# Feasibility of sigmatropic rearrangement on electron-deficient coumarinyl ketones

**Lakshmi Narayan Dutta, Banani De, Godhuli Pal, and Amarendra Patra**

**Abstract:** Different alkyl/aryl 7-hydroxy-8-coumarinyl ketones were converted to 7-*O*-allyl and 7-*O*-cyclohexenyl ethers and the study of hitherto unreported sigmatropic rearrangement on 7-*O*-allyl and 7-*O*-cyclohex-2′-ene-1′-ylcoumarinyl ketones prepared is accounted herein. The rearrangement yielded alkyl/aryl 6-allyl-7-hydroxy-8-coumarinyl ketones **3** and alkyl/aryl 6-cyclohex-2′-en-1′-yl-7-hydroxy-8-coumarinyl ketones **7** as the major products. Interestingly, unusual selectivity was observed in the case of alkyl 7-*O*-allylcoumarinyl ketones. Thus alkyl 3-allyl-7-hydroxy-8-coumarinyl ketones **4** and alkyl 8-allyl-7-hydroxy-6-coumarinyl ketones **5** were the outcome from alkyl 7-*O*-allyl-8-coumarinyl ketones and alkyl 4-methyl-7-*O*-allyl-8-coumarinyl ketones, respectively, albeit in minor yields.

*Key words:* allyloxycoumarinyl ketones, 7-*O*-cyclohex-2′-en-1′-ylcoumarinyl ketones, sigmatropic rearrangement, 3-allylcoumarinyl ketones, 8-allylcoumarinyl ketones.

**Résumé :** On a transformé diverses alkyl/aryl 7-hydroxy-8-coumarinylcétones en leurs éthers, les oxydes de 7-*O*-allyle et 7-*O*-cyclohexényle correspondants, et on rapporte les résultats obtenus lors des réarrangements sigmatropiques qui n'avaient jamais été rapportés antérieurement et qui ont été effectués sur les 7-*O*-allyl- et 7-*O*-cyclohex-2′-én-1′-ulcoumarinylcétones ainsi préparées. Les produits principaux de ces réactions sont les alkyl/aryl 6-allyl-7-hydroxy-8-coumarinylcétones, **3**, et les alkyl/aryl 6-cyclohex-2′-én-1′-yl-7-hydroxy-8-coumarinylcétones, **7**. On a observé une sélectivité inhabituelle intéressante dans le cal des alkyl 7-*O*-allylcoumarinylcétones. Même s'ils n'ont été obtenus qu'avec de faibles rendements, les alkyl 3-allyl-7-hydroxy-8-coumarinylcétones, **4**, et alkyl 8-allyl-7-hydroxy-6-coumarinylcétones, **5**, sont les produits obtenus à partir respectivement des 7-*O*-allyl-8-coumarinylcétones et alkyl 4-méthyl-7-*O*-allyl-8-coumarinylcétones.

*Mots-clés :* allyloxycomarinylcétones, 7-*O*-cyclohex-2′-én-1′-ylcoumarinylcétones, réarrangement sigmatropique, 3-allylcoumarinylcétones, 8-allylcoumarinylcétones.

[Traduit par la Rédaction]

## Introduction

Coumarins (1, 2) have attracted the attention of synthetic organic chemists (3–5) throughout the globe for building up new exotic molecules owing to their well-established range of biological activities (6–10). In quest of newer synthetic methodologies we have successfully carried out a series of systematic studies on the selectivities of different organometallics (11, 12) and ylids (13) involving typical non-concerted processes on coumarinyl ketones and coumarincarboxaldehydes. Under the scope of concerted process we have extensively applied a sigmatropic reaction in the form of thermal Claisen rearrangement for the synthesis of various natural and unnatural coumarins. In spite of a flurry of activity in the synthesis of coumarin employing Claisen rearrangement (14–20), there is virtually no report on the efficacy of the rearrangement on the coumarin moiety bearing further electron-rich and electron-deficient functionalities. Herein we report the findings of an intense investigation on Claisen rearrangement restricting the functionalisation to the electron-deficient coumarinyl ketones.

## Discussion

The starting materials selected for this study, viz. 7-allyloxy-8-coumarinyl alkyl/aryl ketones **2a**–**2h** and 7-cyclohex-2′-en-1′-yloxy-8-coumarinyl alkyl/aryl ketones **6a**–**6h** were prepared from 7-hydroxy-8-coumarinyl alkyl/aryl ketones **1a**–**1h**. The hydroxycoumarinyl ketones could be procured from 7-hydroxycoumarin and 4-methyl-7-hydroxycoumarin, as appropriate, exploiting Fries rearrangement (21). The aforesaid allyl coumarinyl ethers have thus been successfully prepared in good yield by following the usual protocol of refluxing the compounds for 8 h in dry acetone with allyl bromide in the presence of anhydrous $K_2CO_3$. An initial sigmatropic rearrangement study revealed that the allyl ethers failed to record any positive result in solvents like chlorobenzene and polyethylene glycol 400. Consequent to that, the rearrangement was tried and ultimately became successful in *N,N*-diethylaniline. The C–C bond formations showed typical selectivities by yielding 6-allyl substituted coumarinyl ketones **3** and 3-allyl substituted coumarinyl ketones **4** with 7-allyloxy-8-coumarinyl ketones

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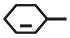
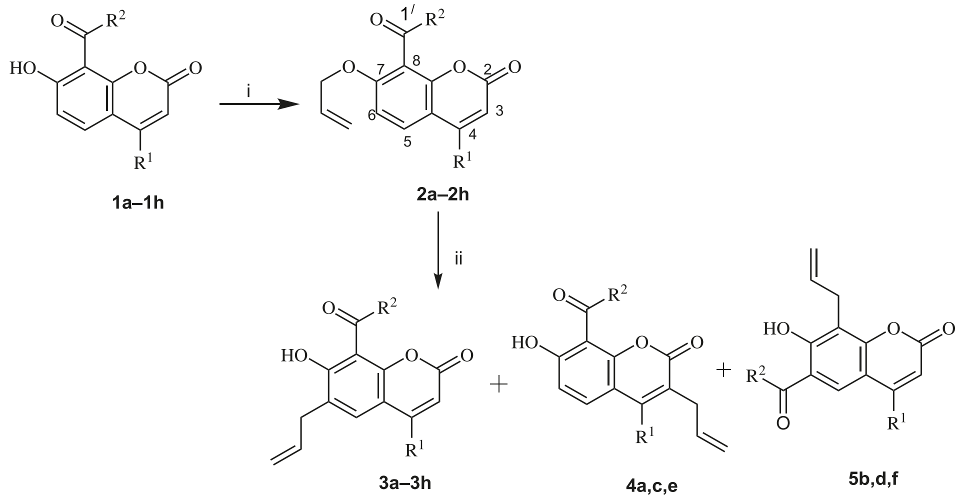
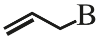
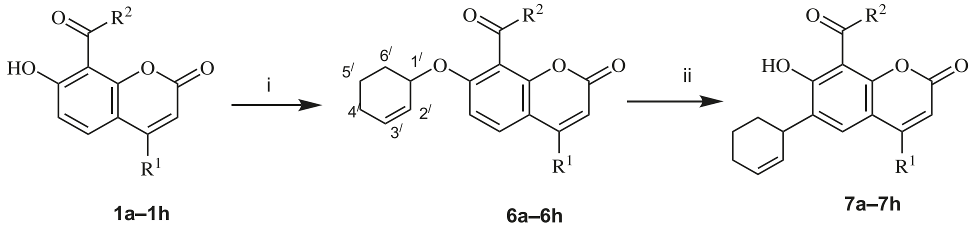
**Scheme 1.** Reagents and conditions: (*i*)  Br, anhyd. $K_2CO_3$, dry $Me_2CO$, 14 h, and reflux; (*ii*) $PhNEt_2$, 195 °C, and 8 h.



**Scheme 2.** Reagents and conditions: (*i*)  Br, $NEt_3$, dry $Me_2CO$, 4 h, and reflux. (*ii*) $Ph_2O$, reflux for 10 min.



**2a**, **2c**, and **2e**, whereas the 4-methyl-7-allyloxy-8-coumarinyl ketones **2b**, **2d**, and **2f** resulted in 6-allyl substituted coumarinyl ketones **3** along with 8-allyl substituted 6-coumarinyl ketones **5** as a consequence of unusual acyl migration. The allyl ethers having benzoyl coumarinyl functionality, **2g** and **2h**, did produce only the usual 6-allyl substituted coumarinyl ketones without any trace of other rearranged products (Scheme 1).

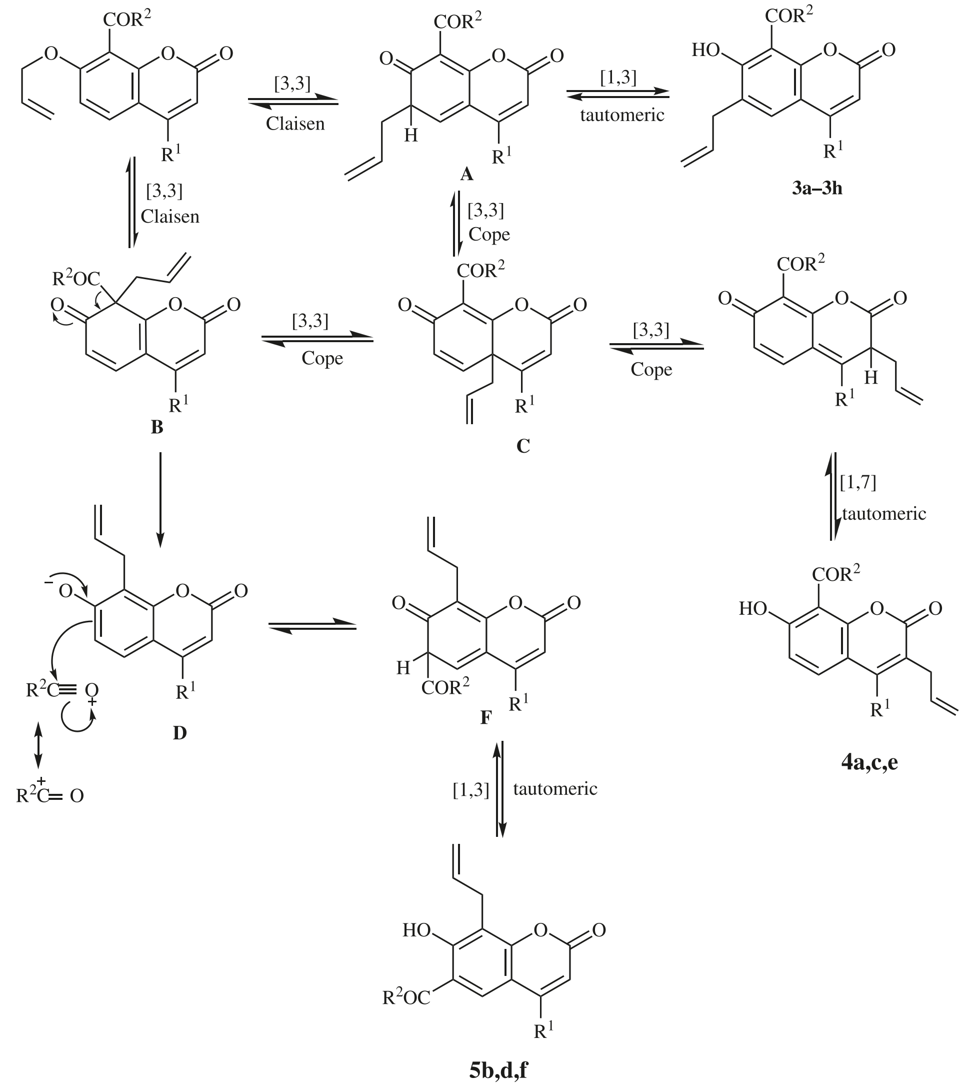
It should be noted that attempted cyclohexenylation of hydroxycoumarinyl ketones following the usual protocol of refluxing in dry acetone with 3-bromocyclohexene in the presence of anhydrous $K_2CO_3$ (22) turned out to be entirely unsuccessful. Finally the problem was overcome through the judicious selection of a base, viz. triethylamine instead of anhydrous $K_2CO_3$ (Scheme 2). It should be emphasized that the study of Claisen rearrangement turned out to be remarkably successful in diphenyl ether as solvent, while the yield was extremely poor when carried out in chlorobenzene (<5%) and *N,N*-diethylaniline (~10%). The cyclohexenyl ethers on Claisen rearrangement underwent regioselective formation of 6-cyclohex-2′-ene-1′-yl-8-coumarinyl alkyl/aryl ketones **7a**–**7h** in good yields (Table 1). No unusual acyl migration or Claisen rearrangement on other positions of coumarin moiety was observed with cyclohexenyl ethers.

The formation of 6-allyl and 6-cyclohexenyl substituted coumarinyl ketones turned out to be quite obvious via an intermediate **A** (Scheme 3). In the formation of 3-allylcoumarinyl ketones, the intermediate **C** may be visualized as a consequence of a [3,3] Cope rearrangement of the intermediate **B** produced via a [3,3] sigmatropic shift. Alternatively, the genesis of 3-allylcoumarinyl ketones from alkyl 7-allyloxy-8-coumarinyl ketones may be rationalized from the intermediate **C** formed via a [3,3] sigmatropic shift, which further underwent Cope rearrangement with the transfer of allyl functionality at the 4a position, leading to the intermediate **C**. The intermediate **C** follows an itinerary of further [3,3] Cope rearrangement followed by [1,7] tautomeric shift to afford the 3-allyl substituted coumarinyl ketones. The 4-methyl-7-allyloxycoumarinyl ketones prefer to follow from the intermediate **B** as an alternative pathway leading to the anionic intermediate **D**, along with the ejected acylium ion R-C≡$O^+$ that may exist, most plausibly enjoying the character of an intimate ion pair though the feasibility of a concerted mechanism cannot be ruled out. On further chemical mutation to intermediate **F**, the 6-acyl-8-allylcoumarinyl ketones are being derived via the [1,3] tautomeric shift.

**Table 1.** Yields of the compounds **2** to **7**.

| | | Substituents | | Yield (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Entry | | $R^1$ | $R^2$ | **2** | **3** | **4** | **5** | **6** | **7** |
| 1 | **a** | H | Me | 83 | 44 | 40 | — | 66 | 60 |
| 2 | **b** | Me | Me | 83 | 46 | — | 33 | 93 | 62 |
| 3 | **c** | H | Et | 84 | 41 | 26 | — | 76 | 62 |
| 4 | **d** | Me | Et | 85 | 42 | — | 26 | 63 | 65 |
| 5 | **e** | H | *n*-Pr | 84 | 43 | 24 | — | 70 | 59 |
| 6 | **f** | Me | *n*-Pr | 84 | 43 | — | 26 | 78 | 61 |
| 7 | **g** | H | Ph | 85 | 47 | — | — | 76 | 59 |
| 8 | **h** | Me | Ph | 85 | 44 | — | — | 89 | 58 |

**Scheme 3.**



The structures of the compounds were unequivocally settled from elemental analyses and extensive spectroscopic investigations. Assignment of the structures of 6-allyl and 8-allylsubstituted coumarinyl ketones posed an interesting problem and could be unequivocally solved by critical analysis of the $^1$H NMR and $^{13}$C NMR spectra, with particular emphasis on the proton signals of C-5 and carbon signals of C-6 and C-8. The proton signals at the 5-position enjoy more deshielding because of the anisotropic effect offered by the newly arrived adjacent ketocarbonyl functionality. On the contrary, the C-6 carbon signal of 8-allyl substituted compounds are more shielded than those of the 6-allyl substituted compounds (23) (Table 2), and the C-8 signals varied oppositely.

**Table 2.** Chemical shift (δ) values of C-5 protons and C-6, C-8 carbon signals.

| | | δ Value | | |
|---|---|---|---|---|
| Compound | Location of ketoalkyl functionality | C-5 proton signal | C-6 carbon signal | C-8 carbon signal |
| **3b** | C-8 | 7.48 | 126.1 | 108.6 |
| **5b** | C-6 | 7.88 | 112.4 | 116.3 |
| **3d** | C-8 | 7.43 | 126.2 | 108.7 |
| **5d** | C-6 | 7.95 | 112.5 | 116.0 |
| **3f** | C-8 | 7.49 | 126.1 | 108.7 |
| **5f** | C-6 | 7.95 | 112.5 | 116.2 |

## Conclusion

In conclusion, it is worth mentioning that an unusual selectivity was observed in the product formation with the introduction of a methyl group at the 4-position of the 7-allyloxy-8-coumarinyl ketone moiety. The changeover in the character of the minor products with the introduction of methyl group at the 4-position of the 8-coumarinyl ketone moiety may be rationalized either from steric or electronic considerations. The plausible explanation of such selectivity in favor of the electronic and (or) steric effect of methyl group can only be confirmed on further study of Claisen rearrangement on 7-allyloxy-8-coumarinyl ketones with varying substituents (Et, *n*-Pr, *i*-Pr, *t*-Bu, CHO, CN, $CO_2Me$, $CH_2OH$) at the 4-position.

## Experimental

All melting points were determined in open capillaries and are uncorrected. IR spectra ($\nu_{max}$ in $cm^{-1}$) were recorded in KBr with a PerkinElmer 883-IR and RXI FT IR spectrophotometers. The UV spectra were measured in 95% ethanol using an Hitachi U 2000 and Lamda 20 ELMER spectrophotometers. The elemental analyses were carried out in a PerkinElmer 240C elemental analyzer. The $^1H$ NMR and $^{13}C$ NMR spectra were recorded in a Bruker AV300 supercon NMR spectrometer operating at 300.13 MHz for proton and 75.47 MHz for carbon, using $CDCl_3$ as solvent and TMS as an internal standard. Mass spectra were recorded on a Finnigan Mat 1020 C, Shimadzu Model GEMS QP1000A, and LC-MS MS Q-TOF-micro spectrometers and a Q TRAP LC/MS/MS system operative at 70 eV. The column chromatographic separation and filtration were performed with silica gel (mesh size 60–120) prepared by Glaxo (India) Ltd and Merck (India) Ltd. Petroleum ether used had a boiling point 60–80 °C.

### Preparation of 7-allyloxycoumarinyl ketones 2a–2h

#### *General procedure*

7-Hydroxycoumarinyl ketones (4.3 mmol) dissolved in dry acetone (50 mL) were treated with allyl bromide (4.9 mmol) and anhydrous $K_2CO_3$ (4.3 mmol) and refluxed under anhydrous conditions on water bath for ~14 h. Excess acetone was distilled off and the residual solid cakelike mass was treated with water (150 mL). The mixture was acidified in cold conditions with cold dil HCl (4 N). The solid separated was filtered out and washed with cold water until it was neutral. The resultant solid was dried and crystallized from EtOAc/petroleum ether to obtain crystals of 7-allyloxycoumarinyl ketones **2a**–**2h**.

#### *Compound 2a*

Mp 68 °C. IR ($cm^{-1}$): 3080, 2980, 1740, 1700, 1620, 1590, 1490, 1400. $^1H$ NMR δ: 2.57 (sharp s, 3H, 1′-$CH_3$), 4.73 (d, $J$ = 5.0 Hz, 2H, $OC\mathit{H}_2CH=CH_2$), 5.34 (d, $J$ = 10.0 Hz, 1H, $OCH_2CH=C\mathit{H}_AH_B$), 5.39 (d, $J$ = 17.0 Hz, 1H, $OCH_2CH=CH_A\mathit{H}_B$), 5.95 (m, 1H, $OCH_2C\mathit{H}=CH_2$), 6.27 (d, $J$ = 9.0 Hz, 1H, 3-H), 6.91 (d, $J$ = 7.2 Hz, 1H, 6-H), 7.45 (d, $J$ = 7.2 Hz, 1H, 5-H), 7.70 (d, $J$ = 9.0 Hz, 1H, 4-H). Anal. calcd. for $C_{14}H_{12}O_4$: C 68.84, H 4.95; found: C 68.79, H 4.90.

#### *Compound 2b*

Mp 108 °C. IR ($cm^{-1}$): 3060, 2995, 1730, 1710, 1605, 1565, 1495, 1380. $^1H$ NMR δ: 2.32 (d, $J$ = 1.0 Hz, 3H, 4-$CH_3$), 2.53 (sharp s, 3H, 1′-$CH_3$), 4.58 (d, $J$ = 6.0 Hz, 2H, $OC\mathit{H}_2CH=CH_2$), 5.23 (d, $J$ = 10.0 Hz, 1H, $OCH_2CH=C\mathit{H}_AH_B$), 5.32 (d, $J$ = 17.0 Hz, 1H, $OCH_2CH=CH_A\mathit{H}_B$), 5.96 (m, 1H, $OCH_2C\mathit{H}=CH_2$), 6.08 (q, $J$ = 1.0 Hz, 1H, 3-H), 6.80 (d, $J$ = 9.0 Hz, 1H, 6-H), 7.47 (d, $J$ = 9.0 Hz, 1H, 5-H). Anal. calcd. for $C_{15}H_{14}O_4$: C 69.75, H 5.46; found: C 69.72, H 5.41.

#### *Compound 2c*

Mp 65 °C. IR ($cm^{-1}$): 3080, 2970, 1750, 1715, 1610, 1570, 1490, 1405, 1300. $^1H$ NMR δ: 1.16 (t, $J$ = 7.0 Hz, 3H, 2′-$CH_3$), 2.86 (q, $J$ = 7.0 Hz, 2H, 1′-$CH_2$), 4.63 (d, $J$ = 6.0 Hz, 2H, $OC\mathit{H}_2CH=CH_2$), 5.30 (d, $J$ = 10.0 Hz, 1H, $OCH_2CH=C\mathit{H}_AH_B$), 5.37 (d, $J$ = 17.0 Hz, 1H, $OCH_2CH=CH_A\mathit{H}_B$), 5.98 (m, 1H, $OCH_2C\mathit{H}=CH_2$), 6.24 (d, $J$ = 9.0 Hz, 1H, 3-H), 6.84 (d, $J$ = 9.0 Hz, 1H, 6-H), 7.43 (d, $J$ = 9.0 Hz, 1H, 5-H), 7.63 (d, $J$ = 9.0 Hz, 1H, 4-H). Anal. calcd. for $C_{15}H_{14}O_4$: C 69.75, H 5.46; found: C 69.70, H 5.41.

#### *Compound 2d*

Mp 70 °C. IR ($cm^{-1}$): 3090, 2990, 1745, 1710, 1605, 1570, 1495, 1380. $^1H$ NMR δ: 1.21 (t, $J$ = 7.0 Hz, 3H, 2′-$CH_3$), 2.39 (d, $J$ = 1.0 Hz, 3H, 4-$CH_3$), 2.91 (q, $J$ = 7.0 Hz, 2H, 1′-$CH_2$), 4.60 (d, $J$ = 5.0 Hz, 2H, $OC\mathit{H}_2CH=CH_2$), 5.45 (d, $J$ = 10.0 Hz, 1H, $OCH_2CH=C\mathit{H}_AH_B$), 5.52 (d, $J$ = 16.0 Hz, 1H, $OCH_2CH=CH_A\mathit{H}_B$), 6.02 (m, 1H, $OCH_2C\mathit{H}=CH_2$), 6.15 (q, $J$ = 1.0 Hz, 1H, 3-H), 6.88 (d, $J$ = 7.2 Hz, 1H, 6-H), 7.51 (d, $J$ = 7.2 Hz, 1H, 5-H). Anal. calcd. for $C_{16}H_{16}O_4$: C 70.57, H 5.92; found: C 70.60, H 5.88.

#### *Compound 2e*

Mp 52 °C. IR : 3080, 2970, 1760, 1710, 1610, 1560, 1490, 1410. $^1H$ NMR δ: 0.93 (t, $J$ = 5.1 Hz, 3H, 3′-$CH_3$), 1.68 (tq, $J$ = 5.1 Hz, 5.1 Hz, 2H, 2′-$CH_2$), 2.77 (t, $J$ = 5.1 Hz, 2H, 1′-$CH_2$), 4.56 (d, $J$ = 6.0 Hz, 2H, $OC\mathit{H}_2CH=CH_2$), 5.23 (d, $J$ = 12.0 Hz, 1H, $OCH_2CH=C\mathit{H}_AH_B$), 5.28 (d, $J$ = 18.0 Hz, 1H, $OCH_2CH=CH_A\mathit{H}_B$), 5.90 (ddt, $J$ = 18.0, 12.0, 6.0 Hz, 1H, $OCH_2C\mathit{H}=CH_2$), 6.17 (d, $J$ = 9.0 Hz, 1H, 3-H), 6.78 (d, $J$ = 9.0 Hz, 1H, 6-H), 7.36 (d, $J$ = 9.0 Hz, 1H, 5-H), 7.57 (d, $J$ = 9.0 Hz, 1H, 4-H). Anal. calcd. for $C_{16}H_{16}O_4$: C 70.57, H 5.92; found: C 70.52, H 5.99.

#### *Compound 2f*

Mp 70 °C. IR ($cm^{-1}$): 3060, 2950, 1735, 1720, 1600, 1560, 1485, 1370. $^1H$ NMR δ: 0.98 (t, $J$ = 7.0 Hz, 3H, 3′-$CH_3$), 1.73 (tq, $J$ = 7.0 Hz, 7.0 Hz, 2H, 2′-$CH_2$), 2.38 (d, $J$ = 1.0 Hz, 3H, 4-$CH_3$), 2.83 (t, $J$ = 7.0 Hz, 2H, 1′-$CH_2$), 4.63 (d, $J$ = 6.0 Hz, 2H, $OC\mathit{H}_2CH=CH_2$), 5.28 (d, $J$ = 10.0 Hz, 1H, $OCH_2CH=C\mathit{H}_AH_B$), 5.37 (d, $J$ = 18.0 Hz, 1H, $OCH_2CH=CH_A\mathit{H}_B$), 5.97 (ddt, $J$ = 18.0, 10.0, 6.0 Hz, 1H, $OCH_2C\mathit{H}=CH_2$), 6.13 (q, $J$ = 1.0 Hz, 1H, 3-H), 6.85 (d, $J$ = 9.0 Hz, 1H, 6-H), 7.52 (d, $J$ = 9.0 Hz, 1H, 5-H). Anal. calcd. for $C_{17}H_{18}O_4$: C 71.31, H 6.34; found: C 71.34, H 6.30.

#### *Compound 2g*

Mp 102 °C. IR : 3065, 2980, 1725, 1675, 1610, 1565, 1495, 1405. $^1H$ NMR δ: 4.58 (d, $J$ = 5.0 Hz, 2H, $OC\mathit{H}_2CH=CH_2$), 5.16 (d, $J$ = 11.0 Hz, 1H, $OCH_2CH=C\mathit{H}_AH_B$), 5.18 (d, $J$ = 17.0 Hz, 1H, $OCH_2CH=CH_A\mathit{H}_B$), 5.83 (m, 1H, $OCH_2C\mathit{H}=CH_2$), 6.24 (d, $J$ = 8.0 Hz, 1H, 3-H), 6.92 (d, $J$ = 8.0 Hz, 1H, 6-H), 7.52 (m, 5H, $C_6H_5$), 7.77 (d, $J$ = 8.0 Hz, 1H, 5-H), 7.88 (d, $J$ = 8.0 Hz, 1H, 4-H). Anal. calcd. for $C_{19}H_{14}O_4$: C 74.50, H 4.60; found: C 74.45, H 4.65.

#### *Compound 2h*

Mp 151 °C. IR : 3090, 2990, 1725, 1680, 1595, 1560, 1490, 1370. $^1H$ NMR δ: 2.44 (d, $J$ = 1.2 Hz, 3H, 4-$CH_3$), 4.60 (br d, $J$ = 7.0 Hz, 2H, $OC\mathit{H}_2CH=CH_2$), 5.15 (d, $J$ = 10.0 Hz, 1H, $OCH_2CH=C\mathit{H}_AH_B$), 5.18 (d, $J$ = 17.0 Hz, 1H, $OCH_2CH=CH_A\mathit{H}_B$), 5.81 (ddt, $J$ = 17.0, 10.0, 7.0 Hz, 1H, $OCH_2C\mathit{H}=CH_2$), 6.14 (q, $J$ = 1.2 Hz, 1H, 3-H), 6.94 (d, $J$ = 9.0 Hz, 1H, 6-H), 7.43 (t, $J$ = 7.8 Hz, 2H, 3′-H and 5′-H), 7.58 (br t, $J$ = 7.8 Hz, 1H, 4′-H), 7.65 (br d, $J$ = 7.8 Hz, 2H, 2′-H and 6′-H), 7.85 (d, $J$ = 9.0 Hz, 1H, 5-H). Anal. calcd. for $C_{20}H_{16}O_4$: C 74.99, H 5.03; found: C 74.94, H 4.98.

## Preparation of 6-allyl-8-coumarinyl alkyl/aryl ketones 3a–3h

### *General Procedure*

The allyloxycoumarinyl ketones **2a**–**2h** (2.0 mmol) dissolved in distilled $PhNEt_2$ (30 mL) were heated at 195 °C for 8 h under anhydrous conditions. $PhNEt_2$ was then distilled off and the residual mass left was dissolved in $CHCl_3$ (30 mL). The $CHCl_3$ solution of the mass was washed successively with cold dil. HCl (3 × 15 mL), a saturated brine solution (1x15 mL), followed by a saturated aqueous solution of $NaHCO_3$ (2 × 15 mL), and again with a saturated brine solution (2 × 15 mL). Removal of solvent after drying over anhydrous $Na_2SO_4$ afforded a semi-solid mass, which was found to be a mixture of three components. Column chromatographic resolution over silica gel yielded the 6-allyl-8-coumarinyl ketones **3a**–**3h** from petroleum ether and EtOAc (99:1) eluate fractions. The products were crystallized from EtOAc/petroleum ether.

### *Compound 3a*

Mp 121 °C. UV–vis (EtOH) $\lambda_{max}$ (log $\epsilon$): 321.7 (4.78), 270.5 (4.76), 254.5 (4.75). IR (cm$^{-1}$): 3080, 2920, 1730, 1710, 1610, 1560, 1400, 1365. $^1$H NMR δ: 2.89 (sharp s, 3H, 1′-$CH_3$), 3.35 (br d, $J$ = 6.5 Hz, 2H, 6-$C\mathit{H}_2CH{=}CH_2$), 5.071 (d, $J$ = 10.0 Hz, 1H, $CH_2CH{=}C\mathit{H}_AH_B$), 5.072 (d, $J$ = 18.0 Hz, 1H, $CH_2CH{=}CH_A\mathit{H}_B$), 6.01 (m, 1H, $CH_2C\mathit{H}{=}CH_2$), 6.20 (d, $J$ = 9.5 Hz, 1H, 3-H), 7.33 (s, 1H, 5-H), 7.57 (d, $J$ = 9.5 Hz, 1H, 4-H), 14.02 (s, 1H, 7-OH). $^{13}$C NMR δ: 33.0 (2°, $\mathit{C}H_2CH{=}CH_2$), 33.7 (1°, 1′-$CH_3$), 108.7 (4°, C-8), 110.3 (4°, C-4a), 112.0 (3°, C-3), 116.9 (2°, $CH_2CH{=}\mathit{C}H_2$), 126.7 (4°, C-6), 133.9 (3°, $CH_2\mathit{C}H{=}CH_2$), 135.1 (3°, C-5), 144.2 (3°, C-4), 154.4 (4°, C-8a), 159.6 (4°, C-2), 165.1 (4°, C-7), 204.3 (4°, C-1′). MS-EI (70 eV) $m/z$: 244 (49.5, M$^+$), 229 (57.2), 216 (19.6), 211 (25.6), 201 (100), 183(12.8), 173 (41.8), 155 (16.6), 145 (29.4), 131 23.5), 115 (92.5). Anal. calcd. for $C_{14}H_{12}O_4$: C 68.84, H 4.95; found: C 68.89, H 4.99.

### *Compound 3b*

Mp 122 °C. IR (cm$^{-1}$): 3080, 2980, 1740, 1715, 1610, 1560, 1450, 1395. $^1$H NMR δ: 2.36 (d, $J$ = 1.0 Hz, 3H, 4-$CH_3$), 2.90 (sharp s, 3H, 1′-$CH_3$), 3.38 (br d, $J$ = 6.5 Hz, 2H, $C\mathit{H}_2CH{=}CH_2$), 5.06 (d, $J$ = 16.0 Hz, 1H, $CH_2CH{=}CH_A\mathit{H}_B$), 5.07 (d, $J$ = 10.0 Hz, 1H, $CH_2CH{=}C\mathit{H}_AH_B$), 5.93 (m, 1H, $CH_2C\mathit{H}{=}CH_2$), 6.10 (q, $J$ = 1.0 Hz, 1H, 3-H), 7.48 (s, 1H, 5-H), 8.86 (s, 1H, 7-OH). $^{13}$C NMR δ: 19.2 (1°, 4-$\mathit{C}H_3$), 33.4 (2°, $\mathit{C}H_2CH{=}CH_2$), 33.9 (1°, 1′-$CH_3$), 108.6 (4°, C-8), 111.1 (3°, C-3), 111.3 (4°, C-4a), 116.8 (2°, $CH_2CH{=}\mathit{C}H_2$), 126.1 (4°, C-6), 130.6 (3°, $CH_2CH{=}CH_2$), 135.3 (3°, C-5), 153.2 (4°, C-4), 153.7 (4°, C-8a), 159.6 (4°, C-2), 164.8 (4°, C-7), 204.7 (4°, C-1′). MS-EI (70 eV) $m/z$: 258 (60.3), 243 (54.4), 230 (21.5), 215 (34.3), 187 (13.2), 115 (27.4), 91 36.7), 77 (41.6), 65 (43.6), 43 (100). Anal. calcd. for $C_{15}H_{14}O_4$: C 69.75, H 5.46; found: C 69.71, H 5.43.

### *Compound 3c*

Mp 110 °C. IR (cm$^{-1}$): 3060, 2960, 1730, 1710, 1620, 1580, 1465, 1400, 1310. $^1$H NMR δ: 1.21 (t, $J$ = 7.0 Hz, 3H, 2′-$CH_3$), 3.40 (q, $J$ = 7.0 Hz, 2H, 1′-$CH_2$), 3.47 (br d, $J$ = 7.0 Hz, 2H, $C\mathit{H}_2CH{=}CH_2$), 5.04 (d, $J$ = 7.0 Hz, 1H, $CH_2CH{=}C\mathit{H}_AH_B$), 5.10 (d, $J$ = 17.0 Hz, 1H, $CH_2CH{=}CH_A\mathit{H}_B$), 5.96 (m, 1H, $CH_2C\mathit{H}{=}CH_2$), 6.24 (d, $J$ = 10.0 Hz, 1H, 3-H), 7.38 (s, 1H, 5-H), 7.62 (d, $J$ = 10.0 Hz, 1H, 4-H), 14.20 (s, 1H, 7-OH). MS-EI (70 eV) $m/z$: 258 (62.4), 243 (2.9), 229 (100), 212 (3.4), 201 (33.3), 185 (3.8), 173 (8.9), 145 (3.4), 128 (2.9), 115 (7.2). Anal. calcd. for $C_{15}H_{14}O_4$: C 69.75, H 5.46; found: C 69.71, H 5.49.

### *Compound 3d*

Mp 125 °C. IR (cm$^{-1}$): 3080, 2960, 1740, 1710, 1610, 1560, 1450, 1395. $^1$H NMR δ: 1.17 (t, $J$ = 7.0 Hz, 3H, 2′-$CH_3$), 2.34 (d, $J$ = 1.0 Hz, 3H, 4-$CH_3$), 3.30 (q, $J$ = 7.0 Hz, 2H, 1′-$CH_2$), 3.35 (br d, $J$ = 6.5 Hz, 2H, $C\mathit{H}_2CH{=}CH_2$), 5.04 (d, $J$ = 17.0 Hz, 1H, $CH_2CH{=}CH_A\mathit{H}_B$), 5.05 (d, $J$ = 10.0 Hz, 1H, $CH_2CH{=}C\mathit{H}_AH_B$), 5.91 (m, 1H, $CH_2C\mathit{H}{=}CH_2$), 6.06 (q, $J$ = 1.0 Hz, 1H, 3-H), 7.43 (s, 1H, 5-H), 14.00 (s, 1H, 7-OH). $^{13}$C NMR δ: 8.2 (1°, 2′-$\mathit{C}H_3$), 19.2 (1°, 4-$\mathit{C}H_3$), 33.5 (2°, $\mathit{C}H_2CH{=}CH_2$), 39.7 (2°, 1′-$CH_2$), 108.7 (4°, C-8), 111.0 (3°, C-3), 111.3 (4°, C-4a), 116.8 (2°, $CH_2CH{=}\mathit{C}H_2$), 126.2 (4°, C-6), 130.3 (3°, $CH_2\mathit{C}H{=}CH_2$), 135.3 (3°, C-5), 153.2 (4°, C-4), 153.7 (4°, C-8a), 159.7 (4°, C-2), 164.7 (4°, C-7), 207.8 (4°, C-1′). MS-EI (70 eV) $m/z$: 272 (49.1), 257 (5.9), 243 (100), 215 (19.6), 201 (2.3), 117 (4.7), 115 (2.5). Anal. calcd. for $C_{16}H_{16}O_4$: C 70.57, H 5.92; found: C 70.60, H 5.87.

### *Compound 3e*

Mp 84 °C. IR (cm$^{-1}$): 3085, 2970, 1735, 1720, 1625, 1565, 1455, 1400. $^1$H NMR δ: 1.05 (t, $J$ = 7.2 Hz, 3H, 3′-$CH_3$), 1.81 (tq, $J$ = 7.2 Hz, 7.2 Hz, 2H, 2′-$CH_2$), 3.35 (t, $J$ = 7.2 Hz, 2H, 1′-$CH_2$), 3.42 (br d, $J$ = 6.6 Hz, 2H, $C\mathit{H}_2CH{=}CH_2$), 5.13 (d, $J$ = 16.0 Hz, 1H, $CH_2CH{=}CH_A\mathit{H}_B$), 5.14 (d, $J$ = 10.0 Hz, 1H, $CH_2CH{=}C\mathit{H}_AH_B$), 5.99 (ddt, $J$ = 16.0, 10.0, 6.6 Hz, 1H, $CH_2C\mathit{H}{=}CH_2$), 6.27 (d, $J$ = 9.5 Hz, 1H, 3-H), 7.38 (s, 1H, 5-H), 7.62 (d, $J$ = 9.5 Hz, 1H, 4-H), 14.16 (s, 1H, 7-OH). MS-EI (70 eV) $m/z$: 272 (43), 257 (8), 244 (1), 229 (100), 201 (10), 173 (3), 115 (5). Anal. calcd. for $C_{16}H_{16}O_4$: C 70.57, H 5.92; found: C 70.55, H 5.99.

### *Compound 3f*

Mp 98 °C. IR (cm$^{-1}$): 3080, 2960, 1740, 1725, 1620, 1560, 1450, 1390. $^1$H NMR δ: 1.03 (t, $J$ = 7.0 Hz, 3H, 3′-$CH_3$), 1.78 (tq, $J$ = 7.0 Hz, 7.0 Hz, 2H, 2′-$CH_2$), 2.40 (d, $J$ = 1.0 Hz, 3H, 4-$CH_3$), 3.32 (t, $J$ = 7.0 Hz, 2H, 1′-$CH_2$), 3.43 (br d, $J$ = 6.5 Hz, 2H, $C\mathit{H}_2CH{=}CH_2$), 5.08 (d, $J$ = 9.0 Hz, 1H, $CH_2CH{=}C\mathit{H}_AH_B$), 5.11 (d, $J$ = 16.0 Hz, 1H, $CH_2CH{=}CH_A\mathit{H}_B$), 5.98 (m, 1H, $CH_2C\mathit{H}{=}CH_2$), 6.13 (q, $J$ = 1.0 Hz, 1H, 3-H), 7.49 (s, 1H, 5-H), 14.07 (s, 1H, 7-OH). $^{13}$C NMR δ: 13.6 (1°, 3′-$\mathit{C}H_3$), 17.7 (2°, 2′-$\mathit{C}H_2$), 19.2 (1°, 4-$\mathit{C}H_3$), 33.4 (2°, $\mathit{C}H_2CH{=}CH_2$), 46.8 (2°, 1′-$\mathit{C}H_2$), 108.7 (4°, C-8), 111.0 (3°, C-3), 111.2 (4°, C-4a), 116.7 (2°, $CH_2CH{=}\mathit{C}H_2$), 126.1 (4°, C-6), 130.2 (3°, $CH_2CH{=}CH_2$), 135.3 (3°, C-5), 153.0 (4°, C-4), 153.6 (4°, C-8a), 159.6 (4°, C-7), 164.7 (4°, C-2), 207.3 (4°, C-1′). MS-EI (70 eV) $m/z$: 286 (61.1), 271 (12.8), 258 (2.9), 253 (8.5), 243 (100), 225 (2.9), 215 (14.5), 201 (2.1), 187 (4.3), 115 (9.8). Anal. calcd. for $C_{17}H_{18}O_4$: C 71.31, H 6.34; found: C 71.25, H 6.30.

### *Compound 3g*

Mp 119 °C. IR (cm$^{-1}$): 3060, 1730, 1710, 1620, 1575, 1450, 1400, 1345. $^1$H NMR δ: 3.49 (br d, *J* = 6.6 Hz, 2H, C*H*$_2$CH=CH$_2$), 5.17 (d, *J* = 12.0 Hz, 1H, CH$_2$CH=C*H*$_A$H$_B$), 5.18 (d, *J* = 15.0 Hz, 1H, CH$_2$CH=CH$_A$*H*$_B$), 6.02 (ddt, *J* = 15.0, 12.0, 6.6 Hz, 1H, CH$_2$C*H*=CH$_2$), 6.16 (d, *J* = 9.0 Hz, 1H, 3-H), 7.43 (s, 1H, 5-H), 7.46 (t, *J* = 9.0 Hz, 2H, 3′-H and 5′-H), 7.59 (d, *J* = 9.0 Hz, 1H, 4-H), 7.61 (br t, *J* = 9.0 Hz, 1H, 4′-H), 7.67 (br d, *J* = 9.0 Hz, 2H, 2′-H and 6′-H), 11.56 (s, 1H, 7-OH). Anal. calcd. for $C_{19}H_{14}O_4$: C 74.50, H 4.60; found: C 74.48, H 4.56.

### *Compound 3h*

Mp 180 °C. IR (cm$^{-1}$): 3060, 1710, 1695, 1590, 1555, 1425, 1365. $^1$H NMR δ: 2.26 (d, *J* = 1.0 Hz, 3H, 4-CH$_3$), 3.68 (br d, *J* = 6.5 Hz, 2H, C*H*$_2$CH=CH$_2$), 5.06 (dq, *J* = 10.0, 1.0 Hz, 1H, CH$_2$CH=C*H*$_A$H$_B$), 5.17 (dq, *J* = 16.0, 1.0 Hz, 1H, CH$_2$CH=CH$_A$*H*$_B$), 5.96 (m, 1H, CH$_2$C*H*=CH$_2$), 6.16 (q, *J* = 1.0 Hz, 1H, 3-H), 7.68 (s, 1H, 5-H), 7.71 (m, 5H, C$_6$H$_5$), 12.76 (s, 1H, 7-OH). Anal. calcd. for $C_{20}H_{16}O_4$: C 74.99, H 5.03; found: C 74.97, H 5.02.

Subsequent elution of the silica column of crude Claisen products from compounds **2a**, **2c**, and **2e** with petroleum ether/EtOAc (96:4, *v*/*v*) afforded the 3-allyl-8-coumarinyl ketones **4a**, **4c**, and **4e**, as appropriate. The products were crystallized from EtOAc/petroleum ether.

### *Compound 4a*

Mp 147 °C. IR (cm$^{-1}$): 3080, 2960, 1730, 1710, 1610, 1400, 1325. $^1$H NMR δ: 2.62 (sharp s, 3H, 1′-CH$_3$), 3.55 (br d, *J* = 7.0 Hz, 2H, 3-C*H*$_2$CH=CH$_2$), 4.99 (d, *J* = 13.0 Hz, 1H, 3-CH$_2$CH=C*H*$_A$H$_B$), 5.00 (d, *J* = 16.0 Hz, 1H, 3-CH$_2$CH=CH$_A$*H*$_B$), 5.90 (ddt, *J* = 16.0, 13.0, 7.0 Hz, 1H, 3-CH$_2$C*H*=CH$_2$), 6.22 (d, *J* = 9.5 Hz, 1H, 6-H), 7.57 (d, *J* = 9.5 Hz, 1H, 5-H), 7.74 (s, 1H, 4-H), 12.93 (s, 1H, 7-OH). $^{13}$C NMR δ: 26.3 (2°, 3-*C*H$_2$CH=CH$_2$), 26.5 (1°, 1′-CH$_3$), 111.3 (4°, C-8), 113.6 (3°, C-6), 115.9 (2°, 3-CH$_2$CH=*C*H$_2$), 116.5 (4°, C-4a), 116.7 (4°, C-3), 129.2 (t, 3-CH$_2$*C*H=CH$_2$), 134.2 (3°, C-5), 143.2 (3°, C-4), 156.7 (4°, C-8a), 159.8 (4°, C-2), 163.5 (4°, C-7), 203.4 (4°, C-1′). MS-EI (70 eV) *m*/*z*: 244 (82.1), 229 (100), 211 (5.9), 201 (55.9), 187 (20.9), 173 (17.9), 155 (3.4), 145 (7.7), 127 (6.4), 115 (29.9). Anal. calcd. for $C_{14}H_{12}O_4$: C 68.84, H 4.95; found: C 68.82, H 4.91.

### *Compound 4c*

Mp 130 °C. IR (cm$^{-1}$): 3080, 2970, 1735, 1710, 1620, 1560, 1450, 1400, 1360. $^1$H NMR δ: 1.24 (t, *J* = 7.0 Hz, 3H, 2′-CH$_3$), 3.08 (q, *J* = 7.0 Hz, 2H, 1′-CH$_2$), 3.60 (br d, *J* = 7.0 Hz, 2H, 3-C*H*$_2$CH=CH$_2$), 5.02 (d, *J* = 10.0 Hz, 1H, 3-CH$_2$CH=C*H*$_A$H$_B$), 5.10 (d, *J* = 17.0 Hz, 1H, 3-CH$_2$CH=CH$_A$*H*$_B$), 5.95 (m, 1H, 3-CH$_2$C*H*=CH$_2$), 6.28 (d, *J* = 10.0 Hz, 1H, 6-H), 7.64 (d, *J* = 10.0 Hz, 1H, 5-H), 7.84 (s, 1 H, 4-H), 13.12 (s, 1 H, 7-OH). MS-EI (70 eV) *m*/*z*: 258 (35.5), 243 (5.1), 229 (100), 201 (54.7), 185 (2.1), 173 (8.5), 145 (3.8), 128 (4.7), 115 (13.6). Anal. calcd. for $C_{15}H_{14}O_4$: C 69.75, H 5.46; found: C 69.70, H 5.42.

### *Compound 4e*

Mp 132 °C. IR (cm$^{-1}$): 3090, 2975, 1740, 1725, 1620, 1570, 1470, 1400. $^1$H NMR δ: 1.04 (t, *J* = 7.2 Hz, 3H, 3′-CH$_3$), 1.80 (tq, *J* = 7.2 Hz, 7.2 Hz, 2H, 2′-CH$_2$), 3.00 (t, *J* = 7.2 Hz, 2H, 1′-CH$_2$), 3.61 (br d, *J* = 6.3 Hz, 2 H, 3-C*H*$_2$CH=CH$_2$), 5.02 (d, *J* = 10.0 Hz, 1H, 3-CH$_2$CH=C*H*$_A$H$_B$), 5.12 (d, *J* = 17.0 Hz, 1H, 3-CH$_2$CH=CH$_A$*H*$_B$), 5.97 (ddt, *J* = 17.0, 10.0, 6.3 Hz, 1H, 3-CH$_2$C*H*=CH$_2$), 6.27 (d, *J* = 9.6 Hz, 1H, 6-H), 7.63 (d, *J* = 9.6 Hz, 1H, 5-H), 7.83 (s, 1H, 4-H), 13.16 (s, 1H, 7-OH). MS-EI (70 eV) *m*/*z*: 272 (40), 257 (10), 244 (1.5), 229 (100), 201 (18), 173 (2), 145 (1), 115 (5). Anal. calcd. for $C_{16}H_{16}O_4$: C 70.57, H 5.92; found: C 70.53, H 5.94.

Further elution of the silica column of Claisen product mixture from compounds **2b**, **2d**, and **2f** afforded the 8-allyl-6-coumarinyl ketones **4b**, **4d**, and **4f**, respectively, from later petroleum ether/EtOAc (96:4, *v*/*v*) eluate fractions and subsequent crystallization from the appropriate solvent–solvent mixture.

### *Compound 5b*

Mp 98 °C. IR (cm$^{-1}$): 3080, 2960, 1730, 1710, 1620, 1590, 1395, 1270. $^1$H NMR δ: 2.43 (d, *J* = 1.0 Hz, 3H, 4-CH$_3$), 2.69 (sharp s, 3H, 1′-CH$_3$), 3.58 (br d, *J* = 7.0 Hz, 2H, 8-C*H*$_2$CH=CH$_2$), 5.00 (d, *J* = 10.0 Hz, 1H, 8-CH$_2$CH=C*H*$_A$H$_B$), 5.08 (d, *J* = 17.0 Hz, 1H, 8-CH$_2$CH=CH$_A$*H*$_B$), 5.94 (m, 1H, 8-CH$_2$C*H*=CH$_2$), 6.16 (q, *J* = 1.0 Hz, 1H, 3-H), 7.88 (s, 1H, 5-H), 12.96 (s, 1H, 7-OH). $^{13}$C NMR δ: 18.6 (1°, 4-CH$_3$), 26.4 (2°, 8-*C*H$_2$CH=CH$_2$), 26.5 (1°, 1′-CH$_3$), 112.4 (q, C-6), 112.6 (3°, C-3), 115.7 (2°, 8-CH$_2$CH=*C*H$_2$), 116.1 (4°, C-4a), 116.3 (4°, C-8), 125.7 (3°, 8-CH$_2$*C*H=CH$_2$), 134.2 (3°, C-5), 151.9 (4°, C-4), 156.1 (4°, C-8a), 159.9 (4°, C-2), 163.1 (4°, C-7), 203.5 (4°, C-1′). Anal. calcd. for $C_{15}H_{14}O_4$: C 69.75, H 5.46; found: C 69.72, H 5.44.

### *Compound 5d*

Mp 110 °C. IR (cm$^{-1}$): 3080, 2960, 1740, 1710, 1620, 1590, 1450, 1395. $^1$H NMR δ: 1.32 (t, *J* = 7.0 Hz, 3H, 2′-CH$_3$), 2.45 (d, *J* = 1.0 Hz, 3H, 4-CH$_3$), 3.15 (q, *J* = 7.0 Hz, 2H, 1′-CH$_2$), 3.68 (br d, *J* = 7.0 Hz, 2H, 8-C*H*$_2$CH=CH$_2$), 5.06 (d, *J* = 10.0 Hz, 1H, 8-CH$_2$CH=C*H*$_A$H$_B$), 5.15 (d, *J* = 18.0 Hz, 1H, 8-CH$_2$CH=CH$_A$*H*$_B$), 5.99 (m, 1H, 8-CH$_2$C*H*=CH$_2$), 6.20 (s, 1H, 4-H), 7.95 (s, 1H, 5-H), 13.20 (s, 1H, 7-OH). $^{13}$C NMR δ: 8.2 (1°, 2′-*C*H$_3$), 18.4 (1°, 4-*C*H$_3$), 26.5 (2°, 8-*C*H$_2$CH=CH$_2$), 31.5 (2°, 1′-CH$_2$), 112.5 (4°, C-6), 112.6 (3°, C-3), 115.8 (2°, 8-CH$_2$CH=*C*H$_2$), 116.0 (4°, C-8), 116.6 (4°, C-4a), 124.8 (3°, 8-CH$_2$*C*H=CH$_2$), 134.5 (3°, C-5), 151.7 (4°, C-4), 156.2 (4°, C-8a), 159.7 (4°, C-2), 163.4 (4°, C-7), 206.2 (4°, C-1′). MS-EI (70 eV) *m*/*z*: 272 (58.5),. 257 (10.6), 243 (100), 215 (29.9), 201 (1.6), 187 (7.2), 159 (1.7), 115 (2.5). Anal. calcd. for $C_{16}H_{16}O_4$: C 70.57, H 5.92; found: C 70.95, H 5.90.

### *Compound 5f*

Mp 128 °C. IR (cm$^{-1}$): 3080, 2960, 1740, 1715, 1620, 1570, 1450, 1390. $^1$H NMR δ: 1.10 (t, *J* = 8.0 Hz, 3H, 3′-CH$_3$), 1.80 (tq, *J* = 8.0 Hz, 8.0 Hz, 2H, 2′-CH$_2$), 2.50 (d, *J* = 1.0 Hz, 3H, 4-CH$_3$), 3.08 (t, *J* = 8.0 Hz, 2H, 1′-CH$_2$), 3.68 (br d, *J* = 7.0 Hz, 2H, 8-C*H*$_2$CH=CH$_2$), 5.08 (d, *J* = 11.0 Hz, 1H, CH$_2$CH=C*H*$_A$H$_B$), 5.18 (d, *J* = 18.0 Hz, 1H, 8-CH$_2$CH=CH$_A$*H*$_B$), 6.00 (m, 1H, 8-CH$_2$C*H*=CH$_2$), 6.24 (s, 1H, 4-H), 7.95 (s, 1H, 5-H), 13.24 (s, 1H, 7-OH). $^{13}$C NMR δ: 13.7 (1°, 3′-*C*H$_3$), 18.0 (2°, 2′-*C*H$_2$), 18.7 (1°, 4-*C*H$_3$), 26.5 (2°, 8-*C*H$_2$CH=CH$_2$), 40.1 (2°, 1′-CH$_2$), 112.5(q, C-6), 112.8 (3°, C-3), 115.8 (2°, 8-CH$_2$CH=*C*H$_2$), 116.2 (4°, C-8), 116.6 (4°, C-4a), 125.0 (3°, 8-CH$_2$*C*H=CH$_2$), 134.5 (3°, C-5), 151.7 (4°, C-4), 156.3 (4°, C-8a), 159.8 (4°, C-2), 163.5 (4°, C-7), 205.8 (4°, C-1′). MS-EI (70 eV) *m/z*: 286 (63.2), 271 (21.3), 258 (3.4), 243 (100), 215 (12.8), 201 (2.5), 187 (8.5), 115 (6.8). Anal. calcd. for $C_{17}H_{18}O_4$: C 71.31, H 6.34; found: C 71.27, H 6.29.

## 7-*O*(Cyclohex-2′-ene-1′-yl)-8-coumarinyl ketones 6a–6h

### *General procedure*

Pure and dried 7-hydroxy-8-coumarinyl ketone **1a–1h** (2.5 mmol) taken in dry acetone (50 mL) were refluxed with 3-bromocyclohexene (0.4 mL, 0.003 mole) and $NEt_3$ (1 mL, 0.726 g, 0.007 mole) for 4 h. After distilling off acetone, water (10 mL) was added, and the content was acidified with cold dil HCl (4 N, 15 mL). The organic part of the mixture was then extracted with $CHCl_3$ (50 mL), which was washed successively with a saturated brine solution (15 mL), a saturated $NaHCO_3$ solution (2 × 15 mL), and again with a saturated brine solution (3 × 15 mL). The $CHCl_3$ layer was dried over anhydrous $Na_2SO_4$ for 30 min, filtered, and excess $CHCl_3$ was distilled off to obtain an oily mass. TLC experiment showed that the oily mass was more polar than the starting material on using 5% EtOAc/benzene as developer solvent. The oily mass was then column chromatographically filtered. Crystals of **6a–6h** were obtained on eluting with 10% EtOAc/petroleum ether and subsequent crystallization of the products.

### *Compound 6a*

Mp 118 °C. IR (cm$^{-1}$): 3071, 2925, 1722, 1666, 1607, 1560, 1489, 1436, 1400. $^1$H NMR δ: 1.66–1.63 (br m, 1H, 6′-H$_{ax}$), 1.93–1.82 (br m, 3H, 5′-H$_2$, 6′-H$_{eq}$), 2.18–2.01 (br m, 2H, 4′-H$_2$), 2.54 (sharp s, 3H, 8-COCH$_3$), 4.89 (br s, 1H, 1′-H), 5.78 (br d, *J* = 12.3 Hz, 1H, 2′-H), 5.98 (br dt, *J* = 11.1 Hz, 3.8 Hz, 1H, 3′-H), 6.21 (d, *J* = 9.6 Hz, 1H, 3-H), 6.90 (d, *J* = 8.7 Hz, 1H, 6-H), 7.41 (d, *J* = 8.7 Hz, 1H, 5-H), 7.76 (d, *J* = 9.6 Hz, 1H, 4-H). $^{13}$C NMR δ: 18.67 (2°, C-5′), 24.90 (2°, C-4′), 28.39 (2°, C-6′), 32.13 (1°, 8-CO*C*H$_3$), 72.81 (3°, C-1′), 110.16 (3°, C-6), 112.83 (4°, C-4a), 113.72 (3°, C-3), 120.87 (4°, C-8), 124.85 (3°, C-2′), 129.29 (3°, C-5), 133.34 (3°, C-3′), 142.85 (3°, C-4), 151.49 (4°, C-8a), 157.53 (4°, C-2), 159.68 (4°, C-7), 198.53 (4°, 8-*C*OCH$_3$). Anal. calcd. for $C_{17}H_{16}O_4$: C 71.82, H 5.67; found: C 71.85, H 5.66.

### *Compound 6b*

Mp 90 °C. IR (cm$^{-1}$): 3418, 3029, 2939, 1724, 1601, 1488, 1378, 1282. $^1$H NMR δ: 1.70–1.62 (br m, 1H, 6′-H$_{ax}$), 1.81–1.75 (br m, 3H, 5′-H$_2$, 6′-H$_{eq}$), 2.08–2.02 (br m, 2H, 4′-H$_2$), 2.36 (d, *J* = 1.0 Hz, 3H, 4-CH$_3$), 2.60 (sharp s, 3H, 8-COCH$_3$), 4.88 (br s, 1H, 1′-H), 5.79 (br dt, *J* = 11.1 Hz, 2.7 Hz, 1H, 2′-H), 5.97 (br dt, *J* = 10.0 Hz, 2.7 Hz, 1H, 3′-H), 6.09 (q, *J* = 1.0 Hz, 1H, 3-H), 6.90 (d, *J* = 8.7 Hz, 1H, 6-H), 7.52 (d, *J* = 8.7 Hz, 1H, 5-H). Anal. calcd. for $C_{18}H_{18}O_4$: C 72.47, H 6.08; found: C 72.48, H 6.05.

### *Compound 6c*

Mp 104 °C. IR (cm$^{-1}$): 3031, 2937, 1725, 1714, 1605, 1560, 1484, 1406. $^1$H NMR δ: 1.17 (t, *J* = 7.2 Hz, 3H, 8-COCH$_2$C*H*$_3$), 1.64–1.59 (br m, 1H, 6′-H$_{ax}$), 1.84–1.73 (br m, 3H, 5′-H$_2$, 6′-H$_{eq}$), 1.92–1.85 (br m, 2H, 4′-H$_2$), 2.82 (q, *J* = 7.2 Hz, 2H, 8-COC*H*$_2$CH$_3$), 4.87 (s, 1H, 1′-H), 5.78 (br dt, *J* = 7.2 Hz, 3.1 Hz, 1H, 2′-H), 5.97 (br dt, *J* = 7.2 Hz, 3.2 Hz, 1H, 3′-H), 6.20 (d, *J* = 9.6 Hz, 1H, 3-H), 6.89 (d, *J* = 8.7 Hz, 1H, 6-H), 7.40 (d, *J* = 8.7 Hz, 1H, 5-H), 7.61 (d, *J* = 9.6 Hz, 1H, 4-H). $^{13}$C NMR δ: 7.55 (1°, 8-COCH$_2$*C*H$_3$), 13.73 (3°, C-3), 18.65 (2°, C-5′), 24.93 (2°, C-4′), 28.42 (2°, C-6′), 38.00 (2°, 8-CO*C*H$_2$CH$_3$), 72.74 (3°, C-1′), 110.14 (3°, C-6), 112.84 (4°, C-4a), 120.85 (4°, C-8), 124.90 (3°, C-2′), 129.10 (3°, C-5), 133.28 (3°, C-3′), 142.85 (3°, C-4), 151.52 (4°, C-8a), 157.54 (4°, C-2), 159.72 (4°, C-7), 201.98 (4°, 8-*C*OCH$_2$CH$_3$). Anal. calcd. for $C_{18}H_{18}O_4$: C 72.47, H 6.08; found: C 72.42, H 6.09.

### *Compound 6d*

Mp 89 °C. IR (cm$^{-1}$): 3035, 2958, 1726, 1668, 1607, 1568, 1490, 1484, 1377. $^1$H NMR δ: 1.18 (t, *J* = 7.2 Hz, 3H, 8-COCH$_2$C*H*$_3$), 1.67–1.61 (br m, 1H, 6′-H$_{ax}$), 1.96–1.90 (br m, 3H, 5′-H$_2$, 6′-H$_{eq}$), 2.14–2.03 (br m, 2H, 4′-H$_2$), 2.37 (d, *J* = 1.0 Hz, 3H, 4-CH$_3$), 2.83 (q, *J* = 7.2 Hz, 2H, 8-COC*H*$_2$CH$_3$), 4.44 (br s, 1H, 1′-H), 5.80 (br d, *J* = 10.5 Hz, 1H, 2′-H), 5.98 (br d, *J* = 10.0 Hz, 1H, 3′-H), 6.11 (q, *J* = 1.0 Hz, 1H, 3-H), 6.91 (d, *J* = 8.8 Hz, 1H, 6-H) 7.52 (d, *J* = 8.8 Hz, 1H, 5-H). Anal. calcd. for $C_{19}H_{20}O_4$: C 73.06, H 6.45; found: C 73.09, H 6.44.

### *Compound 6e*

Mp 72 °C. IR (cm$^{-1}$): 3047, 2929, 1727, 1702, 1607, 1560, 1485, 1458. $^1$H NMR δ: 0.96 (t, *J* = 7.4 Hz, 3H, 8-COCH$_2$CH$_2$C*H*$_3$), 1.67–1.63 (br m, 1H, 6′-H$_{ax}$), 1.72 (tq, *J* = 7.3 Hz, 7.3 Hz, 2H, 8-COCH$_2$C*H*$_2$CH$_3$), 1.84–1.82 (br m, 3H, 5′-H$_2$, 6′-H$_{eq}$), 2.07–2.01 (br m, 2H, 4′-H), 2.81 (t, *J* = 7.2 Hz, 2H, 8-COC*H*$_2$CH$_2$CH$_3$), 4.87 (br s, 1H, 1′-H), 5.79 (br dt, *J* = 10.0 Hz, 2.8 Hz, 1H, 2′-H), 5.97 (br dt, *J* = 10.0 Hz, 3.4 Hz, 1H, 3′-H), 6.20 (d, *J* = 9.5 Hz, 1H, 3-H), 6.87 (d, *J* = 8.7 Hz, 1H, 6-H), 7.39 (d, *J* = 8.7 Hz, 1H, 5-H), 7.60 (d, *J* = 9.5 Hz, 1H, 4-H). $^{13}$C NMR δ: 13.64 (1°, 8-COCH$_2$CH$_2$*C*H$_3$), 16.92 (2°, 8-COCH$_2$*C*H$_2$CH$_3$), 18.66 (2°, C-5′), 24.93 (2°, C-4′), 28.40 (2°, C-6′), 46.76 (2°, 8-CO*C*H$_2$CH$_2$CH$_3$), 72.70 (3°, C-1′), 110.08 (3°, C-6), 112.81 (4°, C-4a), 113.71 (3°, C-3), 120.95 (4°, C-8), 124.90 (3°, C-2′), 129.98 (3°, C-5), 133.23 (3°, C-3′), 142.85 (3°, C-4), 151.54 (4°, C-8a), 157.55 (4°, C-2), 159.71 (4°, C-7), 201.41 (4°, 8-*C*OCH$_2$CH$_2$CH$_3$). Anal. calcd. for $C_{19}H_{20}O_4$: C 73.06, H 6.45; found: C 73.05, H 6.48.

### *Compound 6f*

Mp 64 °C. IR (cm$^{-1}$): 2952, 1735, 1718, 1611, 1570, 1491, 1434, 1408. $^1$H NMR δ: 0.95 (t, *J* = 7.4 Hz, 3H, 8-COCH$_2$CH$_2$C*H*$_3$), 1.67–1.63 (br m, 2H, 6′-H$_2$), 1.71 (tq, *J* = 7.3 Hz, 7.3 Hz, 2H, 8-COCH$_2$C*H*$_2$CH$_3$), 1.92–1.86 (br m, 2H, 5′-H$_2$), 2.07–2.01 (br m, 2H, 4′-H$_2$), 2.36 (d, *J* = 1.0 Hz, 3H, 4-CH$_3$), 2.77 (t, *J* = 7.2 Hz, 2H, 8-COC*H*$_2$CH$_2$CH$_3$), 4.86 (br d, *J* = 2.0 Hz, 1H, 1′-H), 5.78 (br dt, *J* = 10.0 Hz, 2.7 Hz, 1H, 2′-H), 5.96 (br dt, *J* = 10.0 Hz, 3.2 Hz, 1H, 3′-H), 6.07 (q, *J* = 1.0 Hz, 1H, 3-H), 6.89 (d, *J* = 8.9 Hz, 1H, 6-H), 7.50 (d, *J* = 8.9 Hz, 1H, 5-H). Anal. calcd. for $C_{20}H_{22}O_4$: C 73.60, H 6.79; found: C 73.62, H 6.81.

### *Compound 6g*

Mp 99 °C. IR (cm$^{-1}$): 2934, 1728, 1674, 1605, 1560, 1486, 1448, 1402. $^1$H NMR δ: 1.43–1.36 (br m, 1H, 6-H′$_{ax}$), 1.76–1.66 (br m, 3H, 5′-H$_{2,\ 6}$′-H$_{eq}$), 1.90–1.85 (br m, 2H, 4′-H$_2$), 4.82 (br d, *J* = 3.3 Hz, 1H, 1′-H), 5.69 (br dt, *J* = 11.0 Hz, 3.5 Hz, 1.55 Hz, 1H, 2′-H), 5.83 (br dt, *J* =

10.2 Hz, 3.24 Hz, 1H, 3′-H), 5.85 (d, *J* = 9.5 Hz, 1H, 3-H), 6.20 (d, *J* = 8.7 Hz, 1H, 6-H), 7.38 (t, *J* = 7.4 Hz, 2H, 3′′-H and 5′′-H), 7.50 (d, *J* = 8.7 Hz, 1H, 5-H), 7.54 (br t, *J* = 7.5 Hz, 1H, 4′′-H), 7.65 (d, *J* = 9.5 Hz, 1H, 4-H), 7.83 (br d, *J* = 7.18 Hz, 2H, 2′′-H and 6′′-H). Anal. calcd. for $C_{22}H_{18}O_4$: C 76.29, H 5.24; found: C 76.32, H 5.22.

### *Compound 6h*

Mp 130 °C. IR (cm$^{-1}$): 3063, 2905, 1730, 1665, 1608, 1575, 1491, 1440, 1381. $^1$H NMR δ: 1.46–1.41 (br m, 2H, 6′-H$_2$), 1.78–1.66 (br m, 2H, 5′-H$_2$), 1.88–2.00 (br m, 2H, 4′-H$_2$), 2.44 (d, *J* = 1.0 Hz, 3H, 4-CH$_3$), 4.86 (br s, 1H, 1′-H), 5.72 (br d, *J* = 9.8 Hz, 1H, 2′-H), 5.88 (br d, *J* = 9.9 Hz, 1H, 3′-H), 6.13 (q, *J* = 1.0 Hz, 1H, 3-H), 7.00 (d, *J* = 8.7 Hz, 1H, 6-H), 7.42 (t, *J* = 7.4 Hz, 2H, 3′′-H and 5′′-H), 7.57 (br t, *J* = 7.18 Hz, 1H, 4′′-H), 7.64 (d, *J* = 8.7 Hz, 1H, 5-H), 7.83 (br d, *J* = 7.4 Hz, 2H, 2′′-H and 6′′-H). Anal. calcd. for $C_{23}H_{20}O_4$: C 76.65, H 5.59; found: C 76.68, H 5.58.

## 6-(Cyclohex-2′-ene-1′-yl)-7-hydroxy-8-coumarinyl ketones 7a–7h

### *General procedure*

Pure and dry 7-(cyclohex-2′-ene-1′-yloxy)-8-coumarinyl ketones **6a–6h** (1.8 mmol) were taken in Ph$_2$O (10 mL) and refluxed for 10 min. The brown viscous liquid formed was less polar than the starting material (as shown by TLC experiment on using 5% EtOAc/benzene as developer). The brown liquid was then charged on a column of silica gel and eluted with petroleum ether and then with EtOAc/petroleum ether (1:9 *v*/*v*). The crystals of pure Claisen products **7a–7h** were obtained from the later eluate fraction.

### *Compound 7a*

Mp 120 °C. IR (cm$^{-1}$): 3080, 2920, 1745, 1725, 1610, 1560, 1440, 1400, 1360. $^1$H NMR δ: 1.62–1.48 (br m, 4H, 5′-H$_2$, 6′-H$_2$), 2.09–2.00 (br m, 2H, 4′-H$_2$), 2.95 (sharp s, 3H, 8-COCH$_3$), 3.86 (sextet, *J* = 2.8 Hz, 1H, 1′-H), 5.60 (br dt, *J* = 8 Hz, 2.7 Hz, 1H, 2′-H), 5.99 (br dt, *J* = 10.0 Hz, 2.1 Hz, 1H, 3′-H), 6.24 (br d, *J* = 9.5 Hz, 1H, 3-H), 7.42 (s, 1H, 5-H), 7.64 (d, *J* = 9.5 Hz, 1H, 4-H), 14.17 (s, 1H, 7-OH). $^{13}$C NMR δ: 20.40 (2°, C-5′), 25.10 (2°, C-4′), 29.36 (2°, C-6′), 33.57 (1°, 8-CO*C*H$_3$), 33.64 (3°, C-1′), 108.87 (4°, C-4a), 110.27 (4°, C-8), 111.93 (3°, C-3), 128.67 (3°, C-2′), 129.94 (3°, C-5), 132.36 (4°, C-6), 133.19 (3°, C-3′), 144.24 (3°, C-4), 154.45 (4°, C-8a), 159.59 (4°, C-2), 165.03 (4°, C-7), 204.42 (4°, 8-*C*OCH$_3$). MS *m*/*z*: 285.4 [M + H]$^+$. Anal. calcd. for $C_{17}H_{16}O_4$: C 71.82, H 5.67; found: C 71.85, H 5.66.

### *Compound 7b*

Mp 132 °C. IR (cm$^{-1}$): 3060, 2920, 1736, 1710, 1610, 1555, 1430, 1390, 1360. $^1$H NMR δ: 1.53–1.44 (br m, 1H, 6′-H$_{ax}$), 1.62–1.54 (br m, 3H, 5′-H$_2$, 6′-H$_{eq}$), 2.1–1.99 (br m, 2H, 4′-H$_2$), 2.40 (d, *J* = 1.0 Hz, 3H, 4-CH$_3$), 2.93 (sharp s, 3H, 8-COCH$_3$), 3.89 (q, *J* = 3.0 Hz, 1H, 1′-H), 5.62 (br d, *J* = 8.1 Hz, 1H, 2′-H), 5.99 (br dd, *J* = 10.0 Hz, 2.2 Hz, 1H, 3′-H), 6.12 (q, *J* = 1.0 Hz, 1H, 3-H), 7.53 (s, 1H, 5-H), 14.70 (s, 1H, 7-OH). $^{13}$C NMR δ: 19.04 (1°, 4-CH$_3$), 20.53 (2°, C-5′), 25.05 (2°, C-4′), 29.46 (2°, C-6′), 33.87 (1°, 8-CO*C*H$_3$), 33.97 (3°, C-1′), 108.93 (4°, C-4a), 110.96 (3°, C-3), 111.12 (4°, C-8), 128.76 (3°, C-2′), 129.60 (4°, C-6), 129.87 (3°, C-5), 131.81 (3°, C-3′), 153.07 (4°, C-4), 153.80 (4°, C-8a), 159.45 (4°, C-2), 164.61 (4°, C-7), 200.00 (4°, 8-*C*OCH$_3$). MS *m*/*z*: 299.2 [M + H]$^+$, 321.1 [M + Na]. Anal. calcd. for $C_{18}H_{18}O_4$: C 72.47, H 6.08; found: C 72.45, H 6.09.

### *Compound 7c*

Mp 132 °C. IR (cm$^{-1}$): 3020, 2975, 1735, 1715, 1610, 1560, 1445, 1400. $^1$H NMR δ: 1.25 (t, *J* = 7 Hz, 3H, 8-COCH$_2$C*H*$_3$), 1.62–1.48 (br m, 4H, 6′-H$_2$, 5′-H$_2$), 2.09–1.99 (br m, 2H, 4′-H$_2$), 3.41 (q, *J* = 7.0 Hz, 2H, 8-COC*H*$_2$CH$_3$), 3.87 (q, *J* = 2.7 Hz, 1H, 1′-H), 5.62 (br dt, *J* = 7.7 Hz, 2.3 Hz, 1H, 2′-H), 6.00 (br dt, *J* = 10.0 Hz, 3.4 Hz, 1H, 3′-H), 6.25 (br d, *J* = 9.5 Hz, 1H, 3-H), 7.40 (s, 1H, 5-H) 7.64 (d, *J* = 9.5 Hz, 1H, 4-H), 14.28 (s, 1H, 7-OH). $^{13}$C NMR δ: 8.2 (1°, 8-COCH$_2$*C*H$_3$), 20.41 (2°, C-5′), 25.10 (2°, C-4′), 29.37 (2°, C-6′), 33.67 (3°, C-1′), 38.52 (2°, 8-CO*C*H$_2$CH$_3$), 108.64 (4°, C-4a), 110.27 (4°, C-8), 111.61 (3°, C-3), 128.74 (3°, C-2′), 129.90 (3°, C-5), 132.44 (4°, C-6), 132.91 (3°, C-3′), 144.35 (3°, C-4), 154.35 (4°, C-8a), 159.64 (4°, C-2), 165.03 (4°, C-7), 207.63 (4°, 8-*C*OCH$_2$CH$_3$). MS *m*/*z*: 299.2 [M + H]$^+$, 321.2 [M + Na]. Anal. calcd. for $C_{18}H_{18}O_4$: C 72.47, H 6.08; found: C 72.43, H 6.07.

### *Compound 7d*

Mp 114 °C. IR (cm$^{-1}$): 3033, 2980, 1735, 1710, 1610, 1550, 1400, 1320. $^1$H NMR δ: 1.24 (t, *J* = 7.0 Hz, 3H, 8-COCH$_2$C*H*$_3$), 1.49–1.44 (br m, 1H, 6′-H$_{ax}$), 1.66–1.51 (br m, 3H, 5′-H$_2$, 6′-H$_{eq}$), 2.09–2.03 (br m, 2H, 4′-H$_2$), 2.38 (d, *J* = 1.0 Hz, 3H, 4-CH$_3$), 3.41 (q, *J* = 7.0 Hz, 2H, 8-COC*H*$_2$CH$_3$), 3.89 (br s, 1H, 1′-H), 5.63 (br d, *J* = 9.0 Hz, 1H, 2′-H), 6.00 (br dt, *J* = 10.0 Hz, 2 Hz, 1H, 3′-H), 6.13 (sharp q, *J* = 1.0 Hz, 1H, 3-H), 7.53 (s, 1H, 5-H), 14.20 (s, 1H, 7-OH). $^{13}$C NMR δ: 8.29 (1°, 8-COCH$_2$*C*H$_3$), 19.14 (1°, 4-CH$_3$), 20.57 (2°, C-5′), 25.10 (2°, C-4′), 29.51 (2°, C-6′), 33.92 (3°, C-1′), 38.67 (2°, 8-CO*C*H$_2$CH$_3$), 108.47 (4°, C-4a), 110.93 (3°, C-3), 111.15 (4°, C-8), 128.86 (3°, C-2′), 129.34 (3°, C-5), 129.84 (4°, C-6), 131.92 (3°, C-3′), 153.19 (4°, C-4), 153.73 (4°, C-8a), 159.63 (4°, C-2), 164.64 (4°, C-7), 208.00 (4°, 8-*C*OCH$_2$CH$_3$). MS-EI (70 eV) *m*/*z*: 312 (100, M), 283 (81.8), 258 (39), 229 (13.2), 215 (25.5), 203 (9.1), 187 (10), 128 (10), 115 (10), 91 (8.2), 77 (8.2). Anal. calcd. for $C_{19}H_{20}O_4$: C 73.06, H 6.45; found: C 73.09, H 6.46.

### *Compound 7e*

Mp 114 °C. IR (cm$^{-1}$): 3040, 2970, 1730, 1715, 1610, 1550, 1445, 1405, 1310. $^1$H NMR δ: 1.05 (t, *J* = 7.4 Hz, 3H, 8-COCH$_2$CH$_2$C*H*$_3$), 1.59–1.53 (br m, 1H, 6′-H$_{ax}$), 1.64–1.60 (br m, 3H, 5′-H$_2$, 6′-H$_{eq}$), 1.81 (tq, *J* = 7.2 Hz, 7.2 Hz, 2H, 8-COCH$_2$C*H*$_2$CH$_3$), 2.10–2.02 (br m, 2H, 4′-H$_2$), 3.35 (t, *J* = 7.0 Hz, 2H, 8-COC*H*$_2$CH$_2$CH$_3$), 3.86 (br d, *J* = 2.6 Hz, 1H, 1′-H), 5.62 (br dd, *J* = 10.0 Hz, 3.6 Hz, 1H, 2′-H), 5.99 (br dt, *J* = 10.2 Hz, 3.4 Hz, 1H, 3′-H), 6.25 (br d, *J* = 9.5 Hz, 1H, 3-H), 7.41 (s, 1H, 5-H), 7.64 (d, *J* = 9.5 Hz, 1H, 4-H), 14.00 (s, 1H, 7-OH). $^{13}$C NMR δ: 13.70 (1°, 8-COCH$_2$CH$_2$*C*H$_3$), 17.95 (2°, 8-COCH$_2$*C*H$_2$CH$_3$), 20.41 (2°, C-5′), 25.10 (2°, C-4′), 29.37 (2°, C-6′), 33.70 (3°, C-1′), 46.92 (2°, 8-CO*C*H$_2$CH$_2$CH$_3$), 108.79 (4°, C-4a), 110.27 (4°, C-8), 111.88 (3°, C-3), 128.78 (3°, C-2′), 129.93 (3°, C-5), 132.46 (4°, C-6), 132.97 (3°, C-3′), 144.34 (3°, C-4), 154.32 (4°, C-8a), 159.60 (4°, C-2), 165.15 (4°, C-7), 207.28 (4°, 8-

$COCH_2CH_2CH_3$). MS *m/z*: 313.6 $[M + H]^+$. Anal. calcd. for $C_{19}H_{20}O_4$: C 73.06, H 6.45; found: C 73.05, H 6.44.

### *Compound 7f*

Mp 89 °C. IR ($cm^{-1}$): 2958, 1724, 1711, 1603, 1563, 1490, 1448, 1372. $^1H$ NMR δ: 1.04 (t, *J* = 7.4 Hz, 3H, 8-$COCH_2CH_2CH_3$), 1.54–1.50 (br m, 1H, 6′-$H_{ax}$), 1.68–1.55 (br m, 3H, 5′-$H_2$, 6′-$H_{eq}$), 1.80 (tq, *J* = 7.0 Hz, 7.0 Hz, 2H, 8-$COCH_2CH_2CH_3$), 2.19–2.04 (br m, 2H, 4′-$H_2$), 2.40 (d, *J* = 1.0 Hz, 3H, 4-$CH_3$), 3.34 (t, *J* = 7.05 Hz, 2H, 8-$COCH_2CH_2CH_3$), 3.90 (br s, 1H, 1′-H), 5.63 (br d, *J* = 8.1 Hz, 1H, 2′-H), 6.01 (br dt, *J* = 8.0 Hz, 2.2 Hz, 1H, 3′-H), 6.14 (q, *J* = 1.0 Hz, 1H, 3-H), 7.54 (sharp s, 1H, 5-H), 14.17 (s, 1H, 7-OH). $^{13}C$ NMR δ: 13.67 (1°, 8-$COCH_2CH_2CH_3$), 18.02 (2°, 8-$COCH_2CH_2CH_3$), 19.10 (1°, 4-$CH_3$), 20.60 (2°, C-5′), 25.12 (2°, C-4′), 29.54 (2°, C-6′), 47.04 (2°, 8-$COCH_2CH_2CH_3$), 108.94 (3°, C-1′), 108.95 (4°, C-4a), 111.00 (3°, C-3), 111.17 (4°, C-8), 128.91 (3°, C-2′), 129.36 (3°, C-5), 129.86 (3°, C-3′), 131.93 (4°, C-6), 153.09 (4°, C-4), 153.71 (4°, C-8a), 159.74 (4°, C-2), 164.71 (4°, C-7), 207.60 (4°, 8-$COCH_2CH_2CH_3$). MS *m/z*: 327.3 $[M + H]^+$. Anal. calcd. for $C_{20}H_{22}O_4$: C 73.60, H 6.79; found: C 73.63, H 6.77.

### *Compound 7g*

Mp 138 °C. IR ($cm^{-1}$): 3060, 2950, 1730, 1680, 1565, 1440, 1400, 1340. $^1H$ NMR δ: 1.67–1.54 (m, 3H, 5′-$H_2$, 6′-$H_{ax}$), 2.13–2.05 (br m, 3H, 6′-$H_{eq}$, 4′-$H_2$), 3.93 (br s, 1H, 1′-H), 5.69 (br d, *J* = 9.8 Hz, 1H, 2′-H), 6.04 (br dt, *J* = 10.1 Hz, 2.1 Hz, 1H, 3′-H), 6.16 (br d, *J* = 9.5 Hz, 1H, 3-H), 7.46 (t, *J* = 7.4 Hz, 2H, 3′′-H and 5′′-H), 7.46 (s, 1H, 5-H), 7.61 (br t, *J* = 7.3 Hz, 1H, 4′′-H), 7.62 (d, *J* = 9.3 Hz, 1H, 4-H), 7.68 (br d, *J* = 7.3 Hz, 2H, 2′′-H and 6′′-H), 11.64 (s, 1H, 7-OH). MS *m/z*: 347.4 $[M + H]^+$. Anal. calcd. for $C_{22}H_{18}O_4$: C 76.29, H 5.24; found: C 76.33, H 5.22.

### *Compound 7h*

Mp 175 °C. IR ($cm^{-1}$): 3444, 2926, 1735, 1685, 1617, 1560, 1498, 1449, 1399. $^1H$ NMR δ: 1.84–1.62 (br m, 3H, 5′-$H_2$, 6′-$H_{ax}$), 2.29–2.15 (br m, 3H, 6′-$H_{eq}$, 4′-$H_2$), 2.43 (d, *J* = 1.0 Hz, 3H, 4-$CH_3$), 3.97 (br s, 1H, 1′-H), 5.73 (br d, *J* = 10.0 Hz, 1H, 2′-H), 6.07 (br d, *J* = 10.0 Hz, 1H, 3′-H), 6.16 (q, *J* = 1.0 Hz, 1H, 3-H), 7.48 (t, *J* = 7.4 Hz, 2H, 3′′-H and 5′′-H), 7.59 (s, 1H, 5-H), 7.61 (br t, *J* = 7.3 Hz, 1H, 4′′-H), 7.70 (br d, *J* = 7.3 Hz, 2H, 2′′-H and 6′′-H), 11.39 (s, 1H, 7-OH). MS-EI (70 eV) *m/z*: 360 (100, M), 339 (12.7), 332 (14.1), 317 (10.9), 306 (22.7), 279 (13.6), 263 (63.6), 215 (8.2), 165 (8.2), 115 (10.4), 105 (38.2), 77 (34.1) Anal. calcd. for $C_{23}H_{20}O_4$: C 76.65, H 5.59; found: C 76.63, H 5.61.

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