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Photo-rearrangements of some 3-allyloxy-2-phenyl-chromones: Synthesis of vinyl substituted benzopyronopyranes

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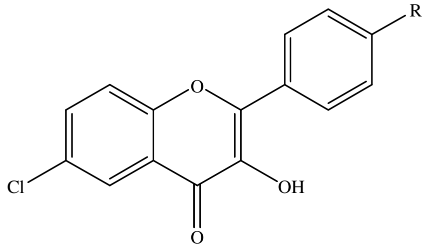
Abstract: Photochemical reactions of some 3-allyloxy-2-phenylchromones have been studied. Photoreactions of the compounds afforded substituted pyronopyrane derivatives through the 1,4-biradicals.

Keywords: Photo-cyclisation; H-abstraction; allyloxychromones; photoreactivity

1. Introduction

The photochemical H-abstraction in the carbonyl compounds has become an important area of research in organic chemistry to synthesize numerous exotic carbocyclic and heterocyclic products which are very difficult to obtain under the thermal routes.[1-11] 3-Alkoxy-2-aryl-chromones are the substrates that undergo easy intramolecular H-abstraction by the photo excited carbonyl chromophore to provide cyclised products.[12-17] In the recent past, we have reported the photo transformations of some 3-alkoxychromones[18-20] where photoreactions occur through intramolecular H-abstraction to furnish angular tetracyclic compounds. In the present study, we wish to report the results of our investigations upon the photolysis of chromones 4a-4f. The major interest behind this study was to synthesize vinyl substituted pyrane derivatives.



1 R=H
2 R=CH_3
3 R=OCH_3

Figure 1. 6-chloro-3-hydroxychromones

2. Results and Discussion

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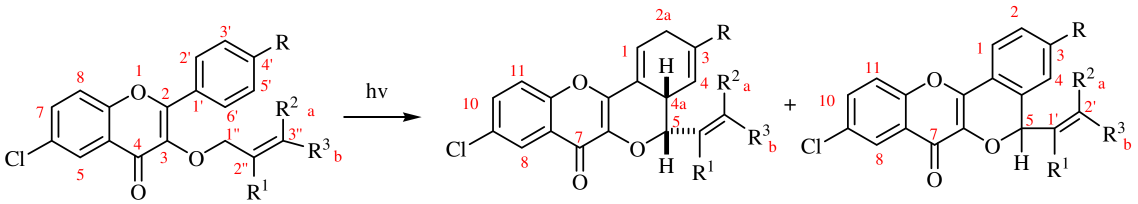
The chromones **4a-4f** used in this study were obtained from the O-alkylation of the 3-hydroxy compounds[21-23] **1-3** with an appropriate alkylating agent (like 3-chloro-2-methylpropene and 1-chloro-3-methyl-2-butene) in the presence of freshly ignited K_2CO_3/dry acetone and $Bu_4N^+I^-$ as phase transfer catalyst (PTC). The use of PTC in these syntheses not only expedited the reaction but also improved the yields of 3-alkoxychromones. The crude chromones were subjected to column chromatography (60-120 mesh) and recrystallization from MeOH afforded **4a-4f** as colorless solids. The structures of these compounds were ascertained from the rigorous analysis of their spectral characterization data (UV-Vis, IR, ^{1}H NMR) (see Experimental Section). The IR spectra of the chromones **4a-4f** exhibited an intense absorption in the region of 1635-1645 cm^{-1} that confirmed an enone moiety in their structure.

The deoxygenated benzene solutions of these chromones were irradiated with pyrex filtered light from the 125 W mercury arc lamp. The progress of these photoreactions was monitored by TLC. The column chromatographic work up of the photolysates yielded dihydrocyclised **5a-5f** and dehydrogenatedcyclised **6a-6f** products (**Scheme 1**). The structures of these pyranes could be assigned from their spectral data (see Experimental Section).



4a-4f **5a-5f** **6a-6f**

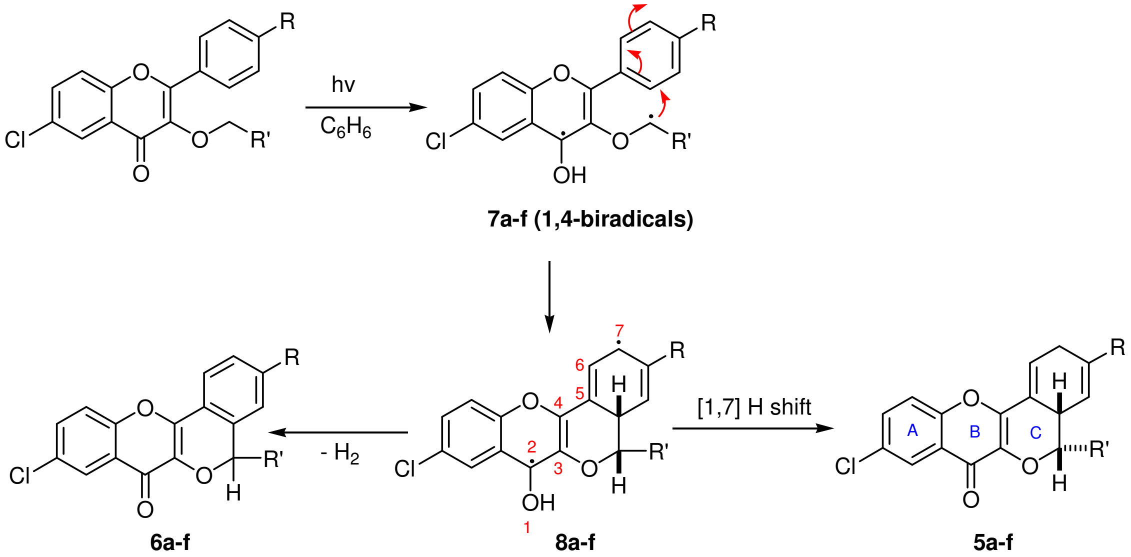
a R = H, $R_1 = CH_3$, $R_2 = R_3 = H$	**5a** (18%)	**6a** (32%)
b $R = CH_3$, $R_1 = CH_3$, $R_2 = R_3 = H$	**5b** (15%)	**6b** (33%)
c $R = OCH_3$, $R_1 = CH_3$, $R_2 = R_3 = H$	**5c** (14%)	**6c** (31%)
d R = H, $R_1 = H$, $R_2 = R_3 = CH_3$	**5d** (17%)	**6d** (35%)
e $R = CH_3$, $R_1 = H$, $R_2 = R_3 = CH_3$	**5e** (16%)	**6e** (34%)
f $R = OCH_3$, $R_1 = H$, $R_2 = R_3 = CH_3$	**5f** (18%)	**6f** (37%)

Scheme 1. Photolysis of chromones

Regarding the major feature of the ^{1}H NMR (400MHz) spectrum of **5a,** are the resonating signals due to H-1, 3, 4, 5, 4a & 2a which appeared at δ 6.85 (1H, br s), 5.81 (1H, dd), 5.71 (1H, d), 4.52 (1H, d), 3.60 (1H, d) and 2.81 (2H, m) respectively. In a double resonance experiment, irradiation of the doublet at 4.52 converted the doublet at 3.60 to singlet and conversely the irradiation of doublet at 3.60 converted the doublet at 4.52 to singlet. Other photoproducts **5b**-**5f** also represented similar kind of spectral pattern. The stereochemical features of the dihydrophenyl compounds **5a-5f** were deduced from the correlation between dihedral angle (ϕ) and coupling constant[24,25] (J). The hydrogen atoms at C-4a and C-5 were disposed *cis* to each other as having coupling constant $J_{4a,5}$=11Hz and dihedral angle $\phi \sim 0^\circ$. Here, pyran ring C is present in the pseudo chair form and R’ group at C-5 occupies pseudo equatorial disposition which is not without precedent because the heavier group always prefers equatorial disposition in cyclohexane.[24,25]

The mass spectra of the dihydro compounds **5a-5f** exhibit the molecular ion (m/z) at the same value as that of the starting compound. It shows that only reorganisation has taken place during the photoreaction. But aromatic compounds **6a-6f** produce molecular ion at a value two mass unit less than the starting chromones. Thus, these are formed by the loss of a hydrogen molecule from the starting chromone. The mass spectra of the photoproducts also exhibit the ion at m/z 154/156 which is obtained through the retro-Diels Alder cleavage of the pyrone moiety.[26-28]

Mechanistically, these phototransformations could be ascribed to the easy intramolecular H-abstraction from C_3-OCH_2- groups by the photoexcited carbonyl chromophores through the six membered cyclic transition state that produced 1,4-biradicals **7a-7f**. These intermediates underwent further cyclisation followed by [1,7]-H migration to yield dihydrocyclised products **5a-5f** while loss of H_2 molecule resulted in the oxidised compounds **6a-6f** (**Scheme 2**).



Scheme 2

3. Conclusion

This photochemical study represents a general and greener method for the synthesis of some novel vinyl substituted benzopyronopyrane derivatives without using any specific and toxic reagent.

4. Experimental Section

4.1. General

Melting points reported are uncorrected. IR spectra were recorded on a Perkin Elmer spectrometer using KBr pellets and UV-Vis spectra on Elico SL-164 spectrometer. ^{1}H NMR spectra were recorded on a 400 MHz Bruker spectrometer using TMS as internal standard. The mass spectra were recorded on Schimatzu QP-5000. TLC plates were coated with silica gel G suspended in MeOH-$CHCl_3$. Silica gel (100-200 mesh) was used for column chromatography.

4.2. Synthesis of 3-allyloxychromones 4a-4c

4.2.1. 6-Chloro-3-(2-methylprop-1-enyloxy)-2-phenyl-4*H*-chromen-4-one (4a)

A suspension of 6-chloro-3-hydroxy-2-phenyl-4*H*-chromen-4-one[21-23] **1** (2.7 g, 0.01 mol), 3-chloro-2-methylpropene (0.91 g, 0.01 mol), freshly ignited K_2CO_3 (1.0 g) and tetrabutylammonium iodide (1.0 g) in dry acetone (25 ml) was refluxed for 1h with stirring. A subsequent filtration of the reaction mixture followed by distillation of the solvent yielded a light yellow solid product that was percolated through a column of silica-gel (60-120 mesh) using petroleum ether-benzene (1:1) as eluent and that was further crystallized from EtOH to afford **4a.**

4a: Yield (2.6 g, 81%); off white powder; m.p. 88-89°C; IR (KBr): 1641 cm^{-1} (C=O); UV-Vis (THF): nm 341, 322, 240; ^{1}H NMR ($CDCl_3$): δ 8.22 (1H, d, J_m=2.6Hz, H-5), 8.09 (2H, m, H-2', 6'), 7.62 (1H, dd, $J_{m,o}$=2.5, 8.8Hz, H-7), 7.51 (3H, m, H-3', 4', 5'), 7.50 (1H, J_o=8.9Hz, H-8), 5.19 (2H, br s, H-α,β), 4.71 (2H, s, H-1"), 1.92 (3H, s, $C_{2''}$-CH_3); MS: *m/z* 326 (M^+, 100%), 271 (37.4), 243 (42.3), 215 (25.5), 172 (32.3), 154 (40.0), 110 (28.5). Anal. Calcd. for $C_{19}H_{15}O_3Cl$: C, 69.84; H, 4.63. Found: C, 69.88; H, 4.59%.

4.2. 2. 6-Chloro-3-(2-methylprop-1-enyloxy)-2-(4-methylphenyl)-4*H*-chromen-4-one (4b)

The chromone **4b** was synthesized by reacting **2**[21-23] (2.85 g, 0.01 mol) with 3-chloro-2-methylpropene (0.91 g, 0.01 mol) under similar conditions as described for **4a**.

4b: Yield (2.65 g, 78%); off white powder; m.p. 95-96°C; IR (KBr): 1635 cm^{-1} (C=O); UV-Vis (THF): nm 338, 317, 252; ^{1}H NMR ($CDCl_3$):δ 8.20 (1H, d, J_m=2.5Hz, H-5), 8.03 (2H, AA' part of AA'XX' system, quasi d, J=7.3 Hz, H-2', 6'), 7.61 (1H, dd, $J_{m,o}$=2.5, 8.9Hz, H-7), 7.45 (1H, d, J_o=8.8Hz, H-8), 7.30 (2H, XX' part of AA'XX' system, quasi d, J=7.3 Hz, H-3', 5'), 5.21 (1H, br s, H-α), 5.02 (1H, H-β), 4.71 (2H, s, H-1"), 1.86 (3H, s, $C_{2''}$-CH_3), 2.44 (3H, s, Cα-CH_3); MS: *m/z* 340 (M^+, 100%), 285 (23.2), 257 (32.7), 229 (35.4), 186 (87.0), 154 (64.6), 110 (48.2). Anal. Calcd. for $C_{20}H_{17}O_3Cl$: C, 70.49; H, 5.03. Found: C, 70.46; H, 4.99%.

4.2.3. 6-Chloro-3-(2-methylprop-1-enyloxy)-2-(4-methoxyphenyl)-4*H*-chromen-4-one(4c)

The chromone **4c** was synthesized by reacting **3**[21-23] (3.0 g, 0.01 mol) with 3-chloro-2-methylpropene (.91 g, 0.01 mol) under similar conditions as used for **4a**.

4c: Yield (2.8 g, 80%); off white powder; m.p. 84-85°C; IR (KBr): 1638 cm^{-1} (C=O); UV-Vis (THF): nm 342, 326, 255; ^{1}H NMR ($CDCl_3$): δ 8.19 (1H, d, J_m=2.4Hz, H-5), 8.12 (2H, AA' part of AA'XX' system, quasi d, *J*=8.9Hz, H-2', 6'), 7.60 (1H, dd, $J_{m,o}$=2.4, 9.0Hz, H-7), 7.53 (1H, d, J_o=9.0Hz, H-8), 7.05 (2H, XX' part of AA'XX' system, quasi d,7.5Hz, H-3', 5'), 5.23 (2H, br s, H-α,β), 4.78 (2H, s, H-1"), 1.95 (3H, s, $C_{2''}$-C***H***$_3$), 3.93 (3H, s, $C_{4'}$-OC***H***$_3$); MS: *m/z* 356 (M^+, 100%), 301 (27.0), 273 (36.7), 245 (28.2), 202 (22.5), 154 (51.0), 110 (53.3). Anal. Calcd. for $C_{20}H_{17}O_4Cl$: C, 67.32; H 4.80. Found: C, 67.35; H, 4.36%.

4.3. Photolysis of 3-allyloxychromones 4a-4c

4.3.1. Photolysis of 6-Chloro-3-(2-methylprop-1-enyloxy)-2-phenyl-4*H*-chromen-4-one (4a)

A deoxygenated solution of **4a** (200 mg, 0.61 mmol) in dry benzene (200 mL) was photolysed with light from a 125 W mercury arc lamp in a pyrex reactor under nitrogen atmosphere for 45 minutes. The progress of reaction was monitored by TLC. The solvent was distilled out under reduced pressure to obtain a dark gummy viscous mass, which was chromatographed over a column of silica gel (100-200 mesh) packed in petroleum ether-benzene (2:3). Elution of column with benzene-EtOAc (3:1) gave starting compound **4a** (20%, co-TLC & m.m.p.), and two new compounds **5a** and **6a**.

5a: Yield (36 mg; 18%); light yellow powder; m.p. 163-164°C; IR (KBr): 1654 cm^{-1} (C=O); UV-Vis (THF): nm 335, 285, 255; ^{1}H NMR ($CDCl_3$): δ 8.22 (1H, d, J_m=2.5Hz, H-8), 7.56 (1H, dd, $J_{m,o}$=2.5, 8.9Hz, H-10), 7.50 (1H, d, J_o=8.9Hz, H-11), 6.85 (1H, br s, H-1), 5.81 (1H, dd, $J_{3,2a}$=2.1Hz, $J_{3,4}$=10.1Hz, H-3), 5.71 (1H, d, $J_{4,3}$=10.0Hz, H-4), 5.10 (2H, d, J_{allyl}=1.4Hz, H-α,β), 4.52 (1H, d,

$J_{5,4a'}$=11.0Hz, H-5), 3.60 (1H, d, $J_{4a,5}$=11.0Hz, H-4a), 2.81 (2H, m, H-2a), 1.91 (3H, s, $C_{1'}$-CH_3); MS: *m/z* 326 (M^+, 80%), 271 (45.5), 243 (35.4), 172 (24.3), 154 (48.3), 126 (25.5), 110 (100). Anal. Calcd. for $C_{19}H_{15}O_3Cl$: C, 69.84; H, 4.63. Found: C, 69.88; H, 4.59%.

6a: Yield (65 mg; 32%); light yellow solid; m.p. 202-204°C; IR (KBr): 1642 cm^{-1} (C=O); UV-Vis (THF): nm 339, 291, 245; ^1H NMR ($CDCl_3$): δ 8.24 (1H, d, J_m=2.6Hz, H-8), 8.10 (1H, dd, $J_{m,o}$=2.5, 8.8Hz, H-1), 7.62 (1H, dd, $J_{m,o}$=2.4, 8.7Hz, H-10), 7.57 (1H, d, J_o=8.9Hz, H-11), 7.50 (3H, m, H-2, 3, 4), 5.07 (2H, d, J_{allyl}=1.2Hz, H-α,β),4.85 (1H, s, H-5), 1.88 (3H, s, $C_{1'}$-CH_3); MS: *m/z* 324 (M^+, 50%), 170 (100), 154 (31.1), 126 (57.3), 110 (41). Anal. Calcd. for $C_{19}H_{13}O_3Cl$ requires C, 70.27; H, 4.03. Found: C, 70.30; H, 4.00%.

4.3.2. Photolysis of 6-Chloro-3-(2”-methylprop-1”-enyloxy)-2-(4-methylphenyl)-4*H*-chromen-4-one *(*4b)

The benzene solution of **4b** (200 mg, 0.58 mmol) was photolysed under similar conditions as described for **4a**. The photolysate on chromatographic separation afforded two new compounds **5b** and **6b**.

5b: Yield (30 mg 15%); light yellow powder; m.p. 168-170°C; IR (KBr): 1656 cm^{-1} (C=O); UV-Vis (THF): nm 341, 290, 252; ^1H NMR ($CDCl_3$): δ 8.23 (1H, d, J_m=2.5Hz, H-8), 7.65 (1H, dd, $J_{m,o}$=2.5, 8.9Hz, H-10), 7.51 (1H, d, J_o=8.9Hz, H-11), 6.80 (1H, br s, H-1), 5.50 (1H, br s, H-4), 5.45 (1H, d, $J_{5,4a}$ =11.0Hz, H-5), 5.11 (2H, d, J_{allyl}=1.4Hz, H-α,β), 3.50 (1H, d, $J_{4a,5}$=11.2Hz, H-4a), 2.15 (3H, s, C_3-CH_3), 2.90 (2H, m, H-2a) 1.94 (3H, s, $C_{1'}$-CH_3); MS: *m/z* 340 (M^+, 75%), 285 (37.5), 257 (22.0), 229 (23.2), 186 (100), 154 (41.1), 126 (66.3), 110 (25.2). Anal. Calcd. for $C_{20}H_{17}O_3Cl$: C, 70.49; H, 5.03. Found: C, 70.46; H, 4.99%.

6b: Yield (65 mg 33%); light yellow powder; m.p. 208-210°C; IR (KBr): 1637 cm^{-1} (C=O); UV-Vis (THF): nm 338, 274, 245; ^1H NMR ($CDCl_3$) δ 8.18 (1H, d, J_m=2.4Hz, H-8), 7.76 (1H, d, J_o=8.0Hz, H-1), 7.60 (1H, dd, $J_{m,o}$=2.6,8.9Hz, H-10), 7.55 (1H, d, J_o=9.0Hz, H-11), 6.98 (2H, m, H-2,4), 5.20 (2H, d, $J_{allyl'}$=1.2Hz, H-α,β), 5.00 (1H, s, H-5), 2.25 (3H, s, C_3-CH_3), 1.89 (3H, s, $C_{1'}$-CH_3); MS: *m/z* 338 (M^+, 90%), 184 (54.0), 154 (34.6), 144 (19.3), 126 (29.7), 110 (100). Anal. Calcd. for $C_{20}H_{15}O_3Cl$: C, 70.90; H, 4.46. Found: C, 70.92; H, 4.43%.

4.3.3. Photolysis of 6-Chloro-3-(2-methylprop-1-enyloxy)-2-(4-methoxyphenyl)-4*H*-chromen-4-one (4c)

The benzene solution of **4c** (200 mg, 0.00056 mol) was photolysed under similar conditions as described for **4a**. The chromatographic work up of photolysate provided the two new compounds **5c** and **6c**.

5c: Yield (28 mg 14%); light yellow powder; m.p. 160-162°C; IR (KBr): 1657 cm^{-1} (C=O); UV-Vis (THF): nm 331, 281, 251; ^1H NMR ($CDCl_3$): δ 8.20 (1H, d, J_m=2.6Hz, H-8), 7.55 (1H, dd, $J_{m,o}$=2.4,8.9Hz, H-10), 7.45 (1H, d, J_o=9.0Hz, H-11), 6.71 (1H, br s, H-1), 5.25 (1H, br s, H-4), 5.15 (2H, d, J_{allyl}=1.4Hz, H-α,β), 4.50 (1H, d, $J_{\square,\square a'}$=10.6Hz, H-5), 4.00 (1H, d, $J_{\square a,\square}$=11.0Hz, H-4a), 3.80 (3H, s, C_3-OCH_3), 2.75 (2H, m, H-2a) 1.80 (3H, s, $C_{1'}$-CH_3); MS: *m/z* 356 (M^+, 70%), 301 (33.1), 273 (34.5), 245 (22.0), 202 (100), 154 (27.1), 126 (18.9), 110 (47.9). Anal. Calcd. for $C_{20}H_{17}O_4Cl$: C, 67.32; H 4.80. Found: C, 67.35; H, 4.36%.

6c: Yield (62 mg 31%); light yellow powder; m.p. 200-202 °C; IR (KBr): 1643 cm^{-1} (C=O); UV-Vis (THF): nm 341, 276, 249; ^{1}H NMR ($CDCl_3$): δ 8.24 (1H, d, J_m=2.4Hz, H-8), 7.80 (1H, d, J_o=8.6Hz, H-1), 7.57 (1H, dd, $J_{m,o}$=2.5, 8.9Hz, H-10), 7.40 (1H, d, J_o=8.9Hz, H-11), 6.98 (1H, dd, $J_{m,o}$=2.4, 8.6Hz, H-2), 6.72 (1H, d, J_m=2.3Hz, H-4), 5.12 (2H, d, $J_{allyl'}$=1.2Hz, H-α,β), 4.95 (1H, s, H-5), 3.87 (3H, s, C_3-OCH_3), 1.88 (3H, s, $C_{1'}$-CH_3); MS: *m/z* 354 (M$^+$, 65%), 200 (26.1), 160 (36.7), 126 (39.4), 110 (100). Anal. Calcd. for $C_{20}H_{15}O_4Cl$: C, 67.71; H, 4.26. Found: C, 67.68; H, 4.30%.

4.4. Synthesis of 3-allyloxychromones 4d-4f

4.4.1. 6-Chloro-3-(3-methylbut-2-enyloxy)-2-phenyl-4*H*-chromen-4-one (4d)

The chromone **4d** was synthesized by reacting **1**$^{21-23}$ (2.7 g, 0.01 mol) with 1-chloro-3-methyl-2-butene (1.1 g, 0.01 mol) under similar conditions as applied for **4a**.

4d: Yield (2.6 g, 77%); off white powder; m.p. 95-96°C; IR (KBr): 1644 cm^{-1} (C=O); UV-Vis (THF): nm 345, 325, 251; ^{1}H NMR ($CDCl_3$): δ 8.18 (1H, d, J_m=2.6Hz, H-5), 8.10 (2H, m, H-2', 6'), 7.62 (1H, dd, $J_{m,o}$=2.4,8.9Hz, H-7), 7.53 (3H, m, H-3',4',5'), 7.51 (1H, J_o=9.0Hz, H-8), 5.61 (1H, bt, *J*=7.0 Hz, H-2''), 4.85 (2H, d, J_{vic}=6.9Hz, H-1''), 1.78 (6H, br s, $C_{3''}$-$(CH_3)_2$); MS: *m/z* 340 (M$^+$, 95%), 271 (26.4), 248 (33.7), 215 (33.7), 186 (21.2), 154 (36.1), 110 (100). Anal. Calcd. for $C_{20}H_{17}O_3Cl$: C, 70.49; H, 5.03. Found: C, 70.51; H, 5.01%.

4.4.2. 6-Chloro-3-(3-methylbut-2-enyloxy)-2-(4-methylphenyl)-4*H*-chromen-4-one (4e)

The chromone **4e** was synthesized by reacting **2**$^{21-23}$ (2.85 g, 0.01 mol) with 1-chloro-3-methyl-2-butene (1.1 g, 0.01 mol) under similar conditions as used for **4a**.

4e: Yield (2.9 g, 82%); off white powder; m.p. 101-102°C; IR (KBr): 1639 cm^{-1} (C=O); UV-Vis (THF): nm 332, 315, 254; ^{1}H NMR ($CDCl_3$):δ 8.20 (1H, d, J_m=2.4Hz, H-5), 8.00 (2H, AA' part of AA'XX' system, quasi d, J=8.8 Hz, H-2',6'), 7.61 (1H, dd, $J_{m,o}$=2.6, 8.9Hz, H-7), 7.50 (1H, d, J_o=8.9Hz, H-8), 7.33 (2H, AA' part of AA'XX' system, quasi d, J=8.8 Hz, J_o=8.5Hz, H-3',5'), 5.61 (1H, bt, J=7.0 Hz, H-2'') 4.85 (2H, d, J_{vic}=7.0Hz, H-1''), 1.82 (6H, br s, $C_{3''}$-$(C\boldsymbol{H_3})_2$), 2.39 (3H, s, $C_{\square'}$-C$\boldsymbol{H_3}$); MS: *m/z* 354 (M$^+$, 100%), 285 (43.0), 257 (47.3), 229 (23.1), 200 (22.9), 154 (45.5), 110 (33.3). Anal. Calcd. for $C_{21}H_{19}O_3Cl$: C, 71.08; H, 5.40. Found: C, 71.12; H, 5.43%.

4.4.3. 6-Chloro-3-(3-methylbut-2-enyloxy)-2-(4-methoxyphenyl)-4*H*-chromen-4-one (4f)

The chromone **4f** was synthesized by reacting **3**$^{21-23}$ (3.0 g, 0.01 mol) with 1-chloro-3-methyl-2-butene (1.1 g, 0.01 mol) under similar conditions as used for **4a**.

4f: Yield (2.9 g, 80%); off white powder; m.p. 92-93°C; IR (KBr): 1638 cm^{-1} (C=O); UV-Vis (THF): nm 342, 322, 252; ^{1}H NMR ($CDCl_3$): δ 8.21 (1H, d, J_m=2.6Hz, H-5), 8.16 (2H, dd, $J_{p,o}$=1.2,9.0Hz, H-2', 6'), 7.63 (1H, dd, $J_{m,o}$=2.4,8.7Hz, H-7), 7.51 (1H, d, J_o=9.0Hz, H-8), 7.03 (2H, dd, $J_{m,o}$=2.6,8.8Hz, H-3', 5'), 5.66 (1H, dd, $J_{allyl,vic}$=1.1,7.0Hz, H-2''), 4.81 (2H, d, J_{vic}=6.8Hz, H-1''), 1.81 (6H, br s, $C_{3''}$-$(C\boldsymbol{H_3})_2$), 3.90 (3H, s, $C_{4'}$-OC$\boldsymbol{H_3}$); MS: *m/z* 370 (M$^+$, 100%), 301 (41.0), 273 (26.3), 245 (33.2), 216 (55.0), 154 (25.7), 110 (64.1). Anal. Calcd. for $C_{21}H_{19}O_4Cl$: C, 68.02; H 5.16. Found: C, 67.99; H, 5.19%.

4.5. Photolysis of 3-allyloxychromones 4d-4f

4.5.1 Photolysis of 6-Chloro-3-(3"-methylbut-2"-enyloxy)-2-phenyl-4*H*-chromen-4-one (4d)

The benzene solution of **4d** (200 mg, 0.58 mmol) was photolysed under similar conditions as described for **4a**. The chromatographic separation of photolysate yielded two new compounds **5d** and **6d**.

5d: Yield (34 mg; 17%); light yellow powder; m.p. 171-172°C; IR (KBr): 1652 cm^{-1} (C=O); UV-Vis (THF): nm 332, 298, 261; ^{1}H NMR ($CDCl_3$): δ 8.20 (1H, d, J_m=2.5Hz, H-8), 7.62 (1H, dd, $J_{m,o}$=2.6,9.0Hz, H-10), 7.50 (1H, d, J_o=8.9Hz, H-11), 6.85 (1H, br s, H-1), 5.35 (1H, d, $J_{1',5}$=6.5Hz, H-1'), 5.85 (1H, dd, $J_{3,2a}$=2.0Hz, $J_{3,4}$=10.0Hz, H-3), 5.70 (1H, d, $J_{4,3}$=10.0Hz, H-4), 4.50 (1H, d, $J_{5,4a'}$=11.0Hz, H-5), 3.60 (1H, d, $J_{4a,5}$=11.0Hz, H-4a), 2.80 (2H, m, H-2a) , 1.81 (6H, s, $C_{2'}$-$(CH_3)_2$); MS: *m/z* 340 (M$^+$, 64%), 271 (32.0), 243 (21.5), 186 (36.7), 154 (9.8), 126 (47.8), 110 (100). Anal. Calcd. for $C_{20}H_{17}O_3Cl$: C, 70.49; H, 5.03. Found: C, 70.51; H, 5.01%.

6d: Yield (70 mg; 35%); light yellow solid; m.p. 214-215°C; IR (KBr): 1643 cm^{-1} (C=O); UV-Vis (THF): nm 342, 292, 240; ^{1}H NMR ($CDCl_3$): δ 8.24 (1H, d, J_m=2.6Hz, H-8), 8.04 (1H, d, $J_{m,o}$=2.3, 8.6Hz, H-1), 7.62 (1H, dd, J_m=2.4Hz, $J_{m,o}$=2.6, 8.9Hz, H-10), 7.57 (1H, d, J_o=8.9Hz, H-11), 7.52-7.55 (3H, m, H-2, 3, 4), 6.15 (1H, d, $J_{1',5}$=6.8Hz, H-1'), 4.85 (1H, d, $J_{5,1'}$=6.5Hz, H-5), 1.85 (6H, s, $C_{2'}$-$(CH_3)_2$); MS: *m/z* 338 (M$^+$, 70%), 184 (100), 154 (28.7), 126 (24.4), 110 (90). Anal. Calcd. for $C_{20}H_{15}O_3Cl$ requires C, 70.90; H, 4.46. Found: C, 70.94; H, 4.50%.

4.5.2. Photolysis of 6-Chloro-3-(3"-methylbut-2"-enyloxy)-2-(4-methylphenyl)-4*H*-chromen-4-one (4e)

The benzene solution of **4e** (200 mg, 0.00056 mol) was photolysed under similar conditions as described for **4a**. The photolysate on chromatographic separation afforded two new compounds **5e** and **6e**.

5e: Yield (32 mg; 16%); light yellow powder; m.p. 175-176°C; IR (KBr): 1650 cm^{-1} (C=O); UV-Vis (THF): nm 330, 285, 250; ^{1}H NMR ($CDCl_3$): δ 8.19 (1H, d, J_m=2.5Hz, H-8), 7.65 (1H, dd, $J_{m,o}$=2.5, 8.9Hz, H-10), 7.51 (1H, d, J_o=8.9Hz, H-11), 6.80 (1H, br s, H-1), 5.50 (1H, br s, H-4), 5.45 (1H, d, $J_{5,4a}$=11.2Hz, H-5), 5.25 (1H, d, $J_{1',5}$=6.9Hz, H-1'), 3.50 (1H, d, $J_{4a,5}$=11.3Hz, H-4a), 2.30 (3H, s, C_3-$C\boldsymbol{H}_3$), 2.90 (2H, m, H-2a) , 1.73 (6H, s, $C_{2'}$-$(CH_3)_2$); MS: *m/z* 354 (M$^+$, 90%), 285 (33.2), 257 (37.7), 200 (29.3), 200 (67.4), 154 (53.7), 126 (31.2), 110 (100). Anal. Calcd. for $C_{21}H_{19}O_3Cl$: C, 71.08; H, 5.40. Found: C, 71.12; H, 5.43%.

6e: Yield (68 mg; 34%); light yellow powder; m.p. 220-221°C; IR (KBr): 1643 cm^{-1} (C=O); UV-Vis (THF): nm 341, 280, 238; ^{1}H NMR ($CDCl_3$) δ 8.26 (1H, d, J_m=2.6Hz, H-8), 7.76 (1H, d, J_o=8.0Hz, H-1), 7.64 (1H, dd, $J_{m,o}$=2.5, 8.9Hz, H-10), 7.52 (1H, d, J_o=9.0Hz, H-11), 6.98 (2H, m, H-2, 4), 6.15 (1H, d, $J_{1',5}$=7.0Hz, H-1'), 5.15 (1H, d, $J_{5,1'}$=6.2Hz, H-5), 2.25 (3H, s, C_3-CH_3), 1.84 (6H, s, $C_{2'}$-$(CH_3)_2$); MS: *m/z* 352 (M$^+$, 100%), 198 (21.1), 154 (57.7), 126 (75.3), 110 (31.7). Anal. Calcd. for $C_{21}H_{17}O_3Cl$: C, 71.49; H, 4.86. Found: C, 71.53; H, 4.90%.

4.5.3. Photolysis of 6-Chloro-3-(3”-methylbut-2”-enyloxy)-2-(4-methoxyphenyl)-4*H*-chromen-4-one (4f)

The benzene solution of **4f** (200 mg, 0.00054 mol) was photolysed under similar conditions as described for **4a**. The chromatographic work up of photolysate provided the two new compounds **5f** and **6f**.

5f: Yield (36 mg; 18%); light yellow powder; m.p. 178-180^{o}C; IR (KBr): 1655 cm^{-1} (C=O); UV-Vis (THF): nm 335, 285, 253; ^{1}H NMR (CDCl$_3$): δ 8.18 (1H, d, J_{m}=2.5Hz, H-8), 7.55 (1H, dd, $J_{m,o}$=2.5, 8.9Hz, H-10), 7.45 (1H, d, J_{o}=8.9Hz, H-11), 6.71 (1H, br s, H-1), 5.29 (1H, d, $J_{1',5}$=6.9Hz, H-1’), 5.25 (1H, br s, H-4), 4.50 (1H, d, $J_{5,4a'}$=10.9Hz, H-5), 4.10 (1H, d, $J_{4\alpha,5}$=11.2Hz, H-4a), 3.80 (3H, s, C$_3$-OCH_3), 2.36 (2H, s, H-2a), 1.77 (6H, s, C$_{2'}$-(CH$_3$)$_2$); MS: *m/z* 370 (M$^+$, 100%), 301 (44.2), 273 (22.1), 245 (35.3), 216 (56.4), 154 (27.3), 126 (29.1), 110 (76.3). Anal. Calcd. for $C_{21}H_{19}O_4Cl$: C, 68.02; H 5.16. Found: C, 67.99; H, 5.19%.

6f: Yield (74 mg; 37%); light yellow powder; m.p. 224-225^{o}C; IR (KBr): 1642 cm^{-1} (C=O); UV-Vis (THF): nm 345, 273, 245; ^{1}H NMR (CDCl$_3$): δ 8.19 (1H, d, J_{m}=2.4Hz, H-8), 7.80 (1H, d, J_{o}=8.6Hz, H-1), 7.57 (1H, dd, $J_{m,o}$=2.4,8.8Hz, H-10), 7.40 (1H, d, J_{o}=8.9Hz, H-11), 6.98 (1H, dd, $J_{m,o}$=2.4, 8.6Hz, H-2), 6.72 (1H, d, J_{m}=2.3Hz, H-4), 6.15 (1H, d, $J_{1',5}$=7.0Hz, H-1’), 5.20 (1H, d, $J_{5,1'}$=6.8Hz, H-5), 3.87 (3H, s, C$_3$-OCH_3), 1.83 (6H, s, C$_{2'}$-(CH$_3$)$_2$); MS: *m/z* 368 (M$^+$, 85%), 214 (33.7), 160 (45.2). 154 (24.0), 126 (28.7), 110 (100). Anal. Calcd. for $C_{21}H_{17}O_4Cl$: C, 68.39; H, 4.65. Found: C, 68.39; H, 4.62%.

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