FULL PAPER

Synthesis of Diverse Oxa-Carbocycle-Annulated Flavones Using the Combined *Claisen* Rearrangement and Ring-Closing Metathesis

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A simple and efficient route for the synthesis of oxepine-, oxocine-, oxepinone-, and dioxocine-angularly annulated flavone skeletons has been developed. The combined *Claisen rearrangemen*t and the ring-closing metathesis are used as key steps for the construction of C_7/C_8–C_6–C_6 tricyclic core structures.

Keywords: Hydroxyflavones, *Claisen* rearrangement, Ring-closing metathesis, *Grubbs*' *I* and *II* catalysts, Oxa-carbocycle-annulated flavones.

Introduction

Flavonoids are the prominent polyphenolic group of secondary metabolites found through the plant kingdom [1]. These compounds naturally occur in fruits, vegetables, seeds, nuts, and flowers [2][3][4], and play significant role in many biological processes [5][6]. Flavonoids exhibit diverse type of properties that are useful for human health by interacting with a wide variety of cellular targets involved in cell signatory pathway in the body. Several therapeutically interesting biological, pharmaceutical activities of certain flavones have been reported, including anticancer [7], anti-HIV [8], antioxidant [9], antimicrobial [10], antiarthritic [11], DNA cleaving [12], antianginous [13], antihepatotoxic [14], anti-inflammatory [15], antimutagenic [16], antiosteoporotic [17], antidiabetic [18], antiulcer [19], antifungal [20], antiallergic [21], vasodilating [22], analgesic [23], antidiarrheal [24], antiviral [25], and various enzyme-inhibitory effects [26]. The benzoxepines and benzoxocines are privileged structural scaffolds in medicinal chemistry because of their presence in several bioactive natural products [27]. The structural features and wide range of biological activity attracted organic chemists for the synthesis of these heterocycles fused to other bioactive heterocycles. Some of the pharmacologically important heterocyclic ring-fused flavones [28] (cyclomorusin and artoflavone A) and oxepine ring containing biologically active natural products [29][30] (ptaeroxylin, heliannuols A) are shown in *Fig. 1*. The ring-closing metathesis (RCM) using *Grubbs*' catalysts (*I* and *II*) is a highly powerful and reliable tool for the construction of a wide range of carbocyclic and heterocyclic ring systems especially for medium to large rings from diene and ene-yne precursors [31][32]. The medium-size rings are difficult to prepare due to enthalpic (increasing strain in transition state) and entropic influences (probability of chain ends meeting). However, to date there is no report of this methodology being employed for the synthesis of angularly heterocycles ring-fused flavones. Several methodologies have been reported for the synthesis of various heterocyclic ring-fused flavones [33], but medium-size oxa-carbocycle-annulated flavones are unknown, probably due to lack of general methods. It appeared to us that a combination of the *Claisen* rearrangement and the RCM could be useful to prepare diverse oxa-unknown medium-sized heterocycle-annulated flavone system of interest. Here, we report a diversity-oriented approach for the synthesis of skeletally different oxa-carbocycle-annulated flavone molecular frameworks (from more readily available starting materials) through the application of the combined *Claisen* rearrangement and RCM. Moreover, the construction of rings is an important strategy of natural product synthesis.

Results and Discussion

7-Hydroxyflavones **1a**,**b** on treating with allylbromide in acetone/K_2CO_3 medium gave 7-allyloxyflavones **2a**,**b**; subsequently, the thermal *Claisen* rearrangement of **2a**,**b** in diphenyl ether solvent under refluxing conditions exclusively produced C(8) regioisomers of **3a**,**b**. Earlier the *Claisen* rearrangement was reported in *N*,*N*-diethylaniline solvent, but we observed that the isolation of the products is simpler in diphenyl ether as compared to the reported

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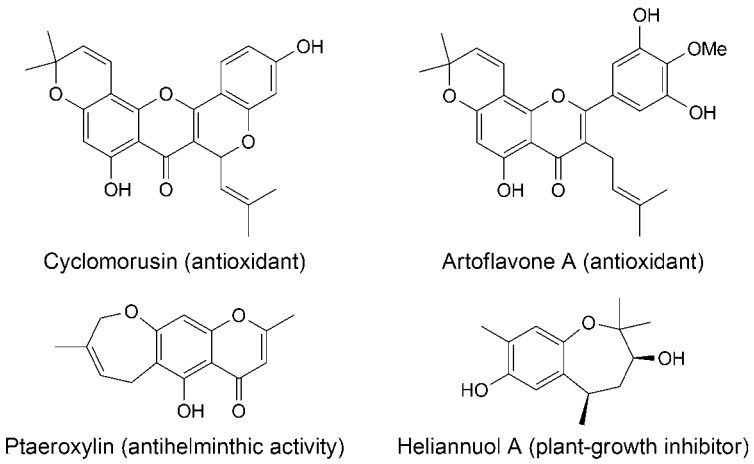
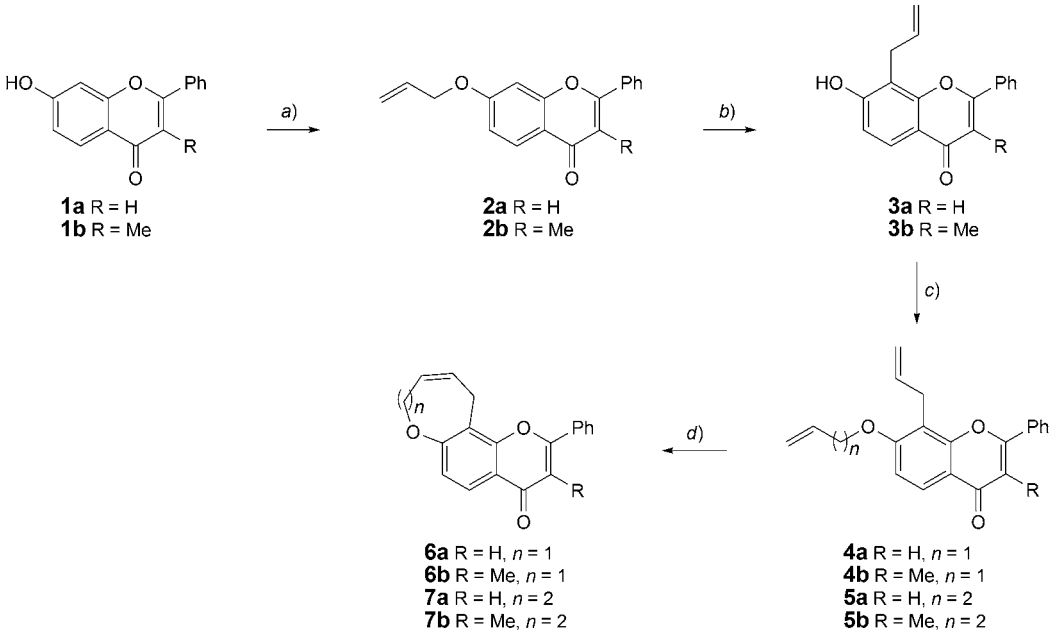


Fig. 1. Some pharmacologically active natural products.

procedure [34]. The rearrangement products **3a**,**b** on further alkylation with allyl bromide in refluxing acetone/K_2CO_3 gave the diene precursors of RCM, 7-allyloxy-8-allylflavones **4a**,**b**, as colorless crystalline solids with 82 – 86% of yields. Similarly, butenyl ethers **5a**,**b** were prepared by treating 8-allyl-7-hydroxyflavones **3a**,**b** with but-3-en-1-yl bromide in acetone/K_2CO_3 medium. The RCM approach is very useful for the synthesis of medium-sized oxacycles; these cyclic ethers are present in many bioactive natural products such as brevetoxins [35]. Treatment of the precursors **4a**,**b** with bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (*Grubbs*' *I* catalyst) (0.01M or 10 mol-%) under refluxing CH_2Cl_2 for 1.5 h resulted in the formation of the desired oxepinoflavones **6a**,**b** in good yields (68 – 75%) (*Scheme 1*). However, when same reaction was carried out at room temperature with varied concentrations of Ru-catalyst, no conversion was observed. Similarly, the RCM of butenyl ethers **5a**,**b** using *Grubbs*' *I* catalyst under refluxing CH_2Cl_2 afforded oxocine derivatives **7a**,**b** with 58 – 64% of yields, but the RCM of compounds **5a**,**b** proved sluggish (12 h). It is known that eight-membered cycloalkenes proved to reverse process, *i.e.*, ring-opening metathesis (ROM), which is not observed in our synthesis. In the ^{1}H-NMR spectra of **6b**, the characteristic signals of newly formed oxepino-ring protons appeared at δ 3.77 (*d*, *J* = 3.5 Hz, 2 H); δ 4.67 (*d*, *J* = 3.0 Hz, 2 H); δ 5.61 – 5.64 (*m*, 1 H) and δ 5.91 – 5.93 (*m*, 1 H).

In order to investigate regioselectivity in the RCM, the 8-allyl-7-allyloxyflavones **4a**,**b**, subjected to *Claisen* rearrangement in *N*,*N*-diethylaniline as solvent under reflux conditions, afforded compounds **8a**,**b**, whereas in diphenyl ether under reflux conditions no conversion was observed. The rearrangement products **8a**,**b** on further alkylation with allyl bromide in refluxing acetone/K_2CO_3 gave the unknown highly substituted 6,8-diallyl-7-allyloxyflavones **9a**,**b** as pale red colored solids, ring-closing metathesis of **9a**,**b** with *Grubbs*' *I* catalyst (0.005M (or) 5 mol-%, 6 h) in CH_2Cl_2 under reflux conditions afforded selectively angularly fused oxepinoflavones **10a**,**b** by leaving some unreacted **9a**,**b**. However, the RCM of **9a**,**b** with 12 mol-% of *Grubbs*' *I* catalyst under refluxing CH_2Cl_2 (2 h) gave unequal amounts of compounds **10a**,**b** (62 – 65%) and linearly fused oxepinoflavones **11a**,**b** (35 – 38%) (*Scheme 2*); exclusive formation of linearly fused 6,7-oxipinoflavones **11a**,**b** was not observed. In order to obtain exclusive compounds, either **10a**,**b** or **11a**,**b**, the RCM was carried out with 12 mol-% of *Grubbs*' *II* catalyst, but as in *Grubbs*' *I* catalyst, the RCM gave the mixture of **10a**,**b** and **11a**,**b**. Attempts to achieve cross-metathesis of compounds **10a**,**b** in refluxing CH_2Cl_2 using 10 mol-% of *Grubbs*' *II* catalyst were also unsuccessful. In the ^{1}H-NMR spectra of **10b**, two *doublet*s at δ 3.49 (*d*, *J* = 6.5 Hz, 2 H); δ 3.74 (*d*, *J* = 5.3 Hz, 2 H); a *doublet* at δ 4.63 (*d*, *J* = 2.5 Hz, 2 H); a *multiplet* at δ 5.08 – 5.10 (*m*, 2 H) and two *multiplet*s at δ 5.52 – 5.58 (*m*, 1 H); δ 5.85 – 5.90 (*m*, 2 H) were assigned to oxepine ring H-atoms and allyl group H-atoms. The structures of **10a**,**b** and **11a**,**b** were further confirmed by NOESY spectra. In the NOESY spectrum of **10b**, the strong correlations are observed between δ 3.49 (C(1″)–CH_2) and δ 7.98 (H–C(5)), weak correlations are observed between δ 3.49 (C(1″)–CH_2) and δ 4.64 (C(8)–OCH_2), δ 3.49 (C(1″)–CH_2) and δ 5.09 (C(3″)–CH_2) (*Fig. 2*). It was also supported by DQFCOSY and HMBC spectrum of **10b**. The HMBC of H–C(1″) correlates with C(6a), C(5), C(2″), C(6), and C(3″), of H–C(8) correlates with C(6a), C(9), and C(10), of H–C(11) correlates with C(12), C(12a), C(9), and C(10). However, in the ^{1}H-NMR spectra of **11b**, two *doublet*s at δ 3.58 (*d*, *J* = 6.5 Hz, 2 H) and δ 3.64 (*d*, *J* = 5.3 Hz, 2 H) were assigned to sixth and eighth position of $ArCH_2$–, a *doublet* at δ 4.64 (*d*, *J* = 2.5 Hz, 2 H) was assigned to OCH_2–, two *multiplet*s at δ 4.99 – 5.04 (*m*, 2 H); δ 5.97 – 6.01 (*m*, 1 H) were assigned to allyl H-atoms and two *multiplet*s at δ 5.44 – 5.47 (*m*, 1 H); δ 5.89 – 5.92 (*m*, 1 H) were assigned to oxepine C=O. In the NOESY spectrum of **11b**, the strong correlations are observed between δ 3.58 (C(6)–CH_2) and δ 7.88 (H–C(5)), δ 3.58

Scheme 1.



a) Allyl bromide (1 equiv.), K_2CO_3, acetone, reflux,4 h. *b*) Diphenyl ether, reflux, 3 h. *c*) Allyl bromide (1 equiv.) or but-3-en-1-yl bromide (1 equiv.), K_2CO_3, acetone, reflux, 6 – 16 h. *d*) *Grubbs*' *I*, CH_2Cl_2, reflux, 1.5 – 12 h.

(C(6)–CH_2), and δ 5.91 (H–C(7)). It was also supported by the DQFCOSY and HMBC spectrum of **11b**. The HMBC of H–C(1″) correlates with C(2″), C(3″), C(10a), C(11), and C(11a), of H–C(6) correlates with C(5a), C(7), C(8), and C(10a), and of H–C(9) correlates with C(10a) and C(8).

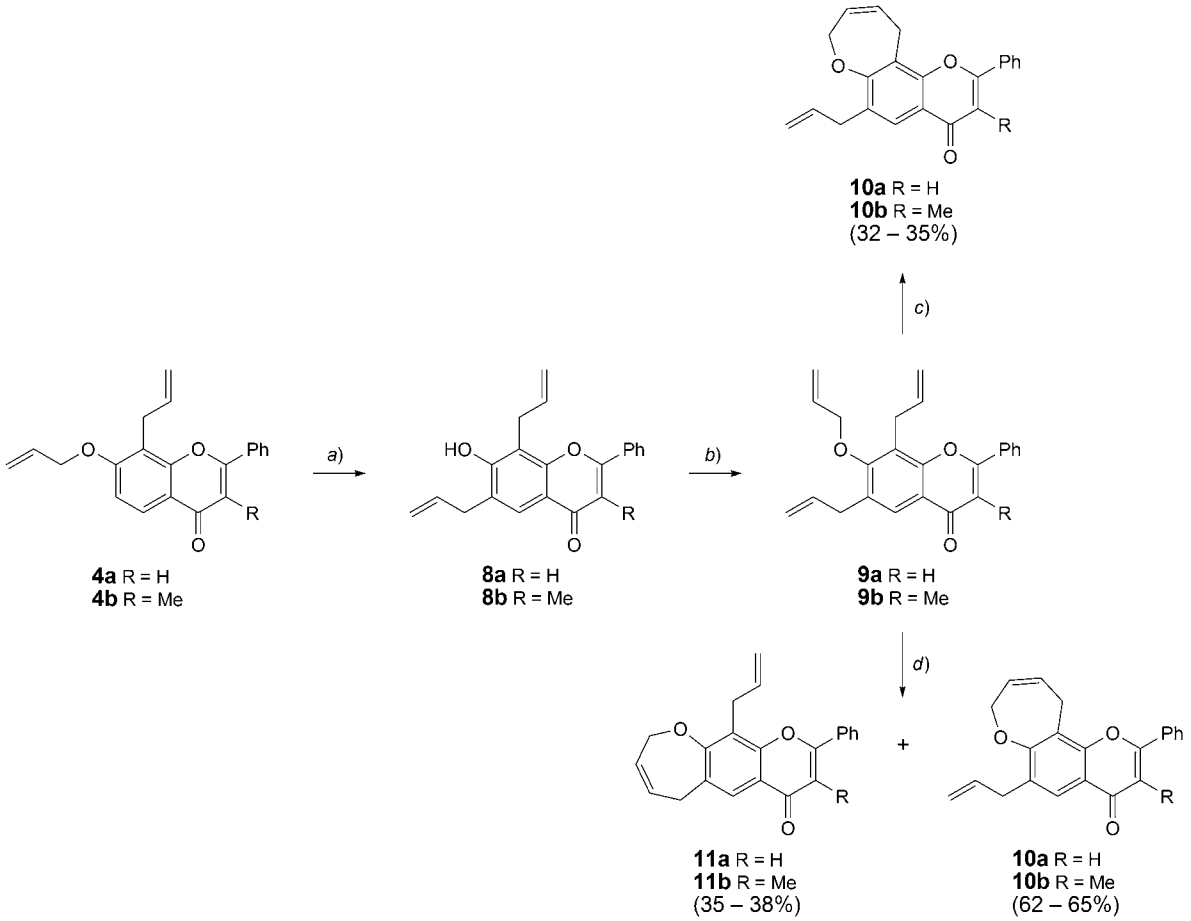
With a view to develop ene-yne metathesis, flavones **3a**,**b** on treating with propargyl bromide in K_2CO_3/acetone under reflux conditions afforded compounds **12a**,**b**. Initially, we tried the RCM of **12a**,**b** with varied concentrations of *Grubbs*' *I* catalyst, but the formation of cyclized product was not observed. Thus, the RCM of **12a**,**b** attempted with *Grubbs*' *II* catalyst (10 mol-%) in CH_2Cl_2 under reflux conditions, underwent the ene-yne RCM and furnished **13a**,**b** with 45 – 52% of yields (*Scheme 3*). In the ^{1}H-NMR spectra of **13b**, the H-atoms of newly formed vinyl oxepine resonated at δ 3.84 (*d*, *J* = 5.8 Hz, 2 H); δ 4.91 (*s*, 2 H); δ 5.01 (*dd*, *J* = 14.5 Hz, 18.1 Hz, 2 H), δ 6.01 (*t*, *J* = 5.8 Hz, 1 H), and δ 6.25 (*dd*, *J* = 11.3 Hz, 17.9 Hz, 1 H).

To further expand the scope of the RCM approach and to develop oxipinoneflavones, the compound 8-allyl-7-hydroxyflavones **3a**,**b** treated with acryloyl chloride in CH_2Cl_2 under cooling conditions gave 7-acryloxy-8-allylflavones **14a**,**b** as white colored solids. Upon the RCM of **14a**,**b** with *Grubbs*' *I* catalyst (0.01M or 10 mol-%, 2.5 h) under refluxing CH_2Cl_2 provided the exclusive formation of angular oxepinoneflavone derivatives **15a**,**b** with 62 – 66% of yields (*Scheme 4*). In the ^{1}H-NMR spectra of **15b**, absence of allylic (=CH_2) and acrylic (=CH_2) was observed, the characteristic signals of newly formed 2-oxooxepine ring protons appeared at δ 3.56 (*d*, *J* = 2.3 Hz, 2 H); δ 5.79 (*d*, *J* = 4.9 Hz, 1 H), and δ 6.40 – 6.44 (*m*, 1 H).

We next turned our attention to the synthesis of dioxocineflavones **18a** – **18c** from 7,8-dihydroxyflavones **16a** – **16c**, which were prepared by *Baker–Venkataraman* rearrangement of 2,3,4-trihydroxyacetophenone and benzoyl chloride under refluxing acetone in the presence of K_2CO_3. These on alkylation with two equivalents of allyl bromide in refluxing acetone/K_2CO_3 medium provided 7,8-diallyloxyflavones **17a** – **17c**. The RCM of **17a** – **17c** with 10 mol-% of *Grubbs*' *I* catalyst under refluxing CH_2Cl_2 afforded dioxicine derivatives **18a** – **18c** with 66 – 76% yields; the formation of **18a** – **18c** is much faster than oxipine derivatives **6a**,**b** (1.5 h) (*Scheme 5*). In the ^{1}H-NMR spectra of **18b**, two *doublet*s at δ 4.91 (*d*, *J* = 1.6 Hz, 2 H) and δ 5.16 (*d*, *J* = 7.0 Hz, 2 H) were assigned to –OCH_2- H-atoms and a *multiplet* at δ 5.92 – 5.96 (*m*, 2 H) was assigned to dioxocino C=O H-atoms.

Subsequently, we concentrated our efforts on the construction of cross-coupling products. The rearrangement products **3a**,**b** on treating with MeI in K_2CO_3/acetone at room-temperature conditions afforded compounds **19a**,**b**, which on treating with *Grubbs*' *I* catalyst did not furnish cross-coupled products. But in the presence of *Grubbs*' *II* catalyst (10 mol-%, 6 h) under refluxing CH_2Cl_2 exclusively gave compounds **20a**,**b** with 52 – 56% yields (*Scheme 6*). In the ^{1}H-NMR spectra of **20b** the characteristic signals of newly formed olefinic C=O H-atoms appeared at δ 3.50 (*d*, *J* = 3.3 Hz, 4 H) and δ 5.55 (*t*, *J* = 3.3 Hz, 2 H).

Scheme 2.



a) *N*,*N*-Diethylaniline, reflux, 3 h. *b*) Allyl bromide (1.1 equiv.), K_2CO_3, acetone, reflux, 8 h. *c*) *Grubbs' I* (5 mol-%), CH_2Cl_2, reflux, 6 h. *d*) *Grubbs' I* (12 mol-%), CH_2Cl_2, reflux, 2 h.

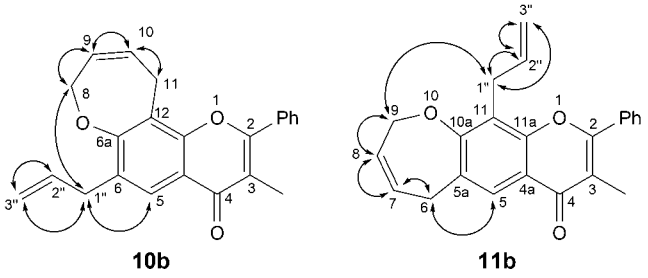


Fig. 2. Important NOESY (H ↔ H) correlations of **10b** and **11b**.

Conclusion

We have successfully used the combined *Claisen* rearrangement and RCM strategy for the synthesis of some potentially bioactive oxepin-, oxepinone-, dioxocin-annulated flavones, and also bisflavones.

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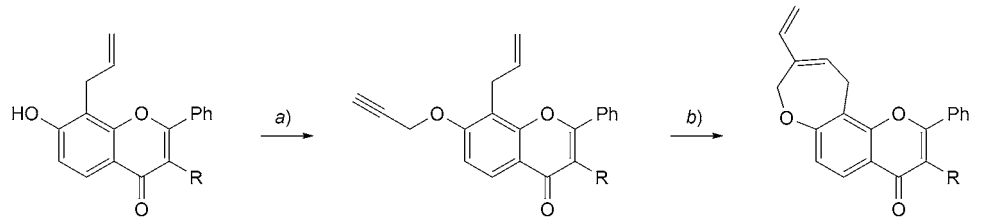
Experimental Part

General

All the experiments were carried out under a N_2 atmosphere. Thin-layer chromatography (TLC): precoated silica gel plates *GF_{254}* (SiO_2; *Merck*, India). Column chromatography (CC): SiO_2 (60 – 120 mesh). IR Spectra: *PerkinElmer 120-000* apparatus (*PerkinElmer*, Germany) in KBr discs; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Bruker DPX-400* spectrometer (*Bruker*, Switzerland) in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. NOESY Spectra: *AVENUE II 500* spectrometer. Elemental analysis: *Thermo Finnigan* CHNS analyzer (*Thermo Finnigan*, Italy).

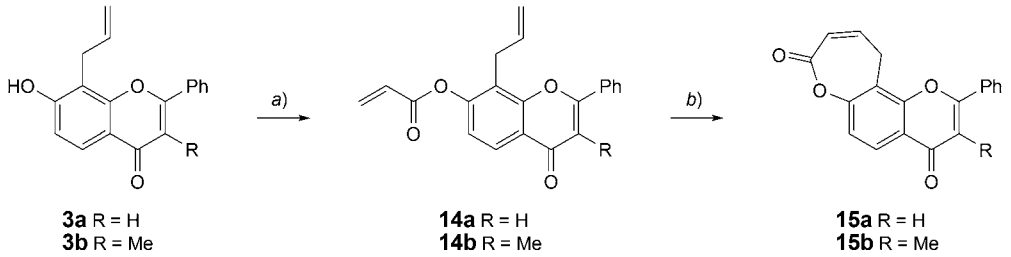
*General Procedure for the Preparation of 7-Hydroxy-2-phenyl-4*H*-chromen-4-one* **1a**,**b** [33]: To the solution of resacetophenone/propiophenones (1 mmol) and K_2CO_3 (4 mmol) in acetone, benzoyl chloride (2 mmol) was added dropwise for about 5 min. The resulting reaction mixture was refluxed for 8 h, acetone was evaporated,

Scheme 3.



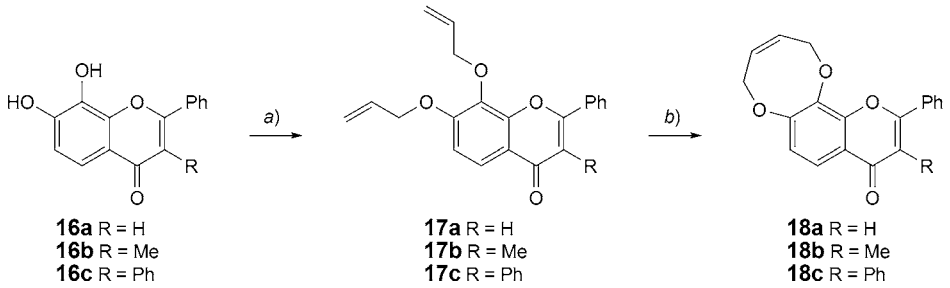
a) Propargyl bromide (1.1 equiv.), K_2CO_3, acetone, reflux, 4 h. *b*) *Grubbs*' *II*, CH_2Cl_2, reflux, 16 h.

Scheme 4.



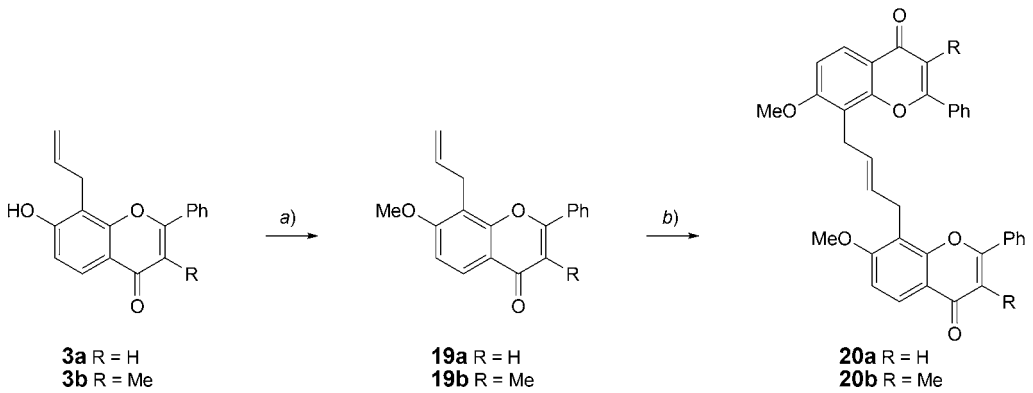
a) Acryloyl chloride (1 equiv.), Et_3N, CH_2Cl_2, 0°, 2 h. *b*) *Grubbs*' *I*, CH_2Cl_2, reflux, 2.5 h.

Scheme 5.



a) Allyl bromide (2.2 equiv.), K_2CO_3, acetone, reflux, 4 h. *b*) *Grubbs*' *I*, CH_2Cl_2, reflux, 2 h.

Scheme 6.



a) MeI (1.1 equiv.), K_2CO_3, acetone, r.t., 2.5 h. *b*) *Grubbs*' *II*, CH_2Cl_2, reflux, 6 h.

and 100 ml of MeOH/H_2O (1:1) was added. Then, the solution was refluxed for 2 h, cooled to r.t., poured into crushed ice, and acidified with 2N HCl. The precipitate was filtered, dried, and recrystallized from MeOH to get compounds **1a**,**b**.

*General Procedure for the Preparation of 7-(Allyloxy)-2-phenyl-4*H*-chromen-4-ones* **2a**,**b** [33]: To the solution of compounds **1a**,**b** (1 mmol) in acetone, allyl bromide (1.2 mmol) and anh. K_2CO_3 (2 mmol) was added. The resulting mixture was refluxed for 4 h, the acetone was evaporated, and ice-cold water was added. The precipitate was filtered and dried to afford compounds **2a**,**b**.

*General Procedure for the Preparation of 8-Allyl-7-hydroxy-2-phenyl-4*H*-chromen-4-ones* **3a**,**b** [33]: Compounds **2a**,**b** (1 mmol) were dissolved in 30 ml of diphenyl ether, the reaction mixture was refluxed for 3 h, and cooled to r.t. Then, 60 ml of petroleum ether (PE) was added, the precipitate was filtered, and dried to afford compounds **3a**,**b** as off-white solids.

*General Procedure for the Preparation of 8-Allyl-7-(allyloxy)-2-phenyl-4*H*-chromen-4-ones* **4a**,**b**: To the solution of compounds **3a**,**b** (1 mmol) in acetone was added anh. K_2CO_3 (2 mmol) and allyl bromide (1.2 mmol) at r.t. The reaction mixture was refluxed for 6 h, acetone was evaporated, and ice-cold water was added. The precipitate was filtered and dried to give compounds **4a**,**b** as off-white solids.

2-Phenyl-8-(prop-2-en-1-yl)-7-(prop-2-en-1-yloxy)-4*H*-1-benzopyran-4-one (**4a**). Yield: 82%. M.p. 109 – 110°. IR (KBr): 1626 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.72 (*d*, *J* = 6.8, 2 H); 4.66 (*d*, *J* = 5.6, 2 H); 5.03 (*dd*, *J* = 1.3, 13.6, 2 H); 5.44 (*dd*, *J* = 1.0, 16.3, 2 H); 5.99 – 6.11 (*m*, 2 H); 6.86 (*s*, 1 H); 7.04 (*d*, *J* = 8.8, 1 H); 7.50 – 7.55 (*m*, 3 H); 7.66 – 7.69 (*m*, 2 H); 8.16 (*d*, *J* = 8.8, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 28.4; 70.2; 110.4; 115.9; 116.9; 117.4; 118.2; 125.4; 126.8; 128.4; 129.1; 130.4; 132.9; 133.8; 136.1; 155.9; 159.1; 161.2; 178.9. ESI-MS: 319 ([*M* + H]$^+$). Anal. calc. for $C_{21}H_{18}O_3$ (318.37): C 79.22, H 5.70; found: C 79.18, H 5.66.

3-Methyl-2-phenyl-8-(prop-2-en-1-yl)-7-(prop-2-en-1-yloxy)-4*H*-1-benzopyran-4-one (**4b**). Yield: 86%. M.p. 99 – 101°. IR (KBr): 1629 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.17 (*s*, 3 H); 3.63 (*d*, *J* = 6.3, 2 H); 4.68 (*d*, *J* = 5.3, 2 H); 5.01 (*dd*, *J* = 0.9, 12.4, 2 H); 5.38 (*dd*, *J* = 1.5, 17.3, 2 H); 5.90 – 6.10 (*m*, 2 H); 6.99 (*d*, *J* = 8.8, 1 H); 7.50 – 7.55 (*m*, 3 H); 7.66 – 7.71 (*m*, 2 H); 8.12 (*d*, *J* = 9.0, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.6; 27.3; 69.3; 109.9; 115.2; 115.8; 115.9; 116.6; 117.6; 125.1; 128.4; 129.0; 130.0; 132.6; 133.7; 135.4; 155.1; 159.9; 160.5; 178.8. ESI-MS: 333 ([*M* + H]$^+$). Anal. calc. for $C_{22}H_{22}O_3$ (332.39): C 79.50, H 6.06; found: C 79.56, H 6.01.

*General Procedure for the Preparation of 8-Allyl-7-(but-3-en-1-yloxy)-2-phenyl-4*H*-chromen-4-ones* **5a**,**b**: To a stirred solution of compounds **3a**,**b** (1 mmol) in acetone was added anh. K_2CO_3 (2 mmol) and 1-bromo-3-butene (1.2 mmol) at r.t. The resulting reaction mixture was refluxed for 16 h, acetone was evaporated, and ice-cold water was added. The precipitate was filtered and dried to give compounds **5a**,**b** as off-white solid.

7-(But-3-en-1-yloxy)-2-phenyl-8-(prop-2-en-1-yl)-4*H*-1-benzopyran-4-one (**5a**). Yield: 54%. M.p. 142 – 144°. IR (KBr): 1628 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.62 (*q*, *J* = 6.3, 2 H); 3.68 (*d*, *J* = 5.1, 2 H); 4.18 (*d*, *J* = 6.2, 2 H); 5.05 (*dd*, *J* = 1.2, 13.4, 2 H); 5.39 (*dd*, *J* = 1.9, 17.5, 2 H); 5.96 – 6.04 (*m*, 2 H); 6.87 (*s*, 1 H); 7.04 (*d*, *J* = 8.8, 1 H); 7.53 – 7.56 (*m*, 3 H); 7.68 – 7.73 (*m*, 2 H); 7.99 (*d*, *J* = 9.0, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 28.2; 34.6; 68.3; 106.4; 110.4; 115.8; 117.1; 117.6; 118.2; 125.4; 128.4; 129.3; 130.2; 133.1; 134.3; 135.9; 156.2; 161.4; 162.8; 178.8. ESI-MS: 333 ([*M* + H]$^+$). Anal. calc. for $C_{22}H_{20}O_3$ (332.39): C 79.50, H 6.06; found: C 79.46, H 6.01.

7-(But-3-en-1-yloxy)-3-methyl-2-phenyl-8-(prop-2-en-1-yl)-4*H*-1-benzopyran-4-one (**5b**). Yield: 58%. M.p. 133 – 135°. IR (KBr): 1625 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.17 (*s*, 3 H); 2.59 (*q*, *J* = 6.1, 2 H); 3.60 (*d*, *J* = 5.5, 2 H); 4.16 (*d*, *J* = 6.8, 2 H); 5.01 (*dd*, *J* = 0.9, 12.4, 2 H); 5.37 (*dd*, *J* = 1.5, 17.3, 2 H); 5.90 – 6.01 (*m*, 2 H); 6.99 (*d*, *J* = 8.8, 1 H); 7.50 – 7.55 (*m*, 3 H); 7.64 – 7.69 (*m*, 2 H); 8.12 (*d*, *J* = 8.5, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.6; 27.3; 33.7; 68.0; 107.1; 109.8; 115.2; 115.6; 116.5; 117.4; 125.1; 128.3; 129.0; 130.0; 133.7; 134.1; 135.5; 155.1; 160.2; 160.6; 178.9. ESI-MS: 347 ([*M* + H]$^+$). Anal. calc. for $C_{23}H_{22}O_3$ (346.42): C 79.74, H 6.40; found: C 79.70, H 6.32.

*General Procedure for the Preparation of 2-Phenyl-8,11-dihydro-4*H*-oxepino[2,3-*h*]chromen-4-ones and (*Z*)-2-Phenyl-8,9-dihydrooxocino[2,3-*h*]chromen-4(12*H*)-ones* (**6a**,**b** and **7a**,**b**): To a solution of the substrates **4a**,**b** (1 mmol) in dry, degassed CH_2Cl_2 (8 ml) was added *Grubbs*' *I* catalyst (5 mol-%) under N_2 atmosphere and the resulting solution was stirred at ambient temp. for 1.5 h. The solvent was evaporated *in vacuo*, the residue was loaded on a pad of silica gel and eluted with 15% AcOEt/hexane to afford **6a**,**b** as colorless solids. The reaction of **5a**,**b** (1 mmol) with *Grubbs*' *I* catalyst under identical conditions led to **7a**,**b** after 12 h. The chromatography on silica gel using 20% AcOEt/hexane as eluent provided pure **7a**,**b** as colorless solids.

8,11-Dihydro-2-phenyl-4*H*-pyrano[2,3-*g*][1]benzoxepin-4-one (**6a**). Yield: 68%. M.p. 139 – 140°. IR (KBr): 1629 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.91 (*d*, *J* = 3.5, 2 H); 4.70 (*d*, *J* = 3.0, 2 H); 5.63 – 5.68 (*m*, 1 H); 5.94 – 6.03 (*m*, 1 H); 6.78 (*s*, 1 H); 7.12 (*d*, *J* = 8.0, 1 H); 7.55 – 7.59 (*m*, 3 H); 7.89 – 7.92 (*m*, 2 H); 8.08 (*d*, *J* = 8.5, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 23.0; 70.5; 107.2; 119.6; 120.4; 123.5; 124.9; 125.8; 126.2; 127.9; 129.2; 131.5; 132.0; 153.7; 163.0; 163.3; 178.3. ESI-MS: 291 ([*M* + H]$^+$). Anal. calc. for $C_{19}H_{14}O_3$ (290.31): C 78.61, H 4.86; found: C 78.58, H 4.81.

8,11-Dihydro-3-methyl-2-phenyl-4*H*-pyrano[2,3-*g*][1]benzoxepin-4-one (**6b**). Yield: 74%. M.p.: 134 – 138°. IR (KBr): 1628 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.16 (*s*, 3 H); 3.77 (*d*, *J* = 3.5, 2 H); 4.67 (*d*, *J* = 3.0, 2 H); 5.61 – 5.64 (*m*, 1 H); 5.91 – 5.93 (*m*, 1 H); 7.08 (*d*, *J* = 8.8, 1 H); 7.53 – 7.66 (*m*, 5 H); 8.11 (*d*, *J* = 8.5, 1 H). ^{13}C-NMR

(100 MHz, $CDCl_3$): 11.6; 22.7; 70.4; 116.9; 118.9; 119.2; 122.8; 125.1; 126.0; 127.7; 128.5; 128.9; 130.1; 133.6; 153.7; 160.6; 162.9; 178.7. ESI-MS: 305 ($[M + H]^+$). Anal. calc. for $C_{20}H_{16}O_3$ (304.34): C 78.93, H 5.30; found: C 78.96, H 5.27.

(10*Z*)-9,12-Dihydro-2-phenyl-4*H*,8*H*-pyrano[2,3-*h*][1]benzoxocin-4-one (**7a**). Yield: 58%. M.p.: 92 – 96°. IR (KBr): 1622 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.54 (*q*, *J* = 6.8, 2 H); 3.71 (*d*, *J* = 7.1, 2 H); 4.24 (*t*, *J* = 4.9, 2 H); 5.74 – 5.76 (*m*, 1 H); 6.08 – 6.11 (*m*, 1 H); 6.80 (*s*, 1 H); 7.14 (*d*, *J* = 8.8, 1 H); 7.56 – 7.71 (*m*, 5 H); 8.14 (*d*, *J* = 8.5, 1 H).). ^{13}C-NMR (100 MHz, $CDCl_3$): 24.1; 30.2; 70.3; 108.4; 115.6; 117.4; 118.2; 125.1; 125.9; 128.2; 129.0; 129.6; 130.1; 133.5; 134.2; 154.7; 158.4; 160.9; 176.8. ESI-MS: 305 ($[M + H]^+$). Anal. calc. for $C_{20}H_{16}O_3$ (304.11): C 78.93, H 5.30; found: C 78.89, H 5.78.

(10*Z*)-9,12-Dihydro-3-methyl-2-phenyl-4*H*,8*H*-pyrano[2,3-*h*][1]benzoxocin-4-one (**7b**). Yield: 64%. M.p.: 82 – 84°. IR (KBr): 1622 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.20 (*s*, 3 H); 2.51 (*q*, *J* = 6.5, 2 H); 3.70 (*d*, *J* = 7.1, 2 H); 4.18 (*t*, *J* = 5.0, 2 H); 5.71 – 5.76 (*m*, 1 H); 6.00 – 6.06 (*m*, 1 H); 7.12 (*d*, *J* = 8.8, 1 H); 7.56 – 7.71 (*m*, 5 H); 8.11 (*d*, *J* = 8.5, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.6; 23.4; 29.6; 73.9; 109.6; 117.0; 118.0; 118.7; 119.2; 124.9; 125.6; 127.9; 128.3; 129.0; 130.2; 132.4; 154.3; 160.8; 161.9; 178.9. ESI-MS: 319 ($[M + H]^+$). Anal. calc. for $C_{21}H_{18}O_3$ (318.37): C 79.22, H 5.70; found: C 79.18, H 5.73.

*General Procedure for the Preparation of 6,8-Diallyl-7-hydroxy-2-phenyl-4*H*-chromen-4-ones* **8a**,**b**: The compounds **4a**,**b** (1 mmol) were dissolved in 20 ml of *N*,*N*-diethylaniline, refluxed in the reaction mixture for 3 h, and cooled to r.t. Then, the solution was acidified with 50 ml of 2N HCl and extracted twice with AcOEt (2 × 40 ml). The organic layer was combined, dried (Na_2SO_4), and evaporated in rota evaporator. The residue was loaded on silica gel and eluted with 20% AcOEt/hexane to afford **8a**,**b** as colorless solids.

7-Hydroxy-2-phenyl-6,8-di(prop-2-en-1-yl)-4*H*-1-benzopyran-4-one (**8a**). Yield: 55%. M.p. 158 – 160°. IR (KBr): 1628 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.62 (*d*, *J* = 6.1, 2 H); 3.71 (*d*, *J* = 5.9, 2 H); 5.08 – 5.19 (*m*, 4 H); 5.99 – 6.10 (*m*, 2 H); 6.88 (*s*, 1 H); 7.02 (*d*, *J* = 8.8, 1 H); 7.53 – 7.58 (*m*, 3 H); 7.69 (*m*, 2 H); 8.01 (*s*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.9; 29.4; 110.4; 115.3; 115.8; 116.2; 117.8; 121.9; 124.2; 127.8; 128.9; 129.4; 131.4; 133.1; 133.8; 153.6; 160.1; 161.2; 177.9. ESI-MS: 319 ($[M + H]^+$). Anal. calc. for $C_{21}H_{18}O_3$ (318.37): C 79.22, H 5.70; found: C 79.15, H 5.74.

7-Hydroxy-3-methyl-2-phenyl-6,8-di(prop-2-en-1-yl)-4*H*-1-benzopyran-4-one (**8b**). Yield: 55%. M.p.: 145 – 147°. IR (KBr): 1626 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.19 (*s*, 3 H); 3.55 (*d*, *J* = 5.9, 2 H); 3.67 (*d*, *J* = 5.9, 2 H); 5.13 – 5.24 (*m*, 4 H); 5.97 – 6.11 (*m*, 2 H); 6.99 (*d*, *J* = 8.8, 1 H); 7.51 – 7.55 (*m*, 3 H); 7.66 – 7.70 (*m*, 2 H); 7.97 (*s*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 10.6; 26.5; 28.6; 108.9; 115.0; 115.6; 116.1; 118.2; 121.3; 123.7; 127.9; 129.0; 131.5; 132.7; 134.1; 134.4; 153.8; 159.1; 160.0; 178.1. ESI-MS: 333 ($[M + H]^+$). Anal. calc. for $C_{22}H_{20}O_3$ (332.39): C 79.50, H 6.06; found: C 79.45, H 6.09.

*General Procedure for the Preparation of 6,8-Diallyl-7-(allyloxy)-2-phenyl-4*H*-chromen-4-ones* **9a**,**b**: To the solution of compounds **8a**,**b** (1 mmol) in acetone was added anh. K_2CO_3 (2 mmol) and allyl bromide (1.2 mmol) at r.t. The reaction mixture was refluxed for 8 h under N_2 atmosphere, acetone was evaporated, and ice-cold water was added. The precipitate was filtered and dried to give compounds **9a**,**b** as off-white solids.

2-Phenyl-6,8-di(prop-2-en-1-yl)-7-(prop-2-en-1-yloxy)-4*H*-1-benzopyran-4-one (**9a**). Yield: 55%. M.p. 136 – 139°. IR (KBr): 1644 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.61 (*d*, *J* = 5.8, 2 H); 3.72 (*d*, *J* = 5.9, 2 H); 4.48 (*d*, *J* = 5.1, 2 H); 4.99 – 5.52 (*m*, 4 H); 6.01 – 6.13 (*m*, 3 H); 6.89 (*s*, 1 H); 7.52 – 7.56 (*m*, 3 H); 7.66 – 7.71 (*m*, 2 H); 8.00 (*s*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.7; 28.5; 68.9; 109.2; 114.4; 115.6; 115.8; 115.9; 116.2; 117.9; 122.9; 128.3; 129.3; 131.8; 132.5; 134.6; 134.8; 135.6; 153.9; 157.1; 160.2; 177.9. ESI-MS: 359 ($[M + H]^+$). Anal. calc. for $C_{24}H_{22}O_3$ (358.43): C 80.42, H 6.19; found: C 80.34, H 6.23.

3-Methyl-2-phenyl-6,8-di(prop-2-en-1-yl)-7-(prop-2-en-1-yloxy)-4*H*-1-benzopyran-4-one (**9b**). Yield: 55%. M.p. 132 – 134°. IR (KBr): 1630 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.19 (*s*, 3 H); 3.54 (*d*, *J* = 5.9, 2 H); 3.66 (*d*, *J* = 5.9, 2 H); 4.43 (*d*, *J* = 4.9, 2 H); 4.98 – 5.49 (*m*, 6 H); 5.99 – 6.14 (*m*, 3 H); 7.51 – 7.55 (*m*, 3 H); 7.65 – 7.69 (*m*, 2 H); 8.03 (*s*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 10.9; 26.4; 28.6; 68.3; 110.9; 114.2; 115.6; 115.9; 116.3; 116.6; 117.6; 123.9; 127.9; 128.6; 130.2; 131.5; 134.1; 134.4; 135.8; 153.3; 156.3; 159.3; 177.7. ESI-MS: 373 ($[M + H]^+$). Anal. calc. for $C_{25}H_{24}O_3$ (372.46): C 80.62, H 6.49; found: C 80.56, H 6.51.

*General Procedure for the Preparation of 6-Allyl-2-phenyl-8,11-dihydro-4*H*-oxepino[2,3-*h*]chromen-4-ones and 11-Allyl-2-phenyl-6,9-dihydro-4*H*-oxepino[3,2-*g*]chromen-4-ones* (**10a**,**b** and **11a**,**b**): To the solution of compounds **9a**,**b** (1 mmol) in 8 ml of dry and degassed CH_2Cl_2, 12 mol-% of *Grubbs' I* catalyst was added under N_2 atmosphere and the solution was refluxed for 2 h. The solvent was evaporated *in vacuo*, the residue was loaded on silica gel and eluted with 12% AcOEt/hexane to afford **10a**,**b** as colorless solids; further elution with 14% AcOEt/hexane afforded **11a**,**b** as colorless solids.

8,11-Dihydro-2-phenyl-6-(2-propen-1-yl)-4*H*-pyrano[2,3-*g*][1]benzoxepin-4-one (**10a**). Yield: 62%. M.p.: 191 – 193°. IR (KBr): 1629 (C=O). ^{1}H-NMR (500 MHz, $CDCl_3$): 3.43 (*d*, *J* = 6.5, 2 H); 3.84 (*d*, *J* = 5.3, 2 H); 4.61 (*d*, *J* = 2.5, 2 H); 5.01 – 5.05 (*m*, 2 H); 5.51 – 5.55 (*m*, 1 H); 5.87 – 5.98 (*m*, 2 H); 6.72 (*s*, 1 H); 7.46 – 7.51 (*m*, 3 H); 7.88 – 7.91 (*m*, 2 H); 7.91 (*s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.8; 29.4; 34.6; 71.1; 116.6; 117.0; 118.1; 124.1; 124.8; 125.6; 127.3; 128.6; 129.1; 130.1; 130.8; 133.5; 136.9; 153.1; 160.2; 160.8; 178.8. ESI-MS: 331 ($[M + H]^+$). Anal. calc. for $C_{22}H_{18}O_3$ (330.38): C 79.98, H 5.49; found: C 79.94, H 5.46.

8,11-Dihydro-3-methyl-2-phenyl-6-(2-propen-1-yl)-4*H*-pyrano[2,3-*g*][1]benzoxepin-4-one (**10b**). Yield: 65%. M.p.: 186 – 188°. IR (KBr): 1631 (C=O). ^{1}H-NMR

(500 MHz, $CDCl_3$,): 2.17 (*s*, 3 H); 3.49 (*d*, *J* = 6.5, 2 H); 3.74 (*d*, *J* = 5.3, 2 H); 4.63 (*d*, *J* = 2.5, 2 H); 5.08 – 5.10 (*m*, 2 H); 5.52 – 5.58 (*m*, 1 H); 5.85 – 5.90 (*m*, 2 H); 7.51 – 7.55 (*m*, 3 H); 7.63 – 7.65 (*m*, 2 H); 7.98 (*s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.7; 29.6; 34.1; 70.2; 116.2; 116.9; 118.9; 123.9; 124.6; 125.2; 127.6; 128.4; 128.9; 130.0; 133.6; 136.6; 152.2; 160.5; 160.9; 178.7. ESI-MS: 345 ($[M + H]^+$). Anal. calc. for $C_{23}H_{20}O_3$ (344.41): C 80.21, H 5.85; found: C 80.24, H 5.79.

6,9-Dihydro-2-phenyl-11-(2-propen-1-yl)-4*H*-pyrano[3,2-*h*][1]benzoxepin-4-one (**11a**). Yield: 38%. M.p.: 215 – 218°. IR (KBr): 1629 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.51 (*d*, *J* = 5.3, 2 H); 3.72 (*d*, *J* = 7.8, 2 H); 4.61 (*d*, *J* = 2.6, 2 H); 5.00 – 5.04 (*m*, 2 H); 5.39 – 5.46 (*m*, 1 H); 5.84 – 5.89 (*m*, 1 H); 6.01 – 6.06 (*m*, 1 H); 6.71 (*s*, 1 H); 7.48 – 7.52 (*m*, 3 H); 7.51 (*s*, 1 H); 7.86 – 7.89 (*m*, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.8; 28.1; 31.3; 71.1; 115.8; 117.4; 118.9; 121.3; 123.1; 125.6; 126.8; 128.9; 128.9; 129.6; 129.6; 130.4; 133.9; 134.6; 135.7; 154.5; 160.8; 161.1; 178.6. ESI-MS: 331 ($[M + H]^+$). Anal. calc. for $C_{22}H_{18}O_3$ (330.38): C 79.98, H 5.49; found: C 79.91, H 5.52.

6,9-Dihydro-3-methyl-2-phenyl-11-(2-propen-1-yl)-4*H*-pyrano[3,2-*h*][1]benzoxepin-4-one (**11b**). Yield: 35%. M.p.: 195 – 196°. IR (KBr): 1629 (C=O). ^{1}H-NMR (500 MHz, $CDCl_3$): 2.17 (*s*, 3 H); 3.58 (*d*, *J* = 6.5, 2 H); 3.64 (*d*, *J* = 5.3, 2 H); 4.64 (*d*, *J* = 2.5, 2 H); 4.99 – 5.04 (*m*, 2 H); 5.44 – 5.47 (*m*, 1 H); 5.89 – 5.92 (*m*, 1 H); 5.97 – 6.01 (*m*, 1 H); 7.50 – 7.53 (*m*, 3 H); 7.63 – 7.65 (*m*, 2 H); 7.88 (*s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.7; 27.8; 31.4; 71.4; 115.5; 117.0; 118.6; 121.1; 122.7; 125.8; 126.6; 128.6; 128.6; 129.0; 129.0; 130.0; 133.6; 134.2; 135.8; 154.2; 160.5; 160.7; 178.8. ESI-MS: 345 ($[M + H]^+$). Anal. calc. for $C_{23}H_{20}O_3$ (344.41): C 80.21, H, 5.85; found: C 80.26, H 5.81.

*General Procedure for the Preparation of 8-Allyl-2-phenyl-7-(prop-2-yn-1-yloxy)-4*H*-chromen-4-ones* **12a**,**b**: To the solution of compounds **3a**,**b** (1 mmol) in acetone was added anh. K_2CO_3 (2 mmol) and propargyl bromide (1.2 mmol) at r.t. The reaction mixture was refluxed for 4 h, acetone was evaporated, and added ice-cold water. The precipitate was filtered and dried to give compounds **12a**,**b** as off-white solids.

2-Phenyl-8-(prop-2-en-1-yl)-7-(prop-2-yn-1-yloxy)-4*H*-1-benzopyran-4-one (**12a**). Yield: 82%. M.p. 151 – 153°. IR (KBr): 1630 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.56 (*t*, *J* = 1.9, 1 H); 3.68 (*d*, *J* = 5.8, 2 H); 4.89 (*s*, 2 H); 5.03 (*dd*, *J* = 1.1, 12.7, 2 H); 5.99 – 6.11 (*m*, 1 H); 6.86 (*s*, 1 H); 7.14 (*d*, *J* = 8.5, 1 H); 7.50 – 7.66 (*m*, 5 H); 8.14 (*d*, *J* = 9.0, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 27.6; 57.1; 110.4; 115.8; 116.9; 117.1; 117.3; 117.8; 126.5; 128.5; 129.2; 129.3; 130.3; 133.9; 134.9; 155.6; 159.3; 165.9; 178.3. ESI-MS: 317 ($[M + H]^+$). Anal. calc. for $C_{21}H_{16}O_3$ (316.35): C 79.73, H 5.10; found: C 79.66, H 5.16.

3-Methyl-2-phenyl-8-(prop-2-en-1-yl)-7-(prop-2-yn-1-yloxy)-4*H*-1-benzopyran-4-one (**12b**). Yield: 82%. M.p. 146 – 148°. IR (KBr): 1627 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.17 (*s*, 3 H); 2.58 (*t*, *J* = 1.8, 1 H); 3.61 (*d*, *J* = 5.3, 2 H); 4.85 (*s*, 2 H); 5.01 (*dd*, *J* = 0.9, 12.4, 2 H); 5.99 – 6.10 (*m*, 1 H); 7.13 (*d*, *J* = 8.8, 1 H); 7.50 – 7.66 (*m*, 5 H); 8.12 (*d*, *J* = 8.8, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.2; 27.2; 56.5; 110.1; 115.3; 116.4; 116.6; 117.2; 117.3; 124.9; 128.3; 128.9; 130.0; 133.5; 135.5; 155.5; 158.8; 160.6; 178.7. ESI-MS: 331 ($[M + H]^+$). Anal. calc. for $C_{22}H_{18}O_3$ (330.38): C 79.98, H 5.48; found: C 79.92, H 5.45.

*General Procedure for the Preparation of 2-Phenyl-9-vinyl-8,11-dihydro-4*H*-oxepino[2,3-*h*]chromen-4-ones* **13a**,**b**: To a solution of the substrates **12a**,**b** (1 mmol) in dry, degassed CH_2Cl_2 (8 ml) was added *Grubbs' II* catalyst (10 mol-%) under N_2 atmosphere and the resulting solution was stirred at ambient temp. for 16 h. The solvent was evaporated *in vacuo*, the residue was loaded on a pad of silica gel and eluted with 20% AcOEt/hexane to afford **13a**,**b** as colorless solids.

9-Ethenyl-8,11-dihydro-2-phenyl-4*H*-pyrano[2,3-*g*][1]benzoxepin-4-one (**13a**). Yield: 52%. M.p.: 63 – 66°. IR (KBr): 1628 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.76 (*d*, *J* = 5.0, 2 H); 4.86 (*s*, 2 H); 5.11 (*dd*, *J* = 11.5, 17.1, 2 H); 5.89 (*t*, *J* = 6.1, 1 H); 6.19 (*dd*, *J* = 10.3, 17.5, 1 H); 6.82 (*s*, 1 H); 7.04 (*d*, *J* = 8.8, 1 H); 7.53 – 7.67 (*m*, 5 H); 8.18 (*d*, *J* = 9.0, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 23.2; 71.1; 109.6; 117.1; 118.2; 119.2; 121.4; 123.4; 124.8; 125.2; 127.3; 128.0; 128.9; 130.4; 132.6; 135.8; 137.0; 154.3; 161.2; 162.8; 178.8. ESI-MS: 317 ($[M + H]^+$). Anal. calc. for $C_{21}H_{16}O_3$ (317.38): C 79.73, H 5.10; found: C 79.70, H 5.55.

9-Ethenyl-8,11-dihydro-3-methyl-2-phenyl-4*H*-pyrano[2,3-*g*][1]benzoxepin-4-one (**13b**). Yield: 46%. M.p.: 68 – 69°. IR (KBr): 1623 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.17 (*s*, 3 H); 3.84 (*d*, *J* = 5.8, 2 H); 4.91 (*s*, 2 H); 5.01 (*dd*, *J* = 14.5, 18.1, 2 H); 6.01 (*t*, *J* = 5.8, 1 H); 6.25 (*dd*, *J* = 11.3, 17.9, 1 H); 7.09 (*d*, *J* = 8.8, 1 H); 7.53 – 7.67 (*m*, 5 H); 8.10 (*d*, *J* = 8.5, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.6; 22.3; 69.3; 111.6; 117.0; 118.8; 118.9; 121.0; 128.1; 128.5; 128.9; 130.2; 133.5; 136.8; 137.0; 153.7; 160.5; 162.6; 178.7. ESI-MS: 331 ($[M + H]^+$). Anal. calc. for $C_{22}H_{18}O_3$ (330.38): C 79.98, H 5.49; found: C 79.92, H, 5.53.

*General Procedure for the Preparation of 8-Allyl-4-oxo-2-phenyl-4*H*-chromen-7-yl Acrylates* **14a**,**b**: To the solution of compounds **3a**,**b** (1 mmol) in 25 ml of dry CH_2Cl_2 was added Et_3N (2 mmol) and acryloyl chloride (1 mmol) at 0 °C. Then the solution was stirred for 2 h, the solvent was evaporated. To the obtained residue 50 ml of ice-cold water was added and extracted twice with AcOEt (2 × 50 ml). The organic layer was washed with water and dried (Na_2SO_4), filtered and evaporated under *vacuo* to give residue, which was purified by column chromatography to afford compounds **14a**,**b** as off - white solids.

4-Oxo-2-phenyl-8-(prop-2-en-1-yl)-4*H*-1-benzopyran-7-yl Prop-2-enoate (**14a**). Yield: 71%. M.p.: 164 – 166°. IR (KBr): 1634 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.61 (*d*, *J* = 6.6, 2 H); 4.99 – 5.08 (*m*, 2 H); 5.86 – 5.96 (*m*, 1 H); 6.13 (*d*, *J* = 11.1, 1 H); 6.38 (*dd*, *J* = 11.1, 18.1, 1 H); 6.66

(*d*, *J* = 17.9, 1 H); 6.94 (*s*, 1 H); 7.21 (*d*, *J* = 2.5, 1 H); 7.51 – 7.64 (*m*, 5 H); 8.25 (*d*, *J* = 7.6, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 32.1; 116.9; 118.4; 120.4; 121.6; 121.9; 123.6; 125.2; 127.8; 129.1; 129.8; 133.6; 134.3; 134.8; 153.1; 155.9; 162.5; 166.1; 180.1. ESI-MS: 333 ([*M* + H]$^+$). Anal. calc. for $C_{21}H_{16}O_4$ (332.35): C 75.89, H 4.85; found: C 75.83, H 4.80.

3-Methyl-4-oxo-2-phenyl-8-(prop-2-en-1-yl)-4*H*-1-benzopyran-7-yl Prop-2-enoate (**14b**). Yield: 76%. M.p.: 159 – 161°. IR (KBr): 1630 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.22 (*s*, 3 H); 3.56 (*d*, *J* = 6.1, 2 H); 4.98 – 5.04 (*m*, 2 H); 5.82 – 5.93 (*m*, 1 H); 6.09 (*d*, *J* = 10.6, 1 H); 6.36 (*dd*, *J* = 10.6, 17.3, 1 H); 6.67 (*d*, *J* = 17.3, 1 H); 7.18 (*d*, *J* = 2.3, 1 H); 7.50 – 7.66 (*m*, 5 H); 8.23 (*d*, *J* = 7.5, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.3; 31.8; 116.8; 118.2; 119.9; 121.4; 122.0; 125.0; 127.6; 128.8; 129.0; 130.3; 133.1; 134.1; 134.2; 152.8; 155.6; 161.9; 165.8; 179.2. ESI-MS: 347 ([*M* + H]$^+$). Anal. calc. for $C_{22}H_{18}O_4$ (346.38): C 76.29, H 5.24; found: C 76.22, H 5.21.

*General Procedure for the Preparation of 2-Phenyl-4*H*-oxepino[2,3-*h*]chromene-4,8(11*H*)-diones* **15a**,**b**: To a solution of the substrates **14a**,**b** (1 mmol) in dry, degassed CH_2Cl_2 (8 ml) was added *Grubbs*' *I* catalyst (5 mol-%) under N_2 atmosphere and the resulting solution was stirred at ambient temp. for 2.5 h. The solvent was evaporated *in vacuo*, the residue was loaded on a pad of silica gel, and eluted with 15% AcOEt/hexane to afford **15a**,**b** as colorless solids.

2-Phenyl-4*H*-pyrano[2,3-*g*][1]benzoxepin-4,8(11*H*)-dione (**15a**). Yield: 62%. M.p.: 128 – 130°. IR (KBr): 1628 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.56 (*d*, *J* = 3.1, 2 H); 5.88 (*d*, *J* = 5.7, 1 H); 6.38 – 6.41 (*m*, 1 H); 6.78 (*s*, 1 H); 7.16 (*d*, *J* = 8.6, 1 H); 7.48 – 7.59 (*m*, 5 H); 8.08 (*d*, *J* = 8.8, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 29.4; 114.3; 115.1; 118.8; 120.4; 121.2; 120.9; 124.9; 127.2; 128.1; 128.4; 129.4; 130.6; 132.6; 135.2; 153.4; 159.6; 162.8; 179.8. ESI-MS: 305 ([*M* + H]$^+$). Anal. calc. for $C_{19}H_{12}O_4$ (304.30): C 74.99, H 3.97; found: C 74.94, H 3.93.

3-Methyl-2-phenyl-4*H*-pyrano[2,3-*g*][1]benzoxepin-4,8(11*H*)-dione (**15b**). Yield: 66%. M.p.: 121 – 123°. IR (KBr): 1631 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.21 (*s*, 3 H); 3.56 (*d*, *J* = 2.3, 2 H); 5.79 (*d*, *J* = 4.9, 1 H); 6.40 – 6.44 (*m*, 1 H); 7.10 (*d*, *J* = 8.6, 1 H); 7.51 – 7.57 (*m*, 5 H); 8.14 (*d*, *J* = 9.0, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.8; 28.3; 116.3; 117.8; 119.7; 120.6; 121.2; 124.8; 127.2; 128.5; 129.0; 130.3; 133.3; 133.6; 134.2; 152.4; 154.9; 160.9; 163.8; 178.6. ESI-MS: 319 ([*M* + H]$^+$). Anal. calc. for $C_{20}H_{14}O_4$ (318.32): C 75.46, H 4.43; found: C 75.48, H 4.41.

*General Procedure for the Preparation of 7,8-Dihydroxy-3-methyl-2-phenyl-4*H*-chromen-4-ones* **16a** – **16c**: To the solution of 1,2,3-trihydroxyacetophenone(1 mmol) and K_2CO_3 (8 mmol) in acetone, benzoyl chloride (3.3 mmol) was added dropwise about 10 min. The resulting reaction mixture was refluxed for 12 h, acetone was evaporated, and 250 ml of MeOH/H_2O (1:1) was added. Then the solution was refluxed for 3 h, cooled to r.t., and poured into crushed ice, acidified with 2N HCl. The precipitate was filtered, dried, and recrystallized in MeOH to yield compounds **16a** – **16c** as light red solids.

*General Procedure for the Preparation of 7,8-Bis(allyloxy)-3-methyl-2-phenyl-4*H*-chromen-4-ones* **17a** – **17c**: To the solution of compounds **16a** – **16c** (1 mmol) in acetone was added anh. K_2CO_3 (5 mmol) and allyl bromide (2.0 mmol). The reaction mixture was refluxed for 4 h, acetone was evaporated, and ice-cold water was added. The precipitate was filtered and dried to give compounds **17a** – **17c** as off-white solids.

2-Phenyl-7,8-bis(prop-2-en-1-yloxy)-4*H*-1-benzopyran-4-one (**17a**). Yield: 78%. M.p. 198 – 199°. IR (KBr): 1641 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 4.65 (*d*, *J* = 5.9, 2 H); 4.79 (*d*, *J* = 5.1, 2 H); 5.19 – 5.23 (*m*, 4 H); 6.02 – 6.14 (*m*, 2 H); 6.84 (*s*, 1 H); 7.09 (*d*, *J* = 8.5, 1 H); 7.52 – 7.56 (*m*, 3 H); 7.67 – 7.69 (*m*, 2 H); 8.01 (*d*, *J* = 8.8, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 70.2; 74.9; 108.3; 115.8; 117.2; 118.4; 118.9; 122.1; 128.5; 129.2; 130.3; 132.6; 133.2; 134.0; 136.1; 151.3; 155.8; 161.1; 178.8. ESI-MS: 335 ([*M* + H]$^+$). Anal. calc. for $C_{22}H_{20}O_4$ (334.37): C 75.43, H 5.43; found: C 75.38, H 5.46.

3-Methyl-2-phenyl-7,8-bis(prop-2-en-1-yloxy)-4*H*-1-benzopyran-4-one (**17b**). Yield: 89%. M.p.: 189 – 191°. IR (KBr): 1637 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.17 (*s*, 3 H); 4.63 (*d*, *J* = 5.8, 2 H); 4.73 (*d*, *J* = 5.0, 2 H); 5.18 – 5.24 (*m*, 4 H); 6.03 – 6.13 (*m*, 2 H); 7.02 (*d*, *J* = 9.03, 1 H); 7.51 – 7.54 (*m*, 3 H); 7.66 – 7.69 (*m*, 2 H); 7.94 (*d*, *J* = 8.8, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.6; 69.9; 74.6; 111.3; 116.7; 117.5; 118.1; 118.3; 121.0; 128.3; 129.0; 130.3; 132.5; 133.6; 133.8; 135.6; 150.8; 155.4; 160.4; 178.4. ESI-MS: 349 ([*M* + H]$^+$). Anal. calc. for $C_{22}H_{20}O_4$ (348.39): C 75.84, H 5.79; found: C 75.81, H 5.76.

2,3-Diphenyl-7,8-bis(prop-2-en-1-yloxy)-4*H*-1-benzopyran-4-one (**17c**). Yield: 89%. M.p. 181 – 183°. IR (KBr): 1644 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 4.60 (*d*, *J* = 5.9, 2 H); 4.71 (*d*, *J* = 5.8, 2 H); 5.21 – 5.26 (*m*, 4 H); 6.06 – 6.15 (*m*, 2 H); 7.14 (*d*, *J* = 9.1, 1 H); 7.21 – 7.46 (*m*, 10 H); 8.14 (*d*, *J* = 8.6, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 69.8; 72.8; 112.6; 116.9; 117.4; 119.8; 121.6; 123.0; 125.6; 127.7; 128.0; 128.6; 128.8; 129.5; 130.4; 131.0; 132.6; 133.6; 134.1; 154.5; 161.0; 162.8; 178.1. ESI-MS: 411 ([*M* + H]$^+$). Anal. calc. for $C_{27}H_{22}O_4$ (410.46): C 79.01, H 5.40; found: C 79.98, H 5.42.

*General Procedure for the Preparation of (Z)-10-Methyl-11-phenyl-2*H*-[1,4]dioxocino[2,3-*h*]chromen-9(5*H*)-ones* **18a** – **18c**: The diallyloxy compounds **17a** – **17c** (1 mmol) in dry CH_2Cl_2 was degassed for 10 min, then *Grubbs*' *I* catalyst (10 mol-%) was added, and the reaction mixture was refluxed for 2 h. The resulting reaction mixture was concentrated under reduced pressure and the crude product was purified by silica gel flash chromatography. The elution of the column with 20% AcOEt and PE mixture gave compounds **18a** – **18c** as colorless solids.

(3*Z*)-2,5-Dihydro-11-phenyl-9*H*-pyrano[2,3-*h*]-1,6-benzodioxocin-9-one (**18a**). Yield: 72%. M.p. 186 – 188°. IR (KBr): 1634 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 4.81 (*d*, *J* = 2.6, 2 H); 5.21 (*d*, *J* = 6.7, 2 H); 5.80 – 5.83 (*m*, 2 H); 6.88 (*s*, 1 H); 7.11 (*d*, *J* = 8.78, 1 H); 7.52 – 7.56 (*m*, 3 H); 7.77 – 7.81 (*m*, 2 H); 7.98 (*d*, *J* = 8.9, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 28.1; 68.2; 68.1; 109.9; 115.8; 116.2; 116.9; 120.4; 124.6; 128.4; 128.8; 132.2; 133.0; 134.6; 135.2; 155.2; 156.8; 160.3; 178.4. ESI-MS: 307 ([*M* + H]$^+$). Anal. calc. for $C_{19}H_{14}O_4$ (306.31): C 74.50, H 4.61; found: C 74.54, H 4.55.

(3*Z*)-2,5-Dihydro-10-methyl-11-phenyl-9*H*-pyrano[2,3-*h*]-1,6-benzodioxocin-9-one (**18b**). Yield: 76%. M.p. 172 – 173°. IR (KBr): 1630 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.16 (*s*, 3 H); 4.91 (*d*, *J* = 1.6, 2 H); 5.16 (*d*, *J* = 7.0, 2 H); 5.92 – 5.96 (*m*, 2 H); 6.92 (*d*, *J* = 9.0, 1 H); 7.52 – 7.56 (*m*, 3 H); 7.64 – 7.68 (*m*, 2 H); 7.88 (*d*, *J* = 9.03, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.7; 66.3; 73.1; 117.3; 117.6; 117.8; 118.0; 121.6; 124.8; 128.4; 128.5; 128.9; 130.1; 133.5; 133.7; 134.0; 151.7; 152.9; 160.1; 178.19. ESI-MS: 321 ([*M* + H]$^+$). Anal. calc. for $C_{20}H_{16}O_4$ (320.34): C 74.99, H 5.03; found: C 74.96, H 5.07.

(3*Z*)-2,5-Dihydro-10,11-diphenyl-9*H*-pyrano[2,3-*h*]-1,6-benzodioxocin-9-one (**18c**). Yield: 66%. M.p.: 156 – 158°. IR (KBr): 1644 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.83 (*d*, *J* = 5.3, 2 H); 4.72 (*d*, *J* = 6.8, 2 H); 5.63 – 5.66 (*m*, 1 H); 5.94 – 5.98 (*m*, 1 H); 7.12 (*d*, *J* = 9.1, 1 H); 7.19 – 7.42 (*m*, 10 H); 8.14 (*d*, *J* = 8.3, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 69.4; 70.8; 118.4; 119.6; 119.9; 122.4; 123.0; 125.7; 127.6; 128.0; 128.3; 129.5; 130.4; 131.2; 132.7; 133.3; 133.7; 153.6; 161.1; 163.3; 177.3. MS-ES+: 383 ([*M* + H]$^+$). Anal. calc. for $C_{25}H_{18}O_4$ (382.41): C 78.52, H 4.74; found: C 78.56, H 4.70.

*General Procedure for the Preparation of 8-Allyl-7-methoxy-2-phenyl-4*H*-chromen-4-ones* **19a**,**b**: To the solution of compounds **3a**,**b** (1 mmol) in acetone was added anh. K_2CO_3 (2 mmol) and MeI (1.1 mmol). The reaction mixture was stirred at r.t. for 2.5 h, acetone was evaporated, and ice-cold water was added. The precipitate was filtered and dried to give compounds **19a**,**b** as colorless solids.

7-Methoxy-2-phenyl-8-(prop-2-en-1-yl)-4*H*-1-benzopyran-4-one (**19a**). Yield: 54%. M.p. 155 – 157°. IR (KBr): 1629 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.64 (*d*, *J* = 5.9, 2 H); 4.06 (*s*, 3 H); 5.03 (*dd*, *J* = 0.9, 12.4, 2 H); 5.96 – 6.08 (*m*, 1 H); 6.88 (*s*, 1 H); 7.13 (*d*, *J* = 8.8, 1 H); 7.51 – 7.58 (*m*, 3 H); 7.78 (*s*, 1 H); 8.21 (*d*, *J* = 9.1, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 28.1, 58.1; 106.6; 115.0, 115.9; 117.8; 118.4, 125.9; 127.8; 128.9; 129.6; 129.9; 130.3; 131.0; 134.6; 155.6; 159.3; 161.6; 178.3. ESI-MS: 293 ([*M* + H]$^+$). Anal. calc. for $C_{19}H_{16}O_3$ (292.33): C 78.06, H 5.52; found: C 78.016, H 5.55.

7-Methoxy-3-methyl-2-phenyl-8-(prop-2-en-1-yl)-4*H*-1-benzopyran-4-one (**19b**). Yield: 68%. M.p. 144 – 146°. IR (KBr): 1636 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.18 (*s*, 3 H); 3.61 (*d*, *J* = 5.8, 2 H); 3.97 (*s*, 3 H); 5.01 (*dd*, *J* = 0.9, 12.4, 2 H); 5.92 – 6.01 (*m*, 1 H); 7.03 (*d*, *J* = 8.8, 1 H); 7.47 – 7.56 (*m*, 3 H); 7.67 (*s*, 1 H); 8.16 (*d*, *J* = 9.0, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.5; 27.2; 56.1; 108.9; 115.2; 115.4; 116.8; 118.4; 125.3; 127.1; 128.8; 129.0; 129.7; 130.1; 130.9; 135.3; 155.0; 158.9; 161.0; 178.6. ESI-MS: 307 ([*M* + H]$^+$). Anal. calc. for $C_{20}H_{18}O_3$ (306.36): C 78.41, H 5.92; found: C 78.36, H 5.88.

*General Procedure for the Preparation of (2*E*)-8,8′-(But-2-ene-1,4-diyl)bis(7-methoxy-2-phenyl-4*H*-chromen-4-one)* (**20a**,**b**): To a solution of the substrates **19a**,**b** (1 mmol) in dry, degassed CH_2Cl_2 (8 ml) was added *Grubbs' II* catalyst (10 mol-%) under N_2 atmosphere, and the resulting solution was stirred at ambient temp. for 6 h. The solvent was evaporated *in vacuo*, the residue was loaded on a pad of silica gel and eluted with 40% AcOEt/hexane to afford **20a**,**b** as off -white solids.

8,8′-(2*E*)-But-2-ene-1,4-diylbis(7-methoxy-2-phenyl-4*H*-1-benzopyran-4-one) (**20a**). Yield: 52%. M.p.: 225 – 228°. IR (KBr): 1626 (C=O); 1634 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.61 (*d*, *J* = 2.9, 4 H); 3.94 (*s*, 6 H); 5.42 (*t*, *J* = 3.5, 2 H); 6.82 (*s*, 2 H); 7.08 (*d*, *J* = 9.1, 2 H); 7.34 – 7.54 (*m*, 10 H); 8.08 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 24.1; 60.6; 110.5; 114.6; 119.2; 119.8; 123.9; 127.2; 129.1; 130.1; 130.6; 131.1; 135.2; 135.9; 153.8; 160.6; 161.4; 179.6. ESI-MS: 580 ([*M* + Na]$^+$). Anal. calc. for $C_{36}H_{28}O_6$ (557.01): C 77.68, H 5.07; found: C 77.62, H 5.09.

8,8′-(2*E*)-But-2-ene-1,4-diylbis(7-methoxy-3-methyl-2-phenyl-4*H*-1-benzopyran-4-one) (**20b**). Yield: 56%. M.p.: 204 – 206°. IR (KBr): 1632 (C=O); 1636 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$): 2.13 (*s*, 6 H); 3.50 (*d*, *J* = 3.3, 4 H); 3.86 (*s*, 6 H); 5.55 (*t*, *J* = 3.3, 2 H); 6.98 (*d*, *J* = 9.0, 2 H); 7.29 – 7.47 (*m*, 10 H); 8.12 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.8; 29.8; 57.6; 111.1; 116.5; 116.8; 118.4; 126.5; 128.5; 128.6; 131.4; 131.9; 132.5; 135.0; 136.9; 156.8; 161.2; 163.8; 181.8. ESI- MS: 585 ([*M* + H]$^+$). Anal. calc. for $C_{38}H_{32}O_6$ (584.66): C 78.06, H 5.52; found: C 78.04, H 5.57.

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