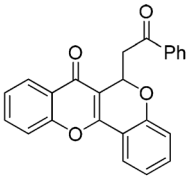
3a (74%)



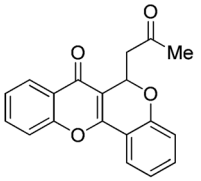
3b (59%)



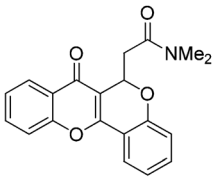
3c (63%)



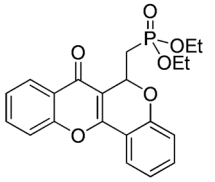
3d (77%)



3e (63%)



3f (47%)



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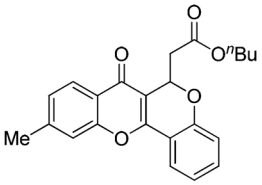
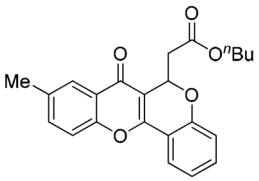
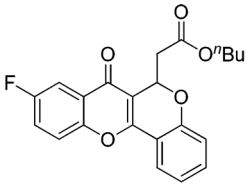


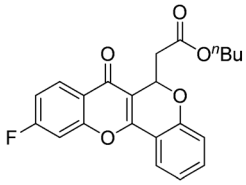
3h (83%)



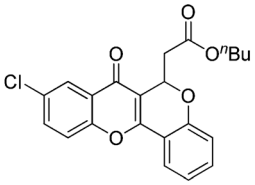
3i (53%)



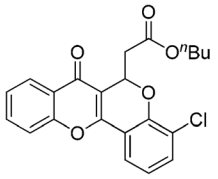
3j (57%)



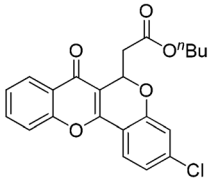
3k (66%)



3l (56%)

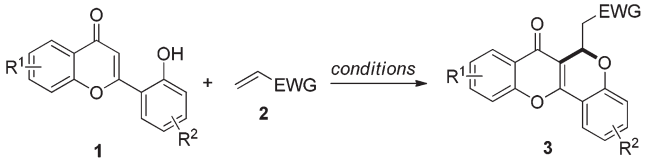


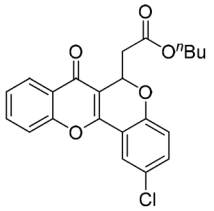
3m (70%)



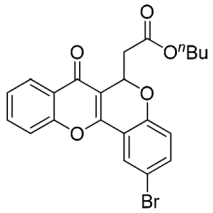
3n (53%)

Table 2 (Contd.)

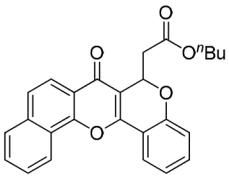




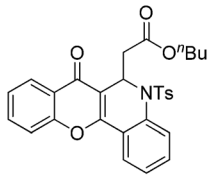
3o (55%)



3p (51%)



3q (52%)



3r (62%)

[a] Reactions were conducted with flavone (1 equiv.), alkene (2 equiv.), $Pd(acac)_2$ (0.2 equiv.), $Cu(OAc)_2$ (3 equiv.), Cs_2CO_3 (2 equiv.), and Al_2O_3 (0.2 equiv.) in *t*-BuOH at 120 °C for 4 h. Yields are reported after isolation and purification by flash silica gel chromatography.

in the sequential reactions, we further investigated the C–N cyclization and were pleased to observe that the *N*-sulfonyl group could be readily utilized, demonstrating that the process was flexible with respect to the substrate type to afford the corresponding cyclization product **3r** in 62% yield.

A proposed mechanism describing the catalytic cycle is illustrated in Fig. 2. The cyclization reaction appeared to follow the initial C–H olefination event. Thus, the electrophilic palladation by the Pd(II) species of the flavone derivative at the C3 position is favorable because the 3-position of the flavone is electron-rich to afford the intermediate **I**. At this point, it remains uncertain whether the phenolic hydroxyl group coordinates as a ligand during the electrophilic palladation of the flavone derivative. Subsequent olefin insertion into the C3-palladated species **I**, followed by C–Pd β-hydride elimination of an intermediate **II** would lead to the C3 alkenylated product **III**. Al_2O_3 is then proposed to coordinate to the carbonyl oxygen and activate the electrophilicity of the α,β-unsaturated ketone system of **2** and **III** to facilitate the alkenylation/C–O cyclization, thereby furnishing the corresponding cyclized product **3**. Furthermore, the enhanced activity observed with Al_2O_3 might be attributed to a pathway where Al_2O_3 competes with Pd/Cu in chelating the chromone substrate.[8]

The utility of the present reaction was broadened by conducting a series of experiments designed to explore the potential applicability of the methodology to the coumarin scaffold **4** (Table 3). Based on the proposed mechanism, we envisaged that the selective C–H functionalization/C–O cyclization reac-

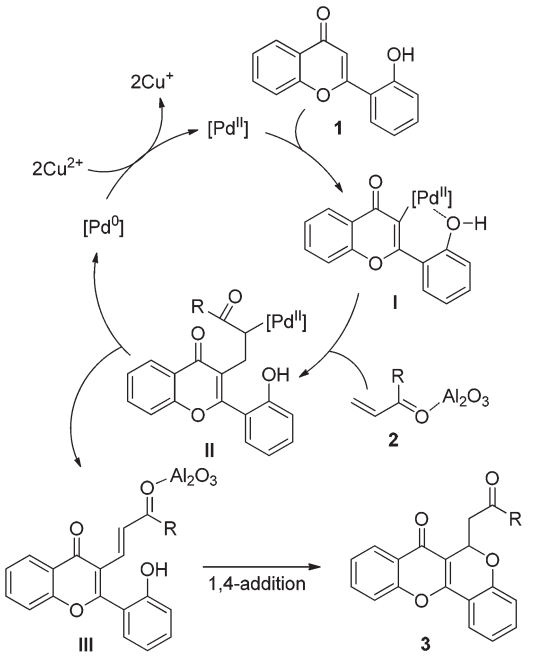


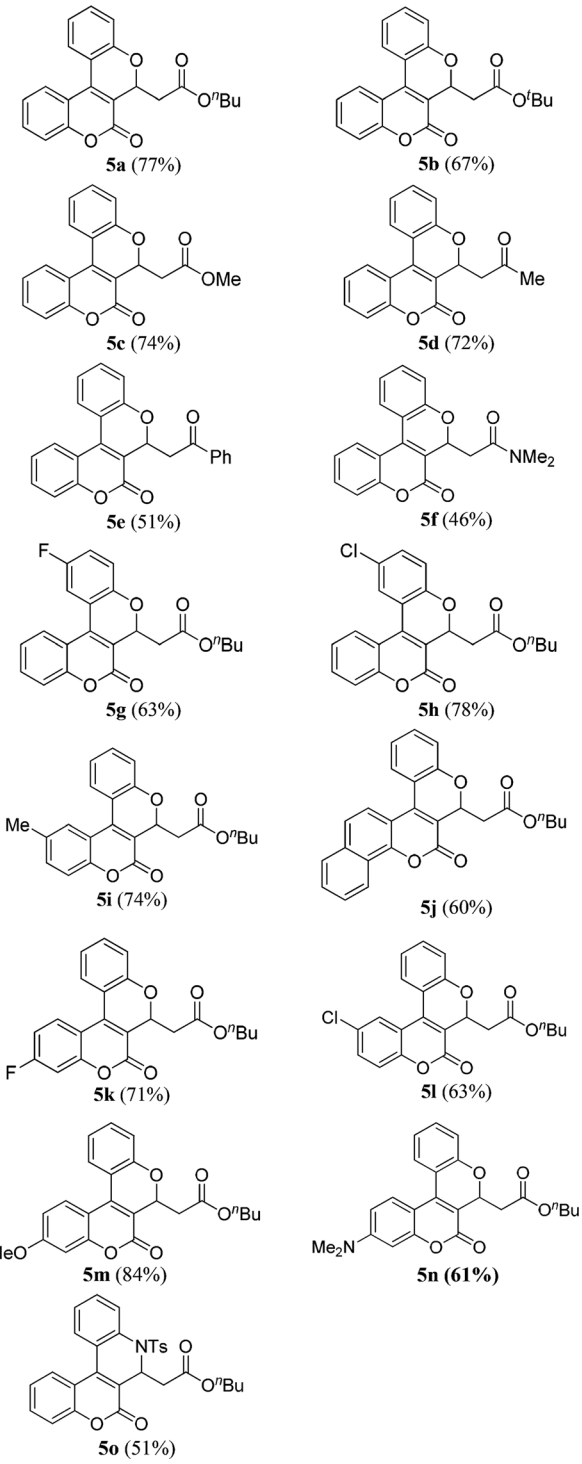
Fig. 2 Proposed mechanistic pathways underlying the present reactions.

tions of the 4-arylcoumarins would be possible because electrophilic palladation of the coumarins at the C3 position was favorable due to the nucleophilic 3-position.[3b] Indeed, the sequential reactions of **4** were very facile under slightly altered reaction conditions in which $Cu(OAc)_2{\cdot}H_2O$ was employed as an oxidant in 1,4-dioxane, thus allowing for the construction of coumarin-annelated benzopyrans in good yields. Unlike the flavone derivatives, the C–O bond formation of coumarin derivatives took place at a comparable reaction rate in the absence of Al_2O_3. We next surveyed the substrate scope, and alkene substrates conjugated with the methyl ester, *tert*-butyl, *n*-butyl, methyl ketone, phenyl ketone, or amide groups all smoothly reacted with 4-arylcoumarin **4** to afford the coumarin-fused benzopyrans **5**. The scope of the coumarin substrates was subsequently examined, and diverse functional groups (*e.g.*, methyl, phenyl, fluoro, chloro, methoxy, naphthyl, and dimethylamino) on the 4-arylcoumarin were found to be compatible with the reaction conditions. Moreover, the one-pot process was carried out on the *N*-sulfonyl substrate leading to the corresponding cyclization product **5o** in a moderate yield.

Conclusions

In summary, we have developed an efficient method for effecting the tandem C–H alkenylation/C–O cyclization reactions *via* the C–H functionalization of flavone derivatives. This synthetic process provides a concise access to a variety of flavone-fused benzopyrans (Table 2). The synthetic utility of

Table 3 Scope of the C–H alkenylation/C–O cyclization of coumarins



the one-pot sequence was further demonstrated by its ability to provide convenient access to coumarin-annelated benzopyrans (Table 3). This methodology allowed the swift development of a wide range of flavone- or coumarin-fused benzopyran derivatives, which are privileged structures in many biologically active compounds. Ongoing studies seek to broaden the scope of the methodology to include related heterocycles and other applications.

Experimental

General methods and materials

Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen using freshly distilled solvents. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F_{254} plates and visualization on TLC was achieved by UV light (254 and 354 nm). Flash column chromatography was undertaken on silica gel (400–630 mesh). ^{1}H NMR was recorded on 600 MHz, 400 MHz or 300 MHz and chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on 100 MHz or 150 MHz and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Mass spectral data were obtained using the EI method. Commercial grade reagents and solvents were used without further purification except as indicated below. Dichloromethane was distilled from calcium hydride. THF was distilled from sodium.

General procedure (GP I) for flavone C–H alkenylation/ C–O cyclization. The flavone derivative (0.063 mmol or 0.095 mmol), $Pd(acac)_2$ (0.2 equiv.), $Cu(OAc)_2$ (3 equiv.), Cs_2CO_3 (2 equiv.), and Al_2O_3 (0.2 equiv.) were combined in *t*-BuOH (0.63 mL) in a cap test tube. The alkene (2 equiv.) was added and the reaction mixture was heated to 120 °C for 4 h. The reaction mixture was monitored by TLC using ethyl acetate–hexanes (1 : 3) as the mobile phase. The reaction mixture was diluted with CH_2Cl_2 and the residue was extracted with aqueous NH_4Cl (3 × 30 mL). The organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography on silica gel to give the desired product.

General procedure (GP II) for coumarin C–H alkenylation/ C–O cyclization. The coumarin derivative (0.063 mmol), $Pd(acac)_2$ (0.2 equiv.), $Cu(OAc)_2{\cdot}H_2O$ (3 equiv.), and Cs_2CO_3 (2 equiv.) were combined in a Schlenk tube under a N_2 atmosphere (balloon). The alkene (2 equiv.) and 1,4-dioxane (0.63 mL) were added and the reaction mixture was heated to 120 °C for 8 h. The reaction mixture was monitored by TLC using ethyl acetate–hexanes (1 : 3) as the mobile phase. The reaction mixture was diluted with CH_2Cl_2 and the residue was extracted with aqueous NH_4Cl (3 × 30 mL). The organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography on silica gel to give the desired product.

Butyl 2-(7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)-acetate (3a). Compound **3a** was prepared (16.9 mg, 74% yield) according to GP I from the flavone derivative (15.0 mg, 0.063 mmol). mp 98–100 °C. IR: ν = 1728, 1642, 1633, 1606, 1416 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.20 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.83 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.69 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.54 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.46–7.35 (m, 2H), 7.07 (td, *J* = 7.6, 1.1 Hz, 1H), 6.94 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.17 (dd, *J* = 9.4, 3.6 Hz, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 2.86 (dd, *J* = 15.1, 9.4 Hz, 1H), 2.78 (dd, *J* = 15.1, 3.6 Hz, 1H), 1.63–1.53 (m, 2H), 1.41–1.30 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 174.4, 169.8, 155.6, 155.3, 155.0, 134.0, 133.7, 125.7, 125.3, 124.0, 123.6, 121.9, 118.0, 115.4, 112.3, 70.5, 64.7, 39.2, 30.6, 19.1, 13.7. HRMS (ESI$^+$) *m*/*z* calcd for $C_{22}H_{20}NaO_5^+$ [M + Na]$^+$: 387.1203, found: 387.1188.

Methyl 2-(7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)-acetate (3b). Compound **3b** was prepared (11.9 mg, 59% yield) according to GP I from the flavone derivative (15.0 mg, 0.063 mmol). mp 187–189 °C. IR: ν = 1737, 1728, 1642, 1604, 1414 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.20 (ddd, *J* = 8.0, 1.7, 0.5 Hz, 1H), 7.83 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.68 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.4, 1.1, 0.5 Hz, 1H), 7.43–7.37 (m, 2H), 7.08 (td, *J* = 7.6, 1.1 Hz, 1H), 6.95 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.17 (dd, *J* = 9.4, 3.6 Hz, 1H), 3.70 (s, 3H), 2.87 (dd, *J* = 15.2, 9.4 Hz, 1H), 2.79 (dd, *J* = 15.2, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 174.4, 170.1, 155.6, 155.2, 155.0, 134.1, 133.8, 125.7, 125.3, 124.0, 123.6, 122.0, 118.0, 118.0, 115.4, 112.2, 70.4, 51.9, 38.9. HRMS (ESI$^+$) *m*/*z* calcd for $C_{19}H_{14}NaO_5^+$ [M + Na]$^+$: 345.0733, found: 345.0713.

***tert*-Butyl 2-(7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)-acetate (3c).** Compound **3c** was prepared (14.5 mg, 63% yield) according to GP I from the flavone derivative (15.0 mg, 0.063 mmol). mp 144–146 °C. IR: ν = 1721, 1467, 1416, 1153 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.20 (ddd, *J* = 8.0, 1.7, 0.5 Hz, 1H), 7.81 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.67 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.53 (ddd, *J* = 8.5, 1.1, 0.5 Hz, 1H), 7.42–7.36 (m, 2H), 7.06 (td, *J* = 7.6, 1.1 Hz, 1H), 6.93 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.12 (dd, *J* = 8.9, 4.1 Hz, 1H), 2.78–2.67 (m, 2H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 174.4, 168.9, 155.6, 155.4, 155.0, 134.0, 133.7, 125.7, 125.2, 124.0, 123.6, 121.8, 118.0, 118.0, 115.5, 112.4, 80.9, 70.7, 40.4, 28.0. HRMS (ESI$^+$) *m*/*z* calcd for $C_{22}H_{20}NaO_5^+$ [M + Na]$^+$: 387.1203, found: 387.1178.

6-(2-Oxo-2-phenylethyl)chromeno[4,3-*b*]chromen-7(6*H*)-one (3d). Compound **3d** was prepared (26.4 mg, 77% yield) according to GP I from the flavone derivative (22.5 mg, 0.095 mmol). mp 180–182 °C. IR: ν = 1677, 1644, 1631, 1606, 1414 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.21 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.06–8.01 (m, 2H), 7.82 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.71–7.66 (m, 1H), 7.54 (td, *J* = 6.9, 6.3, 1.0 Hz, 2H), 7.48–7.39 (m, 3H), 7.38–7.33 (m, 1H), 7.06 (td, *J* = 7.5, 0.9 Hz, 1H), 6.87 (dd, *J* =

8.3, 1.0 Hz, 1H), 6.34 (dd, J = 7.1, 5.3 Hz, 1H), 3.44 (d, J = 2.0 Hz, 1H), 3.43 (s, 1H). ^{13}C NMR (100 MHz, chloroform-d) δ 196.2, 174.6, 155.6, 155.2, 155.0, 136.3, 134.1, 133.8, 133.2, 128.7, 128.5, 125.6, 125.3, 124.0, 123.6, 121.9, 118.2, 118.1, 115.4, 112.7, 70.7, 42.7. HRMS (ESI$^+$) m/z calcd for $C_{24}H_{16}NaO_4^+$ [M + Na]$^+$: 391.0941, found: 391.0939.

6-(2-Oxopropyl)chromeno[4,3-*b*]chromen-7(6*H*)-one (3e). Compound **3e** was prepared (12.1 mg, 63% yield) according to GP I from the flavone derivative (15.0 mg, 0.063 mmol). mp 168–170 °C. IR: ν = 1710, 1598, 1463, 1414 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-d) δ 8.20 (dd, J = 8.0, 1.7 Hz, 1H), 7.83 (dd, J = 7.8, 1.7 Hz, 1H), 7.69 (ddd, J = 8.7, 7.1, 1.7 Hz, 1H), 7.55 (dd, J = 8.4, 1.0 Hz, 1H), 7.44–7.37 (m, 2H), 7.08 (td, J = 7.6, 1.1 Hz, 1H), 6.93 (dd, J = 8.3, 1.0 Hz, 1H), 6.21 (dd, J = 9.9, 3.0 Hz, 1H), 3.02 (dd, J = 15.7, 9.9 Hz, 1H), 2.82 (dd, J = 15.7, 3.0 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, chloroform-d) δ 204.9, 174.5, 155.6, 155.2, 155.0, 134.1, 133.8, 125.7, 125.3, 124.0, 123.7, 122.0, 118.0, 118.0, 115.5, 112.5, 70.0, 47.4, 30.0. HRMS (ESI$^+$) m/z calcd for $C_{19}H_{14}NaO_4^+$ [M + Na]$^+$: 329.0784, found: 329.0764.

***N*,*N*-Dimethyl-2-(7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)acetamide (3f).** Compound **3f** was prepared (15.1 mg, 47% yield) according to GP I from the flavone derivative (22.5 mg, 0.095 mmol). mp 159–161 °C. IR: ν = 1642, 1631, 1600, 1622, 1414 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-d) δ 8.16 (dd, J = 7.9, 1.6 Hz, 1H), 7.80 (dd, J = 7.8, 1.6 Hz, 1H), 7.66 (ddd, J = 8.7, 7.2, 1.7 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.40–7.34 (m, 2H), 7.04 (td, J = 7.7, 0.9 Hz, 1H), 6.99 (dd, J = 8.3, 1.0 Hz, 1H), 6.15 (dd, J = 9.5, 2.9 Hz, 1H), 3.03 (s, 3H), 2.93 (s, 3H), 2.88 (dd, J = 15.0, 9.6 Hz, 1H), 2.76 (dd, J = 15.0, 2.9 Hz, 1H). ^{13}C NMR (100 MHz, chloroform-d) δ 174.6, 168.7, 155.6, 155.4, 154.9, 134.0, 133.7, 125.5, 125.2, 123.9, 123.5, 121.7, 118.2, 118.0, 115.4, 112.7, 70.6, 37.6, 37.5, 35.4. HRMS (ESI$^+$) m/z calcd for $C_{20}H_{17}NNaO_4^+$ [M + Na]$^+$: 358.1050, found: 391.1033.

Diethyl ((7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl) methyl)phosphonate (3g). Compound **3g** was prepared (14.6 mg, 58% yield) according to GP I from the flavone derivative (15.0 mg, 0.063 mmol). mp 118–120 °C. IR: ν = 1644, 1606, 1463, 1421, 1208 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-d) δ 8.20 (dd, J = 8.0, 1.7 Hz, 1H), 7.84 (dd, J = 7.8, 1.6 Hz, 1H), 7.68 (ddd, J = 8.7, 7.1, 1.7 Hz, 1H), 7.54 (dd, J = 8.5, 1.1 Hz, 1H), 7.47–7.36 (m, 2H), 7.09 (td, J = 7.5, 1.1 Hz, 1H), 7.03 (dd, J = 8.3, 1.1 Hz, 1H), 6.08 (td, J = 10.2, 2.8 Hz, 1H), 4.22–4.06 (m, 4H), 2.42 (td, J = 15.2, 10.4 Hz, 1H), 2.24 (ddd, J = 19.2, 15.6, 2.8 Hz, 1H), 1.32 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, chloroform-d) δ 174.3, 155.6, 155.1, 154.8, 134.0, 133.7, 125.7, 125.3, 124.1, 123.6, 122.0, 118.4, 118.0, 115.5, 113.1 (d, J = 14.9 Hz), 69.0 (d, J = 5.8 Hz), 61.8 (dd, J = 16.8, 6.3 Hz), 30.6 (d, J = 139.6 Hz), 16.5 (dd, J = 6.1, 2.3 Hz). HRMS (ESI$^+$) m/z calcd for $C_{21}H_{21}NaO_6P^+$ [M + Na]$^+$: 423.0968, found: 423.0990.

Butyl 2-(10-methyl-7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)acetate (3h). Compound **3h** was prepared (29.8 mg, 83% yield) according to GP I from the flavone derivative (23.8 mg, 0.095 mmol). mp 83–85 °C. IR: ν = 1728, 1638, 1602, 1045 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-d) δ 8.03 (d, J = 8.1 Hz, 1H), 7.75 (dd, J = 7.7, 1.6 Hz, 1H), 7.39–7.30 (m, 1H), 7.29 (s, 1H), 7.17 (d, J = 8.2 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.11 (dd, J = 9.4, 3.6 Hz, 1H), 4.08 (t, J = 6.6 Hz, 2H), 2.82 (dd, J = 15.1, 9.4 Hz, 1H), 2.75 (dd, J = 15.1, 3.6 Hz, 1H), 2.46 (s, 3H), 1.63–1.51 (m, 2H), 1.39–1.29 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-d) δ 174.2, 169.7, 155.6, 155.1, 154.6, 145.1, 133.7, 126.7, 125.3, 123.4, 121.8, 121.6, 117.9, 117.7, 115.4, 112.0, 70.4, 64.6, 39.1, 30.5, 21.8, 19.0, 13.6. HRMS (ESI$^+$) m/z calcd for $C_{23}H_{22}NaO_5^+$ [M + Na]$^+$: 401.1359, found: 401.1343.

Butyl 2-(9-methyl-7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)acetate (3i). Compound **3i** was prepared (12.2 mg, 53% yield) according to GP I from the flavone derivative (15.9 mg, 0.063 mmol). mp 132–134 °C. IR: ν = 1730, 1638, 1602, 1043 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-d) δ 7.96 (ddd, J = 2.2, 1.4, 0.7 Hz, 1H), 7.79 (dt, J = 7.8, 1.1 Hz, 1H), 7.47 (dd, J = 8.5, 2.1 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.39–7.34 (m, 1H), 7.09–7.00 (m, 1H), 6.92 (d, J = 8.2 Hz, 1H), 6.14 (ddd, J = 9.3, 3.7, 0.8 Hz, 1H), 4.09 (t, J = 6.6 Hz, 2H), 2.84 (dd, J = 15.1, 9.3 Hz, 1H), 2.76 (dd, J = 15.2, 3.7 Hz, 1H), 2.43 (s, 3H), 1.62–1.54 (m, 2H), 1.41–1.30 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-d) δ 174.4, 169.8, 155.2, 154.8, 153.8, 135.3, 134.9, 133.8, 125.0, 123.6, 123.6, 121.8, 117.9, 117.7, 115.5, 112.1, 70.5, 64.6, 39.1, 30.6, 20.9, 19.1, 13.7. HRMS (ESI$^+$) m/z calcd for $C_{23}H_{22}NaO_5^+$ [M + Na]$^+$: 401.1359, found: 401.1367.

Butyl 2-(9-fluoro-7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)acetate (3j). Compound **3j** was prepared (13.8 mg, 57% yield) according to GP I from the flavone derivative (16.1 mg, 0.063 mmol). mp 105–107 °C. IR: ν = 1737, 1730, 1633, 1454, 1162 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-d) δ 7.84–7.77 (m, 2H), 7.54 (dd, J = 9.1, 4.1 Hz, 1H), 7.39 (dddd, J = 9.9, 7.3, 2.0, 1.2 Hz, 2H), 7.09–7.03 (m, 1H), 6.93 (d, J = 8.3 Hz, 1H), 6.13 (dd, J = 9.3, 3.6 Hz, 1H), 4.09 (t, J = 6.7 Hz, 2H), 2.84 (dd, J = 15.1, 9.3 Hz, 1H), 2.75 (dd, J = 15.1, 3.6 Hz, 1H), 1.62–1.53 (m, 2H), 1.40–1.30 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-d) δ 173.6 (d, J_{CF} = 2.3 Hz), 169.6, 159.6 (d, J_{CF} = 247.2 Hz), 155.3, 151.7 (d, J_{CF} = 1.6 Hz), 134.2, 125.1 (d, J_{CF} = 7.3 Hz), 123.6, 122.0, 121.7, 120.1 (d, J_{CF} = 8.0 Hz), 118.0, 115.1, 111.7, 110.7 (d, J_{CF} = 23.8 Hz), 70.4, 64.7, 39.1, 30.6, 19.1, 13.6. HRMS (ESI$^+$) m/z calcd for $C_{22}H_{19}FNaO_5^+$ [M + Na]$^+$: 405.1109, found: 405.1102.

Butyl 2-(10-fluoro-7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)acetate (3k). Compound **3k** was prepared (23.8 mg, 66% yield) according to GP I from the flavone derivative (24.2 mg, 0.095 mmol). mp 136–138 °C. IR: ν = 1739, 1633, 1615, 1443, 1065 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-d) δ 8.20 (dd, J = 8.8, 6.3 Hz, 1H), 7.76 (dd, J = 7.8, 1.6 Hz, 1H), 7.41–7.35 (m, 1H), 7.21 (dd, J = 8.9, 2.4 Hz, 1H), 7.12 (td, J = 8.5, 2.4 Hz, 1H), 7.06 (td, J = 7.6, 1.0 Hz, 1H), 6.92 (dd, J = 8.3, 1.1 Hz, 1H), 6.12 (dd, J = 9.4, 3.5 Hz, 1H), 4.09 (t, J = 6.7 Hz, 2H), 2.84 (dd, J = 14.8, 9.4 Hz, 1H), 2.75 (dd, J = 15.1, 3.6 Hz, 1H), 1.62–1.53 (m, 2H), 1.40–1.30 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-d) δ 173.5, 169.6, 165.6 (d, J_{CF} = 255.2 Hz), 156.5 (d, J_{CF} = 13.4 Hz), 155.3, 155.2, 134.2, 128.2 (d, J_{CF} = 10.6 Hz), 123.5, 122.0, 120.8 (d, J_{CF} = 2.4 Hz), 118.0, 115.1,

114.0 (d, J_{CF} = 22.7 Hz), 112.2, 104.8 (d, J_{CF} = 25.6 Hz), 70.4, 64.7, 39.1, 30.6, 19.0, 13.7. HRMS (ESI$^+$) *m*/*z* calcd for $C_{22}H_{19}FNaO_5^+$ [M + Na]$^+$: 405.1109, found: 405.1095.

Butyl 2-(9-chloro-7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)acetate (3l). Compound **3l** was prepared (21.3 mg, 56% yield) according to GP I from the flavone derivative (25.8 mg, 0.095 mmol). mp 111–113 °C. IR: ν = 1733, 1631, 1443, 1156, 1408 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.12 (d, *J* = 2.6 Hz, 1H), 7.84–7.71 (m, 1H), 7.65–7.56 (m, 1H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.42–7.35 (m, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.12 (dd, *J* = 9.3, 3.6 Hz, 1H), 4.08 (t, *J* = 6.7 Hz, 2H), 2.84 (dd, *J* = 15.1, 9.3 Hz, 1H), 2.75 (dd, *J* = 15.0, 3.6 Hz, 1H), 1.61–1.53 (m, 2H), 1.39–1.29 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 173.2, 169.6, 155.3, 155.3, 153.8, 134.3, 133.9, 131.3, 125.1, 124.9, 123.6, 122.0, 119.7, 118.0, 115.0, 112.2, 70.4, 64.7, 39.0, 30.6, 19.0, 13.7. HRMS (ESI$^+$) *m*/*z* calcd for $C_{22}H_{19}ClNaO_5^+$ [M + Na]$^+$: 421.0813, found: 421.0802.

Butyl 2-(4-chloro-7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)acetate (3m). Compound **3m** was prepared (17.5 mg, 70% yield) according to GP I from the flavone derivative (17.2 mg, 0.063 mmol). mp 131–133 °C. IR: ν = 1743, 1620, 1611, 1410, 1067 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.17 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.75–7.63 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.46–7.35 (m, 2H), 6.99 (td, *J* = 7.9, 0.7 Hz, 1H), 6.24 (t, *J* = 6.5 Hz, 1H), 4.15–4.04 (m, 2H), 2.81 (d, 2H), 1.63–1.54 (m, 2H), 1.40–1.30 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 174.3, 169.3, 155.5, 154.1, 150.9, 134.1, 133.9, 125.7, 125.4, 123.8, 123.1, 122.0, 121.9, 118.0, 116.9, 112.5, 71.4, 64.9, 39.4, 30.5, 19.1, 13.7. HRMS (ESI$^+$) *m*/*z* calcd for $C_{22}H_{19}ClNaO_5^+$ [M + Na]$^+$: 421.0813, found: 421.0802.

Butyl 2-(3-chloro-7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)acetate (3n). Compound **3n** was prepared (20.1 mg, 53% yield) according to GP I from the flavone derivative (25.8 mg, 0.095 mmol). mp 80–82 °C. IR: ν = 1728, 1642, 1633, 1598 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.15 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.69–7.64 (m, 1H), 7.50 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.41–7.36 (m, 1H), 7.02 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.92 (d, *J* = 1.9 Hz, 1H), 6.12 (dd, *J* = 8.7, 4.1 Hz, 1H), 4.09 (t, *J* = 6.7 Hz, 2H), 2.87–2.75 (m, 2H), 1.61–1.53 (m, 2H), 1.40–1.29 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 174.2, 169.5, 155.8, 155.4, 154.1, 139.6, 133.9, 125.7, 125.4, 124.5, 123.8, 122.4, 118.2, 117.9, 113.9, 111.9, 71.1, 64.7, 39.2, 30.5, 19.1, 13.6. HRMS (ESI$^+$) *m*/*z* calcd for $C_{22}H_{19}ClNaO_5^+$ [M + Na]$^+$: 421.0813, found: 421.0800.

Butyl 2-(2-chloro-7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)acetate (3o). Compound **3o** was prepared (13.8 mg, 55% yield) according to GP I from the flavone derivative (17.2 mg, 0.063 mmol). mp 107–109 °C. IR: ν = 1724, 1631, 1461, 1408, 1065, 1056 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.18 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.76 (d, *J* = 2.6 Hz, 1H), 7.69 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.57–7.52 (m, 1H), 7.41 (ddd, *J* = 8.0, 7.2, 1.1 Hz, 1H), 7.31 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.13 (dd, *J* = 9.0, 3.8 Hz, 1H), 4.09 (t, *J* = 6.6 Hz, 2H), 2.84 (dd, *J* = 15.2, 9.1 Hz, 1H), 2.77 (dd, *J* = 15.2, 3.8 Hz, 1H), 1.61–1.53 (m, 2H), 1.39–1.29 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 174.3, 169.5, 155.5, 153.7, 134.0, 133.6, 127.1, 125.7, 125.5, 123.9, 123.2, 119.3, 118.1, 116.6, 112.6, 70.8, 64.7, 39.1, 30.5, 19.0, 13.7. HRMS (ESI$^+$) *m*/*z* calcd for $C_{22}H_{19}ClNaO_5^+$ [M + Na]$^+$: 421.0813, found: 421.0803.

Butyl 2-(2-bromo-7-oxo-6,7-dihydrochromeno[4,3-*b*]chromen-6-yl)acetate (3p). Compound **3p** was prepared (21.1 mg, 51% yield) according to GP I from the flavone derivative (30.0 mg, 0.095 mmol). mp 114–116 °C. IR: ν = 1724, 1642, 1629, 1407 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.18 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.90 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.72–7.67 (m, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.45 (ddd, *J* = 8.7, 2.4, 0.7 Hz, 1H), 7.46–7.36 (m, 1H), 6.82 (dd, *J* = 8.8, 0.8 Hz, 1H), 6.13 (dd, *J* = 8.9, 3.9 Hz, 1H), 4.09 (t, *J* = 6.7 Hz, 2H), 2.84 (dd, *J* = 15.2, 9.0 Hz, 1H), 2.77 (dd, *J* = 15.3, 3.9 Hz, 1H), 1.61–1.52 (m, 2H), 1.39–1.29 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 174.3, 169.5, 155.5, 154.2, 153.5, 136.5, 134.0, 126.1, 125.7, 125.5, 123.9, 119.7, 118.0, 117.0, 114.1, 112.6, 70.8, 64.7, 39.1, 30.5, 19.0, 13.7. HRMS (ESI$^+$) *m*/*z* calcd for $C_{22}H_{19}BrNaO_5^+$ [M + Na]$^+$: 465.0308, found: 465.0312.

Butyl 2-(7-oxo-6,7-dihydrobenzo[*h*]chromeno[4,3-*b*]chromen-6-yl)acetate (3q). Compound **3q** was prepared (20.2 mg, 52% yield) according to GP I from the flavone derivative (27.3 mg, 0.095 mmol). mp 104–106 °C. IR: ν = 1739, 1640, 1631, 1410, 1054 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.53–8.45 (m, 1H), 8.08 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.90 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.86 (ddd, *J* = 6.0, 3.8, 1.9 Hz, 1H), 7.70 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.69–7.61 (m, 2H), 7.45–7.35 (m, 1H), 7.15–7.06 (m, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.17 (ddd, *J* = 9.1, 3.7, 1.2 Hz, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 2.89 (dd, *J* = 15.3, 9.2 Hz, 1H), 2.82 (dd, *J* = 15.0, 4.0 Hz, 1H), 1.63–1.55 (m, 2H), 1.40–1.31 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 174.1, 169.8, 155.1, 154.2, 152.7, 135.8, 133.9, 129.3, 128.2, 127.2, 125.3, 123.9, 123.3, 122.0, 121.9, 120.6, 120.2, 118.0, 115.5, 113.3, 70.6, 64.7, 39.1, 30.6, 19.1, 13.7. HRMS (ESI$^+$) *m*/*z* calcd for $C_{26}H_{22}NaO_5^+$ [M + Na]$^+$: 437.1359, found: 437.1368.

Butyl 2-(7-oxo-5-tosyl-6,7-dihydro-5*H*-chromeno[3,2-*c*]quinolin-6-yl)acetate (3r). Compound **3r** was prepared (30.3 mg, 62% yield) according to GP I from the flavone derivative (37.1 mg, 0.095 mmol). mp 131–133 °C. IR: ν = 1744, 1726, 1626, 1410 cm^{-1}. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.12 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.82–7.78 (m, 2H), 7.65–7.57 (m, 2H), 7.44 (td, *J* = 7.6, 1.2 Hz, 1H), 7.40–7.36 (m, 2H), 7.17–7.13 (m, 2H), 6.77–6.72 (m, 2H), 6.04 (dd, *J* = 10.0, 4.6 Hz, 1H), 4.09 (td, *J* = 6.8, 1.4 Hz, 2H), 2.55 (dd, *J* = 14.2, 4.6 Hz, 1H), 2.34 (dd, *J* = 14.2, 10.0 Hz, 1H), 1.78 (s, 3H), 1.69–1.61 (m, 2H), 1.44–1.34 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 174.0, 169.2, 155.2, 154.5, 144.0, 135.8, 134.7, 133.7, 132.5, 129.8, 128.9, 127.6, 126.8, 125.6, 125.2, 123.6, 123.4, 123.1, 117.6, 115.3, 65.0, 49.8, 38.2, 30.5, 20.8, 19.1, 13.7. HRMS (ESI$^+$) *m*/*z* calcd for $C_{29}H_{27}NNaO_6S^+$ [M + Na]$^+$: 540.1451, found: 540.1414.

Butyl 2-(7-oxo-6,7-dihydrochromeno[3,4-*c*]chromen-6-yl)-acetate (5a). Compound **5a** was prepared (17.7 mg, 77% yield) according to GP II from the coumarin derivative (15.0 mg, 0.063 mmol). mp 96–98 °C. IR: ν = 1713, 1604, 1173,

1107 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 8.10 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.58–7.52 (m, 1H), 7.45–7.38 (m, 2H), 7.37–7.27 (m, 1H), 7.18–7.12 (m, 1H), 7.08 (d, J = 8.2 Hz, 1H), 5.86 (ddd, J = 7.5, 6.2, 1.1 Hz, 1H), 4.11 (t, J = 6.7 Hz, 2H), 2.68 (s, 1H), 2.66 (d, J = 0.9 Hz, 1H), 1.67–1.54 (m, 2H), 1.44–1.29 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 169.4, 158.7, 154.6, 153.8, 140.4, 132.8, 131.5, 127.6, 126.4, 124.3, 122.3, 119.8, 119.7, 119.0, 117.8, 116.3, 70.0, 64.8, 35.9, 30.6, 19.1, 13.7. HRMS (ESI^+) m/z calcd for $C_{22}H_{20}NaO_5^+$ $[M + Na]^+$: 387.1203, found: 387.1198.

***tert*-Butyl 2-(7-oxo-6,7-dihydrochromeno[3,4-*c*]chromen-6-yl)-acetate (5b).** Compound **5b** was prepared (24.5 mg, 67% yield) according to GP II from the coumarin derivative (23.8 mg, 0.10 mmol). mp 134–136 °C. IR: ν = 1724, 1693, 1606, 1251, 1149 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 8.09 (dd, J = 8.1, 1.6 Hz, 1H), 7.86 (dd, J = 8.0, 1.6 Hz, 1H), 7.54 (ddd, J = 8.4, 7.2, 1.4 Hz, 1H), 7.41 (dddd, J = 9.7, 8.4, 7.2, 1.4 Hz, 2H), 7.35–7.27 (m, 1H), 7.19–7.09 (m, 1H), 7.07 (dd, J = 8.1, 1.2 Hz, 1H), 5.81 (dd, J = 9.7, 4.2 Hz, 1H), 2.65–2.49 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 168.5, 158.6, 154.7, 153.8, 140.3, 132.8, 131.5, 127.6, 126.4, 124.3, 122.2, 120.0, 119.7, 119.0, 117.8, 116.3, 81.2, 70.1, 36.9, 28.0. HRMS (ESI^+) m/z calcd for $C_{22}H_{20}NaO_5^+$ $[M + Na]^+$: 387.1203, found: 387.1197.

Methyl 2-(7-oxo-6,7-dihydrochromeno[3,4-*c*]chromen-6-yl)-acetate (5c). Compound **5c** was prepared (15.0 mg, 74% yield) according to GP II from the coumarin derivative (15.0 mg, 0.063 mmol). mp 176–178 °C. IR: ν = 1733, 1693, 1604, 1175 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 8.11 (d, J = 7.7 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.59–7.54 (m, 1H), 7.46–7.40 (m, 2H), 7.33 (ddd, J = 8.4, 7.3, 1.2 Hz, 1H), 7.16 (td, J = 7.5, 1.1 Hz, 1H), 7.11 (dd, J = 8.2, 1.2 Hz, 1H), 5.87 (dd, J = 8.2, 5.4 Hz, 1H), 3.71 (s, 3H), 2.70 (d, J = 3.2 Hz, 1H), 2.69 (s, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 169.9, 158.7, 154.5, 153.8, 140.5, 132.9, 131.6, 127.7, 126.4, 124.4, 122.4, 119.8, 119.7, 119.0, 117.9, 116.3, 69.9, 52.0, 35.7. HRMS (ESI^+) m/z calcd for $C_{19}H_{14}NaO_5^+$ $[M + Na]^+$: 345.0733, found: 345.0724.

7-(2-Oxopropyl)chromeno[3,4-*c*]chromen-6(7*H*)-one (5d). Compound **5d** was prepared (13.9 mg, 72% yield) according to GP II from the coumarin derivative (15.0 mg, 0.063 mmol). mp 148–150 °C. IR: ν = 1702, 1691, 1587 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 8.20 (dd, J = 8.2, 1.5 Hz, 1H), 8.05 (dd, J = 7.9, 1.5 Hz, 1H), 7.71 (ddd, J = 8.5, 7.3, 1.5 Hz, 1H), 7.54 (td, J = 8.0, 1.4 Hz, 2H), 7.47 (ddd, J = 8.4, 7.3, 1.3 Hz, 1H), 7.27 (td, J = 7.6, 1.3 Hz, 1H), 7.11 (dd, J = 8.1, 1.2 Hz, 1H), 5.78 (dd, J = 10.1, 2.9 Hz, 1H), 2.86 (dd, J = 16.1, 10.2 Hz, 1H), 2.61 (dd, J = 16.1, 3.0 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 204.6, 157.8, 153.9, 153.1, 139.0, 133.0, 131.8, 128.2, 126.4, 124.8, 122.7, 120.1, 119.1, 118.6, 117.4, 115.7, 68.9, 42.9, 30.2. HRMS (ESI^+) m/z calcd for $C_{19}H_{14}NaO_4^+$ $[M + Na]^+$: 329.0784, found: 329.0778.

7-(2-Oxo-2-phenylethyl)chromeno[3,4-*c*]chromen-6(7*H*)-one (5e). Compound **5e** was prepared (18.6 mg, 51% yield) according to GP II from the coumarin derivative (23.8 mg, 0.10 mmol). mp 202–204 °C. IR: ν = 1701, 1679, 1445, 1197, 1109 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 8.13 (dd, J = 8.2, 1.5 Hz, 1H), 7.98–7.94 (m, 2H), 7.91 (dd, J = 7.9, 1.6 Hz, 1H), 7.60–7.52 (m, 2H), 7.47–7.42 (m, 3H), 7.41–7.39 (m, 1H), 7.37–7.32 (m, 1H), 7.18–7.13 (m, 1H), 7.02 (dd, J = 8.2, 1.3 Hz, 1H), 6.07 (dd, J = 8.6, 4.4 Hz, 1H), 3.31 (d, J = 5.2 Hz, 1H), 3.29 (s, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 195.9, 158.9, 154.7, 153.8, 140.5, 136.3, 133.3, 132.9, 131.6, 128.7, 128.4, 127.6, 126.4, 124.4, 122.3, 120.3, 120.1, 119.0, 117.9, 116.4, 70.1, 39.0. HRMS (ESI^+) m/z calcd for $C_{24}H_{16}NaO_4^+$ $[M + Na]^+$: 391.0941, found: 391.0942.

***N*,*N*-Dimethyl-2-(7-oxo-6,7-dihydrochromeno[3,4-*c*]chromen-6-yl)acetamide (5f).** Compound **5f** was prepared (15.5 mg, 46% yield) according to GP II from the coumarin derivative (23.8 mg, 0.10 mmol). mp 201–203 °C. IR: ν = 1693, 1640, 1111 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 8.09 (dd, J = 8.2, 1.6 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.54 (ddd, J = 8.4, 7.2, 1.4 Hz, 1H), 7.46–7.35 (m, 2H), 7.34–7.29 (m, 1H), 7.14 (t, J = 7.9 Hz, 2H), 5.88 (dd, J = 9.7, 3.2 Hz, 1H), 2.94 (s, 3H), 2.93 (s, 3H), 2.75 (dd, J = 14.9, 9.8 Hz, 1H), 2.64 (dd, J = 14.9, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 168.5, 158.9, 154.9, 153.8, 140.3, 132.8, 131.4, 127.6, 126.4, 124.3, 122.1, 120.4, 119.9, 119.1, 117.8, 116.4, 70.1, 37.5, 35.5, 34.1. HRMS (ESI^+) m/z calcd for $C_{20}H_{17}NNaO_4^+$ $[M + Na]^+$: 358.1050, found: 358.1035.

Butyl 2-(2-fluoro-7-oxo-6,7-dihydrochromeno[3,4-*c*]chromen-6-yl)acetate (5g). Compound **5g** was prepared (15.2 mg, 63% yield) according to GP II from the coumarin derivative (16.1 mg, 0.063 mmol). mp 102–104 °C. IR: ν = 1719, 1480, 1273, 1175 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 8.06 (dd, J = 8.2, 1.5 Hz, 1H), 7.62–7.56 (m, 2H), 7.42 (dd, J = 8.3, 1.3 Hz, 1H), 7.36 (ddd, J = 8.4, 7.3, 1.3 Hz, 1H), 7.15 (ddd, J = 8.9, 7.8, 2.9 Hz, 1H), 7.06 (dd, J = 8.9, 4.9 Hz, 1H), 5.85 (dd, J = 7.3, 6.4 Hz, 1H), 4.11 (t, J = 6.7 Hz, 2H), 2.68 (s, 1H), 2.67 (d, J = 0.9 Hz, 1H), 1.65–1.57 (m, 2H), 1.42–1.32 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 169.3, 158.6 (d, J_{CF} = 28.5 Hz), 155.0 (d, J_{CF} = 259.5 Hz), 150.5, 139.6, 131.8, 125.9, 124.6, 120.9 (d, J_{CF} = 8.1 Hz), 120.8, 119.8 (d, J_{CF} = 8.3 Hz), 119.5 (d, J_{CF} = 23.1 Hz), 118.0, 115.9, 114.0 (d, J_{CF} = 25.5 Hz), 70.2, 64.9, 35.8, 30.6, 19.1, 13.7. HRMS (ESI^+) m/z calcd for $C_{22}H_{19}FNaO_5^+$ $[M + Na]^+$: 405.1109, found: 405.1099.

Butyl 2-(2-chloro-7-oxo-6,7-dihydrochromeno[3,4-*c*]chromen-6-yl)acetate (5h). Compound **5h** was prepared (22.6 mg, 78% yield) according to GP II from the coumarin derivative (17.2 mg, 0.063 mmol). mp 102–104 °C. IR: ν = 1722, 1265, 1246, 1182 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 8.03 (dd, J = 8.2, 1.5 Hz, 1H), 7.85 (d, J = 2.5 Hz, 1H), 7.58 (ddd, J = 8.5, 7.3, 1.5 Hz, 1H), 7.41 (dd, J = 8.4, 1.2 Hz, 1H), 7.39–7.34 (m, 2H), 7.03 (d, J = 8.7 Hz, 1H), 5.85 (dd, J = 7.7, 6.0 Hz, 1H), 4.11 (t, J = 6.7 Hz, 2H), 2.68 (s, 1H), 2.66 (d, J = 1.7 Hz, 1H), 1.64–1.56 (m, 2H), 1.41–1.31 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 169.2, 158.4, 153.7, 153.1, 139.3, 132.5, 131.9, 127.4, 127.2, 125.9, 124.7, 121.1, 120.5, 120.2, 117.9, 115.8, 70.3, 64.9, 35.9, 30.6, 19.0, 13.7. HRMS (ESI^+) m/z calcd for $C_{22}H_{19}ClNaO_5^+$ $[M + Na]^+$: 421.0813, found: 421.0807.

Butyl 2-(11-methyl-7-oxo-6,7-dihydrochromeno[3,4-*c*]chromen-6-yl)acetate (5i). Compound **5i** was prepared (27.6 mg, 74% yield) according to GP II from the coumarin derivative (25.2 mg, 0.10 mmol). IR: ν = 1702, 1387, 1257, 1166 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 7.91–7.82 (m, 2H), 7.41 (ddd, *J* = 8.1, 7.4, 1.5 Hz, 1H), 7.34 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.16 (td, *J* = 7.6, 1.2 Hz, 1H), 7.07 (dd, *J* = 8.2, 1.2 Hz, 1H), 5.83 (t, *J* = 6.9 Hz, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 2.65 (d, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 1.60 (m, 2H), 1.43–1.29 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 169.5, 158.8, 154.5, 151.9, 140.3, 134.0, 132.7, 132.5, 127.6, 126.1, 122.2, 119.7, 119.7, 119.0, 117.4, 115.9, 70.0, 64.7, 35.8, 30.6, 21.1, 19.0, 13.6. HRMS (ESI^+) *m*/*z* calcd for $C_{23}H_{22}NaO_5^+$ $[M + Na]^+$: 401.1359, found: 401.1351.

Butyl 2-(14-oxo-1,14-dihydrobenzo[*h*]chromeno[3,4-*c*]chromen-1-yl)acetate (5j). Compound **5j** was prepared (36.9 mg, 60% yield) according to GP II from the coumarin derivative (43.2 mg, 0.15 mmol). mp 106–108 °C. IR: ν = 1737, 1711, 1604, 1357, 1098 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 8.58–8.50 (m, 1H), 8.03 (d, *J* = 8.9 Hz, 1H), 7.92 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.89–7.81 (m, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.68–7.56 (m, 2H), 7.49–7.40 (m, 1H), 7.18 (td, *J* = 7.7, 1.3 Hz, 1H), 7.11 (dd, *J* = 8.2, 1.2 Hz, 1H), 5.91 (dd, *J* = 7.9, 5.8 Hz, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 2.73 (s, 1H), 2.71 (d, *J* = 2.0 Hz, 1H), 1.69–1.57 (m, 2H), 1.44–1.34 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 169.5, 158.6, 154.7, 151.1, 141.3, 134.3, 132.8, 128.9, 127.9, 127.5, 127.2, 124.1, 123.5, 122.6, 122.3, 121.8, 119.8, 119.3, 119.2, 111.6, 70.1, 64.8, 35.9, 30.6, 19.1, 13.7. HRMS (ESI^+) *m*/*z* calcd for $C_{26}H_{22}NaO_5^+$ $[M + Na]^+$: 437.1359, found: 437.1372.

Butyl 2-(10-fluoro-7-oxo-6,7-dihydrochromeno[3,4-*c*]chromen-6-yl)acetate (5k). Compound **5k** was prepared (17.2 mg, 71% yield) according to GP II from the coumarin derivative (16.1 mg, 0.063 mmol). mp 101–103 °C. IR: ν = 1724, 1611, 1272, 1151 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 8.10 (dd, *J* = 9.0, 5.9 Hz, 1H), 7.82 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.46–7.41 (m, 1H), 7.18–7.04 (m, 4H), 5.84 (dd, *J* = 8.1, 5.5 Hz, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 2.67 (d, *J* = 2.8 Hz, 1H), 2.65 (s, 1H), 1.66–1.54 (m, 2H), 1.42–1.31 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 169.4, 164.0 (d, J_{CF} = 254.8 Hz), 158.4, 155.1 (d, J_{CF} = 12.5 Hz), 154.7, 140.2, 133.1, 128.2 (d, J_{CF} = 9.9 Hz), 127.4, 122.4, 119.9, 118.8, 118.6 (d, J_{CF} = 2.5 Hz), 113.0 (d, J_{CF} = 3.1 Hz), 112.4 (d, J_{CF} = 22.4 Hz), 105.2 (d, J_{CF} = 25.3 Hz), 69.9, 64.8, 35.9, 30.6, 19.1, 13.7. HRMS (ESI^+) *m*/*z* calcd for $C_{22}H_{19}FNaO_5^+$ $[M + Na]^+$: 405.1109, found: 405.1099.

Butyl 2-(11-chloro-7-oxo-6,7-dihydrochromeno[3,4-*c*]chromen-6-yl)acetate (5l). Compound **5l** was prepared (24.8 mg, 63% yield) according to GP II from the coumarin derivative (27.3 mg, 0.10 mmol). mp 93–95 °C. IR: ν = 1719, 1270, 1166 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 8.05 (t, *J* = 1.9 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.54–7.45 (m, 1H), 7.49–7.40 (m, 1H), 7.34 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.21–7.16 (m, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 5.84 (ddd, *J* = 8.3, 5.2, 1.4 Hz, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 2.67 (dd, *J* = 4.0, 1.2 Hz, 1H), 2.65 (d, *J* = 1.0 Hz, 1H), 1.66–1.54 (m, 2H), 1.41–1.31 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 169.3, 158.1, 154.5, 152.2, 139.5, 133.1, 131.5, 129.9, 127.2, 125.9, 122.6, 120.7, 119.8, 119.2, 118.5, 117.4, 69.9, 64.8, 35.8, 30.6, 19.0, 13.6. HRMS (ESI^+) *m*/*z* calcd for $C_{22}H_{19}ClNaO_5^+$ $[M + Na]^+$: 421.0813, found: 421.0808.

Butyl 2-(10-methoxy-7-oxo-6,7-dihydrochromeno[3,4-*c*]chromen-6-yl)acetate (5m). Compound **5m** was prepared (49.8 mg, 84% yield) according to GP II from the coumarin derivative (40.2 mg, 0.15 mmol). mp 135–137 °C. IR: ν = 1701, 1609, 1280, 1167 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 7.98 (d, *J* = 9.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.43–7.38 (m, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.91–6.83 (m, 2H), 5.82 (t, *J* = 6.8 Hz, 1H), 4.10 (t, *J* = 6.6 Hz, 2H), 3.86 (s, 3H), 2.65 (d, *J* = 7.0 Hz, 2H), 1.64–1.56 (m, 2H), 1.43–1.30 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 169.5, 162.3, 158.9, 155.7, 154.6, 140.6, 132.7, 127.6, 127.4, 122.2, 119.7, 119.1, 116.6, 112.5, 109.6, 101.5, 69.9, 64.7, 55.7, 36.1, 30.6, 19.0, 13.7. HRMS (ESI^+) *m*/*z* calcd for $C_{23}H_{22}NaO_6^+$ $[M + Na]^+$: 417.1309, found: 417.1294.

Butyl 2-(10-(dimethylamino)-7-oxo-6,7-dihydrochromeno[3,4-*c*]-chromen-6-yl)acetate (5n). Compound **5n** was prepared (15.5 mg, 61% yield) according to GP II from the coumarin derivative (17.7 mg, 0.063 mmol). mp 95–97 °C. IR: ν = 1728, 1691, 1596 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 7.89 (d, *J* = 9.1 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.39 (ddd, *J* = 8.1, 7.4, 1.5 Hz, 1H), 7.11 (td, *J* = 7.6, 1.2 Hz, 1H), 7.06 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.63 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.56 (d, *J* = 2.6 Hz, 1H), 5.82 (dd, *J* = 8.2, 5.6 Hz, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 3.05 (s, 6H), 2.66 (s, 1H), 2.64 (d, *J* = 2.7 Hz, 1H), 1.65–1.57 (m, 2H), 1.42–1.33 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 169.8, 159.6, 156.1, 154.7, 152.4, 140.9, 132.3, 127.7, 127.2, 122.0, 119.6, 119.6, 113.8, 109.1, 105.5, 98.8, 70.1, 64.7, 40.0, 36.4, 30.6, 19.1, 13.7. HRMS (ESI^+) *m*/*z* calcd for $C_{24}H_{25}NNaO_5^+$ $[M + Na]^+$: 430.1625, found: 430.1628.

Butyl 2-(6-oxo-8-tosyl-7,8-dihydro-6*H*-chromeno[3,4-*c*]quinolin-7-yl)acetate (5o). Compound **5o** was prepared (26.5 mg, 51% yield) according to GP II from the coumarin derivative (39.2 mg, 0.10 mmol). mp 97–99 °C. IR: ν = 1724, 1701, 1354, 1155 cm^{-1}. ^1H NMR (400 MHz, chloroform-*d*) δ 7.83 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.65 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.61 (td, *J* = 7.8, 1.5 Hz, 1H), 7.51–7.41 (m, 2H), 7.27 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.27–7.18 (m, 1H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.64 (d, *J* = 8.1 Hz, 2H), 5.88 (dd, *J* = 10.3, 4.6 Hz, 1H), 4.11 (td, *J* = 6.8, 1.8 Hz, 2H), 2.51 (dd, *J* = 14.3, 4.6 Hz, 1H), 2.13 (dd, *J* = 14.3, 10.4 Hz, 1H), 1.71–1.62 (m, 5H), 1.46–1.34 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 168.8, 158.5, 153.3, 143.9, 140.3, 135.7, 134.3, 131.7, 131.3, 131.3, 129.2, 127.6, 127.4, 126.7, 126.3, 125.8, 123.9, 121.5, 117.4, 115.6, 65.1, 50.8, 36.1, 30.5, 20.8, 19.1, 13.7. HRMS (ESI^+) *m*/*z* calcd for $C_{29}H_{27}NNaO_6S^+$ $[M + Na]^+$: 540.1451, found: 540.1471.

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