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Synthesis of novel oxa-carbocycle annulated flavones and bis-flavones by ring closing/cross metathesis

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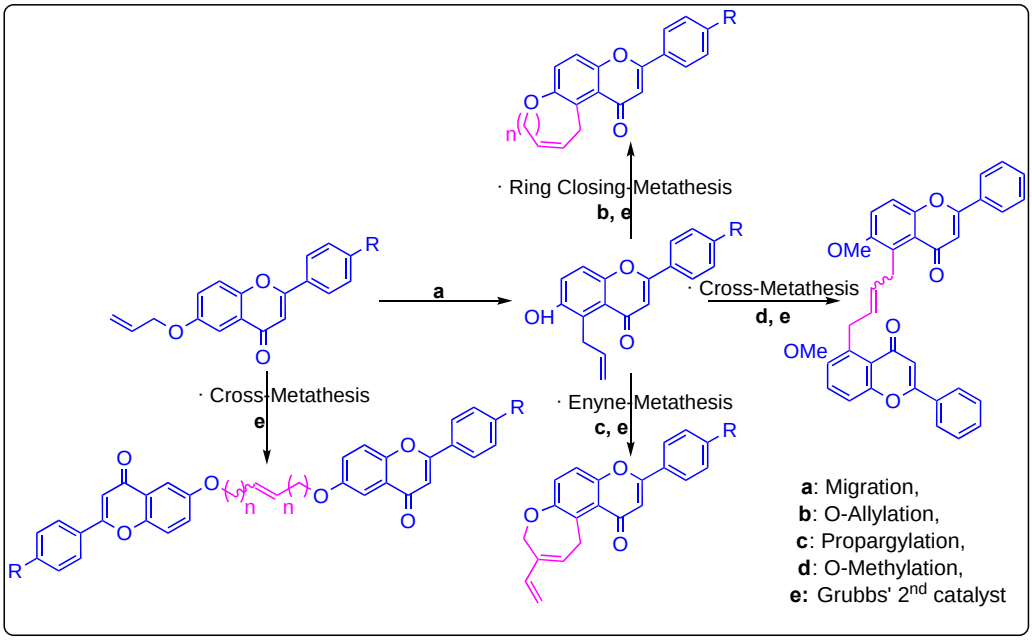
Abstract

A series of new $C_7/C_8/C_9$-C_6-C_6 tricyclic oxa carbocyclic annulated flavones/bis flavones *were* synthesized *via* combined Claisen rearrangement and ring closing/cross metathesis from 6-hydroxy-flavone using Grubbs' 2nd generation catalyst. This synthetic strategy provides a facile and efficient route to a library of diverse tricyclic flavone heterocyclics and bis flavones having different ring systems.



Keywords: 6-Hydroxy-flavone, Claisen rearrangement, Olefin metathesis, Oxa-carbocyclic annulated flavones/bis flavones, Grubbs' 2nd generation catalyst

Introduction

Flavonoids are natural products derived from benzopyrans that form an important group of oxygen heterocycles that are widely distributed in the plant kingdom as secondary metabolites.[1] These perform a variety of plant functions, including flower pigmentation and defence against arthropods and plant microbes.[2] Fruits, vegetables, tea, red wine and juices in particular contain these substances on a regular basis in the human diet.[3] Flavones have numerous biological and pharmacological actions[4,5] such as anti-oxidant, anti-cancer, estrogenic, antibacterial, anti-inflammatory, anti-microbial, ion transport properties and cardiovascular disease protection.[6-12] Some flavonoids participate in a variety of activities in plant biochemistry and physiology including UV ray protection.[13] interaction with soil microbes,[14] enzyme inhibition and nitrogen-fixing module promotion.[15]

For the synthesis of different heterocyclic ring-fused flavones, a number of procedures have been published in the literature; however, medium-sized oxa-carbocycle annulated flavones are very few, most likely because there is no universal technique.[16-19] Entropic and enthalpic forces make it difficult to manufacture medium-sized rings. A number of bioactive natural compounds, including pterulone (**1**) pterulinic acid (**2**), ptaeroxylin (**3**), carpachromene (**4**) and artoflavone A (**5**) contain benzoxepines and benzoxocines, making them privileged structural scaffolds in medicinal chemistry[20-23] (Figure 1).

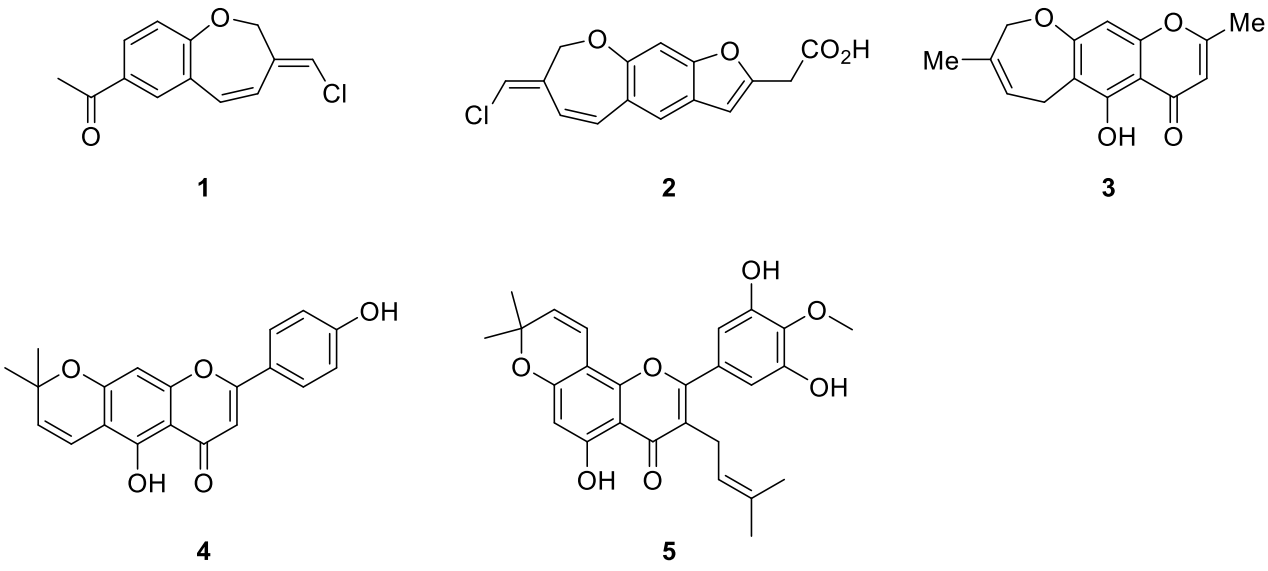


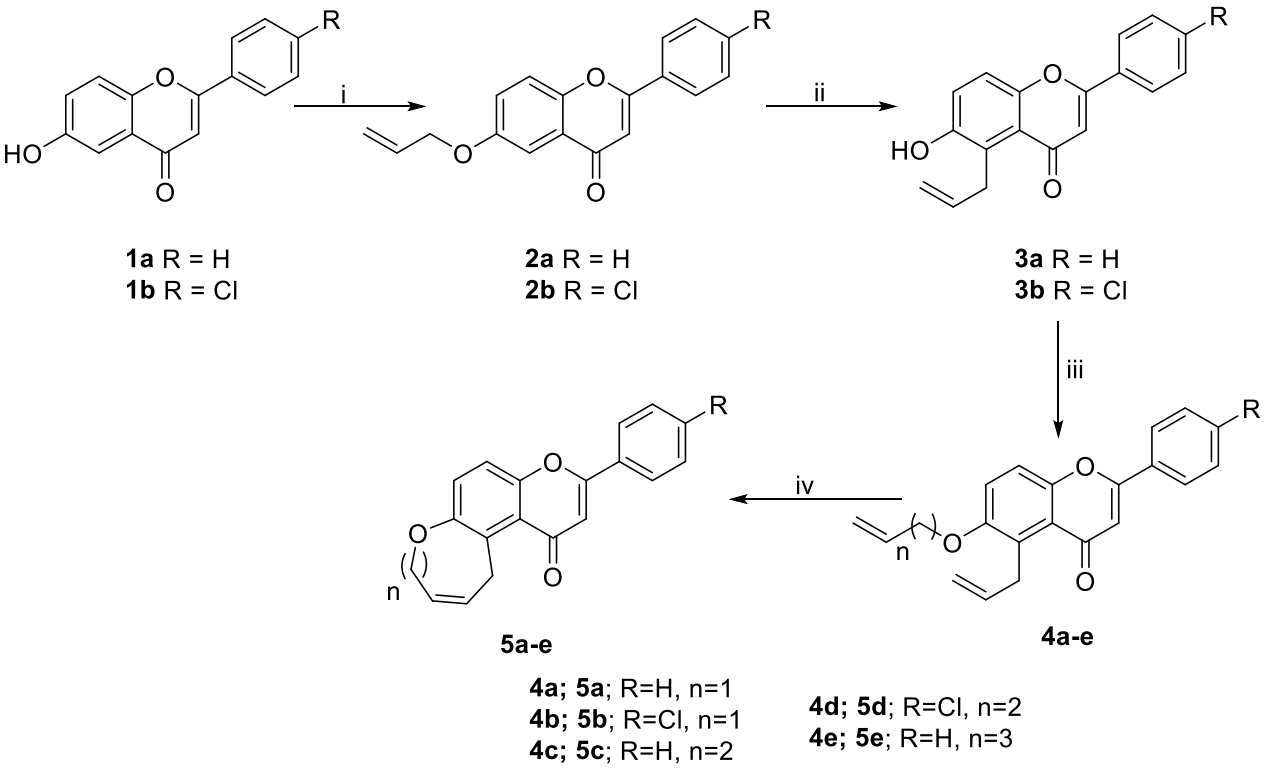
Figure 1. Some biologically active natural products.

The major objective of the current study was to synthesize $C_7/C_8/C_9$-C_6-C_6 tricyclic oxa carbocyclic annulated flavones and oxa-olefin bis flavones *via* combined Claisen rearrangement and olefin metathesis from 6-hydroxy-flavone by using Grubbs' 2nd generation catalyst.[24-26]

Results and Discussion

6-Hydroxy-2-phenyl-4*H*-chromen-4-ones **1a-b** were treated with allyl bromide and K_2CO_3/acetone under reflux conditions yielding[27] **2a-b**, followed by their regiospecific Claisen rearrangement in *N,N*-diethyl aniline at reflux

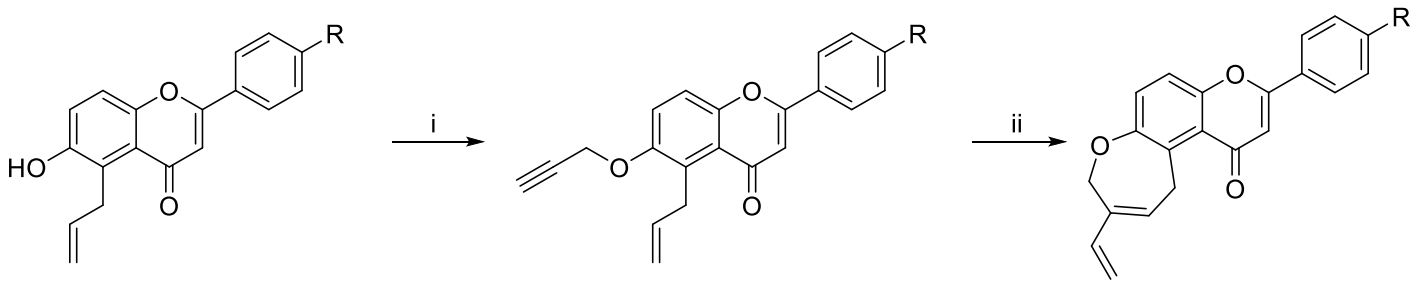
temperature yielding 5-allyl-6-hydroxy-2-phenyl-4*H* chromen-4-ones **3a-b**. The regiospecificity of the Claisen rearrangement of **3a-b** is probably influenced by the electronic effects from the flavone carbonyl and ether oxygen fonctions which gives the relative stability to conformers of the transition state and intermediates for the formation of **3a-b** intermediates. Further alkylation of **3a-b** with allyl bromide and acetone/K_2CO_3 afforded products **4a-e**, ring closing metathesis of 5-allyl-6-(allyloxy)-2-phenyl-4*H*-chromen-4-ones (**4a-e**) with 10 mol % Grubbs' 2nd generation catalyst in degassed dichloromethane under nitrogen, afforded the RCM products 3-phenyl-8,11-dihydro-1*H*-oxepino[3,2-*f*]chromen-1-ones (**5a-e**) in 64-70% yields (Scheme 1). In the ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of **5a** the newly formed oxepino ring protons appeared at δ 5.96–5.85 (m, 1H), 5.39–5.31 (m, 1H), 4.58–4.54 (m, 2H) and 4.49 (ddd, *J* 5.6,3.5,1.9 Hz, 2H), and ^{13}C-NMR ($CDCl_3$, 101 MHz) signals resonated at δ 131.48 (=CH), 129.01 (=CH), 71.61 (-OCH_2) and 23.60 (-CH_2).



Scheme 1. Synthesis of oxa-carbocyclic annulated flavones **5(a-e)**. Reagents and conditions: i) allyl bromide, K_2CO_3, acetone, reflux, 3 h, 80-85% ; ii) *N,N*-diethylaniline, reflux, 4 h, 60%; iii) allyl bromide, but-3-en-1-yl bromide, pent-4-en-1-yl bromide, K_2CO_3, acetone, reflux, 4-6 h, 65-70%; iv) Grubbs' 2nd gen catalyst, CH_2Cl_2, reflux, 4-8 h, 63-70%.

Vinyl oxepino annulated flavones can be made effectively using ring closing enyne metathesis (RCEM). Thus, by alkylating 5-allyl-6-hydroxy-2-phenyl-4*H*-chromen-4-ones (**3a-b**) with propargyl bromide and K_2CO_3/acetone medium at reflux temperature, 5-allyl-2-phenyl-6-(prop-2-yn-1-yloxy)-4*H*-chromen-4-ones (**6a-b**) were produced. Enyne metathesis was employed to cyclize 5-allyl-2-phenyl-6-(prop-2-yn-1-yloxy)-4*H*-chromenones (**6a-b**) in degassed dichloromethane under a nitrogen atmosphere to yield 3-phenyl-9-vinyl-8,11-dihydro-1*H*-oxepino[3,2-*f*]chromen-1-ones (**7a-b**) in 52-55% yield (**Scheme 2**). In the ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of **7a**, the newly constructed vinyl oxepino ring protons appeared at δ 6.25 – 6.01 (m, 1H), 5.28-5.20 (m, 1H), 5.04 (dd, *J* 14.2, 1.7 Hz, 1H), 4.97 (d, *J* 3.4, Hz, 1H), 4.78 (d, *J* 2.4 Hz, 2H), 4.40 – 4.13 (m, 2H), ^{13}C-

NMR ($CDCl_3$, 101 MHz) signals resonated at δ 155.72 (=C), 133.35 (=CH), 120.42 (=CH), 112.72 (=CH_2), 75.54 (-OCH_2), 29.66 (-CH_2).

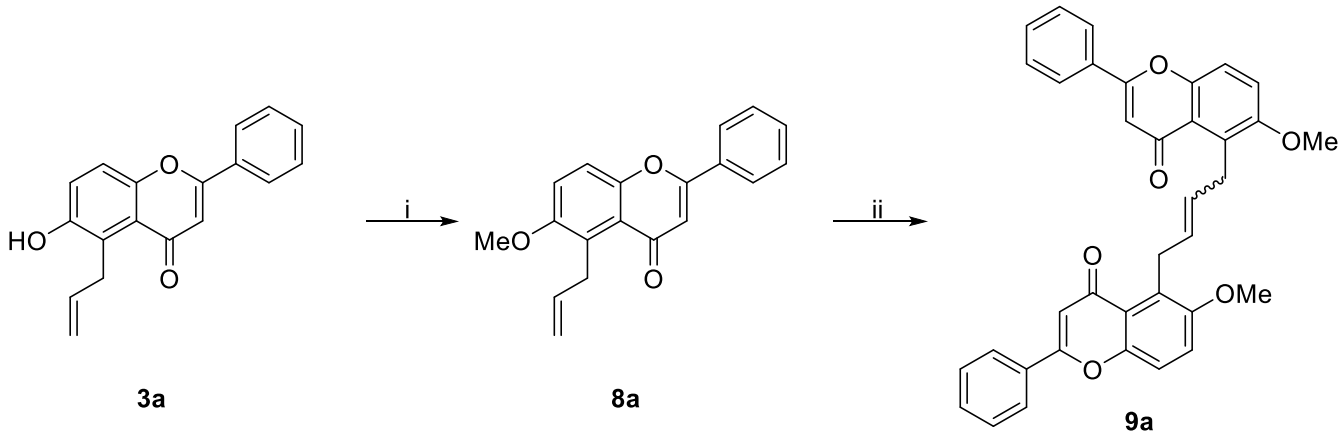


3a-b **6a-b** **7a-b**

3a; 6a; 7a; R = H
3b; 6b; 7b; R = Cl

Scheme 2. Synthesis of Vinyl oxepino annulated flavones **7(a-b)**. Reagents and conditions: i) propargyl bromide, K_2CO_3, acetone, reflux, 4 h, 65-66%; ii) Grubbs' 2nd gen catalyst, CH_2Cl_2, reflux, 8 h, 52-55%.

We focused on preparing cross metathesis products of bis flavones to broaden the scope of olefin metathesis method. 5-Hydroxy 6-allyl flavone (**3a)** was converted into 5-allyl-6-methoxy-2-phenyl-4*H*-chromen-4-one (**8a**) by MeI in acetone/K_2CO_3 at room temperature. Using Grubbs' 2nd generation catalyst in DCM medium under N_2 atmosphere the desired (*E*)-5,5'-(But-2-ene-1,4-diyl)bis(6-methoxy-2-phenyl-4*H*-chromen-4-one) (**9a**) was produced from **8a** in 68% yield (**Scheme 3**). In the ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **9a** the methoxy group protons appeared at δ 3.95 (s, 6H) and the newly-formed olefin protons appeared at δ 5.55 (t, *J* 3.5 Hz,2H) and 4.54 (d, *J* 3.3 Hz, 4H), ^{13}C-NMR ($CDCl_3$, 101 MHz) signals resonated at δ 56.69 (-OMe), 130.87 (=CH) and 24.83 (-CH_2).

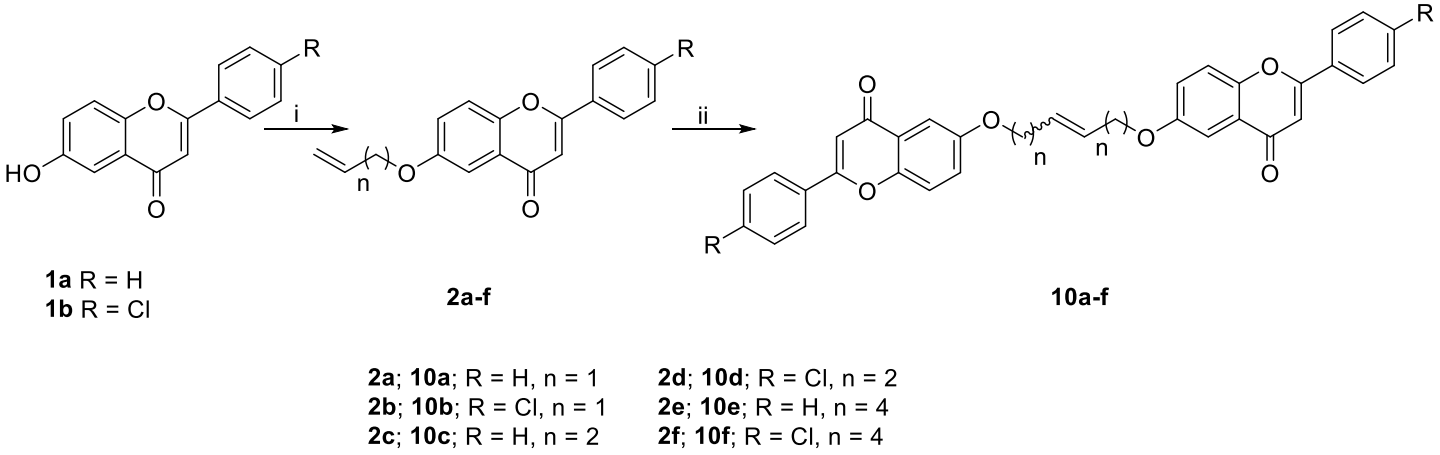


3a **8a** **9a**

Scheme 3. Synthesis of bis-flavones **9a**. Reagents and conditions: i) MeI, K_2CO_3, acetone, r.t., 3 h, 68%. ii) Grubbs' 2nd Catalyst, CH_2Cl_2, reflux, 6 h, 63%.

We subsequently concentrated on expanding cross metathesis to 6-(alkyloxy)-2-phenyl-4*H*-chromen-4-ones (**2a-f**). The alkenyl intermediates **2a-f** were obtained by reacting 6-hydroxy-2-phenyl-4*H*-chromen-4-ones

(**1a-b**) with alkenyl bromides in a K_2CO_3/acetone medium at reflux temperature. Grubbs' 2nd gen catalyst was utilized to create (*E*)-6,6'-(but-2-ene-1,4-diylbis(oxy))bis(2-phenyl-4*H*-chromen-4-one)s (**10a-f**) from **2a-f** in DCM medium under a. N_2 atmosphere in 53-64% yields (**Scheme-4**). In the ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **10a,** newly formed olefin protons appeared at δ 6.18 (dd, *J* 10.1, 4.9 Hz 2H) and 4.71-4.60 (m, 4H), ^{13}C-NMR ($CDCl_3$, 101 MHz) signals appeared at δ 131.87 (=CH) and 69.37 (-OCH_2).



Scheme 4. Synthesis of olefin tethered bis-flavones **10a-f**. Reagents and conditions : i) alkyl bromides, K_2CO_3, acetone, reflux, 4-6 h, 78-85%; ii) Grubbs' 2nd gen catalyst, CH_2Cl_2, reflux, 4-8 h, 53-64%.

Conclusions

We have developed a simple and efficient route for the synthesis of novel oxa-carbocyclic annulated flavones and bis-flavones by combined Claisen rearrangement and ring closing/cross metathesis using Grubbs' 2nd generation catalyst. This synthetic strategy provides an access to develop diverse bioactive new tricyclic flavone heterocyclics and bis flavones having a medium size ring system.

Experimental Section

General. Experimental apparatus and reagents all commercially available starting materials and solvents were reagent grade, and used without further purification. Preparative column chromatography was performed using silica gel 60-120 mesh. Analytical TLC was carried out employing silica gel 60 F254 plates (Merck). Spots were detected by their absorption under UV light. NMR spectra were recorded on a Bruker-400 (^{1}H NMR 400 MHz; ^{13}C, 101 MHz) spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with TMS as an internal reference. Chemical shifts were expressed in ppm, and *J* values are given in Hz. Molecular weights were determined with ESI mass spectra. Melting points (mp) were determined in open capillary tubes on a Buchi 530 melting point apparatus and are uncorrected. IR spectra were recorded on Shimadzu-8400 FT-IR spectrophotometer.

General procedure for the synthesis of 6-(Allyloxy)-2-phenyl-4*H*-chromen-4-ones (2a-b).
To a solution of 6-hydroxy-2-phenyl-4*H*-chromen-4-one (**1a-b)** (1 mmol) and K_2CO_3 (3 mmol) in dry acetone was added allyl bromide (1.5 mmol) under reflux at 70 ^{o}C for 4 h. Progress of the reaction was monitored by

TLC. After completion of the reaction, the acetone was evaporated the reaction mixture poured into cold water and the precipitate formed was filtered off to give the crude products **2a-b** which were purified by column chromatography on silica gel EtOAc/hexane (30:70).

6-(Allyloxy)-2-phenyl-4*H*-chromen-4-one (2a). Colourless solid; Yield 85%; mp: 134-136 °C. IR (KBr, ν_{max}, cm^{-1}): 1732 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* 8.0, 1.5 Hz, 1H), 8.04 (d, *J* 8.3 Hz, 2H, 2H), 7.67 (ddd, *J* 8.6, 7.1, 1.7 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.40 (ddd, *J* 8.0, 7.1, 1.0 Hz, 1H), 7.32 (d, *J* 8.1 Hz, 2H), 6.66 (s, 1H), 5.96 (m, 1H), 5.36 – 5.26 (m, 1H), 5.20 – 5.12 (m, 1H), 4.63 (dt, *J* 6.1, 1.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 178.28, 163.17, 155.93, 151.11, 132.59, 131.87, 131.52, 129.04, 126.25, 124.54, 124.18, 119.57, 106.85, 105.95, 69.37. MS (ESI): *m/z* 279 $[M+H]^+$.

6-(Allyloxy)-2-(4-chlorophenyl)-4*H*-chromen-4-one (2b). Off white solid; Yield 80%; mp: 133-135 °C. IR (KBr, ν_{max}, cm^{-1}): 1730 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.58 (d, *J* 3.1 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.32 (dd, *J* 9.1, 3.1 Hz, 1H), 6.77 (s, 1H), 6.09 (ddt, *J* 17.2, 10.6, 5.3 Hz, 1H), 5.50 – 5.43 (m, 1H), 5.33 (dd, *J* 10.5, 1.3 Hz, 1H), 4.64 (dt, *J* 5.2, 1.3 Hz, 2H, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz,) δ 178.08, 161.97, 156.03, 151.00, 137.77, 132.53, 130.33, 129.37, 127.49, 124.50, 124.31, 119.52, 106.93, 105.97, 69.39. MS (ESI): *m/z* 313 $[M+H]^+$.

General procedure for the synthesis of 5-Allyl-6-hydroxy-2-phenyl-4*H*-chromen-4-ones (3a-b).

6-(Allyloxy)-2-phenyl-4*H*-chromen-4-one (**2a)** (1 mmol) was dissolved in *N,N*-diethyl aniline (30 mL) and the reaction mixture was stirred at 210 °C for 4 h, progress of the reaction was monitored by TLC. After completion of the reaction the mixture was cooled to rt then were added 50 mL of pet ether. The resulting precipitate was filtered off and purified by column chromatography on silica gel EtOAc/n-hexane (40:60) to afford 5-allyl-6-hydroxy-2-phenyl-4*H*-chromen-4-one (**3a)** as colourless solid.

5-Allyl-6-hydroxy-2-phenyl-4*H*-chromen-4-one (3a). Colourless solid; Yield 60%: mp: 130-133 °C. IR (KBr, ν_{max}, cm^{-1}): 1718 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.54 – 7.50 (m, 3H), 7.47 – 7.42 (m, 2H), 6.70 (s, 1H), 6.26 – 5.98 (m, 1H), 5.04 (dq, *J* 17.2, 1.7 Hz, 1H), 4.97 (ddd, *J* 10.1, 3.4, 1.4 Hz, 1H), 4.25 (dt, *J* 6.1, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz,) δ 178.49, 163.40, 163.21, 151.32, 132.43, 132.04, 131.52, 129.21, 126.49, 126.25, 124.54, 124.18, 119.57, 105.95, 28.65. MS (ESI): *m/z* 279 $[M+H]^+$.

5-Allyl-2-(4-chlorophenyl)-6-hydroxy-4*H*-chromen-4-one (3b). Off white solid; Yield 60%: mp: 131-134 °C. IR (KBr, ν_{max}, cm^{-1}): 1722 (C=O). ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.83 (s, 1H), 8.07 (d, *J* 8.2 Hz, 2H), 7.63 (d, *J* 8.2 Hz, 2H), 7.51 (d, *J* 8.9 Hz, 1H), 7.32 (d, *J* 8.9 Hz, 1H), 6.87 (s, 1H), 5.95 (dd, *J* 16.7, 10.1 Hz, 1H), 4.91 (dd, *J* 13.5, 6.2 Hz, 2H), 4.07 (d, *J* 5.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 178.49, 163.40, 163.21, 151.32, 132.43, 132.04, 131.52, 129.21, 126.49, 126.25, 124.54, 124.18, 119.57, 105.95, 28.65. MS (ESI): *m/z* 313 $[M+H]^+$.

General procedure for the synthesis of 5-Allyl-6-(allyloxy)-2-phenyl-4*H*-chromen-4-ones: (4a-e).

To the solution of 5-allyl-6-hydroxy-2-phenyl-4*H*-chromen-4-one **(4a)** (1 mmol) and K_2CO_3 (3 mmol) in dry acetone was added allyl bromide (1.5 mmol) under the reflux at 70 °C for 4-6 h, progress of the reaction was monitored by TLC. After completion of the reaction, the acetone was evaporated the mixture poured into cold water giving a precipitate which was filtered off, and purified by column chromatography on silica gel EtOAc/n-hexane (30:70) to afford **4a**.

5-Allyl-6-(allyloxy)-2-phenyl-4*H*-chromen-4-one (4a). Colourless solid; Yield 70%: mp: 124-126 °C. IR (KBr, ν_{max}, cm^{-1}): 1730 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dt, *J* 8.3, 3.5 Hz, 2H), 7.45 – 7.40 (m, 3H, H-8), 7.34 (d, *J* 9.1 Hz, 1H), 7.20 – 7.16 (m, 1H), 6.61 (s, 1H), 6.11 – 5.93 (m, 2H), 5.37 (dd, *J* 17.3, 1.5 Hz, 1H), 5.23 (dd, *J* 10.6, 1.4 Hz, 1H), 4.98 (dd, *J* 17.2, 1.9 Hz, 1H), 4.89 (dd, *J* 10.1, 1.9 Hz, 1H), 4.53 (dd, *J* 3.5, 1.5 Hz, 2H), 4.19 (d, *J* 6.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.74, 164.51, 161.74, 155.52, 145.79, 136.09, 133.30, 131.57, 131.37, 129.06, 128.14, 127.47, 126.19, 122.46, 117.45, 108.65, 61.41, 30.85. MS (ESI): *m/z* 319 $[M+H]^+$.

5-Allyl-6-(allyloxy)-2-(4-chlorophenyl)-4*H*-chromen-4-one (4b). Off white solid; Yield 65%: mp: 143-146 °C. IR (KBr, ν_{max}, cm^{-1}): 1737 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* 8.0 Hz, 2H), 7.46 (d, *J* 8.0 Hz, 2H), 7.39 (d, *J* 8.9 Hz, 1H), 7.25 (d, *J* 9.4 Hz, 1H), 6.63 (s, 1H), 6.16 – 5.99 (m, 2H), 5.45 (d, *J* 17.2 Hz, 1H), 5.30 (d, *J* 10.3 Hz, 1H), 5.05 (d, *J* 17.1 Hz, 1H), 4.96 (d, *J* 9.7 Hz, 1H), 4.60 (dd, *J* 3.7, 1.4 Hz, 2H), 4.24 (d, *J* 5.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.14, 160.14, 153.43, 152.09, 137.52, 133.05, 130.14, 129.63, 129.27, 127.34, 122.33, 118.88, 117.50, 116.76, 114.62, 108.21, 70.15, 29.94. MS (ESI): *m/z* 353 $[M+H]^+$.

5-Allyl-6-(but-3-en-1-yloxy)-2-phenyl-4*H*-chromen-4-one (4c). Colourless solid; Yield 68%: mp: 145-147 °C. IR (KBr, ν_{max}, cm^{-1}): 1733 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.54 – 7.48 (m, 3H), 7.42 (d, *J* 9.1 Hz, 1H), 7.28 – 7.23 (m, 1H), 6.68 (s, 1H), 6.09 (ddt, *J* 16.4, 10.1, 6.3 Hz, 1H), 5.95 (ddt, *J* 17.0, 10.2, 6.8 Hz, 1H), 5.20 (dd, *J* 17.2, 1.5 Hz, 1H), 5.14 (dd, *J* 10.2, 1.0 Hz, 1H), 5.07 (dd, *J* 17.2, 1.8 Hz, 1H), 4.96 (dd, *J* 10.0, 1.7 Hz, 1H), 4.23 (d, *J* 6.3 Hz, 2H), 4.07 (t, *J* 6.5 Hz, 2H), 2.60 (q, *J* 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.35, 161.69, 155.71, 153.93, 139.49, 134.79, 131.52, 129.01, 128.66, 127.62, 126.15, 121.54, 116.97, 115.87, 108.19, 74.67, 30.18, 26.69. MS (ESI): *m/z* 333 $[M+H]^+$.

5-Allyl-6-(but-3-en-1-yloxy)-2-(4-chlorophenyl)-4*H*-chromen-4-one (4d). Off white solid; Yield 65%: mp: 142-144 °C. IR (KBr, ν_{max}, cm^{-1}): 1728 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.78 (m, 2H), 7.54 – 7.45 (m, 2H), 7.42 (d, *J* 9.1 Hz, 1H), 7.26 (d, *J* 2.8 Hz, 1H), 6.65 (s, 1H), 6.08 (ddt, *J* 16.4, 10.0, 6.3 Hz, 1H), 5.95 (ddt, *J* 17.0, 10.2, 6.8 Hz, 1H), 5.21 (ddd, *J* 17.2, 3.2, 1.5 Hz, 1H), 5.14 (dd, *J* 10.2, 1.6 Hz, 1H), 5.05 (ddd, *J* 17.1, 3.5, 1.5 Hz, 1H), 4.96 (dd, *J* 10.0, 2.1 Hz, 1H), 4.23 (t, *J* 8.4 Hz, 2H), 4.08 (t, *J* 6.5 Hz, 2H), 2.61 (q, *J* 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.43, 161.31, 153.79, 152.02, 137.73, 137.41, 131.74, 131.29, 129.11, 128.96, 126.10, 122.35, 118.14, 116.79, 115.38, 114.49, 108.13, 68.53, 30.20, 28.64. MS (ESI): *m/z* 367 $[M+H]^+$.

5-Allyl-6-(pent-4-en-1-yloxy)-2-phenyl-4H-chromen-4-one (4e). Colourless solid; Yield 65%: mp: 139-142 °C. IR (KBr, ν_{max}, cm^{-1}): 1728 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.53 – 7.47 (m, 3H), 7.44 – 7.40 (m, 1H), 7.25 (t, *J* 3.4 Hz, 1H), 6.68 (s, 1H), 6.10 (ddt, *J* 16.3, 10.0, 6.2 Hz, 1H), 5.87 (ddt, *J* 16.9, 10.2, 6.7 Hz, 1H), 5.15 – 4.89 (m, 4H), 4.29 – 4.17 (m, 2H), 4.02 (t, *J* 6.3 Hz, 2H), 2.29 (ddd, *J* 7.7, 6.8, 1.1 Hz, 2H), 2.02 – 1.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.43, 161.31, 153.79, 152.02, 137.73, 137.41, 131.74, 131.29, 129.04, 126.10, 122.35, 118.14, 116.79, 115.38, 114.49, 108.13, 68.53, 30.20, 29.97, 28.64. MS (ESI): *m/z* 347 $[M+H]^+$.

General procedure for the synthesis of 3-Phenyl-8,11-dihydro-1*H*-oxepino [3,2-*f*]chromen-1-one (5a-e).

Grubbs' 2nd generation catalyst was added to a solution of 5-allyl-6-(allyloxy)-2-phenyl-4*H*-chromen-4-one (**4a**) (1 mmol) in dry degassed CH_2Cl_2 (20 mL) under N_2. The resulting solution was stirred at reflux for 4 h progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated in *vacuo* and the residue was loaded on a pad of silica gel elution with 40% EtOAc/n-hexane afforded 3-phenyl-8,11-dihydro-1*H*-oxepino [3, 2-*f*]chromen-1-one (**5a**) as colourless solid.

3-Phenyl-8,11-dihydro-1*H*-oxepino [3,2-*f*]chromen-1-one (5a). Colourless solid; yield 70%: mp: 140-144 °C. IR (KBr, ν_{max}, cm^{-1}): 1728 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.45 (dd, *J* 3.5, 1.2 Hz, 2H), 7.44 – 7.42 (m, 1H), 7.32-7.26 (m, 2H), 6.63 (s, 1H), 5.96 – 5.85 (m, 1H), 5.39 – 5.31 (m, 1H), 4.58 – 4.54 (m, 2H), 4.49 (ddd, J, 5.6, 3.5, 1.8 JHz. 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.90, 161.55, 155.94, 154.02, 138.67, 131.48, 129.01, 127.32, 126.98, 126.66, 126.16, 121.06, 117.27, 108.30, 71.61, 23.60. HRMS (ESI, *m/z*) Calcd for $C_{19}H_{14}O_3$ 291.1021 $[M+H]^+$, found 291.1015

3-(4-Chlorophenyl) -8,11-dihydro-1*H*-oxepino[3,2-*f*]chromen-1-one (5b). Off white solid; Yield 65%: mp. 140-143 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 1740 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.78 (m, 2H), 7.56 – 7.45 (m, 2H), 7.44 – 7.36 (m, 2H), 6.68 (s, 1H), 6.05 – 5.91 (m, 1H), 5.43 (d, *J* 11.3 Hz, 1H), 4.66 – 4.62 (m, 2H), 4.58 – 4.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.66, 160.34, 156.04, 153.87, 138.74, 137.72, 129.90, 129.32, 127.42, 127.01, 126.57, 120.92, 117.22, 108.33, 71.61, 30.20. HRMS (ESI, *m/z*) Calcd for $C_{19}H_{13}ClO_3$ 325.0631 $[M+H]^+$, found 325.0626

(*Z*)-3-Phenyl-9,12-dihydrooxocino [3,2-*f*]chromen-1(8*H*)-one (5c). Colourless solid; Yield 64%: mp: 144-148 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 1736 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.56 – 7.53 (m, 2H), 7.27 (d, *J* 5.9 Hz, 2H), 7.07 (d, *J* 9.1 Hz, 1H), 6.71 (s, 1H), 5.82 – 5.73 (m, 1H), 5.56 (dd, *J* 14.5, 7.2 Hz, 1H), 4.16 (d, *J* 6.2 Hz, 2H), 3.86 (d, *J* 6.3 Hz, 2H), 2.27 – 2.18 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.20, 160.14, 153.76, 151.97, 137.28, 134.68, 134.39, 130.16, 129.27, 128.79, 127.34, 122.28, 118.33, 117.34, 108.18, 74.66, 29.94, 29.72. MS (ESI): *m/z* 305 $[M+H]^+$.

(*Z*)-3-(4-Chlorophenyl)-9,12-dihydrooxocino[3,2-*f*]chromen-1(8*H*)-one (5d). Off white solid; Yield 68%: mp: 144-147 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 1736 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 2H), 7.46 (dd, *J* 13.6, 5.1 Hz, 4H), 6.61 (s, 1H), 6.00 – 5.85 (m, 1H), 5.68 (dd, 13.7, 7.2, 1 H), 4.16 (dd, *J* 18.5, 6.4 Hz, 2H), 4.07 – 4.04 (m, 2H), 2.58 (d, *J* 6.0 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 180.12, 160.48, 155.82, 153.76, 151.97, 129.51, 129.16, 128.79, 128.72, 128.71, 122.28, 118.33, 117.34, 114.61, 108.21, 68.76, 26.67, 22.72. HRMS (ESI, *m/z*) Calcd for $C_{20}H_{15}ClO_3$ 339.0788 $[M+H]^+$, found 339.0783

(*Z*)-3-Phenyl-8,9,10,13-tetrahydro-1*H*-oxonino[3,2-*f*]chromen-1-one (5e). Colorless solid; Yield 64%; mp: 142-145 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 1737 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.57 – 7.49 (m, 2H), 7.27 (d, *J* 5.9 Hz, 1H), 7.07 (d, *J* 9.1 Hz, 2H), 6.71 (s, 1H), 5.90 – 5.65 (m, 1H), 5.56 (dd, *J* 14.5, 7.2 Hz, 1H), 4.27 – 4.11 (m, 2H), 3.86 (t, *J* 6.3 Hz, 2H), 1.95 – 1.84 (m, 2H), 1.61-1.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.72, 161.20, 154.15, 153.95, 151.87, 131.79, 131.36, 130.03, 129.67, 129.36, 129.19, 128.79, 126.12, 118.29, 108.10, 68.00, 28.85, 28.63, 28.30. ESI-MS: *m/z* 319 $[M+H]^+$.

General procedure for the synthesis of 5-allyl-2-phenyl-6-(prop-2-yn-1-yloxy)-4*H*-chromen-4-one (6a-b).

To a solution of 5-allyl-6-hydroxy-2-phenyl-4*H*-chromen-4-one (**3a)** (1 mmol) in acetone was added anh. K_2CO_3 (3 mmol) and propargyl bromide (1.2 mmol) at rt. The reaction mixture was refluxed for 4 h, progress of the reaction was monitored by TLC. After completion of the reaction, acetone was evaporated and added to ice-cold water. The precipitate was filtered off and purified by column chromatography on silica gel eluted with EtOAc/n-hexane (30:70) to give 5-allyl-2-phenyl-6-(prop-2-yn-1-yloxy)-4*H*-chromen-4-one (**6a)**.

5-Allyl-2-phenyl-6-(prop-2-yn-1-yloxy)-4*H*-chromen-4-one (6a). Colourless solid; Yield 66%: mp: 135-137 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 1742 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.55 – 7.50 (m, 3H), 7.47 – 7.42 (m, 2H), 6.70 (s, 1H), 6.10 (ddt, *J* 16.2, 10.1, 6.1 Hz, 1H), 5.04 (dd, *J,* 14.2,1.7 Hz, 1H), 4.97 (d, *J* 3.4, Hz, 1H), 4.78 (d, *J* 2.4 Hz, 2H), 4.25 (dt, *J* 6.1, 1.4 Hz, 2H), 2.53 (t, *J* 2.4 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 180.18, 161.42, 152.85, 152.44, 137.18, 131.66, 131.37, 130.53, 126.13, 122.49, 119.69, 116.89, 114.64, 108.30, 78.47, 75.88, 57.53, 29.93. MS (ESI): *m/z* 317 $[M+H]^+$.

5-Allyl-2-(4-chlorophenyl)-6-(prop-2-yn-1-yloxy)-4*H*-chromen-4-one (6b). Off-white solid; Yield 65%: mp: 136-139 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 1740 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.51 – 7.46 (m, 2H), 7.44 (d, *J* 1.6 Hz, 2H), 6.66 (s, 1H), 6.23 – 5.99 (m, 1H), 5.07 – 5.00 (m, 1H), 4.97 (ddd, *J* 8.7, 3.3, 2.0 Hz, 1H), 4.78 (d, *J* 2.4 Hz, 2H), 4.23 (dt, *J* 6.0, 1.3 Hz, 2H), 2.51 (t, *J* 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.00, 160.27, 152.71, 152.52, 137.61, 137.08, 130.57, 130.11, 129.32, 127.38, 122.44, 119.71, 114.69, 108.36, 78.42, 75.94, 57.48, 29.91. MS (ESI): *m/z* 351 $[M+H]^+$.

General procedure for the synthesis of 3-Phenyl-9-vinyl-8,11-dihydro-1*H*-oxepino[3,2-*f*] chromen-1-one (7a-b).

Grubbs' 2nd generation catalyst (10 mol %) was added under nitrogen atmosphere to a solution of the substrate 5-allyl-2-phenyl-6-(prop-2-yn-1-yloxy)-4*H*-chromen-4-one (**6a)** (1 mmol) in dry degassed CH_2Cl_2 (20 mL). The resulting solution was stirred at reflux for 6 h while the reaction progress was observed using TLC. After the reaction was complete, the solvent was evaporated in *vacuo*, and the residue was put onto a pad of silica gel eluted with 40% EtOAc/n-hexane to produce 3-Phenyl-9-vinyl-8,11-dihydro-1*H*-oxepino[3,2-*f*] chrome-1-one (**7a**).

3-Phenyl-9-vinyl-8,11-dihydro-1*H*-oxepino [3,2-*f*]chromen-1-one (7a). Colourless solid; Yield 55%: mp: 103-106 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 1739 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.55 – 7.49 (m, 3H), 7.47 – 7.41 (m, 2H), 6.70 (s, 1H), 6.25 – 6.01 (m, 1H), 5.28-5.20 (m, 1H), 5.04 (dd, *J* 17.2, 1.7 Hz, 1H), 4.97 (ddd, *J* 10.1, 3.4, 1.4 Hz, 1H), 4.78 (d, *J* 2.4 Hz, 2H), 4.40 – 4.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.83, 157.17, 156.98, 156.57, 155.72, 133.35, 132.83, 131.88, 131.35, 125.84, 124.61, 124.41, 120.42, 118.16, 117.40, 112.72, 108.36, 75.54, 29.66. HRMS (ESI, *m/z*) Calcd for $C_{21}H_{17}O_3$ 317.1177 $[M+H]^+$, found 317.1172

3-(4-Chlorophenyl)-9-vinyl-8,11-dihydro-1*H*-oxepino[3,2-*f*]chromen-1-one (7b). Off white solid; Yield 52%; mp: 102-104 °C.: FT-IR (KBr, ν_{max}, cm^{-1}): 1735 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* 8.6 Hz, 2H), 7.49 (d, *J* 8.6 Hz, 2H), 7.43 (d, *J* 6.0 Hz, 2H), 6.68 (s, 1H), 6.21 (dd, *J* 18.0, 11.3 Hz, 1H), 6.07 (dd, *J* 11.7, 5.4 Hz, 1H), 5.07 – 4.90 (m, 1H), 4.88 (d, *J* 2.9 Hz, 1H), 4.82-4.58 (m, 2H), 4.61 (d, *J* 6.2 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 175.05, 156.33, 155.24, 141.17, 139.64, 133.32, 133.22, 129.73, 129.18, 128.59, 128.11, 127.66, 125.80, 124.60, 124.14, 107.85, 72.04, 21.56. HRMS (ESI, *m/z*) Calcd for $C_{21}H_{16}ClO_3$ 351.0788 $[M+H]^+$, found 351.0780.

General procedure for the synthesis of 5-Allyl-6-methoxy-2-phenyl-4*H*-chromen-4-one (8a).

To the solution of 5-allyl-6-hydroxy-2-phenyl-4*H*-chromen-4-one (**3a**) (1 mmol) in acetone was added anh. K_2CO_3 (3 mmol) and MeI (1.8 mmol). The reaction mixture was stirred at rt for 8 h ,progress of the reaction was monitored by TLC. After completion of the reaction, acetone was evaporated and ice-cold water was added the precipitate was filtered off and purified by column chromatography, eluted with EtOAc/n-hexane (30:70) to give **8a**.

5-Allyl-6-methoxy-2-phenyl-4*H*-chromen-4-one (8a). Colourless solid; Yield 68%; mp: 153-157 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 1737 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.86 (m, 2H, H-2', 6'), 7.51 (dd, *J* 5.2, 1.9 Hz, 2H, H-3', 5'), 7.46 (d, *J* 9.1 Hz, 1H, H-8), 7.30 (s, 1H, H-4'), 7.27 (d, *J* 7.0 Hz, 1H, H-7), 6.70 (s, *J* 7.0 Hz, 1H, H-3), 6.10 (ddt, *J* 16.2, 10.1, 6.1 Hz, 1H, H-2''), 5.02 (ddd, *J* 17.2, 3.6, 1.7 Hz, 1H, H-3''), 4.96 (ddd, *J* 10.1, 3.4, 1.4 Hz, 1H, H-3''), 4.23 (dt, *J* 6.1, 1.4 Hz, 2H, H-1''), 3.90 (s, 3H, 6-OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.41 (C-4), 161.37 (C-2), 154.42 (C-6), 152.12 (C-8a), 137.35 (C-5, C-1'), 131.77 (C-3', 5'), 131.29 (C-2', 6'), 129.04 (C-4') 126.12 (C-2''), 122.36 (C-4a), 117.31 (C-8), 116.84 (C-7), 114.37 (C-3''), 108.17 (C-3), 56.74 (C-6, -OCH_3), 29.75 (C-1''). ESI-MS: *m/z* 293 $[M+H]^+$.

General procedure for the synthesis of (*E*)-5,5'-(But-2-ene-1,4-diyl)bis(6-methoxy-2-phenyl-4*H*-chromen-4-one) (9a).

Grubbs' 2nd generation catalyst (10 mol %) was added to a solution of the substrate 5-allyl-6-methoxy-2-phenyl-4*H*-chromen-4-one (**8a)** (1 mmol) in dry degassed CH_2Cl_2 and the mixture was refluxed for 6 h, while the reaction was observed by using TLC. After the reaction was complete, the solvent was evaporated in *vacuo* and the residue was put onto a pad of silica gel eluted with 40% EtOAc-hexane to produce (*E*)-5,5'-(but-2-ene-1,4-diyl)bis(6-methoxy-2-phenyl-4*H*-chromen-4-one) (**9a**).

(*E*)-5,5'-(But-2-ene-1,4-diyl)bis(6-methoxy-2-phenyl-4*H*-chromen-4-one) (9a). Colourless solid; Yield 63%: mp: 195-198 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 1739 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* 8.0 Hz, 4H), 7.51-7.42 (m, 6H), 7.44 (d, *J* 9.0 Hz, 2H), 7.33 – 7.25 (m, 3H), 6.68 (s, 2H), δ 5.55 (t, *J* 3.5 Hz, 2H) and 4.54 (d, *J*, 3.3 Hz, 4H) 3.95 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.65, 161.20, 154.58, 152.11, 131.89, 131.19, 130.87, 128.93, 128.27, 126.12, 122.45, 117.25, 116.44, 108.17, 56.69, 24.83. HRMS (ESI, *m/z*) Calcd for $C_{36}H_{29}O_6$ 557.1964 $[M+H]^+$, found 557.1960.

6-(But-3-en-1-yloxy)-2-phenyl-4*H*-chromen-4-one (2c). Colourless solid; Yield 80%; mp: 143-146 °C. IR (KBr, ν_{max}, cm^{-1}): 1736 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.81 (m, 2H), 7.59 (d, *J* 3.1 Hz, 1H), 7.55 – 7.51 (m, 3H), 7.50 (s, 1H), 7.30 (dd, *J* 9.1, 3.1 Hz, 1H), 6.82 (s, 1H), 5.92 (ddt, *J* 17.0, 10.3, 6.7 Hz, 1H), 5.29 – 5.04 (m, 2H), 4.13 (t, *J* 6.7 Hz, 2H), 2.59 (dtd, *J* 6.7, 5.4, 1.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.35, 161.69, 155.71,

153.93, 139.49, 134.79, 131.61, 131.43, 129.01, 128.66, 127.62, 126.15, 121.54, 116.97, 108.19, 74.67, 30.18. MS (ESI): *m/z* 293 $[M+H]^+$.

6-(But-3-en-1-yloxy)-2-(4-chlorophenyl)-4*H*-chromen-4-one (2d). Off white solid; Yield 78%: mp: 142-144 °C. IR (KBr, ν_{max}, cm^{-1}): 1736 (C=O). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 3.0 Hz, 1H), 7.49 (dd, *J* = 8.9, 1.9 Hz, 3H), 7.30 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.77 (s, 1H), 5.92 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.31 – 5.05 (m, 2H), 4.12 (t, *J* = 6.7 Hz, 2H), 2.59 (q, *J* = 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.14, 161.95, 156.42, 150.94, 137.76, 134.13, 130.35, 129.37, 127.49, 124.50, 124.28, 119.46, 117.31, 106.92, 105.62, 67.89, 33.46.MS (ESI): *m/z* 327 $[M+H]^+$.

6-(Hex-5-en-1-yloxy)-2-phenyl-4*H*-chromen-4-one (2e). Colourless solid; Yield 85%: mp: 136-139 °C. IR (KBr, ν_{max}, cm^{-1}): 1740 (C=O). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.57 (d, *J* 3.0 Hz, 1H), 7.54 – 7.50 (m, 3H), 7.48 (s, 1H), 7.30 – 7.26 (m, 1H), 6.81 (s, 1H), 5.84 (ddt, *J* 16.9, 10.2, 6.7 Hz, 1H), 5.17 – 4.91 (m, 2H), 4.07 (t, *J* 6.5 Hz, 2H), 2.15 (dd, *J* 14.3, 7.2 Hz, 2H), 1.91 – 1.78 (m, 2H), 1.59 (dq, *J* 15.0, 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.37, 163.12, 156.51, 150.98, 138.44, 131.92, 131.48, 129.04, 126.24, 124.55, 124.12, 119.46, 114.88, 106.83, 105.45, 68.52, 33.41, 28.56. MS (ESI): *m/z* 321 $[M+H]^+$.

2-(4-Chlorophenyl)-6-(hex-5-en-1-yloxy)-4*H*-chromen-4-one (2f). Off White solid; Yield 78%: mp: 140-143 °C. IR (KBr, ν_{max}, cm^{-1}): 1741 (C=O). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* 8.6 Hz, 2H), 7.57 (d, *J* 3.0 Hz, 1H), 7.49 (dd, *J* 8.9, 2.9 Hz, 3H), 7.34 (d, *J* 7.2 Hz 1H), 6.78 (s, 1H), 6.42 (d, *J* 15.8 Hz, 1H), 6.24 (dt, *J* 15.8, 6.9 Hz, 2H), 4.09 (t, *J* 6.5 Hz, 2H), 2.31 (q, *J* 6.8 Hz, 2H), 1.94 – 1.84 (m, 2H), 1.68 (dt, *J* 14.8, 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.40, 163.12, 156.54, 150.97, 131.93, 131.48, 130.38, 129.03, 124.54, 124.16, 119.45, 106.82, 105.46, 68.32, 32.29, 28.57, 26.07. MS (ESI): *m/z* 355 $[M+H]^+$

General procedure for the synthesis of (*E*)-6,6'-(But-2-ene-1,4-diylbis(oxy))bis(2-phenyl-4*H*-chromen-4-one) (10a-f).

Grubbs' 2nd generation catalyst (10 mol %) was added to a solution of 6-(allyloxy)-2-phenyl-4*H*-chromen-4-one (**2a**) (1 mmol) in dry degassed CH_2Cl_2 (10 mL). The resulting solution was stirred for 6 h while the progress of the reaction was monitored by TLC. Once the reaction was complete, the solvent was evaporated in *vacuo* and the residue was loaded on a pad of silica gel and eluted with 60% AcOEt/hexane to afford (*E*)-6,6'-(But-2-ene-1,4-diylbis(oxy))bis(2-phenyl-4*H*-chromen-4-one) (**10a**).

(*E*)-6,6'-(But-2-ene-1,4-diylbis(oxy))bis(2-phenyl-4*H*-chromen-4-one) (10a). Colorless solid; Yield 64%; mp.: 196-199 °C. IR (KBr, ν_{max}, cm^{-1}): 1743 (C=O); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92-7.79 (m, 3H), 7.57-7.42 (m, 11H), 7.35 (m, 3H), 6.82 (s, 2H), 6.18 (dd, *J* 10.1, 4.9 Hz 2H), 4.71-4.60 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.28, 163.17, 155.93, 151.11, 132.59, 131.87, 131.52, 129.04, 126.25, 124.18, 119.57, 118.19, 106.85, 105.95, 69.37. HRMS (ESI, *m/z*) Calcd for $C_{34}H_{24}O_6$ 529.1651 $[M+H]^+$, found 529.1645.

(*E*)-6,6'-(But-2-ene-1,4-diylbis(oxy))bis(2-(4-chlorophenyl)-4*H*-chromen-4-one) (10b). Off white solid; Yield 60%; mp: 200-203 °C. IR (KBr, ν_{max}, cm^{-1}): 1741 (C=O). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.67 (m, 4H), 7.61 (d, *J* 2.6 Hz, 2H), 7.57 (d, *J* 2.7 Hz, 4H), 7.50 (d, *J* 2.6 Hz 2H), 7.35 (d, *J* 2.8 Hz, 2H), 6.77 (s, 2H), 6.16-5.87 (m, 2H), 4.71-4.50 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.14, 161.78, 156.32, 150.94, 137.65, 134.13, 130.09, 129.37, 129.00, 127.37, 124.00, 119.41, 117.26, 106.92, 105.66, 67.89. HRMS (ESI, *m/z*) Calcd for $C_{34}H_{23}Cl_2O_6$ 597.0871 $[M+H]^+$, found 597.0862.

(*E*)-6,6'-(Hex-3-ene-1,6-diylbis(oxy))bis(2-phenyl-4*H*-chromen-4-one) (10c). Colourless solid; Yield 56%: mp; 197-200 °C. IR (KBr, ν_{max}, cm^{-1}): 1739 (C=O). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* 5.6, 2.1 Hz, 4H), 7.59 (d, *J* 2.9 Hz, 2H), 7.52 (d, *J* 4.3 Hz, 8H), 7.30 (dd, *J* 9.1, 1.9 Hz, 2H), 6.82 (s, 2H), 5.69 (dd, *J* 8.9, 4.1 Hz, 2H), 4.12 (t, *J* 6.5 Hz, 4H), 2.69 – 2.55 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.85, 162.57, 151.55, 151.35, 131.49, 129.03, 129.87, 128.52, 126.26, 124.19, 119.50, 106.84, 105.69, 68.89, 32.44. HRMS (ESI, *m/z*) Calcd for $C_{36}H_{29}O_6$ 557.1964 $[M+H]^+$, found 557.1959.

(*E*)-6,6'-(Hex-3-ene-1,6-diylbis(oxy))bis(2-(4-chlorophenyl)-4*H*-chromen-4-one) (10d). Off white solid; Yield 53%; mp: 202-205 °C. IR (KBr, ν_{max}, cm^{-1}): 1743 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 4H), 7.57 (d, *J* 2.9 Hz, 2H), 7.49 (d, *J* 8.2 Hz, 6H), 7.32 – 7.29 (m, 2H), 6.78 (s, 2H), 5.68 (t, *J* 4.7 Hz, 2H), 4.11 (t, *J* 6.6 Hz, 4H), 2.63 (dt, J 16.0, 5.7 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.40, 163.12, 156.54, 150.97, 131.93, 131.48, 130.38, 129.03, 126.25, 124.54, 124.16, 119.45, 106.82, 105.46, 68.60, 32.22. HRMS (ESI, *m/z*) Calcd for $C_{36}H_{27}Cl_2O_6$ 625.1184 $[M+H]^+$, found 625.1175.

(*E*)-6,6'-(Dec-5-ene-1,10-diylbis(oxy))bis(2-phenyl-4*H*-chromen-4-one) (10e). Colourless solid; Yield 62%: mp: 199-201 °C. IR (KBr, ν_{max}, cm^{-1}): 1738 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 4H), 7.57 (d, *J* 3.0 Hz, 2H), 7.53 – 7.50 (m, 6H), 7.49 – 7.47 (m, 2H), 7.30 (d, *J* 3.0 Hz, 2H), 6.81 (s, 2H), 5.47 (dd, *J* 8.3, 4.6 Hz, 2H), 4.08 – 4.05 (m, 4H), 2.10 (dd, *J* 11.5, 6.7 Hz, 4H), 1.85 – 1.81 (m, 4H), 1.59 – 1.54 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.40, 163.12, 156.54, 150.97, 131.93, 131.48, 130.38, 129.03, 126.25, 124.54, 124.16, 119.45, 106.82, 105.46, 68.60, 32.22, 28.57, 25.89. HRMS (ESI, *m/z*) Calcd for $C_{40}H_{37}O_6$ 613.2590 $[M+H]^+$, found 613.2581.

(*E*)-6,6'-(Dec-5-ene-1,10-diylbis(oxy))bis(2-(4-chlorophenyl)-4*H*-chromen-4-one) (10f). Off white solid; Yield 58%: mp: 207-210 °C. IR (KBr, ν_{max}, cm^{-1}): 1741 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 4H), 7.55 (d, *J* 3.1 Hz, 2H), 7.51 – 7.46 (m, 6H), 7.29 (d, *J* 2.7 Hz, 2H), 6.76 (s, 2H), 5.47 (t, *J* 3.6 Hz, 2H), 4.05 (t, *J* 6.5 Hz, 4H), 2.13 – 2.06 (m, 4H), 1.86 – 1.80 (m, 4H), 1.58 – 1.53 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.20, 161.91, 156.63, 150.84, 137.74, 130.39, 129.36, 127.48, 126.48, 124.48, 124.27, 119.40, 106.87, 105.46, 68.61, 32.21, 28.54, 25.86. HRMS (ESI, *m/z*) Calcd for $C_{40}H_{35}Cl_2O_6$ 681.1810 $[M+H]^+$, found 681.1802.

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Supplementary Material

Supplementary material (^{1}H NMR, ^{13}C NMR and HRMS spectrum of the compounds **1a-b, 2a-f, 3a-b, 4a-e, 5a-e, 6a-b, 7a-b, 8a, 9a, 10a-f**) associated with this article can be found in the website.

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