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Domino Reactions of 1,3-Bis-Silyl Enol Ethers with Benzopyrylium Triflates: Efficient Synthesis of Fluorescent 6*H*-Benzo[*c*]chromen-6-ones, Dibenzo[*c,d*]chromen-6-ones, and 2,3-Dihydro-1*H*-4,6-dioxachrysen-5-ones

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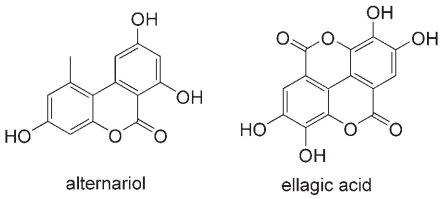
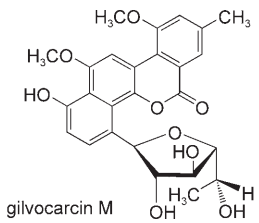
Abstract: The condensation of 1,3-bis-silyl enol ethers with benzopyrylium triflates, generated in situ by the reaction of chromones with Me_3SiOTf, afforded functionalized 2,3-dihydrobenzopyrans; treatment of the latter with NEt_3 or BBr_3 resulted in a domino retro-Michael–aldol–lactonization reaction and the formation of a variety of 7-hydroxy-6*H*-benzo[*c*]chromen-6-ones. The hydroxy group was functionalized by using Suzuki cross-coupling reactions. The methodology reported was applied to the synthesis of the natural product autumnariol and a new fluorescence dye, which exhibits promising optical properties. 2,3-Dihydro-1*H*-4,6-dioxachrysen-5-ones were prepared by condensation of chromones with 1,3-bis-silyl enol ethers containing a remote chloride group, domino retro-Michael–aldol–lactonization, and an intramolecular Williamson reaction.

Keywords: chromones · domino reactions · heterocycles · lactones · natural products

Introduction

Functionalized 6*H*-benzo[*c*]chromen-6-ones (dibenzo[*b*,*d*]pyran-6-ones, biaryl lactones) are present in a variety of pharmacologically relevant natural products. Autumnariol has been isolated from onions of *Eucomis autumnalis* Greab. (Liliaceae),[1] and a number of related natural products, such as autumnariniol,[2] alternariol,[3] and altenuisol[4] are known.[5] 6*H*-Benzo[*c*]chromen-6-ones represent specific inhibitors of endothelic cell[6] and oestrogene receptor[7] growth. Related structures, such as ellagic and coruleoellagic acid, contain an additional lactone bridge.[8] These compounds occur both as glycosides and aglycons and have been mainly isolated from plant sources. Dibenzo[*c,d*]chromen-6-ones (benzo[*d*]naphthopyran-6-ones) can be regarded as benzo-annulated 6*H*-benzo[*c*]chromen-6-ones and occur in a number of antibiotics and antitumor agents isolated from *Streptomyces*, for example, the gilvocarcins, chrysomycins, and ravidomycins.[9]





The classic approach to the synthesis of 6*H*-benzo[*c*]chromen-6-ones relies on the cyclization of *o*-bromobenzoic acids with phenols; however, this method is limited to acti-

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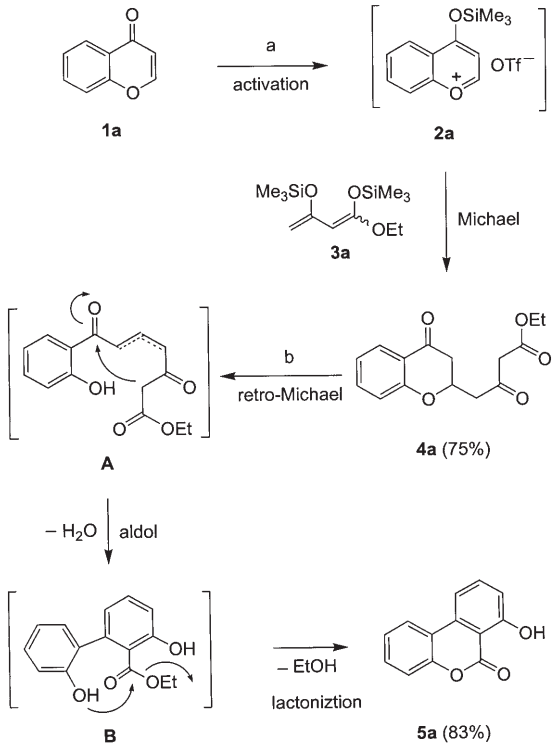
vated substrates and the yields are often low.[10] More recently, a number of syntheses utilizing transition-metal-catalyzed reactions have been reported. For example, 6*H*-benzo[*c*]chromen-6-ones can been obtained by the intramolecular Pd^{II}-catalyzed coupling reactions of aryl benzoates.[11] An efficient and versatile synthesis of 6*H*-benzo[*c*]chromen-6-ones—developed by Snieckus et al.—relies on sequential directed *ortho*-metalation (DoM)/Suzuki reactions.[12] A related approach, based on sequential [3+3] Suzuki cyclization reactions, has recently been reported by us.[13] Zhou et al. reported the palladium-catalyzed insertion of carbon oxide into boroxarenes, which are readily synthesized from *ortho*-hydroxybiaryls.[14]

In the course of their elegant work related to the synthesis of polyketides,[15] Harris et al. reported the synthesis of 9-*O*-methylalternariol by the condensation of the dianion of acetylacetone with a protected salicylate.[16] This work inspired us to develop an alternative approach to 6*H*-benzo[*c*]chromen-6-ones: some years ago, we reported[17] the condensation of 1,3-bis-silyl enol ethers[18] with 4-silyloxybenzopyrylium triflates, generated in situ from chromones,[19] to give 2,3-benzopyrans; the latter were transformed into 7-hydroxy-6*H*-benzo[*c*]chromen-6-ones by domino retro-Michael–aldol–lactonization reactions. Herein, we report full details of these studies. With regard to our preliminary communication,[17] the preparative scope has been considerably extended and a great variety of 7-hydroxy-6*H*-benzo[*c*]chromen-6-ones and dibenzo[*c,d*]chromen-6-ones are now available; the hydroxy group can be functionalized by Suzuki cross-coupling reactions. In addition, the natural product autumnariol was prepared by our methodology. Notably, 7-hydroxy-6*H*-benzo[*c*]chromen-6-ones exhibit strong fluorescence and, based on optimization studies, a potentially useful blue fluorescence dye has been developed. 2,3-dihydro-1*H*-4,6-dioxachrysen-5-ones have also been prepared by using domino retro-Michael–aldol–lactonization reactions of novel chloro-substituted 1,3-bis-silyl enol ethers.

Abstract in German: *Die Umsetzung von 1,3-Bis-Silylenolethern mit Benzopyryliumtriflaten, in situ generiert durch Behandlung von Chromonen mit Me_3SiOTf, liefert funktionalisierte 2,3-Dihydrobenzopyrane; deren Umsetzung mit NEt_3 oder BBr_3 ermöglicht die Herstellung einer großen Bandbreite von 7-Hydroxy-6*H*-benzo[c]chromen-6-onen durch neuartige Domino Retro-Michael–Aldol–Lactonisierungs Reaktionen. Die Hydroxylgruppe der Produkte kann durch Suzuki Kreuzkupplungsreaktionen funktionalisiert werden. Die entwickelte Methodik wurde erfolgreich zur Darstellung des Naturstoffs Autumnariol und zur Synthese eines neuen Fluoreszenzfarbstoffes eingesetzt. Weiterhin wurden 2,3-Dihydro-1H-4,6-dioxachrysen-5-one basierend auf der Umsetzung von Chromonen mit Chloralkyl-substituierten 1,3-Bis-Silylenolethern hergestellt.*

Results and Discussion

Optimization: The reaction of parent chromone (**1a**) with 1,3-bis-silyl enol ether **3a**[20] in the presence of Me_3SiOTf afforded the 2,3-dihydrobenzopyran **4a** with very good regioselectivity (Scheme 1). Treatment of **4a** with NEt_3 afforded



Scheme 1. Mechanism for the formation of 7-hydroxy-6*H*-benzo[*c*]chromen-6-one **5a**: a) 1) Me_3SiOTf (1.3 equiv), 20 °C, 1 h; 2) **3a** (1.3 equiv), CH_2Cl_2, 0→20 °C, 12 h; 3) HCl (10 %); b) NEt_3 (2.0 equiv), EtOH, 20 °C, 12 h.

the 7-hydroxy-6*H*-benzo[*c*]chromen-6-one **5a**. Optimal yields (up to 62 % over two steps) were obtained after a careful optimization process: the presence of Me_3SiOTf was mandatory for the activation of **1a**, and thus the in situ generation of benzopyrylium triflate **2a**.[19] In contrast to our original protocol,[17] the use of base (2,6-lutidine) is not required (0→20 °C, 12 h). Hydrochloric acid (10 %) was used for the aqueous workup to completely hydrolyze the silyl enol ether groups of intermediate **A**. With regards to the second step in the synthesis, the base (NEt_3), solvent (EtOH), temperature (20 °C), and reaction time (12 h) played an important role. Stirring of the solution under reflux resulted in a shorter reaction time (1 h), but also a decreased yield (64 % versus 83 %). A dramatic decrease in the yield was observed when the base or solvent was changed (LDA/THF, NEt_3/THF, KO*t*Bu/EtOH, or K_2CO_3/EtOH). The treatment of a stirred solution of **4a** in CH_2Cl_2 with BBr_3 (8.0 equiv) for 12 h at 20 °C, followed by the addi-

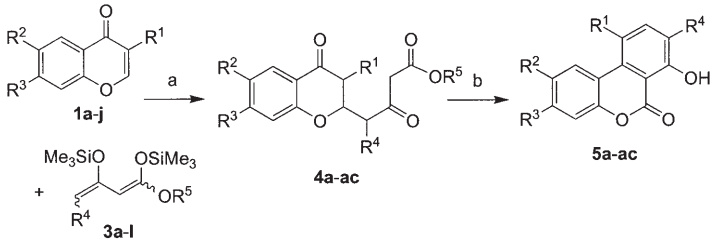
tion of water afforded **5a**, however, again in reduced yield (55% versus 83%).

A domino retro-Michael–aldol–lactonization reaction (Scheme 1) is responsible for the formation of **5a** from **4a**. The base-induced retro-Michael reaction initially results in formation of intermediate **A**, which subsequently undergoes an aldol reaction, followed by the elimination of water to produce intermediate **B**. Finally, 7-hydroxy-6*H*-benzo[*c*]-chromen-6-one **5a** is formed by lactonization.

Preparative scope: The preparative scope of our methodology was studied (Table 1). The reaction of **1a** with 1,3-bis-silyl enol ethers **3a–i**, prepared from the corresponding β-ketoesters, afforded the 2,3-dihydrobenzopyrans **4a–i**, which were transformed into the alkyl-substituted 7-hydroxy-6*H*-benzo[*c*]chromen-6-ones **5a–i** (R^4 = Alkyl, Allyl, or Bn). By starting with **3j**, readily synthesized from methyl 4-methoxyacetoacetate, the methoxy-substituted 6*H*-benzo[*c*]chromen-6-one **5j** was prepared; treatment of the latter with BBr_3 afforded the 7,8-di(hydroxy)-6*H*-benzo[*c*]chromen-6-one **5k**. The benzyloxy-substituted 6*H*-benzo[*c*]chromen-6-one **5l** was prepared from **1a** and 1,3-bis-silyl enol ether **3k**. Next, we studied variation of the chromone. Thus, 7-hydroxy-6*H*-benzo[*c*]chromen-6-ones **5m–x**, containing various substituents at carbon atoms C-2 or C-3, were prepared from chromones **1b–h** (R^2, R^3 = Me, MeO, OH, BnO, Cl, or Br). The reaction of **3a** with 3-methylchromone (**1i**) afforded **4y**, which was transformed into **5y**; this compound contains a methyl group at carbon C-10 (R^1 = Me). The cyano-substituted 7-hydroxy-6*H*-benzo[*c*]chromen-6-ones **5z–ac** (R^1 = CN) were prepared from 1,3-bis-silyl enol ethers **3b,c,f,l** and 3-cyanochromone (**1j**). 7,8-Di(hydroxy)-6*H*-benzo[*c*]chromen-6-ones **5o** and **5w** were prepared in high yields by the reaction of BBr_3 with **5n** and **5v**, respectively.

The structure of **5q** was independently confirmed by crystal structure analysis (Figure 1). The 6*H*-benzo[*c*]chromen-6-one core structure is flat and an intramolecular hydrogen bond O(3)–H···O(2) is observed. The latter was observed for all products, as determined by ^{1}H NMR spectroscopic analysis.

Table 1. Synthesis of 7-hydroxy-6*H*-benzo[*c*]chromen-6-ones **5a–ac**.[a]



1	3	5	R^1	R^2	R^3	R^4	R^5	Yield **5** [%][b]
a	**a**	**a**	H	H	H	H	Et	62
a	**b**	**b**	H	H	H	Me	Me	54
a	**c**	**c**	H	H	H	Et	Et	58
a	**d**	**d**	H	H	H	Allyl	Et	43
a	**e**	**e**	H	H	H	Bn	Et	20
a	**f**	**f**	H	H	H	*n*Bu	Et	48
a	**g**	**g**	H	H	H	*n*Hex	Et	45
a	**h**	**h**	H	H	H	*n*Hep	Et	48
a	**i**	**i**	H	H	H	*n*Oct	Et	51
a	**j**	**j**	H	H	H	OMe	Me	65
		k	H	H	H	OH	–	84[c]
a	**k**	**l**	H	H	H	OBn	Et	20
b	**a**	**m**	H	Me	H	H	Et	54
c	**a**	**n**	H	OMe	H	H	Et	61
		o	H	OH	H	H	–	87[d]
d	**a**	**p**	H	Cl	H	H	Et	56
d	**b**	**q**	H	Cl	H	Me	Me	57
d	**f**	**r**	H	Cl	H	*n*Bu	Et	59
d	**g**	**s**	H	Cl	H	*n*Hex	Et	56
e	**a**	**t**	H	Br	H	H	Et	47
f	**a**	**u**	H	Cl	Me	H	Et	62
g	**a**	**v**	H	H	OMe	H	Et	51
		w	H	H	OH	H	–	91[e]
h	**a**	**x**	H	H	OBn	H	Et	48
i	**a**	**y**	Me	H	H	H	Et	48
j	**b**	**z**	CN	H	H	Me	Me	34
j	**c**	**aa**	CN	H	H	Et	Et	34
j	**l**	**ab**	CN	H	H	*n*Pr	Et	37
j	**f**	**ac**	CN	H	H	*n*Bu	Et	42

[a] Reaction conditions: a) 1) Me_3SiOTf (1.3 equiv), 20°C, 1 h; 2) **3a–l** (1.3 equiv), CH_2Cl_2, 0→20°C, 12 h; 3) HCl (10%); b) NEt_3 (2.0 equiv), EtOH, 20°C, 12 h. [b] Isolated yields based on chromones **1a–j**. [c] from **5j**. [d] from **5n**. [e] from **5v**.

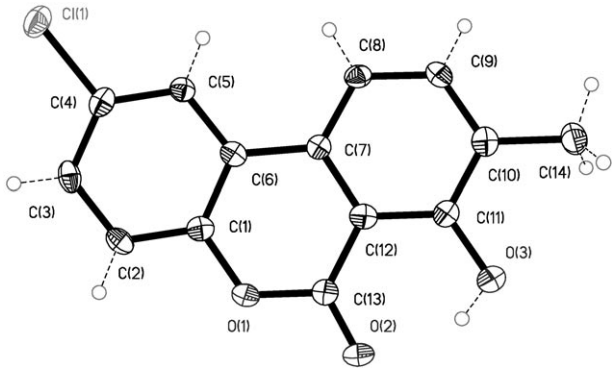
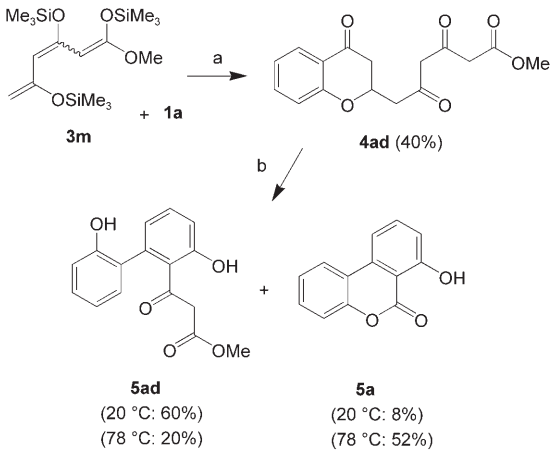


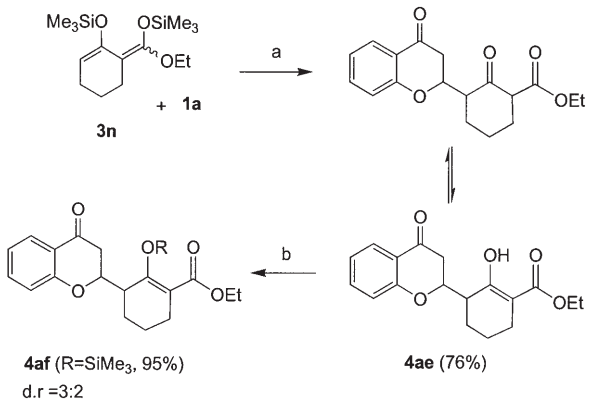
Figure 1. ORTEP-plot of **5q**. Selected bond lengths [Å] and angles [°]: O(1)-C(13) 135.5(3), O(1)-C(1) 137.7(3), C(1)-C(6) 139.4(3), O(2)-C(13) 121.6(3), O(3)-C(11) 135.2(3), C(6)-C(7) 146.0(3), C(7)-C(12) 140.7(3), C(10)-C(11) 139.7(4), O(2)-C(13)-O(1) 115.9(2), O(2)-C(13)-C(12) 125.2(2), O(1)-C(13)-C(12) 118.9(2).

The reaction of **1a** with 1,3,5-tris-silyl enol ether **3m**[21] afforded the masked pentaketide **4ad**; the reaction of the latter with NEt_3 at 20°C afforded the biaryl **5ad** (Scheme 2). Unexpectedly, when the reaction was carried out under reflux the biaryl **5ad** was isolated in a yield of only 20% and the 6*H*-benzo[*c*]chromen-6-one **5a** was formed, presumably by the formation of a hemiketal, followed by a retro-aldol reaction with extrusion of methyl acetate.

The reaction of cyclic 1,3-bis-silyl enol ether **3n**[22] with **1a** afforded the condensation product **4ae** as a mixture of diastereomers and keto/enol tautomers (Scheme 3); to simplify the NMR spectra, **4ae** was transformed into the silyl enol ether **4af**. Only starting material was recovered in the reaction of **4ae** with NEt_3/EtOH.

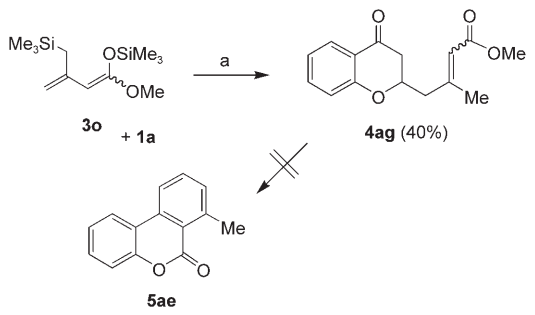


Scheme 2. Reaction of 1,3,5-tris-silyl enol ether **3m** with **1a**: a) 1) Me_3SiOTf (1.3 equiv), 20 °C, 1 h; 2) **3m** (1.3 equiv), CH_2Cl_2, 0→20 °C, 12 h; 3) HCl (10%); b) NEt_3 (2.0 equiv), EtOH (12 h, 20 °C or 3 h, 78 °C).



Scheme 3. Reaction of cyclic 1,3-bis-silyl enol ether **3n** with **1a**: a) 1) Me_3SiOTf (1.3 equiv), 20 °C, 1 h; 2) **3a** (1.3 equiv), CH_2Cl_2, 0→20 °C, 12 h; 3) HCl (10%); b) Me_3SiCl, benzene, 20 °C.

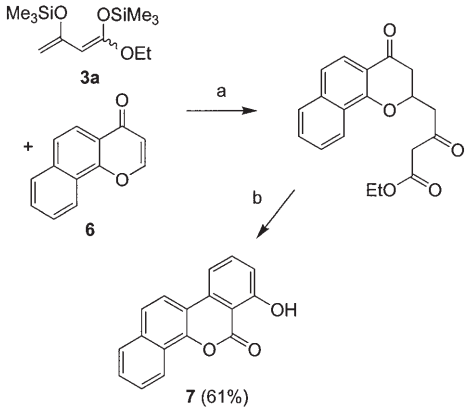
The reaction of **1a** with silyl enol ether **3o**, a carba-analogue of **3a**,[20] afforded the condensation product **4ag**; however, this product could not be transformed into the 6*H*-benzo[*c*]chromen-6-one **5ae** (Scheme 4). This result suggests



Scheme 4. Reaction of silyl enol ether **3o** with **1a**: a) 1) Me_3SiOTf (1.3 equiv), 20 °C, 1 h; 2) **3a** (1.3 equiv), CH_2Cl_2, 0→20 °C, 12 h; 3) HCl (10%).

that the presence of a 1,3-dicarbonyl unit is mandatory for a domino retro-Michael–aldol–lactonization reaction to proceed.

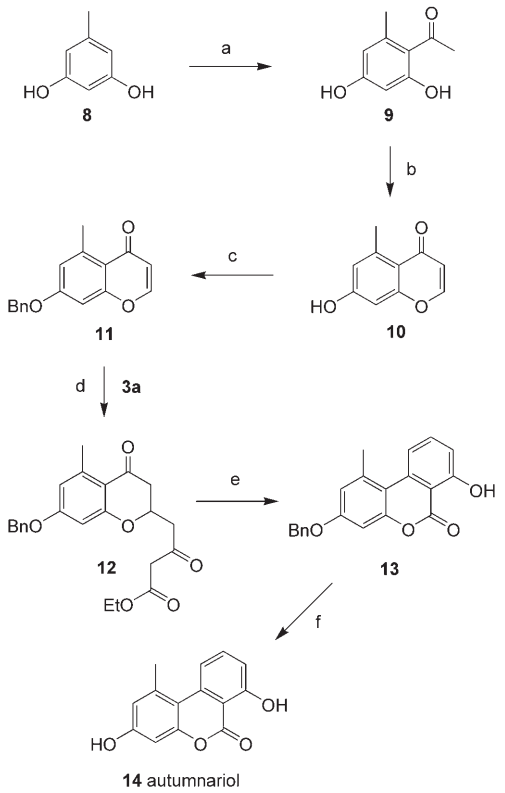
Synthesis of 7-hydroxydibenzo[*c,d*]chromen-6-ones: The condensation reaction of benzo[*h*]chromone (**6**) with 1,3-bis-silyl enol ether **3a**, followed by NEt_3-mediated domino retro-Michael–aldol–lactonization, afforded 7-hydroxydibenzo[*c,d*]chromen-6-one (**7**) (Scheme 5).



Scheme 5. Synthesis of 7-hydroxydibenzo[*c,d*]chromen-6-one **7**: a) 1) Me_3SiOTf (1.3 equiv), 20 °C, 1 h; 2) **3a** (1.3 equiv), CH_2Cl_2, 0→20 °C, 12 h; 3) HCl (10%); b) NEt_3 (2.0 equiv), EtOH, 20 °C, 12 h.

Synthesis of autumnariol: Farkas et al. reported[23] the first synthesis of autumnariol. This synthesis was based on methodology reported by Hurtley;[10] however, the condensation of orcine (orcinol, **8**) with 2-bromo-6-methoxybenzoic acid, the key step in the synthesis, produced a yield of only 19% for the expected product. Snieckus et al. reported an efficient synthesis of autumnariol, which ultilized the Suzuki reaction of [3,4-dimethoxy-2-(diisopropylcarbamoyl)phenyl]-boronic acid with 2,4-dimethoxy-6-methylbromobenzene.[12] We have developed the following alternative synthesis, based on our own methodology. The acetylation of orsinol (**8**) afforded the acetophenone **9**, which was transformed into the chromone **10** by treatment with triethylorthoformate in the presence of perchloric acid (Scheme 6). Benzylation of **10** produced **11**, which was transformed into the 2,3-dihydrobenzopyran **12** by reaction with **3a**. Treatment of **12** with NEt_3/EtOH afforded the 7-hydroxy-6*H*-benzo[*c*]-chromen-6-one **13**. Debenzylation with BBr_3 finally afforded autumnariol (**14**) in 4% yield (over six steps).

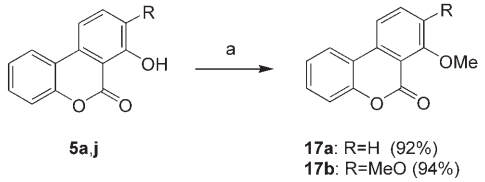
Functionalization of 7-hydroxy-6*H*-benzo[*c*]chromen-6-ones: Next we studied the functionalization of the hydroxy group of 7-hydroxy-6*H*-benzo[*c*]chromen-6-ones **5** by Suzuki cross-coupling reactions. Thus, 7-hydroxy-6*H*-benzo[*c*]chromen-6-one **5a** was transformed into the triflate **15** in 91% yield. The Suzuki reaction of **5a** with a number of boronic acids afforded, under standard conditions, 7-aryl-6*H*-ben-



Scheme 6. Synthesis of autumnariol: a) MeCN (2.0 equiv), $ZnCl_2$ (0.3 equiv), Et_2O, 3 h, 20 °C, 41 %; b) $HC(OEt)_3$ (10 equiv), $HClO_4$ (1.3 equiv), 12 h, 0→20 °C, 56 %; c) BnCl (1.0 equiv), K_2CO_3 (0.5 equiv), EtOH, 7 h, reflux, 76 %; d) 1) Me_3SiOTf (0.3 equiv), 30 min; 2) **3a** (1.3 equiv), CH_2Cl_2, 6 h, 0→20 °C; 3) HCl (10 %), 67 %; e) 1) NEt_3 (2.0 equiv), EtOH, 12 h, 20 °C; 2) 12 h, reflux, 34 %, 81 % b.o.r.s.m (b.o.r.s.m = based on recovered starting material); f) BBr_3 (4 equiv), CH_2Cl_2, 1 h, 0 °C, 92 %.

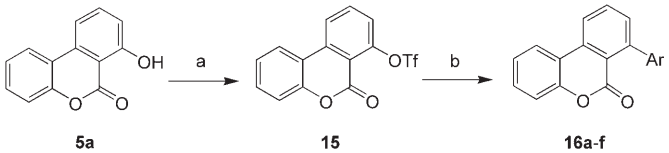
zo[*c*]chromen-6-ones **16a–f** in good to very good yields (Table 2).

Fluorescence of 6*H*-benzo[*c*]chromen-6-ones: A number of fluorescent materials are known in organic chemistry; however, blue fluorescence is more rare than fluorescence at other wavelengths. For technical applications of blue fluorescent materials a fluorescence maximum in the range of 450–480 nm is desirable; in addition, the Stokes shift should be less than 50 nm. Most of the 6*H*-benzo[*c*]chromen-6-ones reported herein exhibit a blue–green fluorescence in the range of approximately 480–500 nm (Table 3) and the Stokes shift is rather large (ca. 150 nm). The thienyl-substituted 6*H*-benzo[*c*]chromen-6-one **16f** produces a promising fluorescence maximum (452 nm); however, the Stokes shift is again rather large. Much to our satisfaction, 6*H*-benzo[*c*]-chromen-6-ones **5j** and **5l**, which contain a methoxy- and a benzyloxy group at carbon C-8, exhibit a fluorescence maximum at approximately 456 nm and a Stokes shift at 65 nm. To further optimize these properties, the methoxy-substituted 6*H*-benzo[*c*]chromen-6-ones **17a** and **17b** were prepared by the methylation of **5a** and **5j** (Scheme 7). However, the methylation resulted in a hypsochromic effect and a shift of the fluorescence to (**17a**: 374 nm; **17b**: 406 nm) the UV rather than the visible region. In conclusion, the best results were obtained for 6*H*-benzo[*c*]chromen-6-ones **5j** and **5l**.



Scheme 7. Synthesis of **17a,b**: a) 1) K_2CO_3 (1.5 equiv), 20 °C, acetone; 2) Me_2SO_2 (1.1 equiv), 0 °C; 3) 6 h, reflux; 4) 12 h, 20 °C.

Table 2. Synthesis of 7-aryl-6*H*-benzo[*c*]chromen-6-ones **16a–f** by Suzuki reactions of triflate **15**.[a]



16	Ar	Yield [%][b]
a	Ph	92
b	4-MeC_6H_4	86
c	4-$(MeO)C_6H_4$	79
d	3,4,5-$(MeO)_3C_6H_2$	89
e	4-ClC_6H_4	74
f	2-Thienyl	66

[a] Reaction conditions a) Tf_2O (1.6 equiv), pyridine (2.0 equiv), CH_2Cl_2, −78→20 °C, 10 h, 91 %; b) K_3PO_4 (1.6 equiv), $ArB(OH)_2$ (1.3 equiv), Pd-$(PPh_3)_4$ (3 mol %), 4–12 h, 100 °C. [b] Isolated yields.

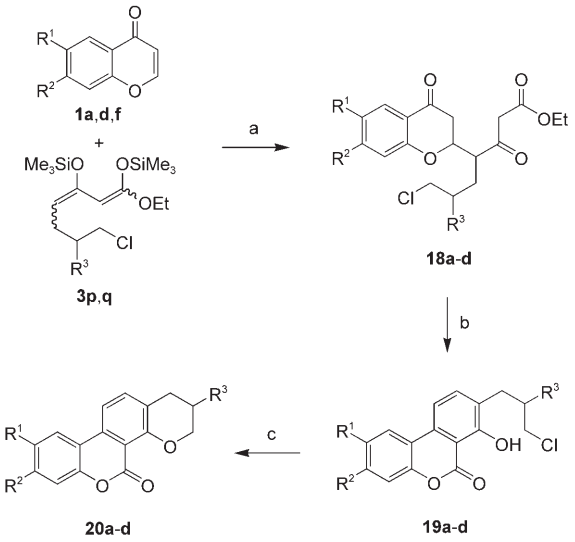
Synthesis of 2,3-dihydro-1*H*-4,6-dioxachrysen-5-ones: The Me_3SiOTf-mediated condensation of chromone (**1a**) with 1,3-bis-silyl enol ether **3p**, prepared from ethyl 7-chloro-3-oxoheptanoate, afforded the corresponding 2,3-dihydrobenzopyran **18a**, which was transformed into the 6*H*-benzo[*c*]-chromen-6-one **19a** by a NEt_3-mediated domino retro-Michael–aldol–lactonization reaction (Scheme 8, Table 4). Treatment of **19a** with sodium hydride in the presence of tetrabutylammonium iodide (TBAI) afforded the 2,3-dihydro-1*H*-4,6-dioxachrysen-5-one **20a**. Similarly, **20b** and **20c** were prepared from **3p** and from chromones **1d** and **1f**. The condensation of **1a** with 1,3-bis-silyl enol ether **3q**, prepared from ethyl 7-chloro-6-methyl-3-oxoheptanoate, and subsequent domino reaction produced **19d**, which was transformed into 2,3-dihydro-1*H*-4,6-dioxachrysen-5-one **20d**.

The Me_3SiOTf-mediated condensation of benzo[*h*]chromone (**6**) with 1,3-bis-silyl enol ether **3p** afforded the 2,3-dihydronaphthopyran **21**; this was transformed into 7-hydroxydibenzo[*c*,*d*]chromen-6-one (**22**) by treatment with NEt_3. The reaction of **22** with NaH/TBAI afforded the 3,4-dihydro-2*H*-1,13-dioxapicen-14-one **23** (Scheme 9).

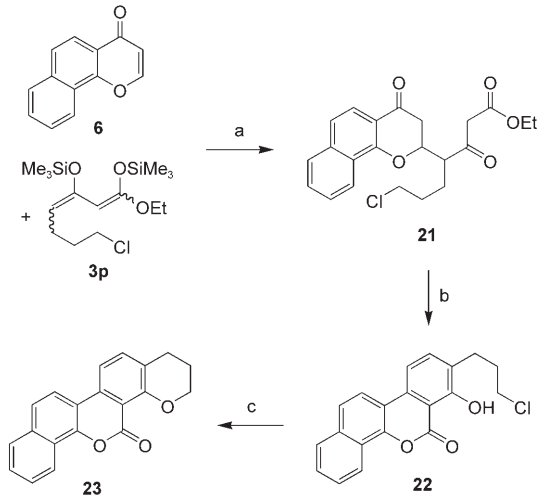
Table 3. UV/Vis absorption and fluorescence of 6*H*-benzo[*c*]chromen-6-ones.

Compound	λ_{max} [nm][a]	$F\lambda_{max}$ [nm][a]	Compound	λ_{max} [nm][a]	$F\lambda_{max}$ [nm][a]
5a	357	489	**5s**	345	495
5b	342	499	**5t**	340	483
5c	345	498	**5u**	340	485
5d	372	499	**5v**	345	407
5e	350	499	**5w**	345	481
5f	345	496	**5x**	350	486
5g	345	497	**5y**	348	493
5h	345	495	**5z**	345	489
5i	345	498	**5aa**	340	485
5j	392	457	**5ac**	345	479
5l	392	456	**7**	350	403
5m	340	484	**15**	345	380
5n	345	468	**16a**	350	420
5o	345	415	**16f**	335	452
5p	340	486	**17a**	342	374
5q	345	500	**17b**	340	406
5r	345	490			

[a] Solvent: CH_3CN.



Scheme 8. Synthesis of 2,3-dihydro-1*H*-4,6-dioxachrysen-5-ones **20a-d**: a) 1) Me_3SiOTf (1.3 equiv), 0°C, 1 h; 2) **3p,q** (1.3 equiv), CH_2Cl_2, 12 h; 3) HCl (10%); b) NEt_3, EtOH, 12 h, 20°C; c) NaH (1.5 equiv), TBAI (2.0 equiv), THF, 20°C, 20 h.



Scheme 9. Synthesis of 3,4-dihydro-2*H*-1,13-dioxapicen-14-one **23**: a) 1) Me_3SiOTf (1.3 equiv), 0°C, 1 h; 2) **3p** (1.3 equiv), CH_2Cl_2, 12 h; 3) HCl (10%); b) NEt_3, EtOH, 12 h, 20°C; c) NaH (1.5 equiv), TBAI (2.0 equiv), THF, 20°C, 20 h.

Table 4. Products and yields.

19/20	R^1	R^2	R^3	**19** [%][a]	**20** [%][a]
a	H	H	H	58	64
b	Cl	H	H	55	61
c	Cl	Me	H	57	69
d	H	H	Me	52	52

[a] Isolated yields.

Conclusion

The condensation of 1,3-bis-silyl enol ethers with benzopyrylium triflates, generated in situ by the reaction of chromones with Me_3SiOTf, afforded functionalized 2,3-dihydrobenzopyrans; treatment of the latter with NEt_3 or BBr_3 resulted in a domino retro-Michael–aldol–lactonization reaction. This methodology allows for the convenient synthesis of a great variety of 6*H*-benzo[*c*]chromen-6-ones, including the natural product, autumnariol and a novel blue fluorescence dye. 2,3-Dihydro-1*H*-4,6-dioxachrysen-5-ones were also prepared by the reaction of chromones with 1,3-bis-silyl enol ethers containing a remote chloride group.

Experimental Section

General comments: All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectra (MS) were obtained by electron ionization (EI, 70 eV), chemical ioni-

zation (CI, H_2O) or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60–200 mesh) was used. Melting points are uncorrected.

General procedure for the synthesis of 7-hydroxy-6*H*-benzo[*c*]chromen-6-ones (5a–ac): Me_3SiOTf (1.3 equiv) was added to chromone **1** (1.0 equiv) at 20 °C. After stirring for 1 h, CH_2Cl_2 (8 mL) and the 1,3-bis-silyl enol ether **3** (1.3 equiv) were added at 0 °C. For products **4a**–**4e**, **4j**, and **4l**, 2,6-lutidine (1.3 equiv) was added after the addition of CH_2Cl_2. The mixture was stirred for 12 h at 20 °C and was then poured into an aqueous solution of hydrochloric acid (10 %). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×80 mL). The combined organic layers were washed with water, dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. Polar side-products were removed by flash-column chromatography (silica gel, *n*-hexane/EtOA*c* 1:1) to give the 2,3-dihydrobenzopyran **4**. Products **4a**–**4e**, **4j**, and **4l** were subsequently isolated and characterized, and samples of each of these products were transformed into the 6*H*-benzo[*c*]chromen-6-ones **5**. All other derivatives of **4** were not characterized; directly after their isolation, they were completely transformed into **5.**

NEt_3 (2.0 equiv) was added to a solution of **4** in EtOH (10 mL) and the mixture was stirred for 12 h at 20 °C. After this time, aqueous hydrochloric acid (1 M) and Et_2O (50 mL) were added. The organic layer was separated and the aqueous layer was extracted with Et_2O (3×100 mL). The combined organic layers were washed with water, dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc 20:1→3:1) to give **5**.

Ethyl 3-oxo-4-(4-oxochroman-2-yl)butanoate (4a): The starting materials **1a** (500 mg, 3.42 mmol), Me_3SiOTf (0.80 mL, 4.4 mmol), 2,6-lutidine (0.52 mL, 4.4 mmol), and **3a** (1.22 g, 4.4 mmol) produced **4a** as a colorless solid (708 mg, 75 %). ^1H NMR (keto/enol 9:1, $CDCl_3$, 250 MHz): δ = 1.07 (t, J = 6.5 Hz, 3H; CH_3), 2.59 (m, 2H; chain CH−CH_2), 2.78 (dd, J = 17.2, 5.3 Hz, 1H; ring CH_2), 3.02 (dd, J = 17.2, 7.1 Hz, 1H; ring CH_2), 3.38 (s, 2H; chain CH_2), 4.00 (q, J = 6.5 Hz, 2H; OCH_2), 4.74 (m, 1H; C*H*−CH_2, keto tautomer), 4.65 (m; 1H; C*H*−CH_2, enol tautomer), 4.95 (s, 1H; =C*H*−, enol tautomer), 6.70–6.85 (m, 2H; Ar), 7.25 (t, J = 7.8 Hz, 1H; Ar), 7.62 ppm (dd, J = 7.8, 1.5 Hz, 1H; Ar); ^{13}C NMR ($CDCl_3$, 62.5 MHz); keto tautomer: δ = 13.53 (CH_3), 41.70, 46.77, 49.13 (CH_2), 60.86 (OCH_2), 72.92 (CH), 117.34 (CH), 120.29 (C), 121.02, 126.29, 135.50 (CH), 160.46, 166.30, 190.76, 198.97 ppm (C); IR (KBr): $\tilde{\nu}$ = 3427 (w), 3005 (m), 2991 (m), 2965 (m), 2948 (m), 2920 (m), 2906 (m), 1737 (s), 1707 (s), 1607 (s), 1578 (m), 1474 (s), 1459 (s), 1403 (s), 1316 (s), 1302 (s), 1278 (s), 1153 cm^{-1} (s); MS (70 eV): *m/z* (%): 276 (20) $[M]^+$, 231 (3), 203 (7), 147 (100); HRMS (EI, 70 eV): *m/z*: calcd for $C_{15}H_{16}O_5$: 276.0997 $[M]^+$; found: 276.0997 ± 2 ppm; elemental analysis (%) calcd for $C_{15}H_{16}O_5$: C 65.21, H 5.84; found: C 65.11, H 5.68.

7-Hydroxy-6*H*-benzo[*c*]chromen-6-one (5a): The starting materials **4a** (150 mg, 0.54 mmol) and NEt_3 (55 mg, 0.54 mmol) produced **5a** as a colorless solid (95 mg, 83 %). ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.06 (d, J = 8.2 Hz, 1H; Ar), 7.30–7.40 (m, 2H; Ar), 7.47 (dt, J = 5.5, 1.5 Hz, 1H; Ar), 7.56 (d, J = 8.0 Hz, 1H; Ar), 7.70 (t, J = 8.0 Hz, 1H; Ar), 8.03 (dd, J = 5.5, 1.5 Hz, 1H; Ar), 11.36 ppm (s, 1H; OH); ^{13}C NMR (APT, $CDCl_3$, 50.3 MHz): δ = 106.10 (C), 112.14, 116.46, 117.68 (CH), 118.25 (C), 123.32, 125.15, 130.59 (CH), 135.19 (C), 137.26 (CH), 150.50, 162.43, 165.39 ppm (C); IR (KBr): $\tilde{\nu}$ = 3433 (m), 1686 (s), 1612 (s), 1573 (m), 1450 (s), 1269 (s), 1242 (s), 1209 (s), 1182 (s), 1108 (m), 1077 (m), 815 (m), 754 (s), 725 (m), 689 (m), 670 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} = 357, 313, 286 nm; UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 351 (3.89), 338 (3.94), 300 (3.48), 290 (3.54), 276 (3.88), 263 nm (4.01); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 489 nm (358 nm); MS (EI, 70 eV): *m/z* (%): 212 (100) $[M]^+$, 184 (10); HRMS (EI, 70 eV): *m/z*: calcd for $C_{13}H_8O_3$: 212.0473 $[M]^+$; found: 212.0473 ± 2 ppm.

Methyl 3-oxo-4-(4-oxochroman-2-yl)pentanoate (4b): The starting materials **1a** (500 mg, 3.42 mmol), Me_3SiOTf (0.80 mL, 4.4 mmol), 2,6-lutidine (0.52 mL, 4.4 mmol), and **3b** (1.22 g, 4.4 mmol) produced **4b** as a colorless solid (572 mg, 61 %, d.r. = 3:2, keto/enol 15:1). A diastereomer of unknown configuration was separated and isolated in a diastereomerically enriched form (d.r. = 10:1). ^1H NMR ($CDCl_3$, 250 MHz); major diastereomer (keto/enol 20:1): δ = 1.20 (d, J = 6.5 Hz, 3H; CH_3), 2.75 (m, 2H; ring CH_2), 3.22 (quint, J = 7.0 Hz, 1H; C*H*CH_3), 3.63 (s, 2H; chain CH_2), 3.75 (s, 3H; OCH_3), 4.65 (m, 1H; C*H*−CH_2, keto tautomer), 6.92 (d, J = 8.0 Hz, 1H; Ar), 7.02 (t, J = 7.0 Hz, 1H; Ar), 7.49 (t, J = 7.0 Hz, 1H; Ar), 7.85 ppm (dd, J = 8.0, 1.5 Hz, 1H; Ar); ^{13}C NMR ($CDCl_3$, 62.5 MHz); keto tautomer: δ = 11.98 (CH_3), 40.04, 49.27 (CH_2), 49.90 (CH), 52.21 (CH_3), 60.86 (OCH_2), 79.05 (CH), 117.61 (CH), 120.73 (C), 121.61, 126.74, 135.99 (CH), 160.65, 167.11, 190.90, 203.79 ppm (C); IR (KBr): $\tilde{\nu}$ = 2925 (w), 2888 (m), 2852 (m), 1749 (s), 1737 (s), 1694 (s), 1606 (s), 1576 (m), 1536 (s), 1465 (s), 1437 (m), 1404 (m), 1350 (m), 1320 (s), 1304 (s) 1263 (s), 1230 (s), 1153 (s), 1029 (m), 1012 (s), 876 (m), 767 (s), 552 cm^{-1} (m); MS (70 eV): *m/z* (%): 276 (20) $[M]^+$, 231 (3), 203 (7), 147 (100); HRMS (EI, 70 eV): *m/z*: calcd for $C_{15}H_{16}O_5$: 276.0997 $[M]^+$; found: 276.0997 ± 2 ppm.

7-Hydroxy-8-methyl-6*H*-benzo[*c*]chromen-6-one (5b): The starting materials **4b** (54 mg, 0.20 mmol) and NEt_3 (20 mg, 0.20 mmol) produced **5b** as a colorless solid (39 mg, 88 %). ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.38 (s, 3H; CH_3), 7.30 (m, 2H; Ar), 7.42 (m, 2H; Ar), 7.55 (d, J = 8.0 Hz, 1H; Ar), 7.95 (dd, J = 8.0, 1.5 Hz, 1H; Ar), 11.55 ppm (s, 1H; OH); ^{13}C NMR (APT, $CDCl_3$, 50.3 MHz): δ = 15.65 (CH_3), 105.30 (C), 111.42, 117.49 (CH), 118.49 (C), 122.90, 124.98 (CH), 125.97 (C), 129.92 (CH), 132.61 (C), 138.20 (CH), 150.19, 160.36, 165.72 ppm (C); IR (KBr): $\tilde{\nu}$ = 2956 (m), 2923 (m), 2852 (m), 1681 (s), 1610 (m), 1462 (m), 1449 (m), 1416 (m), 1270 (s), 1255 (s), 1197 (m), 1128 (s), 822 (m), 751 (s), 722 (m), 671 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε) = 342 (3.87), 299 (3.57), 290 (3.60), 277 (3.87), 262 (3.93), 232 nm (4.39); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 499 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 226 (100) $[M]^+$, 197 (9); HRMS (EI, 70 eV): *m/z*: calcd for $C_{14}H_{10}O_3$: 226.0630 $[M]^+$; found: 226.0630 ± 2 ppm; elemental analysis calcd (%) for $C_{14}H_{10}O_3$: C 74.33, H 4.45; found: C 74.52, H 4.80.

Ethyl 3-oxo-4-(4-oxochroman-2-yl)hexanoate (4c): The starting materials **1a** (500 mg, 3.42 mmol), Me_3SiOTf (0.80 mL 4.4 mmol), 2,6-lutidine (0.52 mL, 4.4 mmol), and **3c** (1.22 g, 4.4 mmol) produced **4c** as a colorless solid (716 mg, 69 %, d.r. = 2:1, keto/enol 2.5:1). ^1H NMR ($CDCl_3$, 250 MHz); keto tautomer: δ = 0.92, 1.22 (2×t, J = 6.5 Hz, 3H; CH_3), 1.22, 1.65, 1.90 (3×m, 2H; C$H_2$$CH_3$), 2.65 (m, 2H; ring CH_2), 3.21 (m, 1H; C*H*$CH_2$$CH_3$), 3.60 (s, 2H; chain CH_2), 4.18 (m, 2H; OCH_2), 4.50, 4.62 (m, 1H; C*H*−CH_2, keto tautomer), 6.90–7.05 (m, 2H; Ar), 7.41 (t, J = 7.0 Hz, 1H; Ar), 7.80 ppm (dd, J = 8.0, 1.5 Hz, 1H; Ar); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 11.19, 11.58, 14.06, 14.16 (CH_3), 20.57, 21.51, 39.83, 41.08, 50.90 (CH_2), 51.90, 56.06 (*C*H$CH_2$$CH_3$), 60.29, 61.43 ($OCH_2$), 77.17, 78.15 (CH), 92.53, 117.74, 117.85 (CH), 120.94, 120.99 (C), 121.46, 121.73, 126.85, 126.98, 136.01 (CH), 160.86, 161.11, 166.63, 172.21, 175.07, 191.50, 191.95, 203.56 ppm (C); IR (neat): $\tilde{\nu}$ = 3427 (w), 3005 (m), 2971 (m), 2936 (m), 2879 (m), 1745 (s), 1694 (s), 1650 (s), 1607 (s), 1464 (s), 1307 (s), 1227 (s), 1150 (m), 1031 (m), 706 cm^{-1}(m); MS (70 eV) *m/z* (%): 304 (11) $[M]^+$, 275 (9), 147 (100); HRMS (EI, 70 eV): *m/z*: calcd for $C_{17}H_{20}O_5$: 304.1310 $[M]^+$; found: 304.1310 ± 2 ppm; elemental analysis calcd (%) for $C_{17}H_{20}O_5$: C 67.09, H 6.62; found: C 66.36, H 6.22.

8-Ethyl-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (5c): The starting materials **4c** (95 mg, 0.31 mmol) and NEt_3 (32 mg, 0.31 mmol) produced **5c** as a colorless solid (63 mg, 84 %). ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.23 (t, J = 7.0 Hz, 3H; CH_3), 2.75 (t, J = 7.0 Hz, 2H; CH_2), 7.30 (m, 2H; Ar), 7.42 (m, 1H; Ar), 7.47 (d, J = 8.0 Hz, 1H; Ar), 7.57 (d, J = 8.0 Hz, 1H; Ar), 7.98 (dd, J = 8.0, 1.5 Hz, 1H; Ar), 11.60 ppm (s, 1H; OH); ^{13}C NMR (APT, $CDCl_3$, 50.3 MHz): δ = 13.55 (CH_3), 22.75 (CH_2), 105.40 (C), 111.61, 117.49 (CH), 118.51 (C), 122.92, 124.99, 129.93 (CH), 131.85, 132.58 (C), 136.63 (CH), 150.21, 160.13, 165.82 ppm (C); IR (KBr): $\tilde{\nu}$ = 3432 (m), 2963 (m), 2930 (m), 2872 (m), 1663 (s), 1610 (s), 1444 (s), 1436 (s), 1266 (s), 1253 (s), 1199 (m), 1139 (s), 1090 (m), 829 (m), 758 (s), 725 (m), 670 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε) = 342 (4.02), 299 (3.69), 290 (3.77), 277 (3.97), 263 (4.04), 232 (4.50), 204 nm (4.50); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 498 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 240 (60) $[M]^+$, 225 (100); HRMS (EI, 70 eV): *m/z*: calcd for $C_{15}H_{12}O_3$: 240.0786 $[M]^+$; found: 240.0786 ± 2 ppm; elemental analysis calcd (%) for $C_{15}H_{12}O_3$: C 74.98, H 5.03; found: C 74.67, H 5.30.

Ethyl 3-oxo-4-(4-oxochroman-2-yl)hept-6-enoate (4d): The starting materials **1a** (500 mg, 3.42 mmol), Me_3SiOTf (0.80 mL, 4.4 mmol), 2,6-lutidine (0.52 mL, 4.4 mmol), and **3d** (1.22 g, 4.4 mmol) produced **4d** as a colorless solid (698 mg, 64%) and as a mixture of diastereomers and keto/enol tautomers. ^{1}H NMR ($CDCl_3$, 250 MHz); keto tautomer: $\delta = 1.10$–1.30 (m, 3H; CH_3), 2.40–2.70 (m, 2H; ring CH_2), 2.75 (m, 1H; chain CH−C*H*), 3.30–3.50 (m, 2H; C*H*$_2$−CH=CH$_2$), 3.56 (s, 2H; chain CH_2), 4.20 (m, 2H; OCH_2), 4.65 (m, 1H; ring C*H*−CH_2, keto tautomer), 5.00–5.15 (m, 2H; CH=C*H*$_2$), 5.65–5.85 (m, 1H; C*H*=CH_2), 6.90–7.05 (m, 2H; Ar), 7.45 (t, $J = 7.0$ Hz, 1H; Ar), 7.85 ppm (dd, $J = 8.0$, 1.5 Hz, 1H; Ar); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 14.04$, 14.13 (CH_3), 29.61, 31.62, 39.71, 40.90, 50.81 (CH_2), 50.01, 54.28 (CH), 60.30, 61.39 (OCH_2), 76.65, 77.64 (CH), 117.42, 118.40 (CH=*C*H$_2$), 117.71, 117.84 (CH), 120.93, 121.54 (C), 120.96, 121.77, 126.85, 126.98, 134.54, 135.99 (CH), 160.80, 160.99, 166.54, 172.17, 174.42, 191.22, 191.64, 202.88 ppm (C); IR (KBr): $\tilde{\nu} = 3400$ (w), 2980 (s), 2917 (s), 1744 (s), 1712 (s), 1694 (s), 1608 (s), 1579 (m), 1465 (s), 1445 (m), 1300 (s), 1228 (s), 1150 (m), 1030 (m), 921 (m), 766 cm^{-1} (m); MS (70 eV): *m/z* (%): 316 (6) $[M]^+$, 298 (3), 275 (36), 147 (100); HRMS (EI, 70 eV): *m/z*: calcd for $C_{18}H_{20}O_5$: 316.1311 $[M]^+$; found: 316.1311 ± 2 ppm; elemental analysis calcd (%) for $C_{18}H_{20}O_5$: C 68.34, H 6.37; found: C 68.17, H 6.29.

8-Allyl-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (5d): The starting materials **4d** (345 mg, 0.24 mmol) and NEt_3 (24 mg, 0.24 mmol) produced **5d** as a colorless solid (184 mg, 67%). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 3.42$ (d, $J = 5.0$ Hz, 2H; CH_2), 5.14 (dd, $J = 8.0$, 1.0 Hz, 2H; CH=C*H*$_2$), 6.02 (m, 1H; C*H*=CH_2), 7.15–7.55 (m, 6H; Ar), 7.83 (d, $J = 6.0$ Hz, 1H; Ar), 11.58 ppm (s, 1H; OH); ^{13}C NMR (APT, $CDCl_3$, 50.3 MHz): $\delta = 33.93$ (CH_2), 105.28 (C), 111.50 (CH), 116.39 (CH_2), 117.30 (CH), 118.14 (C), 122.80, 124.90 (CH), 127.62 (C), 129.96 (CH), 132.84 (C), 135.43, 137.20 (CH), 150.03, 159.75, 165.48 ppm (C); IR (KBr): $\tilde{\nu} = 3433$ (m), 3076 (m), 1670 (s), 1611 (s), 1450 (s), 1433 (s), 1412 (s), 1316 (m), 1269 (s), 1246 (s), 1214 (s), 1124 (s), 1089 (m), 920 (m), 830 (m), 756 (s), 669 cm^{-1} (m); UV/Vis (CH_3CN): $\lambda_{max} = 372$, 306, 295 nm; UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 344 nm (4.02); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 499 nm (372 nm); MS (EI, 70 eV): *m/z* (%): 252 (100) $[M]^+$, 237 (68); HRMS (EI, 70 eV): *m/z*: calcd for $C_{16}H_{12}O_3$: 252.0786 $[M]^+$; found: 252.0786 ± 2 ppm.

Ethyl 3-oxo-4-(4-oxochroman-2-yl)-5-phenylpentanoate (4e): The starting materials **1a** (500 mg, 3.42 mmol), Me_3SiOTf (0.80 mL, 4.4 mmol), 2,6-lutidine (0.52 mL, 4.4 mmol), and **3e** (1.22 g, 4.4 mmol) produced **4e** as a colorless solid (702 mg, 56%, keto/enol 5:1, mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 250 MHz); keto tautomer: $\delta = 1.25$ (t, $J = 7.0$ Hz, 3H; CH_3), 2.75 (m, 2H; chain CH−C*H*, ring CH_2), 3.05 (m, 1H; ring CH_2), 3.35 (s, 2H; chain CH_2), 4.15 (q, $J = 7.0$ Hz, 2H; OCH_2), 4.65 (m, 1H; ring C*H*−CH_2, keto tautomer), 6.90–7.30 (m, 7H; Ar), 7.45 (m, 1H; Ar), 7.88 (d, $J = 8.0$ Hz, 1H; Ar); IR (cap): $\tilde{\nu} = 2979$ (s), 2935 (s), 2904 (s), 1745 (s), 1712 (s), 1655 (s), 1607 (s), 1580 (m), 1472 (s), 1464 (s), 1426 (m), 1406 (m), 1368 (m), 1305 (s) 1228 (s), 1181 (s), 1150 (s), 1030 (s), 843 (s), 765 (s), 702 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%): 366 (16) $[M]^+$, 291 (37), 275 (22), 219 (60), 147 (100).

8-Benzyl-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (5e): The starting materials **4e** (165 mg, 0.45 mmol) and NEt_3 (46 mg, 0.45 mmol) produced **5e** as a colorless solid (49 mg, 36%). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 4.05$ (s, 2H; CH_2), 7.20–7.55 (m, 10H; Ar), 7.95 (t, $J = 7.0$ Hz, 1H; Ar), 11.73 ppm (s, 1H; OH); ^{13}C NMR (APT, $CDCl_3$, 50.3 MHz): $\delta = 35.23$ (CH_2), 105.65 (C), 111.72, 117.51 (CH), 118.33 (C), 122.97, 125.05, 126.25, 127.32, 128.49, 129.00, 130.15 (CH), 133.18, 137.85, 139.72, 150.26, 160.01, 165.71 ppm (C); IR (KBr): $\tilde{\nu} = 3434$ (m), 1676 (s), 1611 (s), 1453 (m), 1415 (m), 1315 (m), 1266 (s), 1251 (m), 1122 (s), 1087 (w), 816 (m), 755 (s), 728 (m), 698 (m), 671 cm^{-1} (m); UV/Vis (CH_3CN): $\lambda_{max} = 342$, 279, 258, 250, 219 nm; UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 345 (4.02), 301 (3.77), 292 (3.87), 279 (4.05), 266 nm (4.13); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 499 nm (350 nm); MS (EI, 70 eV): *m/z* (%): 302 (100) $[M]^+$, 225 (12); HRMS (EI, 70 eV): *m/z*: calcd for $C_{20}H_{14}O_3$: 302.0943 $[M]^+$; found: 302.0943 ± 2 ppm.

8-Butyl-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (5f): The starting materials **1a** (205 mg, 1.4 mmol), Me_3SiOTf (404 mg, 1.8 mmol), **3f** (482 mg, 1.8 mmol), and NEt_3 (283 mg, 0.39 mL, 2.8 mmol) in EtOH (12 mL) produced **5f** as a colorless solid (180 mg, 48%). M.p. 64 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.96$ (t, $J = 7.3$ Hz, 3H; CH_3), 1.41 (m, 2H; CH_2), 1.61 (m, 2H; CH_2), 2.70 (m, 2H; CH_2), 7.29 (m, 2H; Ar), 7.41 (m, 2H; Ar), 7.53 (d, $J = 7.9$ Hz, 1H; Ar), 7.93 (m, 1H; Ar), 11.58 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta = 13.93$ (CH_3), 22.52, 29.29, 31.41 (CH_2), 105.44 (C), 111.48, 117.45 (CH), 118 51 (C), 122.89, 124.96, 129.01 (CH), 130.59, 132.59 (C), 137.41 (CH), 160.20 (C), 165.79 ppm (C=O); IR (KBr): $\tilde{\nu} = 3421$ (w), 3066 (w), 2956 (m), 2929 (m), 2867 (w), 1667 (s), 1614 (m), 1455 (m), 1417 (m), 1311 (m), 1265 (s), 1235 (s), 1214 (s), 1131 (s), 757 cm^{-1} (s); UV/Vis (CH_3CN): λ_{max} (lg ε): 342 (3.93), 299 (3.53), 290 (3.62), 277 (3.87), 263 (3.96), 233 (4.44), 206 nm (4.36 nm); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 345 nm (496 nm); MS (EI, 70 eV): *m/z* (%): 268 (41) $[M]^+$, 225 (100), 186 (3), 143 (19), 130 (27), 114 (9), 70 (17), 57 (46), 39 (14); HRMS (EI, 70 eV): *m/z*: calcd for $C_{17}H_{16}O_3$: 268.1099 $[M]^+$; found: 268.1099 ± 2 ppm.

8-Hexyl-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (5g): The starting materials **1a** (205 mg, 1.4 mmol), Me_3SiOTf (404 mg, 1.8 mmol), **3g** (645 mg, 1.8 mmol), and NEt_3 (283 mg, 0.39 mL, 2.8 mmol) in EtOH (12 mL) produced **5g** as a colorless solid (186 mg, 45%). M.p. 63 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.89$ (t, $J = 7.0$ Hz, 3H; CH_3), 1.25–1.57 (m, 6H; 3 × CH_2), 1.60–1.68 (m, 2H; CH_2), 2.73 (t, $J = 7.50$ Hz 2H; CH_2), 7.34 (m, 2H; Ar), 7.48 (m, 2H; Ar), 7.51 (d, $J = 8.0$ Hz, 1H; Ar), 8.01 (d, $J = 7.4$ Hz, 1H; Ar), 11.58 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta = 14.09$ (CH_3), 22.62, 29.14, 29.27, 29.67, 31.71 (CH_2), 105.59 (C), 111.57, 117.45 (CH), 118 65 (C), 122.99, 125.04, 129.99 (CH), 130.76, 132.72 (C), 137.55 (CH), 150.33, 160.32 (C), 165.93 ppm (C=O); IR (KBr): $\tilde{\nu} = 3061$ (w), 2953 (m), 2926 (m), 2857 (m), 1666 (s), 1614 (m), 1457 (m), 1417 (m), 1312 (w), 1268 (s), 1249 (s), 1213 (s), 1130 (s), 757 cm^{-1} (s); UV/Vis (CH_3CN): λ_{max} (lg ε): 343 (3.95), 300 (3.64), 290 (3.72), 277 (3.94), 263 (4.00), 233 (4.46), 204 nm (4.47); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}) = 497 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 296 $[M]^+$ (25), 25), 249 (13), 225 (100), 197 (13), 151 (15), 114 (14), 102 (11), 41 (15); HRMS (EI, 70 eV): *m/z*: calcd for $C_{19}H_{20}O_3$: 296.1412 $[M]^+$; found: 296.1412 ± 2 ppm.

8-Heptyl-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (5h): The starting materials **1a** (205 mg, 1.4 mmol), Me_3SiOTf (404 mg, 1.8 mmol), **3h** (671 mg, 1.8 mmol), and NEt_3 (283 mg, 0.39 mL, 2.8 mmol) in EtOH (15 mL) produced **5h** as a colorless solid (209 mg, 48%). M.p. 75 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.88$ (t, $J = 6.25$ Hz, 3H; CH_3), 1.34 (m, 8H; CH_2), 1.64 (m, 2H; CH_2), 2.68 (m, 2H; CH_2), 7.30 (m, 2H; Ar), 7.42 (m, 2H; Ar), 7.54 (d, $J = 8.0$ Hz, 1H; Ar), 7.95 (d, $J = 8.6$ Hz, 2.0 Hz, 1H; Ar), 11.59 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta = 14.08$ (CH_3), 22.65, 29.27, 29.45, 29.48, 29.62, 31.87 (CH_2), 105.46 (C), 111.49, 117.48 (CH), 118 55 (C), 122.91, 124.97, 129.91 (CH), 130.66, 132.59 (C), 137.43 (CH), 150.23, 160.22 (C), 165.81 ppm (C=O); IR (KBr): $\tilde{\nu} = 3434$ (m), 3085 (w), 2956 (m), 2922 (s), 2850 (m), 1680 (s), 1643 (w), 1614 (m), 1495 (m), 1409 (m), 1353 (w), 1328 (w), 1317 (w), 1265 (s), 1214 (m), 1133 (s), 832 (m), 807 (w), 756 (s), 671 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 343 (3.94), 300 (3.54), 290 (3.63), 278 (3.88), 263 (3.96), 233 (3.06), 206 (4.34), 203 nm (4.36); fluorescence (CH_3CN): λ_{ex} ($F\lambda_{max}$): 495 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 310 (42) $[M]^+$, 249 (4), 224 (100), 197 (3), 165 (2), 151 (8), 114 (6), 91 (3); HRMS (FT-ICR): calcd. for $C_{20}H_{23}O_3$: 311.16471 $[M+1]^+$; found: 311.16397.

7-Hydroxy-8-octyl-6*H*-benzo[*c*]chromen-6-one (5i): The starting materials **1a** (234 mg, 1.6 mmol), Me_3SiOTf (467 mg, 2.1 mmol), **3i** (813 mg, 2.1 mmol), and NEt_3 (324 mg, 0.45 mL, 3.2 mmol) in EtOH (15 mL) produced **5i** as a colorless solid (265 mg, 51%). M.p. 61 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.89$ (t, $J = 6.9$ Hz, 3H; CH_3), 1.35 (m, 10H; CH_2), 1.64 (m, 2H; CH_2), 2.72 (t, $J = 7.6$ Hz, 2H; CH_2), 7.31 (m, 2H; Ar), 7.40–7.59 (br m, 3H; Ar), 7.99 (d, $J = 8.0$ Hz; 1H; Ar), 11.62 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta = 14.09$ (CH_3), 22.66, 29.17, 29.32, 29.44, 29.66, 31.83 (CH_2), 105.75 (C), 111.55, 117.56 (CH), 118.63 (C), 122.97, 125.03, 129.98 (CH), 130.74, 132.70 (C), 137.53 (CH), 150.31, 160.30 (C), 165.91 ppm (C=O); IR (KBr): $\tilde{\nu} = 3434$ (m), 3434 (m), 3050 (w), 2956 (m), 2923 (s), 2854 (m), 1683 (s), 1613 (m), 1451 (m), 1414 (m), 1355 (w), 1316 (m), 1268 (s), 1213 (m), 1135 (s), 1102 (w), 1082 (w), 814 (w), 765 (s), 757 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 343 (3.96), 300 (3.56), 290 (3.65), 277 (3.89), 263 (3.98), 233 nm (4.46); fluorescence (CH_3CN): λ_{ex} ($F\lambda_{max}$): 498 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 324

(37) $[M]^+$, 306 (3), 249 (6), 225 (100), 197 (5), 151 (7), 114 (6), 41 ppm (4); HRMS (FT-ICR): calcd for $C_{21}H_{25}O_3$: 325.18036 $[M+1]^+$; found: 325.17950.

Methyl 4-methoxy-3-oxo-4-(4-oxochroman-2-yl)butanoate (4j): The starting materials **1a** (300 mg, 2.05 mmol), Me_3SiOTf (0.48 mL, 2.70 mmol), 2,6-lutidine (0.31 mL, 2.70 mmol), and **3j** (0.898 g, 2.70 mmol) produced **4j** as a colorless solid (455 mg, 76%) and as a mixture of diastereomers and keto/enol tautomers. ^{1}H NMR ($CDCl_3$, 250 MHz); major isomer: $\delta=$ 2.50 (dd, $J=17.0$, 2.5 Hz, 1H; ring CH_2), 2.90 (dd, $J=17.0$, 12.5 Hz, 1H; ring CH_2), 3.50 (s, 2H; chain CH_2), 3.60 (s, 3H; OCH_3), 4.03 (d, $J=$ 2.5 Hz, 1H; chain C*H*–CH), 4.75 (td, $J=12.5$, 2.5 Hz, 1H; ring CH), 6.90 (m, 2H; Ar), 7.35 (t, $J=7.0$ Hz, 1H; Ar), 7.75 ppm (dd, $J=8.0$, 1.5 Hz, 1H; Ar); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta=36.53$, 37.21, 45.22, 45.86 (CH_2), 51.50, 52.24, 58.26, 59.42 (OCH_3), 77.72, 81.80, 88.50, 90.12 (CH), 117.34, 117.50 (CH), 120.29, 120.48 (C), 121.10, 121.18, 126.50, 126.54, 135.60, 135.64 (CH), 160.40, 160.56, 166.22, 171.80, 172.22, 190.30, 191.22, 202.50 ppm (C); IR (cap): $\tilde{\nu}=3427$ (w), 2954 (m), 2918 (m), 1748 (s), 1723 (s), 1694 (s), 1607 (s), 1474 (s), 1446 (s), 1403 (m), 1322 (s), 1301 (s), 1265 (s), 1227 (s), 1149 (s), 1085 (m), 1034 (m), 767 cm^{-1} (m); MS (70 eV): *m/z* (%): 292 (12) $[M]^+$, 261 (3), 2042 (7), 147 (100); HRMS (EI, 70 eV): *m/z*: calcd for $C_{15}H_{16}O_6$: 292.0947 $[M]^+$; found: 292.0947 ± 2 ppm; elemental analysis calcd (%) for $C_{15}H_{16}O_6$: C 61.64, H 5.51; found: C 61.40, H 4.98.

7-Hydroxy-8-methoxy-6*H*-benzo[*c*]chromen-6-one (5j): The starting materials **4j** (110 mg, 0.38 mmol) and NEt_3 (38 mg, 0.38 mmol) produced **5j** as a colorless solid (78 mg, 85%). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta=4.00$ (s, 3H; OMe), 7.25–7.50 (m, 4H; Ar), 7.52 (d, $J=7.0$, 1H; Ar), 7.97 (d, $J=7.0$ Hz, 1H; Ar), 11.55 ppm (s, 1H; OH); ^{13}C NMR (APT, $CDCl_3$, 50.3 MHz): $\delta=56.37$ (CH_3), 106.30 (C), 111.94, 117.52 (CH), 118.38 (C), 118.97, 122.49, 125.15 (CH), 126.57 (C), 129.39 (CH), 147.62, 149.68, 151.86, 165.40 ppm (C); IR (KBr): $\tilde{\nu}=3433$ (m), 2924 (m), 1660 (s), 1608 (m), 1691 (m), 1468 (s), 1442 (s), 1332 (m), 1278 (s), 1208 (m), 1144 (s), 1054 (s), 774 (s), 751 (m), 689 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε) = 399, 318, 272 nm; UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 357 (3.91), 306 (3.97), 294 (3.92), 285 (3.95), 266 nm (3.96); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 457 nm (400 nm); MS (EI, 70 eV): *m/z* (%): 242 (100) $[M]^+$, 227 (22), 213 (18), 199 (63); HRMS (EI, 70 eV): *m/z*: calcd for $C_{14}H_{10}O$: 242.0579 $[M]^+$; found: 242.0579 ± 2 ppm; elemental analysis calcd (%) for $C_{14}H_{10}O_4$: C 69.42, H 4.16; found: C 69.72, H 4.31.

Methyl 4-(benzyloxy)-3-oxo-4-(4-oxochroman-2-yl)butanoate (4l): The starting materials **1a** (500 mg, 3.42 mmol), Me_3SiOTf (0.80 mL, 4.4 mmol), 2,6-lutidine (0.52 mL, 4.4 mmol), and **3k** (1.22 g, 4.4 mmol) produced **4l** as a colorless solid (778 mg, 62%) and as a mixture of diastereomers and keto/enol tautomers. Major isomer: ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta=1.10$–1.30 (2×t, $J=7.0$ Hz, 3H; CH_3), 2.50–2.75 (m, 1H; ring CH_2), 2.85–3.05 (m, 1H; ring CH_2), 2.75 (m, 1H; chain CH–C*H*), 3.58, 3.75 (2×d, $J=14.0$ Hz, 2×1H; chain CH_2), 4.05–4.25 (m, 2H; OCH_2), 4.35 (dd, $J=8.0$, 2.0 Hz; chain CH), 4.75, 4.80 (2×d, $J=10.0$ Hz, 2H; chain CH_2), 4.90 (m, 1H; ring CH), 6.95 (m, 2H; Ar), 7.20–7.35 (m, 5H; Ph), 7.40 (m, 1H; Ar), 7.82 ppm (d, $J=8.0$ Hz, 1H; Ar); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta=14.11$, 14.21 (CH_3), 29.67, 31.24, 39.03, 39.23, 46.52, 60.61, 61.48, 72.62, 74.29, 77.16, 78.31, 84.47, 91.29, 112.95, 117.84, 118.10, 120.72, 12.86, 121.51, 121.87, 125.25, 125.78, 126.72, 126.85, 128.26, 128.34, 128.58, 128.72, 136.02, 136.53, 155.36, 160.60, 167.11, 171.94, 172.44, 191.19, 191.63, 203.88 ppm; IR (cap): $\tilde{\nu}=3400$ (w), 2980 (m), 2930 (m), 1741 (s), 1721 (s), 1696 (s), 1607 (s), 1473 (s), 1464 (s), 1402 (m), 1321 (s), 1301 (s), 1262 (m), 1226 (s), 1150 (s), 1084 (m), 1030 (m), 766 (m), 699 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 382 $[M]^+$ [3), 258 (22), 236 (22), 147 (56), 91 (100); HRMS (EI, 70 eV): *m/z*: calcd for $C_{22}H_{22}O_6$: 382.1416 $[M]^+$; found: 382.1416 ± 2 ppm; elemental analysis calcd (%) for $C_{22}H_{22}O_6$: C 69.10, H 5.80; found: C 68.93, H 5.55.

8-(Benzyloxy)-7-Hydroxy-6*H*-benzo[*c*]chromen-6-one (5l): The starting materials **4l** (329 mg, 0.86 mmol) and NEt_3 (87 mg, 0.86 mmol) produced **5l** as a colorless solid (93 mg, 34%). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta=$ 5.21 (s, 2H; CH_2Ph), 7.20–7.55 (m, 10H; Ar), 7.90 (d, $J=6.5$ Hz, 1H; Ar), 11.58 ppm (s, 1H; OH); ^{13}C NMR (APT, $CDCl_3$, 50.3 MHz): $\delta=$ 71.37 (CH_2), 106.51 (C), 111.80, 117.45 (CH), 118.27 (C), 122.08, 122.49, 125.09 (CH), 127.23 (C), 127.32, 128.09, 128.62, 129.43 (CH), 136.31, 146.39, 149.67, 152.55, 165.62 ppm (C); IR (KBr): $\tilde{\nu}=3062$ (m), 1666 (s), 1609 (m), 1479 (m), 1455 (s), 1422 (m), 1329 (m), 1264 (s), 1205 (m), 1141 (s), 1024 (s), 758 (s), 734 (m), 698 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε) = 392 nm; UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 357 nm (3.98); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 456 nm (392 nm); MS (EI, 70 eV): *m/z* (%): 318 $[M]^+$ (52), 227 (20), 199 (16), 91 (100); HRMS (EI, 70 eV): *m/z*: calcd for $C_{20}H_{14}O_4$: 318.0892 $[M]^+$; found: 318.0892 ± 2 ppm.

7-Hydroxy-2-methyl-6*H*-benzo[*c*]chromen-6-one (5m): The starting materials **1b** (176 mg, 1.1 mmol), Me_3SiOTf (311 mg, 1.4 mmol), **3a** (393 mg, 1.4 mmol), and NEt_3 (223 mg, 0.31 mL, 2.2 mmol) in EtOH (8 mL) produced **5m** as a colorless solid (134 mg, 54%). M.p. 168 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=2.23$ (s, 3H; CH_3), 7.03 (dd, $J=8.3$, 0.9 Hz, 1H; Ar), 7.19–7.28 (m, 2H; Ar), 7.51 (dd, $J=8.0$, 1.2 Hz, 1H; Ar), 7.67 (t, $J=$ 8.0 Hz, 1H; Ar), 7.75 (br s, 1H; Ar), 11.40 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta=21.08$ (CH_3), 106.08 (C), 111.99 (CH), 115.98 (C), 116.23, 117.34 (CH), 117.53, 117.77 (C), 123.22 (CH), 131.49 (CH), 134.76, 135.23, 135.44 (C), 137.08 (CH), 148.57 (C), 162.41, 165.51 ppm (C); IR (KBr): $\tilde{\nu}=3064$ (m), 2875 (w), 1666 (s), 1611 (s), 1575 (s), 1508 (m), 1497 (m), 1455 (s), 1357 (m), 1328 (m), 1274 (s), 1246 (s), 1215 (s), 1172 (m), 1106 (m), 1081 (m), 818 (s), 811 (s), 737 (s), 680 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 350 (3.89), 337 (3.94), 306 (3.44), 294 (3.36), 277 (3.83), 267 (3.95), 233 (4.42), 208 nm (4.32); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 484 nm (340 nm); MS (EI, 70 eV): *m/z* (%): 226 $[M]^+$ (100), 197 (18), 169 (12), 141 (6), 115 (9), 57 (6); HRMS (EI, 70 eV): *m/z*: calcd for $C_{14}H_{10}O_3$: 226.0630 $[M]^+$; found: 226.0630 ± 2 ppm.

7-Hydroxy-2-methoxy-6*H*-benzo[*c*]chromen-6-one (5n): The starting materials **1c** (246 mg, 1.4 mmol), Me_3SiOTf (311 mg, 1.4 mmol), **3a** (499 mg, 1.8 mmol), and NEt_3 (283 mg, 0.39 mL, 2.8 mmol) in EtOH (12 mL) produced **5n** as a colorless solid (207 mg, 61%). M.p. 169 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=3.90$ (s, 3H; OCH_3), 7.04–7.08 (m, 2H; Ar), 7.28 (d, $J=10.7$ Hz, 1H; Ar), 7.41 (d, $J=2.9$ Hz, 1H; Ar), 7.50 (dd, $J=8.0$, 0.7 Hz, 1H; Ar), 7.70 (t, $J=10.7$ Hz, 1H; Ar), 11.46 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta=55.84$ (OCH_3), 106.14 (C), 106.65, 112.15, 116.61, 117.47, 118.66 (CH), 118.82, 135.12 (C), 137.14 (CH), 144.87, 156.73, 162.56, 165.52 ppm (C); IR (KBr): $\tilde{\nu}=3082$ (w), 2993 (w), 2929 (w), 1664 (s), 1622 (s), 1576 (s), 1502 (m), 1459 (s), 1405 (m), 1338 (m), 1264 (s), 1250 (s), 1206 (s), 1172 (m), 1108 (m), 1088 (m), 817 (s), 724 (m), 691 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 342 (4.01), 272 (3.92), 237 (4.52), 218 nm (4.38); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 468 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 242 $[M]^+$ (100), 227 (35), 199 (15), 171 (10), 145 (6), 115 (4), 89 (3); elemental analysis calcd (%) for $C_{14}H_{10}O_4$: C 69.42, H 4.16; found: C 69.76, H 4.51.

2-Chloro-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (5p): The starting materials **1d** (181 mg, 1.0 mmol), Me_3SiOTf (289 mg, 1.3 mmol), **3a** (357 mg, 1.3 mmol), and NEt_3 (202 mg, 0.23 mL, 2.0 mmol) in EtOH (8 mL) produced **5p** as a colorless solid (138 mg, 56%). M.p. 190 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.10$ (dd, $J=8.1$, 0.6 Hz, 1H; Ar), 7.30 (d, $J=$ 8.8 Hz, 1H; Ar), 7.42 (dd, $J=8.8$, 2.3 Hz, 1H; Ar), 7.49 (d, $J=8.1$, 0.7 Hz, 1H; Ar), 7.72 (t, 8.1 Hz, 1H; Ar), 7.94 (d, $J=2.3$ Hz, 1H; Ar), 11.27 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta=105.95$ (C), 112.31, 117.33, 119.11 (CH), 119.62 (C), 123.13, 130.53 (CH), 130.73, 133.91 (C), 137.45 (CH), 148.87, 162.53, 164.87 ppm (C); IR (KBr): $\tilde{\nu}=$ 3120 (w), 2980 (w), 1679 (s), 1618 (m), 1449 (s), 1455 (w), 1267 (m), 1237 (m), 1211 (s), 1172 (m), 1085 (m), 813 (s), 691 cm^{-1} (s); UV/Vis (CH_3CN): λ_{max} (lg ε): 349 (3.96), 335 (4.00), 295 (3.37), 276 (3.83), 267 (3.95), 259 (3.94), 234 (4.50), 215 nm (3.44); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 486 nm (340 nm); MS (EI, 70 eV): *m/z* (%): 246 $[M]^+$ (100), 218 (12), 183 (6), 155 (8), 126 (6), 105 (4); elemental analysis calcd (%) for $C_{13}H_7ClO_3$: C 63.31, H 2.86; found: C 63.21, H 3.25.

2-Chloro-7-hydroxy-8-methyl-6*H*-benzo[*c*]chromen-6-one (5q):[24] The starting materials **1d** (181 mg, 1.0 mmol), Me_3SiOTf (289 mg, 1.3 mmol), **3b** (357 mg, 1.3 mmol), and NEt_3 (202 mg, 0.23 mL, 2.0 mmol) in EtOH (8 mL) produced **5q** as a colorless solid (149 mg, 57%). M.p. 201 °C; ^{1}H NMR ([D$_6$]DMSO, 300 MHz): $\delta=2.29$ (s, 3H; CH_3), 7.48 (d, $J=$ 8.8 Hz, 1H; Ar), 7.61 (dd, $J=8.8$, 2.4 Hz, 1H; Ar), 7.76 (d, $J=8.0$ Hz, 1H; Ar), 7.90 (d, $J=8.0$ Hz, 1H; Ar), 8.42 (d, $J=2.4$ Hz, 1H; Ar), 11.43 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta=15.36$

(CH_3), 105.22 (C), 113.10, 119.22 (CH), 120.02 (C), 123.45 (CH), 126.09, 129.61 (C), 130.08 (CH), 131.40 (C), 138.57 (CH), 148.51, 159.21 (C–OH), 164.80 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3437 (m), 3084 (w), 1675 (s), 1623 (m), 1435 (s), 1386 (m), 1345 (w), 1317 (m), 1265 (s), 1219 (w), 1198 (w), 1135 (s), 1097 (s), 823 (m), 808 (m), 725 (s), 642 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 341 (4.03), 308 (3.59), 297 (3.56), 281 (3.91), 267 (3.97), 234 (4.52), 215 nm (4.43); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 500 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 260 (100) $[M]^+$, 231 (10), 197 (7), 169 (5), 139 (7), 114 (3); HRMS (EI, 70 eV): *m/z*: calcd for $C_{14}H_9O_3Cl$: 260.0240 $[M]^+$; found: 260.0240 ± 2 ppm.

2-Chloro-7-hydroxy-8-butyl-6*H*-benzo[*c*]chromen-6-one (5r): The starting materials **1d** (289 mg, 1.6 mmol), Me_3SiOTf (467 mg, 2.1 mmol), **3f** (494 mg, 2.1 mmol), and NEt_3 (324 mg, 0.45 mL, 3.2 mmol) in EtOH (15 mL) produced **5r** as a colorless solid (285 mg, 59%). M.p. 129°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.96 (t, *J* = 7.3 Hz, 3H; CH_3), 1.40 (sext, *J* = 7.5 Hz, 2H; CH_2), 1.63 (m, 2H; CH_2), 2.72 (t, *J* = 7.7 Hz, 2H; CH_2), 7.23 (d, *J* = 8.8 Hz, 1H; Ar), 7.36 (m, 2H; Ar), 7.56 ppm (d, *J* = 8.0 Hz, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 13.95 (CH_3), 22.57, 29.40, 31.38 (CH_2), 105.30 (C), 111.71, 118.93, 122.74, 129.89 (CH), 130.58, 131.34, 131.69 (C), 137.58 (CH), 148.62, 160.38 (C), 165.33 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3432 (w), 3132 (m), 3105 (m), 3073 (m), 2965 (s), 2931 (s), 2890 (m), 2867 (s), 1430 (s), 1385 (m), 1345 (m), 1316 (s), 1269 (s), 1234 (s), 1217 (s), 1128 (s), 1093 (s), 837 (m), 777 (w), 742 (s), 728 (s), 643 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 343 (4.06), 308 (3.72), 296 (3.71), 281 (3.99), 267 (4.02), 234 (4.56), 213 nm (4.53); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 490 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 302 (44) $[M]^+$, 273 (5), 258 (100), 168 (3), 151 (7), 107 (3), 74 (9); elemental analysis calcd (%) for $C_{17}H_{15}ClO_3$: C 67.44, H 4.99; found: C 67.22, H 5.28.

2-Chloro-7-hydroxy-8-hexyl-6*H*-benzo[*c*]chromen-6-one (5s): The starting materials **1d** (289 mg, 1.6 mmol), Me_3SiOTf (467 mg, 2.1 mmol), **3g** (753 mg, 2.1 mmol) and NEt_3 (324 mg, 0.45 mL, 3.2 mmol) in EtOH (15 mL) produced **5s** as a colorless solid (297 mg, 56%). M.p. 75°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.90 (t, *J* = 6.9 Hz, 3H; CH_3), 1.38 (m, 6H; CH_2), 1.60 (m, 2H; CH_2), 2.71 (m, 2H; CH_2), 7.23 (d, *J* = 8.8 Hz, 1H; Ar), 7.36 (dd, *J* = 8.0, 2.2 Hz, 2H; Ar), 7.56 (d, *J* = 8.0 Hz, 1H; Ar), 7.87 (d, *J* = 2.3 Hz, 1H; Ar), 11.49 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 14.07 (CH_3), 22.59, 29.14, 29.15, 29.66, 31.66 (CH_2), 105.25 (C), 111.67, 118.88 (CH), 119.91 (C), 122.69, 129.84 (CH), 130.54, 131.28, 131.69 (C), 137.53 (CH), 148.58, 160.33 (C), 165.29 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3437 (w), 3134 (w), 3104 (w), 3074 (w), 2949 (m), 2928 (s), 2865 (m), 2852 (m), 1669 (s), 1613 (m), 1569 (w), 1479 (m), 1431 (s), 1387 (m), 1342 (w), 1317 (m), 1268 (s), 1244 (m), 1216 (s), 1130 (m), 1095 (s), 834 (m), 809 (m), 779 (w), 748 (w), 729 (s), 643 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 343 (4.09), 308 (3.58), 297 (3.56), 281 (3.94), 267 (4.01), 235 (4.58), 124 nm (4.53); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 495 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 330 (40) $[M]^+$, 273 (7), 256 (100), 168 (2), 151 (2), 70 (2); elemental analysis calcd (%) for $C_{19}H_{19}ClO_3$: C 68.98, H 5.78; found: C 68.85, H 5.89.

2-Bromo-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (5t): The starting materials **1e** (225 mg, 1.0 mmol), Me_3SiOTf (289 mg, 1.3 mmol), **3a** (357 mg, 1.3 mmol), and NEt_3 (202 mg, 0.23 mL, 2.0 mmol) in EtOH (8 mL) produced **5t** as a colorless solid (137 mg, 47%). M.p. 186°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.13 (dd, *J* = 8.2, 1.0 Hz, 1H; Ar), 7.27 (d, *J* = 8.7 Hz, 1H; Ar), 7.56–7.62 (m, 2H; H-3, Ar), 7.75 (t, *J* = 8.2 Hz, 1H; Ar), 8.16 (d, *J* = 2.2 Hz, 1H; Ar), 11.27 ppm (s, 1H; OH); ^{13}C NMR (APT, $CDCl_3$, 75.5 MHz): δ = 105.96 (C), 112.34, 117.34 (CH), 118.17 (C), 119.41 (CH), 120.07 (C), 126.18, 133.39 (CH), 133.82 (C), 137.48 (CH), 149.37, 162.52, 164.84 ppm (C); IR (KBr): $\tilde{\nu}$ = 3162 (w), 3150 (w), 2980 (w), 1691 (s), 1618 (m), 1606 (m), 1566 (m), 1450 (s), 1274 (s), 1266 (s), 1249 (m), 1238 (s), 1213 (s), 1178 (s), 1135 (m), 1108 (m), 1077 (s), 812 (s), 799 (w), 723 (w), 688 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 349 (3.89), 336 (3.92), 296 (3.36), 277 (3.79), 267 (3.90), 258 (3.90), 221 nm (4.66); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 483 nm (340 nm); MS (EI, 70 eV): *m/z* (%): 290 (100) $[M]^+$, 264 (12), 211 (13), 183 (16), 155 (20), 127 (9), 77(6), 63 (8); HRMS (EI, 70 eV): *m/z*: calcd for $C_{13}H_7O_3Br$: 289.9579 $[M]^+$; found: 289.9579 ± 2 ppm.

2-Chloro-7-hydroxy-3-methyl-6*H*-benzo[*c*]chromen-6-one (5u): The starting materials **1f** (195 mg, 1.0 mmol), Me_3SiOTf (289 mg, 1.3 mmol), **3a** (357 mg, 1.3 mmol) and NEt_3 (202 mg, 0.23 mL, 2.0 mmol) in EtOH (8 mL) produced **5u** as a colorless solid (162 mg, 62%). M.p. 206°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.32 (s, 3H; CH_3), 7.12 (dd, *J* = 8.1, 0.8 Hz, 1H; Ar), 7.51 (s, 1H; Ar), 7.82 (t, *J* = 8.1 Hz, 1H; Ar), 7.91 (dd, *J* = 8.1, 0.8 Hz, 1H; Ar), 8.40 (s, 1H; Ar), 11.25 ppm (s, 1H; OH); ^{13}C NMR (DEPT, [D_6]DMSO, 75.5 MHz): δ = 19.15 (CH_3), 104.85 (C), 111.55, 115.81 (CH), 116.54 (C), 118.63, 122.68 (CH), 130.22, 133.67 (C), 136.80 (CH), 138.36, 147.85, 161.45, 164.22 ppm (C); IR (KBr): $\tilde{\nu}$ = 3430 (m), 3052 (w), 1691 (s), 1615 (s), 1586 (m), 1562 (m), 1456 (s), 1376 (m), 1277 (m), 1250 (s), 1220 (s), 1175 (m), 1163 (s), 1089 (s), 1011 (m), 811 (s), 718 (m), 690 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 352 (3.98), 338 (4.02), 307 (3.61), 295 (3.56), 278 (3.98), 268 (4.02), 222 nm (4.82); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 485 nm (340 nm); MS (EI, 70 eV): *m/z* (%): 260 (100) $[M]^+$, 231 (5), 168 (4), 139 (7), 70 (3); HRMS (EI, 70 eV): *m/z*: calcd for $C_{14}H_9O_3Cl$: 260.0240 $[M]^+$; found: 260.0240 ± 2 ppm.

7-Hydroxy-3-methoxy-6*H*-benzo[*c*]chromen-6-one (5v): The starting materials **1g** (234 mg, 1.6 mmol), Me_3SiOTf (467 mg, 2.1 mmol), **3a** (576 mg, 2.1 mmol), and NEt_3 (324 mg, 0.45 mL, 3.2 mmol) in EtOH (14 mL) produced **5v** as a colorless solid (265 mg, 51%). M.p. 167°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.89 (s, 3H; OCH_3), 6.86 (d, *J* = 2.5 Hz, 1H; Ar), 6.94 (dd, *J* = 8.8, 2.6 Hz, 1H; Ar), 6.99 (dd, *J* = 8.3, 0.8 Hz, 1H; Ar), 7.46 (dd, *J* = 8.0, 0.4 Hz, 1H; Ar), 7.68 (t, *J* = 8.1 Hz, 1H; Ar), 7.92 (d, *J* = 8.9 Hz, 1H; Ar), 11.32 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 55.73 (OCH_3), 101.49 (CH), 105.20, 111.34 (C), 111.44, 113.12, 115.19 (CH), 124.37, 135.70 (C), 137.35 (CH), 151.85, 161.62, 162.45, 165.66 ppm (C); IR (KBr): $\tilde{\nu}$ = 3094 (m), 3066 (m), 3024 (w), 1682 (s), 1623 (s), 1570 (m), 1524 (w), 1488 (m), 1465 (s), 1438 (s), 1352 (m), 1314 (s), 1298 (s), 1253 (s), 1223 (m), 1169 (s), 1084 (s), 1027 (w), 856 (w), 803 (s), 724 (s), 691 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 346 (4.03), 302 (3.88), 268 (4.09), 241 (4.39), 211 nm (4.54); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 407 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 242 (100) $[M]^+$, 198 (24), 171 (7), 114 (10), 89 (2), 64 (3); HRMS (FT-ICR): calcd for $C_{14}H_{11}O_4$: 243.06519 $[M+1]^+$; found: 243.06537.

3-(Benzyloxy)-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (5x): The starting materials **1h** (303 mg, 1.20 mmol), Me_3SiOTf (347 mg, 1.56 mmol), **3a** (428 mg, 1.56 mmol), and NEt_3 (246 mg, 0.43 mL, 2.43 mmol) in EtOH (12 mL) produced **5x** as a colorless solid (128 mg, 48%). M.p. 144°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.17 (s, 3H; CH_3), 5.15 (s, 2H; OCH_2), 6.93 (d, *J* = 2.5 Hz, 1H; Ar), 7.01 (m, 2H; Ar), 7.34–7.47 (br m, 5H; Ph), 7.68 (t, *J* = 8.2 Hz, 1H; Ar), 7.92 (d, *J* = 8.8 Hz, 1H; Ar), 11.31 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 70.50 (OCH_2), 102.61 (CH), 105.25 (C), 111.50 (CH), 111.61, 113.82, 115.29, 124.44, 127.54, 128.37, 128.77 (CH), 135.68, 135.91 (C), 137.40 (CH), 151.78, 160.68, 162.47, 165.67, 173.42 ppm (C); IR (KBr): $\tilde{\nu}$ = 3091 (w), 2958 (w), 2926 (m), 1688 (s), 1611 (s), 1573 (w), 1465 (m), 1438 (w), 1394 (w), 1371 (w), 1309 (w), 1290 (m), 1249 (s), 1217 (m), 1188 (m), 1170 (s), 1146 (s), 1082 (s), 1024 (m), 1010 (m), 796 (m), 749 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max}: 346, 302, 291, 269, 237, 209 nm; fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 486 nm (350 nm); MS (EI, 70 eV): *m/z* (%): 318 (43) $[M]^+$, 91 (100).

7-Hydroxy-10-methyl-6*H*-benzo[*c*]chromen-6-one (5y): The starting materials **1i** (160 mg, 1.0 mmol), Me_3SiOTf (289 mg, 1.3 mmol), **3a** (357 mg, 1.3 mmol), and NEt_3 (202 mg, 0.23 mL, 2.0 mmol) in EtOH (8 mL) produced **5y** as a colorless solid (109 mg, 48%). M.p. 144°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.75 (s, 3H; CH_3), 7.05 (d, *J* = 8.6 Hz, 1H; Ar), 7.41–7.48 (m, 2H; Ar), 7.56–7.62 (m, 1H; Ar), 7.69 (d, *J* = 8.6 Hz, 1H; Ar), 8.38 (dd, *J* = 8.0, 1.3 Hz, 1H; Ar), 11.63 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 24.08 (CH_3), 106.47 (C), 116.24, 117.37 (CH), 119.34 (C), 124.89 (CH), 125.19 (C), 127.45, 130.13 (CH), 132.56 (C), 142.10 (CH), 149.93 (C), 160.27 (C–OH), 165.35 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3250 (w), 3002 (w), 2900 (m), 2870 (m), 1679 (s), 1599 (s), 1575 (m), 1481 (m), 1467 (s), 1446 (s), 1434 (m), 1309 (m) 1267 (s), 1236 (s) 1213 (s), 1198 (s), 1129 (m) 1082 (m), 801 (m), 760 (s), 734 (m), 674 (m), 625 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 345 (3.92), 298 (3.18), 263 (4.01), 239 (4.45), 232 (4.47), 204 nm (4.42); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 493 nm (348 nm); MS (EI, 70 eV): *m/z* (%): 226 (100) $[M]^+$,

197 (18), 181 (10), 141 (8); HRMS (EI, 70 eV): *m/z*: calcd for $C_{14}H_{10}O_3$: 226.0630 $[M]^+$; found: 226.0630 ± 2 ppm.

7-Hydroxy-8-methyl-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile (5z): The starting materials **1j** (171 mg, 1.0 mmol), Me_3SiOTf (289 mg, 1.3 mmol), **3b** (357 mg, 1.3 mmol), and NEt_3 (202 mg, 0.23 mL, 2.0 mmol) in EtOH (10 mL) produced **5z** as a colorless solid (85 mg, 34 %). M.p. 238 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.38 (s, 3H; CH_3), 7.41–7.49 (m, 2H; Ar), 7.59–7.64 (m, 1H; Ar), 7.87 (s, 1H; Ar), 9.18 (dd, J = 2.3, 1.4 Hz; Ar), 12.66 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 15.47 (CH_3), 96.11 (*C*−CN), 106.15 (CN), 116.71 (C), 117.89 (CH), 119.55 (C), 125.04, 125.72 (CH), 127.55 (C), 132.15 (CH), 135.30 (C), 143.76 (CH), 150.28, 164.70, 165.05 ppm (C); IR (KBr): $\tilde{\nu}$ = 3420 (w), 2970 (w), 2830 (w), 2212 (s), 1684 (s), 1600 (s), 1459 (s), 1412 (m), 1388 (m), 1326 (m), 1262 (s) 1219 (m), 1170 (s), 1147 (s), 1112 (s), 811 (m), 764 (s), 666 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 350 (3.81), 338 (3.34), 311 (4.02), 299 (3.95), 288 (3.96), 254 (4.48), 206 nm (4.52); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 489 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 251 (100) $[M]^+$, 222 (18), 194 (14), 177 (8), 140 (10), 71 (6); elemental analysis calcd (%) for $C_{15}H_9NO_3$: C 71.98, H 3.61, N 5.60; found: C 71.71, H 4.20, N 5.70.

7-Hydroxy-8-ethyl-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile (5aa): The starting materials **1j** (171 mg, 1.0 mmol), Me_3SiOTf (289 mg, 1.3 mmol), **3c** (393 mg, 1.3 mmol), and NEt_3 (202 mg, 0.23 mL, 2.0 mmol) in EtOH (10 mL) produced **5aa** as a colorless solid (98 mg, 37 %). M.p. 183 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.30 (t, J = 7.2 Hz, 3H; CH_2CH_3), 2.78 (q, J = 7.2 Hz, 2H; CH_2CH_3), 7.41–7.49 (m, 2H; Ar), 7.59–7.62 (m, 1H; Ar), 7.88 (s, 1H; Ar), 9.19 (dd, J = 2.3, 1.4 Hz, 1H; Ar), 12.71 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 12.98 (CH_3), 22.51 (CH_2), 96.32, 106.29, 116.80 (C), 117.92 (CH), 119.78 (C), 125.11, 125.76, 132.18 (CH), 133.23, 135.31 (C), 142.34 (CH), 150.34, 164.21, 165.20 ppm (C); IR (KBr): $\tilde{\nu}$ = 3150 (w), 2971 (w), 2939 (w), 2877 (w), 2219 (m), 1675 (s), 1600 (s), 1459 (s), 1440 (m), 1422 (s), 1361 (w), 1338 (m), 1316 (m), 1273 (s), 1250 (m), 1221 (m), 1169 (s), 1155 (m), 1115 (m), 817 (s), 796 (m), 764 cm^{-1} (s); UV/Vis (CH_3CN): λ_{max} (lg ε): 383 (3.11), 351 (3.78), 338 (3.79), 311 (3.97), 300 (3.92), 289 (3.93), 255 (4.45), 208 nm (4.44); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 485 nm (340 nm); MS (EI, 70 eV): *m/z* (%): 265 (64) $[M]^+$, 251 (94), 211 (3), 58 (7), 32 (23); HRMS (EI, 70 eV): *m/z*: calcd for $C_{16}H_{11}O_3N$: 265.0739 $[M]^+$; found: 265.0739 ± 2 ppm.

7-Hydroxy-8-propyl-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile (5ab): The starting materials **1j** (205 mg, 1.2 mmol), Me_3SiOTf (347 mg, 1.6 mmol), **3l** (428 mg, 1.6 mmol), and NEt_3 (242 mg, 0.28 mL, 2.4 mmol) in EtOH (12 mL) produced **5ab** as a colorless solid (124 mg, 37 %). M.p. 172 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.01 (t, J = 7.4 Hz, 3H; CH_3), 1.69 (m, 2H; CH_2CH_3), 2.74 (t, J = 7.3 Hz, 2H; $ArCH_2$), 7.45 (m, 2H; Ar), 7.61 (m, 1H; Ar), 7.86 (s, 1H; Ar), 9.20 (dd, J = 8.1, 1.3 Hz, 1H; Ar), 12.69 ppm (s, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz,): δ = 13.81 (CH_3), 21.89 (CH_2CH_3), 31.21 ($ArCH_2$), 96.09, 106.20, 116.63 (C), 117.82 (CH), 119.60 (C), 124.94, 125.66 (CH), 131.74 (C), 132.11 (CH), 135.16 (C), 143.06 (CH), 150.20, 164.48, 165.03 ppm (C); IR (KBr): $\tilde{\nu}$ = 3434 (m), 2961 (m), 2875 (m), 2219 (m), 1678 (s), 1602 (s), 1459 (s), 1416 (s), 1357(m), 1325 (s), 1270 (s), 1224 (m), 1168 (s), 1115 (m), 814 (m), 791 (w), 761 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 351 (3.83), 339 (3.86), 311 (4.03), 299 (3.96), 289 (3.96), 255 (4.48), 208 nm (4.47); MS (EI, 70 eV): *m/z* (%): 279 (43) $[M]^+$, 264 (12), 250 (100), 222 (4), 206 (2), 164 (4), 139 (5), 77 (50), 43 (4); HRMS (EI, 70 eV): *m/z*: calcd for $C_{17}H_{13}NO_3$: 279.0895 $[M]^+$; found: 279.0895 ± 2 ppm.

8-Butyl-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile (5ac): The starting materials **1j** (257 mg, 1.5 mmol), Me_3SiOTf (433 mg, 1.95 mmol), **3f** (645 mg, 1.95 mmol), and NEt_3 (304 mg, 0.42 mL, 3.0 mmol) in EtOH (10 mL) produced **5ac** as a colorless solid (237 mg, 54 %). M.p. 132 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.98 (t, J = 7.3 Hz, 3H; CH_3), 1.42 (m, 2H; CH_2), 1.65 (m, 2H; CH_2), 2.74 (t, J = 7.6 Hz, 2H; $ArCH_2$), 7.39–7.47 (m, 2H; Ar), 7.60 (m, 1H; Ar), 7.84 (s, 1H; Ar), 9.15 (dd, J = 8.3, 1.4 Hz, 1H; Ar), 12.67 (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 13.88 (CH_3), 22.47, 28.99, 30.86 (CH_2), 96.18, 106.28, 116.72 (C), 117.88 (CH), 119.68 (C), 125.03, 125.73 (CH), 132.05 (C), 132.16 (CH), 135.21 (C), 143.06 (CH), 150.28, 164.51, 165.12 ppm (C); IR (KBr): $\tilde{\nu}$ = 3126 (w), 2958 (w), 2929 (w), 2866 (w), 2219 (m), 1679 (s), 1602 (s), 1458 (s), 1414 (s), 1352 (m), 1326 (s), 1268 (s), 1213 (m), 1169 (s), 1114 (m), 805 (m) 791 (m), 765 (s), 739 (m), 668 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 351 (3.86), 339 (3.88), 311 (4.04), 299 (3.95), 289 (3.96), 255 (4.50), 207 nm (4.53); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 479 nm (345); MS (EI, 70 eV): *m/z* (%): 293 (100) $[M]^+$, 250 (26), 222 (3), 210 (3), 164 (79), 161 (18), 70 (3); HRMS (EI, 70 eV): *m/z*: calcd for $C_{18}H_{15}O_3N$: 293.1052 $[M]^+$; found: 293.1052 ± 2 ppm.

Methyl 6-(2′,3′-dihydrochromon-2′-yl)-3,5-dioxohexanoate (4ad): TMSOTf (0.93 g, 4.20 mmol) was added to a solution of **1a** (0.47 g, 3.22 mmol) in CH_2Cl_2 (1 mL) at 20 °C and the solution was stirred for 1 h. After this time, CH_2Cl_2 (5 mL), 2,6-lutidine (0.45 g, 4.20 mmol) and **3m** (1.56 g, 4.20 mmol, dissolved in CH_2Cl_2 (5 mL)) were added to the reaction mixture. This mixture was stirred for 15 min and then warmed to 20 °C and stirred for a further 3 h. An aqueous solution of HCl (10 %) was added to the mixture and the organic and the aqueous layers were separated; the latter was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered, and the resulting filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, petroleum ether/ether 5:1→1:2) to give **4ad** (0.39 g, 41 %) as a yellow solid. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.75 (dd, ^2J = 17, ^3J = 5 Hz, 1H; 0.5 × CH_2CH, A of AB), 2.79 (m, 2H; CH_2COH), 2.92 (dd, ^2J = 15, ^3J = 7 Hz, 1H; 0.5 × CH_2CH, B of AB), 3.37 (s, 2H; CH_2CO_2Me), 3.75 (s, 3H; CH_3), 4.88 (m, 1H; CH−O), 5.73 (s, 1H; =CH), 7.00 (m, 2H; 2 × CH, Ar), 7.48 (m, 1H; CH, Ar), 7.86 ppm (m, 1H; CH, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 42.49, 43.00, 44.60 (CH_2), 52.47 (CH_3), 74.07 (*C*HCH$_2$), 101.27 (=CH), 117.85 (CH, Ar), 120.79 (C), 121.60, 126.89, 136.05 (CH, Ar), 160.87, 167.61, 186.72, 188.13, 191.17 ppm (C); MS (EI, 70 eV): δ = 304 (16) $[M]^+$, 273 (4), 203 (4), 160 (7), 147 (100), 121 (15), 101 (6), 92 (4), 69 (5), 43 (2); elemental analysis calcd (%) for $C_{16}H_{16}O_6$: C 63.15, H 5.30; found: C 63.21, H 5.35.

Methyl 3-(2′,3-dihydroxy-1′,1-biphenyl-2-yl)-3-oxopropionate (5ad): NEt_3 (0.33 g, 3.27 mmol) was added to a solution of **4ad** (0.20 g, 0.67 mmol) in EtOH (7 mL) and the solution was stirred at 20 °C for 12 h. After this time, an aqueous solution of HCl (1 M, 30 mL) was added to the mixture. The organic and aqueous layers were then separated and the latter was extracted with ether (2 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, petroleum ether/ether 40:1→4:1) to give **5ad** (60 %) as a yellow solid. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.64 (s, 3H; CH_3), 3.89 (s, 2H; CH_2), 6.75 (m, 1H; CH, Ar), 6.83 (m, 2H; 2 × CH, Ar), 7.05 (m, 1H; CH, Ar), 7.28 (m, 1H; CH, Ar), 7.50 ppm (m, 2H; 2 × CH, Ar); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 38.78 (CH_2), 52.32 (CH_3), 113.50, 118.18, 118.68, 119.19 (CH, Ar), 119.97, 129.54 (C, Ar), 132.18, 133.70 (CH, Ar), 135.37 (C, Ar), 136.30 (CH, Ar), 158.42, 163.06 (C, Ar), 172.66 (C=O), 202.24 ppm (CO_2CH_3); MS (EI, 70 eV): 286 (79) $[M]^+$, 268 (24), 255 (31), 226 (100), 213 (46), 197 (51), 181 (14), 165 (8), 121 (44), 77 (6), 65 ppm (8); HRMS (EI, 70 eV): *m/z*: calcd for $C_{16}H_{14}O_5$: 286.0841 $[M]^+$; found: 286.0841 ± 2 ppm.

2,3-Dihydrobenzopyran (4ae): The starting materials **1a** (300 mg, 2.05 mmol), Me_3SiOTf (0.48 mL, 2.70 mmol), 2,6-lutidine (0.31 mL, 2.70 mmol), and **3n** (0.898 g, 2.70 mmol) produced **4ae** as a colorless solid (493 mg, 76 %). ^{1}H NMR ($CDCl_3$, 250 MHz); mixture of diastereomers and keto/enol tautomers: δ = 1.22 (m, 3H; CH_3), 1.40–3.00 (m, 10H; CH, CH_2), 4.15 (q, 2H; OCH_2), 5.00 (m, 1H; CH−O), 6.90 (m, 2H; Ar), 7.40 (m, 1H; Ar), 7.79 (m, 1H; Ar), 12.47, 12.53 ppm (2 × s, 1H; OH, enol tautomer); IR (KBr): $\tilde{\nu}$ = 3400 (w), 2940 (m), 1742 (s), 1694 (s), 1650 (m), 1607 (s), 1579 (m), 1464 (s), 1401 (m), 1377 (m), 1306 (s), 1252 (m), 1226 (s), 1150 (m), 1083 (m), 1026 (m), 766 cm^{-1} (m); MS (70 eV) *m/z* (%): 316 (10) $[M]^+$, 170 (18), 147 (100); HRMS (EI, 70 eV): *m/z*: calcd for $C_{18}H_{20}O_5$: 316.1310 $[M]^+$; found: 316.1310 ± 2 ppm.

2,3-Dihydrobenzopyran (4af): NEt_3 and Me_3SiCl were added to a solution of **4ae** in THF and the mixture was stirred for 12 h. After this time, the solvent was removed in vacuo, hexane was added, and the suspension was filtered. The resulting filtrate was concentrated in vacuo to give **4af** as a yellow oil (279 mg, 95 %). The product was obtained as a 3:2 mixture of diastereomers. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.12 (2 × s, 9H; $SiMe_3$), 1.25 (2 × t, J = 7.0 Hz, 3H; CH_3), 1.40–2.95 (m, 9H; CH_2, CH),

4.15 (q, $J=7.0$ Hz, 2H; OCH_2), 4.75–4.85 (2×m, 1H; ring CH−O), 6.90 (m, 2H; Ar), 7.40 (m, 1H; Ar), 7.82 ppm (d, $^3J=8.0$ Hz, 1H; Ar); ^{13}C NMR ($CDCl_3$, 62.5 MHz); major diastereomer: $\delta=1.28$, 1.49 ($SiMe_3$), 14.23 (CH_3), 20.17, 20.73, 23.09, 23.26, 25.28, 26.68, 37.95, 40.72 (CH_2), 44.48, 45.01 (CH), 59.56, 59.63 (OCH_2), 76.49, 78.19 (H), 112.82, 113.29 (C), 117.64, 117.96, 120.54, 120.63, 126.69, 126.81, 135.64, 135.69 (CH), 155.80, 156.85, 161.33, 161.75, 166.86, 167.09, 192.38 ppm (C); MS (EI, 70 eV): *m/z* (%): 388 $[M]^+$, 12), 373 (50), 242 (18), 196 (30), 147 (100).

2,3-Dihydrobenzopyran (4ag): The starting materials **1a** (200 mg, 1.36 mmol), Me_3SiOTf (0.32 mL, 1.78 mmol), 2,6-lutidine (0.21 mL, 1.78 mmol), and **3o** (0.513 g, 1.78 mmol) produced **4ag** as a colorless solid (138 mg, 40%, mixture of *E*/*Z* isomers). A small sample of a pure isomer was isolated. ^{1}H NMR ($CDCl_3$, 250 MHz); isomeric mixture: $\delta=$ 2.21 (s, 3H; CH_3), 2.50 (dd, $^2J=17.0$, $^3J=5.0$ Hz, 1H; ring CH_2), 2.65 (d, $J=7.0$ Hz, 2H; chain CH−CH_2), 2.75 (dd, $^2J=17.0$, $^3J=7.2$, 1H; ring CH_2), 3.67 (s, 3H; OCH_3), 4.62 (m, 1H; C*H*−CH_2), 5.75 (s, 1H; =CH−CO_2Me), 6.95 (m, 2H; Ar), 7.45 (t, $J=7.6$ Hz, 1H; Ar), 7.85 ppm (dd, $^3J=7.6$, $^4J=1.5$ Hz, 1H; Ar); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta=26.85$ (CH_3), 42.75, 42.92, 44.38, 44.44 (CH_2), 51.22 (OCH_3), 75.43, 75.81 (CH), 117.73, 117.77 (CH), 120.82, 120.87 (C), 120.97, 121.45, 121.48, 121.62, 126.95, 135.90, 135.95, 136.14 (CH), 153.76, 153.97, 160.96, 161.01, 166.11, 191.47, 191.87 ppm (C); IR (KBr): $\tilde{\nu}=2951$ (m), 1717 (s), 1693 (s), 1650 (m), 1606 (s), 1465 (s), 1304 (m), 1227 (m), 1152 (m), 1119 (m), 1079 (w), 1032 (w), 858 (m), 766 cm^{-1} (m); MS (70 eV) *m/z* (%): 260 (8) $[M]^+$, 147 (100); HRMS (EI, 70 eV): *m/z*: calcd for $C_{15}H_{16}O_4$: 260.1049 $[M]^+$; found: 260.1049±2 mD; elemental analysis calcd (%) for $C_{15}H_{16}O_4$: C 69.21, H 6.19; found: C 69.09, H 6.25.

General procedure for the synthesis of 7,8-di(hydroxy)-6*H*-benzo[*c*]chromen-6-ones (5k, 5o, and 5w): BBr_3 (4.0 equiv) was added to a solution of **5j,n,v** (1.0 equiv) in CH_2Cl_2 (10 mL per 1.0 mmol) at 0°C. The reaction mixture was warmed to 20°C over 3 h, and was then poured into an aqueous solution of hydrochloric acid (10%) and stirred for 30 min at 20°C. After this time, the organic and the aqueous layers were separated and the latter was extracted with Et_2O (4×30 mL). The combined organic layers were dried (Na_2SO_4), filtered, and the resulting filtrate was concentrated in vacuo. The residue produced was purified by column chromatography (silica gel, *n*-hexane/EtOAc 10:1→3:1) to give **5k,o,w**.

7,8-Dihydroxy-6*H*-benzo[*c*]chromen-6-one (5k): The starting materials **5j** (65 mg, 0.25 mmol) in CH_2Cl_2 (3 mL) and BBr_3 (501 mg, 0.19 mL, 1.0 mmol) produced **5k** as a colorless solid (48 mg, 84%). M.p. 196°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=5.79$ (s, 1H; OH), 7.32–7.45 (m, 4H; Ar), 7.55 (d, $J=8.6$ Hz, 1H; Ar), 7.98 (dd, $J=8.0$, 1.5 Hz, 1H; Ar), 11.37 ppm (s, 1H; OH); ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta=106.34$ (C), 112.82, 117.73 (CH), 118.68 (C), 122.60, 122.67, 125.31 (CH), 126.73 (C),129.42 (CH) 144.50, 148.37, 149.94 (C), 165.64 ppm (C=O); IR (KBr): $\tilde{\nu}=3397$ (m), 3169 (m), 3075 (m), 1675 (s), 1604 (m), 1465 (m), 1434 (m), 1391 (w), 1283 (s), 1276 (s), 1245 (m), 1198 (m), 1139 (s), 826 (w), 753 (m), 677 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 355 (3.85), 303 (3.83), 294 (3.82), 263 (3.87), 234 (4.39), 203 nm (4.25); MS (EI, 70 eV): *m/z* (%): 228 (100) $[M]^+$, 200 (7), 192 (12), 166 (31), 135 (5), 114 (10), 81 (2), 70 (8), 57 (11); elemental analysis calcd (%) for $C_{13}H_8O_4$ (228.2): C 68.42, H 3.53; found: C 68.05, H 3.79.

2,7-Dihydroxy-6*H*-benzo[*c*]chromen-6-one (5o): The starting materials **5n** (168 mg, 0.69 mmol) in CH_2Cl_2 (8 mL) and BBr_3 (695 mg, 0.26 mL, 2.78 mmol) produced **5o** as a colorless solid (137 mg, 87%). M.p. 242°C; ^{1}H NMR ([D$_6$]DMSO, 300 MHz): $\delta=7.02$ (dd, $J=8.9$, 2.7 Hz, 1H; Ar), 7.15 (dd, $J=8.2$, 0.9 Hz, 1H; Ar), 7.32 (d, $J=2.7$ Hz, 1H; Ar), 7.56 (d, $J=2.7$ Hz, 1H; Ar), 7.73 (dd, $J=7.1$, 0.9 Hz, 1H; Ar), 7.82 (t, $J=8.1$ Hz, 1H; Ar), 9.82 (s, 1H; OH), 11.34 ppm (s, 1H; OH); ^{13}C NMR (DEPT, [D$_6$]DMSO, 75.5 MHz): $\delta=105.78$ (C), 108.49, 112.93, 116.11, 118.29 (CH), 118.50 (C), 118.74 (CH), 134.99 (C), 137.65 (CH), 143.34, 154.68, 161.39 (C), 164.81 ppm (C=O); IR (KBr): $\tilde{\nu}=3530$ (s), 3424 (s), 1672 (s), 1616 (s), 1598 (m), 1573 (s), 1498 (m), 1453 (s), 1337 (m), 1265 (s), 1232 (s), 1202 (s), 1174 (s), 1107 (m), 851 (w), 816 (m), 716 (w), 692 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 342 (3.98), 272 (3.91), 237 (4.49), 217 nm (4.39); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 415 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 228 (100) $[M]^+$, 200 (7), 173 (9), 146 (4), 136 (3), 114 (10), 88 (2), 55 (8), 28 (9); HRMS (FT-ICR): calcd for $C_{13}H_9O_4$: 229.04954 $[M+1]^+$; found: 229.04938.

3,7-Dihydroxy-6*H*-benzo[*c*]chromen-6-one (5w): The starting materials **5v** (197 mg, 0.81 mmol) in CH_2Cl_2 (8 mL) and BBr_3 (815 mg, 0.31 mL, 3.25 mmol) produced **5w** as a colorless solid (168 mg, 91%). M.p. 238°C; ^{1}H NMR ([D$_6$]DMSO, 300 MHz): $\delta=6.78$ (d, $J=2.4$ Hz, 1H; Ar), 6.86 (dd, $J=8.7$, 2.4 Hz, 1H; Ar), 6.96 (dd, $J=8.1$, 1.0 Hz, 1H; Ar), 7.67 (dd, $J=8.1$, 1.0 Hz, 1H; Ar), 7.75 (t, $J=8.1$ Hz, 1H; Ar), 8.11 (d, $J=8.7$ Hz, 1H; Ar), 10.50 (br s, 1H; OH), 11.18 ppm (s, 1H; OH); ^{13}C NMR (DEPT, [D$_6$]DMSO, 75.5 MHz): $\delta=102.95$ (CH), 104.66, 109.60 (C), 112.01, 113.86, 114.39, 125.41 (CH), 135.90 (C), 137.75 (CH), 151.51, 160.08, 161.32, 164.91 ppm (C=O); IR (KBr): $\tilde{\nu}=3181$ (m), 2150 (w), 2350 (w), 1741 (s), 1414 (s), 1679 (s), 1656 (s), 1603 (s), 1575 (s), 1466 (s), 1391 (m), 1371 (m), 1314 (m), 1291 (s), 1256 (s), 1231 (s), 1185 (m), 1161 (m), 1131 (m), 1027 (m), 850 (m), 805 (w), 757 (m), 650 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 307 (3.67), 269 (3.99), 234 (3.99), 212 nm (4.16); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 481 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 228 (4) $[M]^+$, 177 (14), 163 (92), 137 (100), 107 (36), 81 (10), 70 (27), 43 (38), 29 (48).

7-Hydroxydibenzo[*c*,*d*]chromen-6-one (7): The synthesis of **7** was carried out according to the procedure as given for the synthesis of **5a**. The starting materials **6** (294 mg, 1.5 mmol), Me_3SiOTf (433 mg, 1.95 mmol), **3a** (535 mg, 1.95 mmol) and NEt_3 (304 mg, 0.42 mL, 3.0 mmol) in EtOH (10 mL) produced **7** as a colorless solid (239 mg, 61%). M.p. 205°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.12$ (dd, $J=8.2$, 1.0 Hz, 1H; Ar), 7.63–7.69 (m, 3H; Ar), 7.76–7.83 (m, 2H; Ar), 7.91 (dd, $J=7.2$, 2.2 Hz, 1H; Ar), 8.04 (d, $J=8.9$, 1H; Ar), 8.57 (dd, $J=7.2$, 1.8 Hz, 1H; Ar), 11.43 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta=106.22$ (C), 112.54 (CH), 113.52 (C), 116.14, 119.53, 122.06 (CH), 123.65 (C), 125.09, 127.30, 127.67, 128.04 (CH), 134.27, 135.87 (C), 137.43 (CH), 146.49 (C), 162.54, 165.37 ppm (C=O); IR (KBr): $\tilde{\nu}=2362$ (m), 1685 (s), 1622 (s), 1590 (m), 1567 (m), 1496 (m), 1452 (m), 1372 (m), 1363 (m), 1284 (m), 1236 (s), 1185 (s), 1109 (s), 801 (s), 733 (m), 696 (w), 672 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 364 (4.03), 349 (4.09), 306 (3.83), 294 (3.88), 267 (4.51), 258 (4.40), 238 nm (4.71); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 403 nm (350 nm); MS (EI, 70 eV): *m/z* (%): 262 (100) $[M]^+$, 97 (1), 70 (2), 57 (1).

Synthesis of autumnariol

1-(2,4-Dihydroxy-6-methylphenyl)ethanone (9): Acetonitrile (1.86 g, 2.37 mL, 28.6 mmol) and dry $ZnCl_2$ (0.56 g, 4.29 mmol) was added to a solution of 3,5-dihydroxytoluene (1.76 g, 14.3 mmol) in Et_2O (10 mL). Hydrogen chloride gas was then bubbled through the mixture, and the resulting precipitate was filtered off and dissolved in water. This solution was neutralized by using aqueous ammonia solution and was subsequently stirred for 30 min at 100°C. The crude product was recrystallized from water to give **9** as a colorless solid (975 mg, 41%). M.p. 158°C (lit.[1] 132–133°C); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=2.56$ (s, 3H; CH_3), 2.63 (s, 3H; CH_3), 5.27 (s, 1H; OH), 6.23–6.26 (m, 2H; Ar), 13.41 (s, 1H; OH).

7-Hydroxy-5-methyl-4*H*-chromen-4-one (10): Perchloric acid (60%, 933 mg, 0.56 mL, 5.81 mmol) was added to a solution of **9** (725 mg, 4.36 mmol) in $HC(OEt)_3$ (6.46 g, 7.18 mL, 43.6 mmol) at 0°C. The reaction mixture was warmed to 20°C over 12 h. The precipitated crude product was filtered and washed with water. Finally, the residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc 3:1) to give **10** as a red solid (430 mg, 56%). M.p. 229°C; ^{1}H NMR ([D$_6$]DMSO, 300 MHz): $\delta=2.65$ (s, 3H; CH_3), 6.10 (d, $J=5.9$ Hz, 1H; C=CH), 6.66 (m, 2H; Ar), 8.02 (d, $J=5.9$ Hz, 1H; C=CH), 10.64 ppm (br s, 1H; OH); ^{13}C NMR (DEPT, [D$_6$]DMSO, 75.5 MHz): $\delta=22.57$ (CH_3), 100.75 (CH; Ar), 113.23 (CH), 115.66 (C), 116.83 (CH; Ar), 141.78 (C), 154.39 (CH), 159.19, 161.11 (C), 177.73 ppm (C=O); IR (KBr): $\tilde{\nu}=3421$ (m), 3199 (m), 3109 (m), 3004 (m), 1640 (s), 1620 (s), 1696 (s), 1553 (s), 1485 (s), 1447 (s), 1412 (s), 1353 (s), 1326 (m), 1300 (s), 1286 (s), 1208 (m), 1160 (m), 1121(s), 1099 (s), 1067 (m), 1039 (m), 1009 (w), 959 (w), 882 (m), 844 (s), 826 (m), 619 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 299 (3.74), 289 (3.79), 258 (3.81), 248 (4.08), 240 nm (4.11); MS (EI, 70 eV): *m/z* (%): 176 (100) $[M]^+$, 147 (20), 122 (14), 105 (2), 91 (8), 70 (6), 66 (7), 51 (8); HRMS (EI, 70 eV): *m/z*: calcd for $C_{10}H_8O_3$: 176.0473 $[M]^+$; found: 176.0473±2 ppm.

7-(Benzyloxy)-5-methyl-4*H*-chromen-4-one (11): A mixture of **10** (357 mg, 2.03 mmol), benzylic chloride (257 mg, 0.23 mL, 2.03 mmol), and K_2CO_3 (140 mg, 1.02 mmol) in EtOH (50 mL) was stirred under reflux for 7 h. After this time, the solvent was removed in vacuo and the residue was filtered off and washed with water (3 mL) to give **11** as a dark red solid (410 mg, 76%). M.p. 114°C; ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ=2.51 (s, 3H; CH_3), 5.22 (s, 2H; OCH_2), 6.16 (d, J=5.9 Hz, 1H; C=CH), 6.88 (d, J=2.5 Hz, 1H; Ar), 7.01 (d, J=2.5 Hz, 1H; Ar), 7.36–7.50 (m, 5H; Ph), 8.07 ppm (d, J=5.9 Hz, 1H; C=CH); ^{13}C NMR (DEPT, [D$_6$]DMSO, 75.5 MHz): δ=22.38 (CH_3), 69.66 (OCH_2), 99.87 (CH; Ar), 113.23 (CH), 116.62 (CH), 116.66 (CH; Ar), 127.78, 128.02, 128.47 (CH, Ph), 136.10 (C), 154.58 (CH), 158.98, 161.10 (C), 177.63 ppm (C=O); IR (KBr): $\tilde{\nu}$=3064 (w), 3035 (w), 2966 (m), 2925 (m), 1651 (s), 1600 (s), 1568 (s), 1494 (w), 1454 (s), 1407 (m), 1380 (s), 1281 (s), 1243 (s), 1154 (s), 1090 (m), 1070 (m), 1023 (m), 964 (w), 914 (w), 846 (m), 829 8 m), 756 (m), 745 (m), 696 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 299 (3.90), 289 (3.92), 274 (3.97), 248 (4.26), 240 (4.34), 212 nm (3.48); MS (EI, 70 eV): *m/z* (%): 266 (50) $[M]^+$, 175 (1), 147 (7), 91 (100), 77 (4), 66 (19), 39 (5); HRMS (EI, 70 eV): *m/z*: calcd for $C_{17}H_{14}O_3$: 266.0943 $[M]^+$; found: 266.0943±2 ppm.

Ethyl 4-(7-(benzyloxy)-3,4-dihydro-5-methyl-4-oxo-2*H*-chromen-2-yl)-3-oxobutanoate (12): A mixture of **11** (231 mg, 0.87 mmol) and Me_3SiOTf (58 mg, 0.26 mmol) was stirred for 30 min at 20°C. After this time, CH_2Cl_2 (15 mL) was added, and the mixture was cooled to 0°C and **3a** (310 mg, 1.13 mmol) was added. The reaction mixture was warmed to 20°C over 12 h, and was subsequently poured into an aqueous solution of hydrochloric acid (10%, 10 mL). The organic and the aqueous layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (5× 40 mL). The combined organic layers were washed with water, dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc 5:1→1:1) to give **12** as an orange solid (230 mg, 67%). M.p. 114°C; ^{1}H NMR ($CDCl_3$, 300 MHz; keto/enol 9:1): δ=1.35 (t, J=7.2 Hz, 3H; OCH_2CH_3), 2.61 (s, 3H; CH_3), 2.73 (m, 2H; chain CH−CH_2), 2.87 (dd, J=16.9, 5.1 Hz, 1H; ring CH), 3.15 (dd, J=16.9, 5.1 Hz, 1H; ring CH_2), 3.54 (s, 2H; C(O)CH_2), 4.21 (q, J=7.2 Hz, 2H; OCH_2CH_3), 4.91 (m, 1H; C*H*−CH_2, keto tautomer), 5.06 (s, 2H; OCH_2Ph), 5.11 (m, 1H, C*H*−CH_2, enol tautomer), 5.30 (s; =C*H*−, enol tautomer), 6.36 (d, J=2.5 Hz, 1H; Ar), 6.46 (d, J=2.5 Hz, 1H; Ar), 7.33–7.38 (m, 5H; Ph), 12.15 ppm (s, 1H; enol OH); ^{13}C NMR ($CDCl_3$, 75.5 MHz); keto tautomer: δ=14.12 (OCH_2CH_3), 23.1 (CH_3), 43.60, 47.42, 49.96 (CH_2), 61.62 (OCH_2CH_3), 70.06 (OCH_2Ph), 72.96, 100.02 (CH; Ar), 127.48, 128.28, 128.70 (CH; Ph), 135.98, 144.33, 163.39, 164.06, 166.75 (C), 191.08 (C=O, ester), 199.22 ppm (C=O, ketone); IR (KBr): $\tilde{\nu}$=3433 (w), 2980 (w), 2934 (w), 2907 (w), 1740 (s), 1718 (s), 1671 (s), 1606 (s), 1569 (s), 1454 (s), 1405 (w), 1381 (m), 1339 (m), 1307 (w), 1271 (s), 1204 (m), 1160 (s), 1092 (w), 1028 (m), 844 (w), 754 (w), 698 (m), 664 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 307 (3.74), 273 (4.26), 220 nm (4.35); MS (EI, 70 eV): *m/z* (%): 396 (22) $[M]^+$, 351 (5), 266 (18), 240 (84), 147 (3), 91 (100), 65 (12); HRMS (FT-ICR): calcd for $C_{23}H_{25}O_6$: 397.16456 $[M+1]^+$; found: 397.16577.

3-(Benzyloxy)-7-hydroxy-1-methyl-6*H*-benzo[*c*]chromen-6-one (13): NEt_3 (81 mg, 0.11 mL, 0.80 mmol) was added to a solution of 2,3-dihydrobenzopyrane **12** (158 mg, 0.40 mmol) in EtOH (8 mL) was added at 0°C. After stirring for 12 h at 20°C and for 12 h under reflux, an aqueous solution of hydrochloric acid (10%, 8 mL) was added. The organic and the aqueous layers were then separated and the latter was extracted with CH_2Cl_2 (6×15 mL). The combined organic layers were washed with water, dried (Na_2SO_4), filtered, and the resulting filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc 20:1→1:1) to give the recovered starting material **12** (92 mg, 58%) and product **13** as a colorless solid (45 mg, 34%, 81% based on the recovered starting material). M.p. 195°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.81 (s, 3H; CH_3), 5.12 (s, 2H; OCH_2Ph), 6.84 (dd, J=9.9, 2.9 Hz, 1H; Ar), 7.02 (dd, J=7.9, 1.1 Hz, 1H; Ar), 7.32–7.47 (m, 6H; Ar), 7.64–7.74 ppm (m, 2H; Ar); IR (KBr): $\tilde{\nu}$=3065 (w), 3032 (w), 2962 (m), 2926 (m), 2855 (w), 1671 (s), 1606 (s), 1470 (m), 1465 (m), 1351 (m), 1326 (w), 1300 (m), 1233 (s), 1186 (s), 1161 (s), 1112 (m), 1093 (s), 1052 (w), 1014 (m), 812 (m), 745 (m), 692 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max}: 347, 283, 244, 208 nm; fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 409 nm (350 nm); MS (EI, 70 eV): *m/z* (%): 332 (65) $[M]^+$, 242 (5), 213 (6), 157 (5), 128 (7), 115 (4), 91 (100), 66 (15); HRMS (EI, 70 eV): *m/z*: calcd for $C_{21}H_{16}O_4$: 332.1049 $[M]^+$; found: 332.1049±2 ppm.

3,7-Dihydroxy-1-methyl-6*H*-benzo[*c*]chromen-6-one (autumnariol) (14): BBr_3 (120 mg, 0.5 mL, 0.48 mmol) was added to a solution of **13** (39 mg, 0.12 mmol) in CH_2Cl_2 (5 mL) at 0°C. The reaction mixture was then warmed to 20°C over 2 h and poured into an aqueous solution of hydrochloric acid (10%). The organic and the aqueous layers were separated and the latter was extracted with Et_2O (5×10 mL). The combined organic layers were then dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc 3:1) to give **14** as a colorless solid (27 mg, 92%). M.p. 195°C; ^{1}H NMR ([D$_6$]DMSO/[D$_4$]MeOH 10:1, 300 MHz): δ=2.75 (s, 3H; CH_3), 6.68 (d, J=2.6 Hz, 1H; Ar), 7.75 (d, J=2.7 Hz, 1H; Ar), 7.02 (m, 1H; Ar), 7.78 (m, 2H; Ar), 10.36 ppm (s, 1H; OH), 11.62 ppm (s, 1H; OH); ^{13}C NMR (DEPT, [D$_6$]DMSO/[D$_4$]MeOH 10:1, 75.5 MHz): δ=25.23 (CH_3), 101.57 (C), 104.92, 109.06 (CH), 114.35, 116.11, 117.66, 136.70 (C), 137.45 (CH), 138.33, 152.94, 158.41, 161.74, 165.05 ppm (C); IR (KBr): $\tilde{\nu}$=2969 (s), 2928 (s), 2869 (s), 1739 (m), 1722 (m), 1674 (m), 1648 (m), 1605 (s), 1569 (m), 1454 (s), 1407 (m), 1382 (m), 1363 (m), 1275 (s), 1202 (m), 1158 (s), 1091 (m), 1027 (m), 841 (w), 743 (m), 700 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max}: 353 (2.97), 308 (2.78), 296 (2.85), 269 (3.37), 246 (3.93), 217 nm (4.41); MS (EI, 70 eV): *m/z* (%): 242 (100) $[M]^+$, 213 (8), 185 (4), 171 (4), 157 (3), 128 (4), 114 (4), 70 (2), 64 (2), 28 ppm (2); HRMS (EI, 70 eV): *m/z*: calcd for $C_{14}H_{10}O_4$: 242.0579 $[M]^+$; found: 242.0579±2 ppm.

6-Oxo-6*H*-benzo[*c*]chromen-7-yl triflourmethanesulfonate (15): Pyridine (185 mg, 2.34 mmol) and Tf_2O (429 mg, 1.52 mmol) were added to a solution of **5a** (250 mg, 1.17 mmol) in CH_2Cl_2 (8 mL) at −78°C. The reaction mixture was then warmed to 20°C over 10 h. After this time, the solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc 5:1) to give **15** as a colorless solid (366 mg, 91%). M.p. 181°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.32–7.45 (m, 3H; Ar), 7.56 (dt, J=7.8, 1.5 Hz, 1H; Ar), 7.89 (t, J=8.2 Hz, 1H; Ar), 8.04 (dd, J=8.0, 1.6 Hz, 1H; Ar), 8.19 ppm (dd, J=8.4, 0.6 Hz, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz) δ=114.65, 116.57 (C), 117.78 (CH), 118.82 (quart, J=321 Hz; CF_3), 122.28, 122.79, 123.36, 125.01, 131.81, 135.66 (CH), 138.05, 149.99, 151.36 (C), 156.74 ppm (C=O); IR (KBr): $\tilde{\nu}$=1732 (s), 1615 (s), 1561 (w), 1459 (m), 1427 (s), 1301 (m), 1252 (s), 1225 (s), 1208 (s), 1168 (m), 1144 (s), 1057 (s), 1031 (w), 931 (s), 889 (m), 824 (s), 758 (s), 601 cm^{-1} (s); UV/Vis (CH_3CN): λ_{max} (lg ε): 320 (3.96), 301 (3.91), 290 (3.85), 271 (4.12), 260 (4.15), 228 (4.52), 220 (4.52), 214 (4.52), 208 (4.51), 206 nm (4.51); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 380 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 344 (100) $[M]^+$, 281 (7), 280 (50), 252 (20), 214 (3), 211 (5), 182 (34), 155 (46), 127 (28), 126 (12), 77 (10), 70 (16); elemental analysis calcd (%): for $C_{14}H_7O_5SF_3$: C 48.84, H 2.05; found C 48.70, H 1.99.

General procedure for the synthesis of 7-aryl-6*H*-benzo[*c*]chromen-6-ones (16): Tetrakis(triphenylphosphine)palladium (3 mol%) was added to a solution of **15** (1.0 equiv), K_3PO_4 (1.6 equiv), and the boronic acid (l.3 equiv) in 1,4-dioxane (3 mL) at 20°C under inert atmosphere. After stirring under reflux for 4–12 h, the solution was cooled to 20°C, filtered, and the resulting filter cake was thoroughly washed with Et_2O. The filtrate was concentrated in vacuo and the residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc 10:1) to give **16**.

7-Phenyl-6*H*-benzo[*c*]chromen-6-one (16a): The starting materials **15** (92 mg, 0.27 mmol), phenylboronic acid (42 mg, 0.35 mmol), K_3PO_4 (93 mg, 0.43 mmol), and $Pd(Ph_3)_4$ (9 mg, 8 μmol) produced **16a** as a colorless solid (reaction time: 6 h, 66 mg, 92%). M.p. 114°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.35 (m, 4H; Ar), 7.39–7.51 (br m, 5H; Ar), 7.80 (t, J=7.6 Hz, 1H; Ar), 8.10 (dd, J=7.9, 1.2 Hz, 1H; Ar), 8.18 ppm (dd, J=8.9, 1.2 Hz, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ=117.50 (CH), 118.71 (C), 121.19, 123.11, 124.25, 127.29, 127.80, 128.24, 130.49, 132.36, 133.58 (CH), 136.17, 141.92, 146.94, 151.50, 159.23 ppm (C); IR (KBr): $\tilde{\nu}$=3400 (w), 3075 (w), 1737 (s), 1594 (m), 1460 (m), 1271 (m), 1247 (m), 1212 (s), 1100 (m), 1045 (s), 757 (s), 699 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 324 (3.89), 301 (3.78), 291 (3.71), 271 (4.11), 246

(4.29), 229 (4.49), 222 (4.48), 210 nm (452); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 420 nm (350 nm); MS (EI, 70 eV): *m/z* (%): 272 (100) $[M]^+$, 255 (6), 225 (70), 215 (15), 187 (3), 151 (6), 114 (5), 95 (3), 64 (2), 43 (3); elemental analysis calcd (%) for $C_{19}H_{12}O_2$: C 83.81, H 4.44; found: C 83.39, H 4.92.

7-*p*-Tolyl-6*H*-benzo[*c*]chromen-6-one (16b): The starting materials **15** (100 mg, 0.29 mmol), 4-toloylboronic acid (57 mg, 0.38 mmol), K_3PO_4 (100 mg, 0.46 mmol), and $Pd(Ph_3)_4$ (10 mg, 9 μmol) produced **16b** as a colorless solid (reaction time: 8 h, 72 mg, 87%). M.p. 120°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.54$ (s, 3H; CH_3), 7.25 (d, $J = 5.6$ Hz, 4H; Ar), 7.31–7.36 (m, 2H; Ar), 7.41–7.52 (m, 2H; Ar), 7.79 (t, $J = 7.9$ Hz 1H; Ar), 8.10–8.18 ppm (m, 2H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta = 21.35$ (CH_3), 117.49 (CH), 118.15, 118.73 (C), 121.02, 123.09, 124.22, 128.29, 128.59, 130.44, 132.48, 133.56 (CH), 136.77, 136.96, 138.98, 147.02, 151.50, 159.25 ppm (C); IR (KBr): $\tilde{\nu} = 3425$ (w), 2921 (w), 1724 (s), 1595 (s), 1571 (m), 1515 (m), 1458 (s), 1401 (w), 1311 (w), 1271 (s), 1248 (s), 1212 (s), 1103 (m), 1046 (s), 1008 (w), 828 (m), 812 (m), 788 (w), 758 (s), 695 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 326 (3.89), 301 (3.74), 290 (3.71), 255 (4.28), 229 (4.49), 215 nm (4.52); MS (EI, 70 eV): *m/z* (%): 285 (100) $[M]^+$, 269 (5), 242 (3), 226 (3), 202 (3), 176 (2), 142 (10), 136 (3), 101 (3), 89 (2), 64 (2); elemental analysis calcd (%) for $C_{20}H_{14}O_2$: C 83.90, H 4.93; found: C 82.25, H 5.07.

7-(4-Methoxyphenyl)-6*H*-benzo[*c*]chromen-6-one (16c): The starting materials **15** (100 mg, 0.29 mmol), 4-methoxyphenylboronic acid (57 mg, 0.38 mmol), K_3PO_4 (100 mg, 0.46 mmol), and $Pd(Ph_3)_4$ (10 mg, 9 μmol) produced **16c** as a colorless solid (reaction time: 12 h, 69 mg, 79%). M.p. 127°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 3.87$ (s, 1H; OCH_3), 6.97 (m, 2H; Ar), 7.27–7.36 (m, 4H; Ar), 7.42 (dd, $J = 7.5$, 1.1 Hz, 1H; Ar), 7.48 (m, 1H; Ar), 7.79 (t, $J = 8.0$ Hz, 1H; Ar), 8.13 ppm (m, 2H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta = 55.19$ (OCH_3), 113.26, 117.37 (CH), 118.09, 118.58 (C), 120.87, 123.06, 124.17, 129.52, 130.38, 132.53, 133.52 (CH), 134.12, 136.16, 146.62, 151.39, 158.93, 159.28 ppm (C); IR (KBr): $\tilde{\nu} = 3442$ (w), 3110 (w), 3005 (w), 2960 (w), 2920 (w), 2805 (w), 1732 (s), 1609 (s), 1514 (s), 1460 (s), 1407 (m), 1311 (w), 1288 (m), 1276 (m), 1244 (s), 1211 (s), 1179 (m), 1096 (m), 1046 (s), 1006 (m), 828 (m), 790 (w), 761 (m), 697 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 334 (3.93), 288 (3.91), 259 (4.29), 229 (4.56), 223 (4.54), 215 nm (4.55); MS (EI, 70 eV): *m/z* (%): 302 (100) $[M]^+$, 287 (5), 259 (11), 231 (2), 202 (8), 175 (3), 150 (7), 101 (4), 70 (5), 28 (21); elemental analysis calcd (%) for $C_{20}H_{14}O_3$: C 79.46, H 4.67; found: C 79.43, H 4.64.

7-(3,4,5-Trimethoxyphenyl)-6*H*-benzo[*c*]chromen-6-one (16d): The starting materials **15** (103 mg, 0.30 mmol), 3,4,5-trimethoxyphenylboronic acid (83 mg, 0.39 mmol), K_3PO_4 (104 mg, 0.48 mmol), and $Pd(Ph_3)_4$ (10 mg, 9 μmol) produced **16d** as a colorless solid (reaction time: 8 h, 97 mg, 89%). M.p. 165°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 3.86$ (s, 6H; OCH_3), 3.93 (s, 3H; OCH_3), 6.54 (s, 2H; Ar), 7.33–7.37 (m, 2H; Ar), 7.44–7.50 (m, 2H; Ar), 7.80 (t, $J = 7.7$ Hz, 1H; Ar), 8.12 (dd, $J = 8.0$, 1.2 Hz, 1H; Ar), 8.18 ppm (dd, $J = 8.2$, 1.1 Hz, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta = 56.13$, 56.31, 60.98 (OCH_3), 104.66, 105.79, 117.47 (CH), 118.06, 118.64 (C), 121.25, 123.14, 124.32, 130.57, 132.36, 133.57 (CH), 136.21, 137.33, 137.49, 146.82, 151.47, 152.69, 153.42 (C), 159.01 ppm (C=O); IR (KBr): $\tilde{\nu} = 3461$ (br), 3452 (w), 3450 (w), 2936 (w), 1743 (s), 1584 (s), 1510 (m), 1463 (s), 1415 (m), 1286 (m), 1248 (s), 1229 (s), 1209 (m), 1127 (s), 1099 (m), 1045 (m), 1006 (m), 818 (w), 756 (m), 701 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 329 (3.87), 299 (3.81), 289 (3.84), 270 (4.18), 260 (4.23), 229 (4.56), 208 nm (4.72); MS (EI, 70 eV): *m/z* (%): 362 (100) $[M]^+$, 347 (37), 333 (6), 289 (9), 261 (17), 233 (12), 205 (4), 165 86), 88 (2); elemental analysis calcd (%) for $C_{22}H_{18}O_5$: C 72.29, H 5.01; found: C 71.77, H 5.06.

7-(4-Chlorophenyl)-6*H*-benzo[*c*]chromen-6-one (16e): The starting materials **15** (99 mg, 0.29 mmol), 4-chlorophenylboronic acid (58 mg, 0.37 mmol), K_3PO_4 (100 mg, 0.46 mmol), and $Pd(Ph_3)_4$ (10 mg, 9 μmol) produced **16e** as a colorless solid (reaction time: 12 h, 65 mg, 74%). M.p. 129°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.27$ (m, 3H; Ar), 7.32–7.42 (m, 4H; Ar), 7.50 (m, 1H; Ar), 7.81 (t, $J = 7.8$ Hz, 1H; Ar), 8.11 (dd, $J = 8.6$, 1.8 Hz, 1H; Ar), 8.20 ppm (dd, $J = 8.2$, 1.1 Hz, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta = 117.49$ (CH), 117.93, 18.62 (C), 121.56, 123.12, 124.36, 2×128.01, 129.60, 129.64, 130.64, 132.22 (CH), 133.34 (C), 133.72 (CH), 136.29, 140.32, 145.59, 151.42 (C), 159.23 ppm (C=O); IR (KBr): $\tilde{\nu} = 3432$ (m), 3089 (w), 1732 (s), 1594 (s), 1496 (m), 1458 (m), 1413 (m), 1392 (m), 1309 (m), 1271 (m), 1251 (s), 1215 (s), 1109 (m), 1091 (m), 1051 (s), 1008 (m), 836 (m), 810 (m), 754 (s), 689 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 325 (3.87), 302 (3.74), 290 (3.68), 271 (4.10), 249 (4.29), 229 (4.47), 214 (4.49), 210 nm (4.49); MS (EI, 70 eV): *m/z* (%): 306 (100) $[M]^+$, 231 (49), 175 (25), 150 (9), 95 (12), 55 (23), 28 (21); elemental analysis calcd (%) for $C_{19}H_{11}ClO_2$: C 74.39, H 3.61; found: C 74.73, H 4.02.

7-(4-Thiophen-2-yl)-)-6*H*-benzo[*c*]chromen-6-one (16f): The starting materials **15** (103 mg, 0.30 mmol), 2-thiophenylboronic acid (50 mg, 0.39 mmol), K_3PO_4 (104 mg, 0.48 mmol), and $Pd(Ph_3)_4$ (10 mg, 9 μmol) produced **16f** as a colorless solid (reaction time: 12 h, 55 mg, 66%). M.p. 161°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.07$–7.13 (m, 2H; thiophenyl), 7.32–7.36 (m, 2H; thiophenyl), 7.42 (dd, $J = 5.1$, 1.4 Hz, 1H; Ar), 7.49 (m, 1H; Ar), 7.59 (dd, $J = 7.5$, 1.1 Hz, 1H; Ar), 7.79 (t, $J = 7.8$ Hz, 1H; Ar), 8.09 (dd, $J = 8.0$, 1.8 Hz, 1H; thiophenyl), 8.19 ppm (dd, $J = 8.2$, 1.0 Hz, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta = 117.50$ (CH), 117.89, 119.57 (C), 122.01, 123.11, 124.30, 125.90, 126.79, 130.66, 133.45, 133.56 (CH), 136.44, 139.10, 142.77 (C), 151.47 (C–O), 158.78 ppm (C=O); IR (KBr): $\tilde{\nu} = 3102$ (w), 3070 (w), 2361 (w), 1731 (s), 1693 (m), 1611 (m), 1592 (m), 1462 (m), 1434 (w), 1406 (w), 1314 (w), 1294 (m), 1254 (s), 1205 (s), 1189 (m), 1133 (w), 1104 (m), 1046 (s), 1027 (s), 855 (w), 821 (m), 788 (w), 752 (s), 708 (s), 689 (m), 664 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 333 (3.86), 299 (3.86), 291 (3.88), 270 (4.21), 260 (4.27), 229 nm (4.49); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 452 nm (335 nm); MS (EI, 70 eV): *m/z* (%): 278 (9) $[M]^+$, 277 (7), 208 (12), 189 (4), 167 (6), 148 (18), 72 (5), 58 (11), 46 (46), 45 (100); HRMS (FT-ICR): calcd for $C_{17}H_{11}O_2S$: 279.04743 $[M+1]^+$; found: 279.04760.

General procedure for the synthesis of (17a,b): K_2CO_3 (1.5 equiv) was added to a solution of **5** (1.0 equiv) in acetone (10 mL per 1.0 mmol). After cooling to 0°C, Me_2SO_4 (1.1 equiv) was added dropwise. After stirring for 6 h under reflux and for 12 h at 20°C, the solvent was removed in vacuo and the resulting residue was poured onto ice water. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2 (5×30 mL). The combined organic layers were washed with water, dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc 5:1) to give **17**.

7-Methoxy-6*H*-benzo[*c*]chromen-6-one (17a): The starting materials **5a** (143 mg, 0.59 mmol) in acetone (9 mL), K_2CO_3 (192 mg, 0.88 mmol), and Me_2SO_4 (82 mg, 0.07 mL, 0.65 mmol) produced **17a** as a colorless solid (114 mg, 92%). M.p. 132°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 4.04$ (s, 3H; OCH_3), 7.05 (dd, $J = 7.8$, 1.4 Hz, 1H; Ar), 7.26–7.33 (m, 2H; Ar), 7.45 (m, 1H; Ar), 7.67–7.73 (m, 2H; Ar), 8.00 ppm (dd, $J = 7.9$, 1.4 Hz, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta = 56.40$ (OCH_3), 109.95 (C), 111.05, 113.54, 117.29 (CH), 117.71 (C), 123.23, 124.09, 130.55, 135.69 (CH), 137.46, 151.51, 157.82 (C), 162.22 ppm (C=O); IR (KBr): $\tilde{\nu} = 3439$ (m), 3068 (m), 2969 (w), 2938 (w), 2842 (w), 1732 (s), 1602 (s), 1569 (s), 1501 (w), 1467 (s), 1442 (w), 1418 (m), 1339 (w), 1267 (s), 1245 (s), 1209 (s), 1138 (w), 1089 (m), 1024 (s), 904 (w), 810 (m), 761 (s), 681 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 340 (3.96), 329 (3.99), 302 (3.61), 291 (3.54), 272 (3.93), 259 (4.01), 238 (4.46), 230 (4.47), 207 nm (4.47); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 374 nm (342 nm); MS (EI, 70 eV): *m/z* (%): 253 (6), 226 (42) $[M]^+$, 197 (35), 183(13), 168 (11), 165 (11), 155 (10), 141 (14), 137 (8), 112 (10), 85 (3), 55 (5); elemental analysis calcd (%) for $C_{14}H_{10}O_3$: C 74.33, H 4.46; found: C 73.96, H 4.71.

7,8-Dimethoxy-6*H*-benzo[*c*]chromen-6-one (17b): The starting materials **5j** (117 mg, 0.55 mmol) in acetone (7 mL), K_2CO_3 (178 mg, 0.83 mmol), and Me_2SO_4 (82 mg, 0.07 mL, 0.65 mmol) produced **17b** as a colorless solid (117 mg, 94%). M.p. 120°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 3.97$, 4.00 (s, 3H; OCH_3), 7.24–7.30 (m, 2H; Ar), 7.36–7.42 (m, 2H; Ar), 7.84 (d, $J = 8.9$ Hz, 1H; Ar), 7.93 ppm (dd, $J = 7.6$, 1.1 Hz, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): $\delta = 56.47$, 61.51 (OCH_3), 115.76 (C), 117.25, 117.73 (CH), 117.90 (C), 119.33, 122.32, 124.26 (CH), 128.70 (C), 129.44 (CH), 150.62, 151.64, 153.62, 157.60 ppm (C); IR (KBr): $\tilde{\nu} = 3442$ (w), 3082 (w), 2928 (s), 2850 (s), 1733 (s), 1604 (m), 1507 (m), 1477 (s), 1460 (s), 1396 (w), 1306 (m), 1279 (s), 1210 (m), 1132 (m), 1089 (m), 1039 (s),

1005 (s), 920 (w), 832 (m), 775 (m), 751 (m), 734 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 340 (3.75), 305 (3.94), 294 (3.88), 279 (4.02), 271 (3.91), 232 (4.39), 215 nm (4.36); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 406 nm (340 nm); MS (EI, 70 eV): *m/z* (%): 256 (41) $[M]^+$, 227 (22), 213 (4), 155 (11), 125 (7), 97 (23), 83 (20), 72 (22), 58 (39), 43 (26). HRMS (FT-ICR): calcd for $C_{15}H_{13}O_4$: 257.08084 $[M+1]^+$; found: 257.08104.

Synthesis of 6*H*-benzo[*c*]chromen-6-ones (19a–d): Products **19a–d** were prepared by following the procedure as given for the synthesis of 7-hydroxy-6*H*-benzo[*c*]chromen-6-ones **5**.

8-(3′-Chloropropyl)-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (19a): The starting materials **1a** (438 mg, 3.0 mmol), Me_3SiOTf (866 mg, 3.9 mmol), **3p** (1.26 g, 3.6 mmol), and NEt_3 (607 mg, 0.83 mL, 6.0 mmol) in EtOH (40 mL) produced **19a** as a yellow solid (502 mg, 58%). M.p. 96°C; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.17 (m, 2H; $CH_2CH_2CH_2Cl$), 2.92 (t, J = 7.1 Hz, 2H; $ArCH_2$), 3.58 (t, J = 6.5 Hz, 2H; CH_2Cl), 7.33–7.39 (m, 2H; Ar), 7.50 (m, 2H; Ar), 7.54 (d, J = 8.0 Hz, 1H; Ar), 7.63 (d, J = 8.0 Hz, 1H; Ar), 8.03 (dd, J = 7.7, 1.6 Hz, 1H; Ar), 11.65 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 27.18, 31.17 (CH_2), 44.47 (CH_2Cl), 105.74 (C), 111.72, 117.60 (CH), 118.42 (C), 123.05, 125.13 (CH), 128.36 (C), 130.24 (CH), 133.35 (C), 137.95 (CH), 150.33 (C), 160.38 (C–OH), 165.77 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3060 (m), 2958 (m), 2938 (m), 1686 (s), 1615 (m), 1448 (m), 1418 (m), 1352 (w), 1306 (m), 1270 (s), 158 (s), 1216 (s), 1127 (s), 1088 (m), 1027 (w), 815 (m), 756 (s), 714 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 341 (3.87), 299 (3.44), 290 (3.54), 277 (3.82), 263 (3.89), 233 (4.36), 207 nm (4.17); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 493 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 288 (5) $[M]^+$, 253 (4), 225 (16), 206 (9), 171 (6), 143 (8), 119 (19), 114 (32), 70 (17), 55 (43); HRMS (FT-ICR): calcd for $C_{16}H_{14}ClO_3$: 289.06260 $[M+1]^+$; found: 289.06283.

2-Chloro-8-(3′-chloropropyl)-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (19b): The starting materials **1d** (578 mg, 3.2 mmol), Me_3SiOTf (947 mg, 0.77 mL, 4.26 mmol), **3p** (1.46 g, 4.26 mmol), and NEt_3 (648 mg, 0.89 mL, 6.4 mmol) in EtOH (40 mL) produced **19b** as a yellow solid (569 mg, 55%). M.p. 118°C; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.16 (m, 2H; $CH_2CH_2CH_2Cl$), 2.93 (t, J = 7.1 Hz, 2H; $ArCH_2$), 3.58 (t, J = 6.5 Hz, 2H; CH_2Cl), 7.31 (d, J = 8.8 Hz, 1H; Ar), 7.48 (d, J = 8.1 Hz, 1H; Ar), 7.65 (d, J = 8.1 Hz, 1H; Ar), 7.97 (d, J = 2.4 Hz, 1H; Ar), 11.59 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 27.28 (CH_2Ar), 31.65 (CH_2), 44.44 (CH_2Cl), 105.65 (C), 111.98, 119.07 (CH), 119.87 (C), 122.92 (CH), 129.43 (C), 130.22 (CH), 130.76, 132.14 (C), 138.14 (CH), 148.76 (C), 160.55 (C–OH), 165.35 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3435 (s), 1682 (s), 1622 (m), 1433 (w), 1394 (w), 1261 (m), 11219 (w), 1141 (w), 1096 (m), 823 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 341 (4.06), 308 (3.64), 296 (3.61), 281 (3.95), 267 (3.99), 235 (4.53), 215 nm (4.43); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 491 nm (342 nm); MS (EI, 70 eV): *m/z* (%): 324/322 (4/6) $[M]^+$, 287 (20), 259 (46) $[M-C_2H_4Cl]^+$, 221 (3), 184 (2).

2-Chloro-8-(3′-chloropropyl)-7-hydroxy-3-methyl-6*H*-benzo[*c*]chromen-6-one (19c): The starting materials **1f** (641 mg, 3.29 mmol), Me_3SiOTf (952 mg, 0.78 mL, 4.28 mmol), **3p** (1.50 g, 4.28 mmol), and NEt_3 (666 mg, 0.91 mL, 6.58 mmol) in EtOH (40 mL) produced **19c** as a yellow solid (632 mg, 57%). M.p. 156°C; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.16 (m, 2H; $CH_2CH_2CH_2Cl$), 2.46 (s, 3H; OCH_3), 2.91 (t, J = 7.1 Hz, 2H; $ArCH_2$), 3.59 (t, J = 6.5 Hz, 2H; CH_2Cl), 7.23 (s, 1H; Ar), 7.43 (d, J = 8.0 Hz, 1H; Ar), 7.62 (d, J = 8.0 Hz, 1H; Ar), 7.95 (s, 1H; Ar), 11.59 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 20.32 (CH_3), 27.25 ($ArCH_2$), 31.71 (CH_2), 44.47 (CH_2Cl), 105.49 (C), 111.66 (CH), 117.59 (C), 119.48, 123.14 (CH), 128.76, 131.16, 132.42 (C), 138.12 (CH), 138.86, 148.64 (C), 160.50 (C–OH), 165.57 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3133 (w), 2961 (w), 2933 (w), 1689 (s), 1615 (s), 1477 (m), 1444 (m), 1427 (m), 1376 (m), 1335 (w), 1313 (m), 1276 (m), 1242 (s), 1181 (m), 1165 (m), 1144 (s), 1105 (s), 1008 (m), 877 (w), 816 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 344 (4.06), 308 (3.66), 296 (3.63), 281 (4.05), 271 (4.08), 238 (4.58), 214 nm (4.53); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 496 nm (345 nm); MS (EI, 70 eV): *m/z* (%): 338 (100) $[M]^+$, 301 (16), 273 (61), 245 (3), 165 (5), 151 (6), 76 (18); HRMS (FT-ICR): calcd for $C_{17}H_{15}Cl_2O_3$: 337.03928 $[M+1]^+$; found: 337.03964.

8-(3′-Chloro-2-methylpropyl)-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (19d): The starting materials **1a** (438 mg, 3.0 mmol), Me_3SiOTf (867 mg, 0.71 mL, 3.90 mmol) **3q** (1.42 g, 3.90 mmol), and NEt_3 (607 mg, 0.83 mL, 6.0 mmol) in EtOH (40 mL) produced **19d** as a yellow solid (472 mg, 52%). M.p. 72°C; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.07 (d, J = 6.7 Hz, 3H; CH_3), 2.34 (m, 1H; CH), 2.72 (dd, J = 13.4, 7.1 Hz, 1H; $ArCH_2$, A of AB), 2.87 (dd, J = 13.4, 7.1 Hz, 1H, $ArCH_2$, B of AB) 3.46 (dd, J = 10.8, 4.7 Hz, 1H; CH_2Cl, A of AB), 3.54 (dd, J = 10.8, 4.7 Hz, 1H; CH_2Cl, B of AB), 7.37 (dd, J = 7.7, 0.9 Hz, 1H; Ar), 7.46–7.56 (m, 3H; Ar), 7.54 (d, J = 8.0 Hz, 1H; Ar), 7.62 (d, J = 8.0 Hz, 1H; Ar), 8.03 (dd, J = 8.2, 1.2 Hz, 1H; Ar), 11.68 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz,): δ = 17.79 (CH_3), 34.28 ($ArCH_2$), 35.23 (CH), 50.78 (CH_2Cl), 105.78 (C), 111.65, 117.61 (ArCH), 118.45 (C), 123.08, 125.17 (ArCH), 127.71 (C), 130.28 (ArCH), 133.44 (C), 138.65 (ArCH), 150.38, 160.55 (C), 165.80 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3133 (w), 2961 (w), 2933 (w), 1689 (s), 1615 (s), 1477 (m), 1444 (m), 1427 (m), 1376 (m), 1335 (w), 1313 (m), 1276 (m), 1242 (s), 1181 (m), 1165 (m), 1144 (s), 1105 (s), 1008 (m), 877 (w), 816 (w), 753 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 342 (4.00), 299 (3.65), 290 (3.74), 277 (3.98), 263 (4.05), 233 (4.50), 206 nm (4.47); fluorescence (CH_3CN): $F\lambda_{max}$ (λ_{ex}): 494 nm (343 nm); MS (EI, 70 eV): *m/z* (%): 302 (7) $[M]^+$, 267 (8), 225 (55), 197 (2), 151 (3), 114 (2), 104 (2); elemental analysis calcd (%) for $C_{17}H_{15}ClO_3$: C 67.44, H 4.99; found: C 67.28, H 5.11.

General procedure for the synthesis of dioxachrysenones (20a–d): NaH (1.5 equiv) and TBAI (2.0 equiv) were added to a solution of **19** (1.0 equiv) in THF at 20°C. After stirring for 20 h, the solvent was removed in vacuo, and the resulting residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc 3:1→1:1) to give **20**.

2,3-Dihydro-1*H*-4,6-dioxachrysen-5-one (20a): The starting materials **19a** (101 mg, 0.35 mmol), NaH (11 mg, 0.46 mmol), and TBAI (259 mg, 0.70 mmol) in THF (1 mL) produced **20a** as a colorless solid (56 mg, 64%). M.p. 192°C; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.12 (m, 2H; $CH_2CH_2CH_2$), 2.91 (t, J = 6.4 Hz, 2H; $ArCH_2$), 4.47 (t, J = 5.1 Hz, 2H; OCH_2), 7.29 (m, 2H; Ar), 7.44 (m, 2H; Ar), 7.59 (d, J = 8.1 Hz, 1H; Ar), 7.99 ppm (dd, J = 8.0, 1.3 Hz, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 21.25 ($CH_2CH_2CH_2$), 25.45 ($ArCH_2$), 67.59 (OCH_2), 109.97 (C), 112.68, 117.96 (CH), 118.03 (C), 122.89 (CH), 123.14 (C), 125.03, 130.11 (CH), 135.42 (C), 136.51 (CH), 151.41, 158.12, 15840 ppm (C); IR (KBr): $\tilde{\nu}$ = 2964 (m), 2930 (m), 2901 (m), 1731 (s), 1599 (s), 1565 (m), 1505 (s), 1477 (s), 1445 (m), 1406 (m), 1322 (m), 1301 (s), 1282 (w), 1265 (s), 1243 (m), 1190 (w), 1160 (w), 1108 (m), 1095 (s), 1083 (s), 1051 (s), 956 (m), 815 (m), 769 cm^{-1} (s); UV/Vis (CH_3CN): λ_{max} (lg ε): 349 (3.75), 337 (3.77), 304 (3.41), 293 (3.41), 276 (3.71), 267 (3.76), 259 (3.75), 239 (4.24), 233 (4.27), 208 nm (4.28); MS (EI, 70 eV): *m/z* (%): 252 (100) $[M]^+$, 224 (9), 196 (7), 168 (12), 139 (10), 126 (5), 114 (3), 75 (4).

9-Chloro-2,3-dihydro-1*H*-4,6-dioxachrysen-5-one (20b): The starting materials **19b** (112 mg, 0.35 mmol), NaH (11 mg, 0.46 mmol), and TBAI (259 mg, 0.70 mmol) in THF (1 mL) produced **20b** as a colorless solid (61 mg, 61%); M.p. 209°C; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.11 (m, 2H; $CH_2CH_2CH_2$), 2.92 (t, J = 6.5 Hz, 2H; $ArCH_2$), 4.46 (t, J = 5.1 Hz, 2H; OCH_2), 7.24 (d, J = 8.7 Hz, 1H; Ar), 7.37 (dd, J = 8.8, 2.3 Hz, 1H; Ar), 7.50 (m, 2H; Ar), 7.94 ppm (d, J = 2.4 Hz, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz,): δ = 21.15 ($CH_2CH_2CH_2$), 25.46 ($ArCH_2$), 67.65 (OCH_2), 109.45 (C), 112.72, 118.68 (CH), 119.47 (C), 122.72 (CH), 124.04, 129.47 (C), 130.00 (CH), 134.13 (C), 136.66 (CH), 149.79, 157.52, 158.11 ppm (C); IR (KBr): $\tilde{\nu}$ = 3438 (m), 2948 (w), 2928 (w), 1737 (s), 1599 (s), 1563 (s), 1495 (m), 1476 (s), 1423 (m), 1387 (m), 1302 (s), 1262 (s), 1184 (m), 1096 (s), 1081 (m), 1049 (m), 882 (w), 816 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 352 (4.02), 338 (4.04), 312 (3.63), 300 (3.49), 279 (3.85), 270 (3.94), 260 (3.92), 264 (4.52), 213°nm (4.49); MS (EI, 70 eV): *m/z* (%): 286 (21) $[M]^+$, 170 (16), 88 (39), 72 (51), 57 (100; $C_3H_5O^+$).

9-Chloro-2,3-dihydro-8-methyl-1*H*-4,6-dioxachrysen-5-one (20c): The starting materials **19c** (126 mg, 0.36 mmol), NaH (13 mg, 0.47 mmol), and TBAI (266 mg, 0.72 mmol) in THF (1 mL) produced **20c** as a colorless solid (75 mg, 69%). M.p. 216°C; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.11 (m, 2H; $CH_2CH_2CH_2$), 2.35 (s, 3H; CH_3), 2.90 (t, J = 6.5 Hz, 2H; $ArCH_2$), 4.45 (t, J = 5.1 Hz, 2H; OCH_2), 7.17 (s, 1H; Ar), 7.46 (m, 2H; Ar), 7.92 ppm (s, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 20.27 (CH_3), 21.21 ($CH_2CH_2CH_2$), 25.44 ($ArCH_2$), 67.63 (OCH_2), 109.24 (C), 112.51 (CH), 117.25 (C), 119.10, 122.98 (CH), 123.42, 129.93, 134.41

(C), 136.63 (CH), 138.52, 149.69, 157.81, 158.06 ppm (C); IR (KBr): $\tilde{\nu}$ = 3444 (w), 2929 (w), 2878 (w), 1743 (s), 1597 (s), 1556 (m), 1473 (s), 1418 (m), 1373 (m), 1303 (m), 1259 (s), 1178 (m), 1100 (s), 1052 (m), 944 (w), 875 (w), 817 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 353 (4.04), 340 (4.06), 312 (3.67), 299 (3.53), 279 (3.95), 270 nm (3.94); MS (EI, 70 eV): *m/z* (%): 300 (100) $[M]^+$, 272 (10), 244 (8), 237 (5), 184 (24), 151 (9), 125 (6), 102 (5).

2,3-Dihydro-2-methyl-1*H*-4,6-dioxachrysen-5-one (20d): The starting materials **19d** (309 mg, 1.02 mmol), NaH (36.7 mg, 1.53 mmol), and TBAI (753 mg, 2.04 mmol) in THF (1 mL) produced **20d** as a colorless solid (142 mg, 52%). M.p. 223 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.11 (d, J = 6.6 Hz, 3H; CH_3), 2.26 (m, 1H; CH), 2.55 (d, J = 9.9 Hz, 1H; $ArCH_2$), 2.94 (ddd, J = 16.5, 5.1, 2.1 Hz, 1H; $ArCH_2$), 3.89 (t, J = 10.8 Hz, 1H; OCH_2), 4.52 (ddd, J = 10.8, 3.6, 2.4 Hz, 1H; OCH_2), 7.33–7.36 (m, 2H; Ar), 7.43 (m, 2H; Ar), 7.59 (d, J = 8.2 Hz, 1H; Ar), 7.98 ppm (dd, J = 7.9, 1.5 Hz, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 16.83 (CH_3), 26.09 (CH), 33.73 ($ArCH_2$), 72.74 (OCH_2), 109.33 (C), 112.77, 117.24 (ArCH), 118.06 (C), 122.87 (ArCH), 122.89 (C), 123.99, 130.05 (ArCH), 135.35 (C), 136.43 (ArCH), 151.38, 157.49, 158.20 ppm (C); IR (KBr): $\tilde{\nu}$ = 3432 (m), 2959 (m), 2924 (m), 1871 (m), 1729 (s), 1599 (s), 1567 (m), 1476 (s), 1404 (s), 1346 (m), 1289 (s), 1262 (s), 1231 (s), 1196 (m), 1112 (s), 1068 (s), 1017 (s), 928 (m), 769 (s), 676 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (lg ε): 349 (4.03), 337 (4.04), 304 (3.68), 293 (3.65), 276 (3.96), 267 (4.02), 259 (4.00), 239 (4.49), 233 (4.52), 208 nm (4.51); MS (EI, 70 eV): *m/z* (%): 266 (38) $[M]^+$, 251 (5), 224 (15), 196 (7), 168 (12), 139 (14), 76 (5); HRMS (EI, 70 eV): *m/z*: calcd for $C_{17}H_{14}O_3$: 266.0943 $[M]^+$; found: 266.0943 ± 2 ppm.

8-(3-Chloropropyl)-7-hydroxydibenzo[*c*,*h*]chromen-6-one (22): The reaction was carried following the general procedure as given for the synthesis of **5a**. The starting materials **6** (612 mg, 3.12 mmol), Me_3SiOTf (901 mg, 0.73 mL, 4.06 mmol), **3p** (1.43 g, 4.06 mmol), and NEt_3 (631 mg, 0.86 mL, 6.24 mmol) in EtOH (40 mL) produced **22** as a yellow solid (602 mg, 57%). M.p. 179 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.19 (m, 2H; $CH_2CH_2CH_2$), 2.95 (t, J = 7.1 Hz, 2H; $ArCH_2$), 3.60 (t, J = 6.5 Hz, 2H; CH_2Cl), 7.60–7.69 (m, 4H; Ar), 7.79 (d, J = 8.9 Hz, 1H; Ar), 7.90 (dd, J = 7.4, 1.9 Hz, 1H; Ar), 8.02 (d, J = 8.9 Hz, 1H; Ar), 8.55 (dd, J = 7.4, 1.2 Hz, 1H; Ar), 11.71 ppm (s, 1H; OH); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 27.23 ($ArCH_2$), 31.77 (CH_2), 44.53 (CH_2Cl), 105.91 (C), 112.17 (CH), 113.73 (C), 119.45, 122.02 (CH), 123.70 (C), 125.12, 127.32, 127.72, 127.92 (CH), 128.08, 134.08, 134.15 (C), 138.19 (CH), 146.22 (C), 160.50 (C–OH), 165.80 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3432 (m), 3131 (w), 3064 (w), 2953 (w), 2929 (w), 1682 (s), 1623 (s), 1498 (s), 1446 (s), 1402 (m), 1343 (m), 1251 (s), 1226 (s) 1153 (m), 1127 (s), 800 (m), 778 (w), 745 (m), 615 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (lg ε): 368 (4.08), 354 (4.16), 308 (3.98), 296 (3.99), 269 (4.53), 259 (4.43), 240 (4.73), 219 nm (4.57); MS (EI, 70 eV): *m/z* (%): 338 (41) $[M]^+$, 302 (28), 275 (100), 247 (5), 218 (12), 184 (19), 125 (6); elemental analysis calcd (%) for $C_{20}H_{15}ClO_3$: C 70.90, H 4.46; found: C 70.72, H 4.75.

3,4-Dihydro-2*H*-1,13-dioxapicen-14-one (23): The reaction was carried out following the general procedure as given for the synthesis of dioxachrysenones **20**. The starting materials **22** (107 mg, 0.31 mmol), NaH (9.8 mg, 0.41 mmol), and TBAI (233 mg, 0.63 mmol) in THF (1 mL) produced **23** as a colorless solid (602 mg, 57%). M.p. 205 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.12 (m, 2H; $CH_2CH_2CH_2$), 2.96 (t, J = 6.7 Hz, 2H; $ArCH_2$), 4.49 (t, J = 5.0 Hz, 2H; OCH_2), 7.49 (d, J = 8.2 Hz, 1H; Ar), 7.57–7.66 (m, 3H; Ar), 7.71 (d, J = 8.2 Hz, 1H; Ar), 7.85 (dd, J = 7.2, 2.0 Hz, 1H; Ar), 7.99 (d, J = 8.9 Hz, 1H; Ar), 8.60 ppm (dd, J = 8.9, 1.0 Hz, 1H; Ar); ^{13}C NMR (DEPT, $CDCl_3$, 75.5 MHz): δ = 21.28 ($CH_2CH_2CH_2$), 25.44 ($ArCH_2$), 67.60 (OCH_2), 109.57 (C), 112.99, 119.57, 122.58 (CH), 122.78, 123.66 (C), 123.88 (CH), 126.82 (C), 126.84, 127.47, 127.86 (CH), 134.09, 136.08 (C), 136.59 (CH), 147.37, 158.04, 158.05 ppm (C); IR (KBr): $\tilde{\nu}$ = 3440 (w), 2980 (w), 2150 (w), 1657 (m), 1546 (m) 1444 (s), 1257 (m), 1245 (m), 1201 (s), 1176 (s), 1145 (s), 1131 (s), 1096 (s), 1027 (m), 879 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 302 (100) $[M]^+$, 274 (7), 246 (5), 218 (13), 148 (11).

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[24] CCDC-281282 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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