A New Route to Pyranocoumarins and Their Benzannulated Derivatives

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Abstract: A new protocol based on sequential applications of three atom-economic processes viz. Claisen rearrangement, olefin isomerisation, and ring-closing diene metathesis has been developed to access a range of linear and angularly fused pyranocoumarin derivatives. Incorporation of enyne (in place of diene) metathesis and Diels–Alder reaction in the sequence has allowed the corresponding benzannulated derivatives to be prepared in good yields.

Key words: heterocycle, metathesis, rearrangement, Diels–Alder reaction, isomerization

Coumarins are widely distributed in nature and are found in all parts of plants.[1] Several heteroannulated coumarins of both the linear and angular type display interesting biological activities.[2] Among them, pyranocoumarins are of special importance because of their broad spectrum of biological activities.[3–5] Compounds **1**–**3** (Figure 1) are good examples in this regard, and a great number of methodologies have been developed to access such targets. Amongst them, Trost's palladium-catalysed addition of activated phenols to alkynoates,[6] Nicolaou's Knoevenagel transesterification on solid phase,[7] Liu's gold-catalysed annulation,[8] Yadav's domino Knoevenagel/hetero-Diels–Alder protocol,[9] and multi-component protocols[10] are notable, among others.[11] Moreover, fusion of a benzene ring onto pyranocoumarins has been reported to impart significant changes to the biological and material properties.[12] Therefore, the synthesis of benzo-fused pyranocoumarins continue to be developed.[13] Nevertheless, the development of a common route to angular- and linearly fused pyranocoumarins and their benzo-fused analogues remains important. Several years ago, we reported a sequence of Claisen rearrangement and ring-closing metathesis (RCM) reaction to prepare various medium-ring-sized oxacycle-fused coumarin derivatives **I**–**IV** (Scheme 1).[14] The methodology has found application in the preparation of related systems.[15] We realised that incorporation of an isomerisation step in the sequence would lead to a general and simple synthesis of pyranocoumarin derivatives in a similar fashion; that is, the conversion **II** → **V** → **VI**.

Additionally, the propargyl ether **VII**, derived from the isomerised phenol **V**, on ring-closing enyne metathesis (RCEYM) may lead to the formation of dienes of type **VIII**, which, on Diels–Alder reaction with a suitable dienophile followed by aromatisation of the cycloadduct, would constitute a general synthesis of benzannulated pyranocoumarin derivatives of the type **IX**.

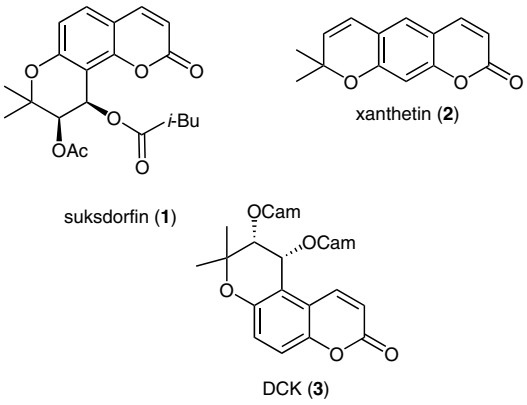
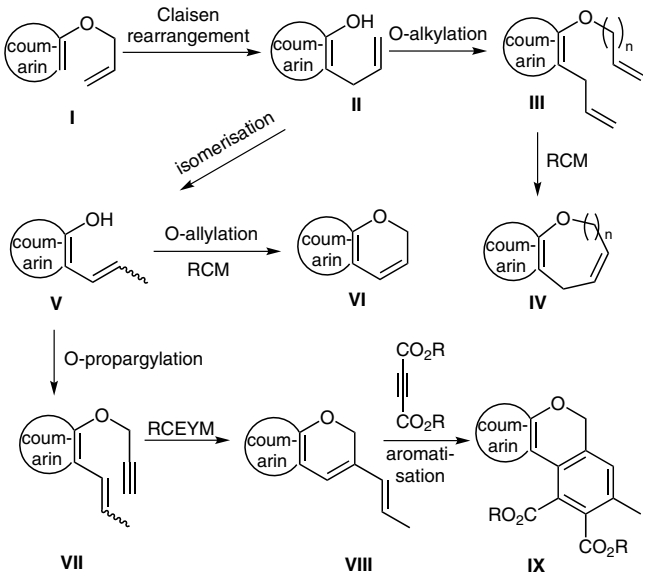


Figure 1 Representative pyran ring fused biologically active coumarins; Cam = camphanoyl



Scheme 1 Synthetic plan

Our synthesis started with the Claisen rearrangement of allyl ether **4** (Scheme 2), obtained by O-allylation of 4-methyl-7-hydroxycoumarin. Claisen rearrangement of **4** was previously carried out[16] by either heating neat or to reflux in *N*,*N*-diethylaniline. We found that the rearrangement also proceeded well upon heating diphenyl ether to reflux, and product isolation was less tedious under the developed conditions. Moreover, the rearranged phenol **5**

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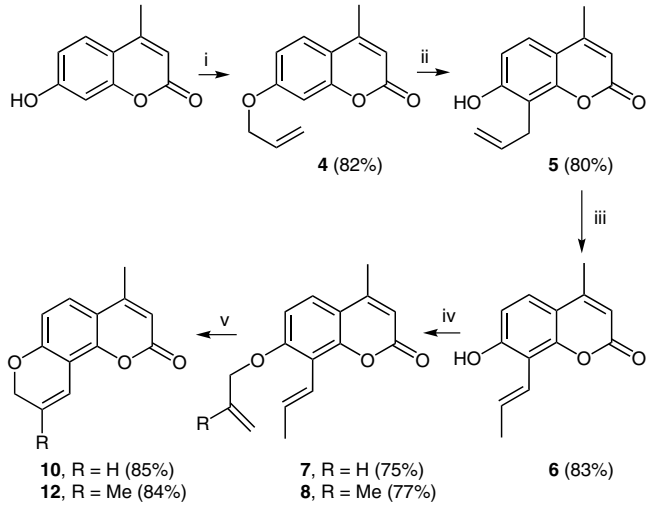
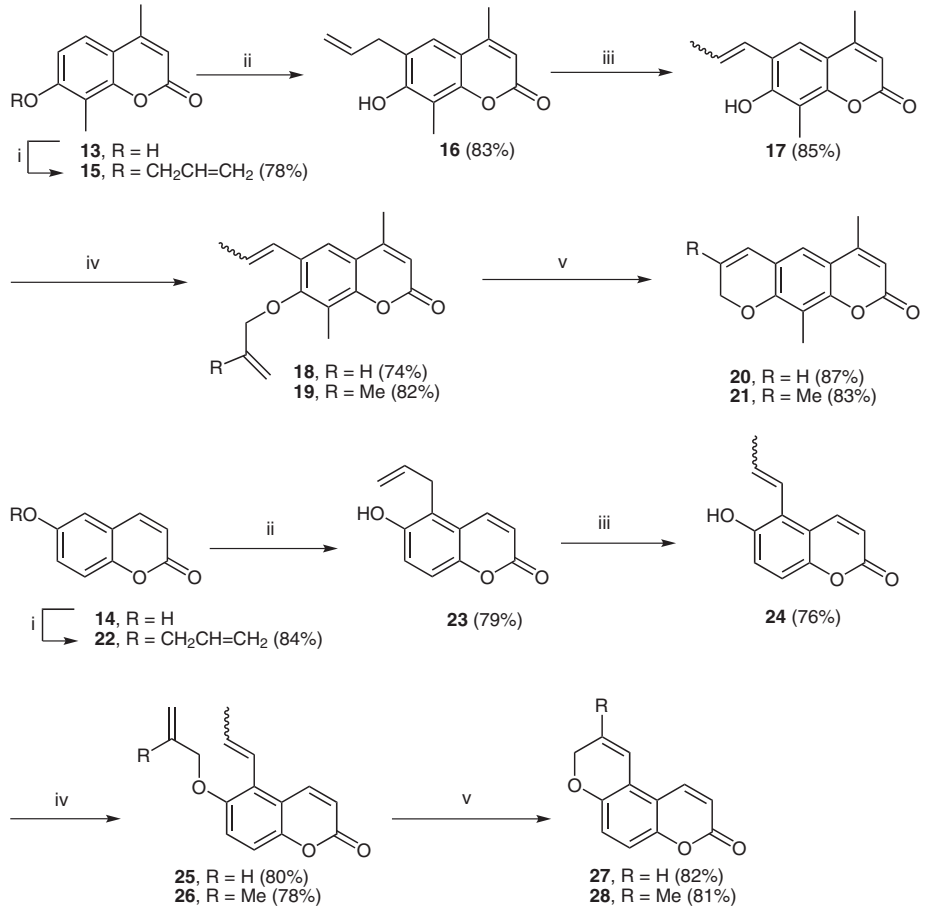


Scheme 2 *Reagents and conditions*: (i) allyl bromide, acetone, K_2CO_3, reflux; (ii) diphenyl ether, reflux; (iii) $RuClH(CO)(PPh_3)_3$ (2 mol%), benzene, reflux; (iv) allyl bromide/3-chloro-2-methyl-propene, K_2CO_3, acetone, reflux; (v) catalyst **9**/catalyst **11** (5 mol%), anhydrous benzene, reflux.

was obtained as the only regioisomer in 80% yield. $[Ru(CO)HCl(PPh_3)_3]$[17] is known to catalyse the isomerisation of terminal double bonds and has found use in many isomerisation/RCM sequences for the synthesis of carbocyclic and heterocyclic systems.[18] We were pleased to observe that when a solution of **5** in anhydrous benzene was heated to reflux in the presence of 2 mol% of the said ruthenium catalyst for 24 hours under a nitrogen atmosphere, the expected isomerised product **6** was formed in 83% yield and as a single isomer. The isomer was identified as *E* from the coupling constant in the NMR spectrum, in which the required proton appeared at δ = 6.62 ppm (d, J = 16 Hz, 1 H). Subsequent O-allylation of the isomerised product **6** with allyl bromide afforded **7** in 75% yield. Ring-closing metathesis of **7** with Grubbs first-generation catalyst **9** [bis(tricyclohexylphosphine)benzylidine-ruthenium(II)] in benzene heated to reflux proceeded well to provide the desired pyranocoumarin **10** in 85% yield. Similarly, O-allylation of **6** with methallyl chloride afforded the O-tethered diene **8**. However, RCM of the latter with catalyst **9** was problematic. Switching to the Grubbs second-generation catalyst **11** [benzylidene [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro (tricyclohexylphosphine)ruthenium] resolved the problem and the desired product **12** was obtained in a overall yield of 35% over a linear sequence of five steps.



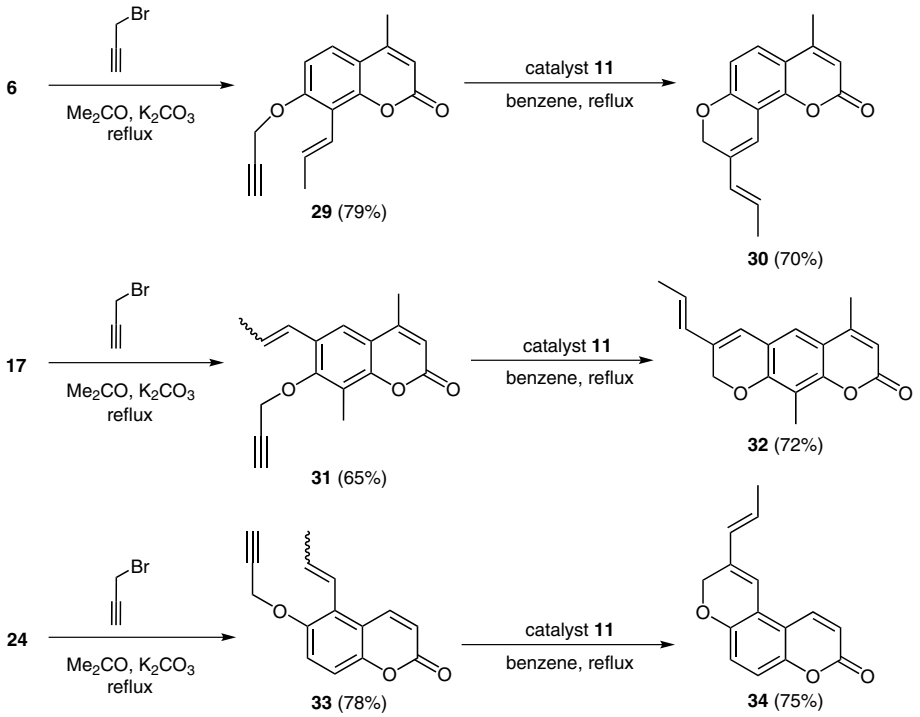
Scheme 3 *Reagents and conditions*: (i) allyl bromide, acetone, K_2CO_3, reflux; (ii) diphenyl ether, reflux; (iii) $RuClH(CO)(PPh_3)_3$ (2 mol%), benzene, reflux; (iv) allyl bromide/3-chloro-2-methyl-propene, K_2CO_3, acetone, reflux; (v) catalyst **9**/**11** (5 mol%), anhydrous benzene, reflux.

With optimised conditions in hand, we then turned our attention to study the scope and generality of the methodology. Coumarin derivatives with angular- and linearly fused heterocyclic motifs have attracted the attention of both chemists and biologists. We therefore employed the sequence of reactions on two other easily obtainable hydroxycoumarin derivatives: 4,8-dimethyl-7-hydroxycoumarin (**13**) and 6-hydroxycoumarin (**14**). Thus, *O*-allyl ether **15**, prepared by O-allylation of **13**, underwent clean rearrangement upon heating to reflux in diphenyl ether to provide the known rearranged phenol **16** (Scheme 3). Isomerisation of the latter with $[Ru(CO)HCl(PPh_3)_3]$ proceeded smoothly and produced the isomerised olefin **17** but as a mixture of *E*/*Z*-isomers in a ratio of approximately 3:1 in favour of the *E*-isomer. The *E*-isomer could be separated with difficulty, for characterisation. However, for synthetic purposes, the mixture was carried through because the isomeric identity was lost in the subsequent RCM reaction. Repetition of the sequences detailed for the conversion **7**→**10** and **8**→**12** on **17**; i.e., further O-allylation leading to the dienes **18**/**19** followed by their RCM with catalysts **9** or **11**, provided the linearly fused pyranocoumarin derivatives **20** and **21** in good overall yields of 35.4 and 37.5%, respectively. Similarly, starting with 6-allyloxycoumarin (**22**) the isomerised phenol **24** was prepared (mostly *E*) and converted into the angularly fused pyranocoumarin derivatives **27** and **28** in comparable yields.

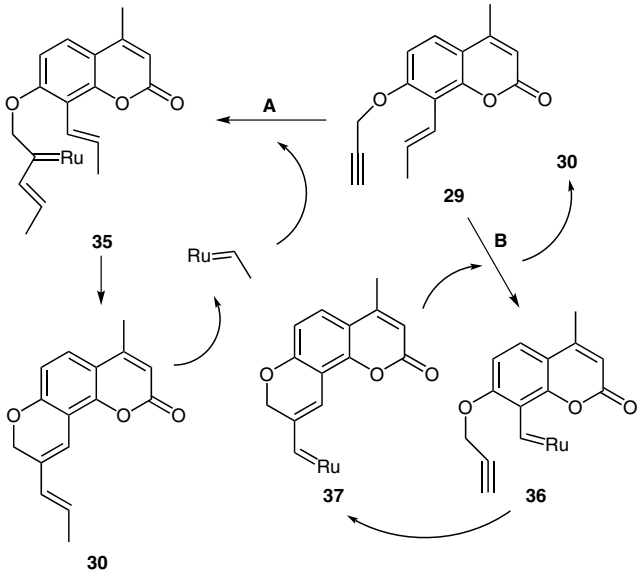
Ruthenium-catalysed ring-closing enyne metathesis (RCEYM) has become a powerful tool with which to construct heterocyclic derivatives.[19] The efficacy of the process has been increased by combining other synthetic transformations either before or after the metathesis step.[20] We,[21] and others[22] have reported a sequential Claisen rearrangement/RCEYM/Diels–Alder reaction as a cascade route to oxepin ring-fused heterocycles. We became interested in including the isomerisation step in this sequence to prepare benzannulated pyranocoumarin derivatives. Thus, the phenolic OH group in **6** was reacted with propargyl bromide under conventional conditions to obtain the O-tethered enyne derivative **29** (Scheme 4). RCEYM reactions of olefins other than terminal olefins have been less well documented compared with those of terminal olefins. In the few instances studied, interesting mechanistic and stereochemical observations have been made.[23] However, heteroatom-tethered enynes have been reported to show poor selectivity.[24] It was observed that RCEYM of **29** proceeded sluggishly in the presence of the second generation catalyst **11** under the optimised conditions to provide diene **30** (70%), mostly as the *E*-isomer but contaminated with the *Z*-isomer (5–10%), which could not be separated. Similarly, enyne derivatives **31** and **33** provided the corresponding dienes **32** and **34** in similar yields and stereochemical identity.

Mechanistically, the reaction may follow either the 'ene-then-yne' or 'yne-then-ene' pathways[25] (Scheme 5). In path A, the ruthenium carbene complex may coordinate with the alkyne part of the substrate **29** to form a new intermediate complex **35**, which, on subsequent cyclisation, will produce the product **30**. In this case, the reaction will be expected to exhibit stereoselectivity similar to that of a cross-enyne metathesis reaction.

On the other hand, the carbene complex **36** will result if the reaction occurs at the ene site (pathway B). The complex **36** will cyclise to produce a new complex **37**, which



Scheme 4 RCEYM of O-tethered enyne derivatives



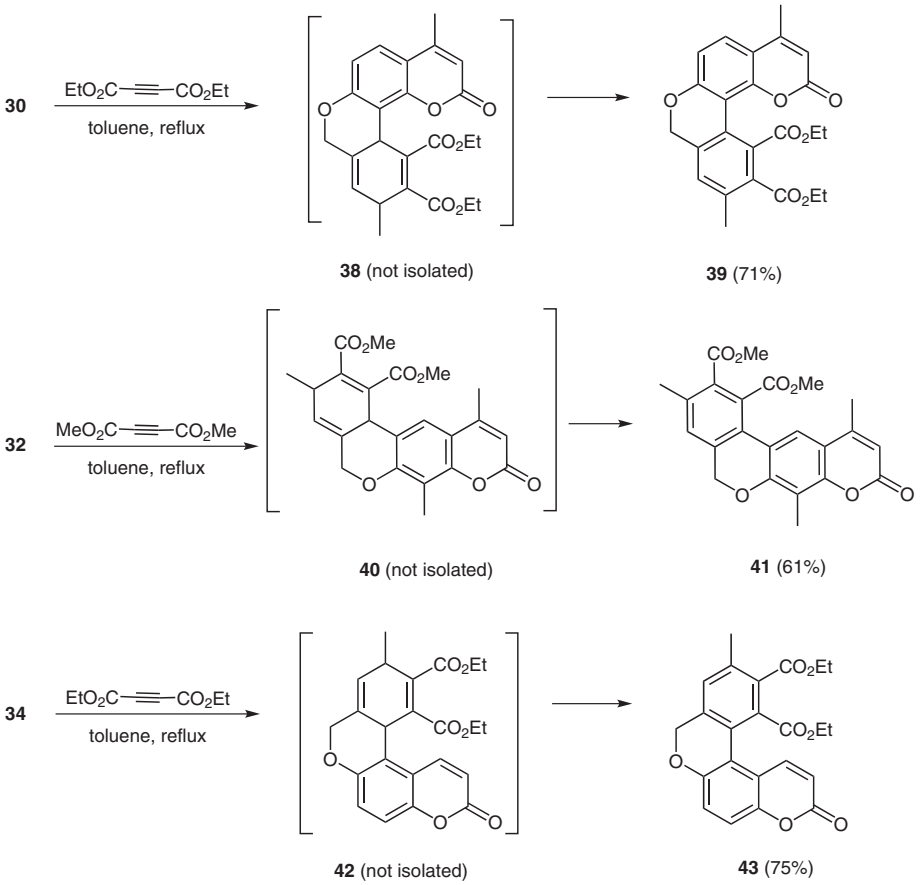
Scheme 5 Representation of plausible catalytic pathways: 'yne-then-ene' pathway (A) and 'ene-then-yne' pathway (B)

may then react with the olefin part of a second substrate molecule, leading to the 1,3-diene product **30**. The stereoselectivity in this case will be similar to that of a cross-ene metathesis. It is interesting to note that diene **30** is obtained as the major (90–95%) isomer, which has little precedence.

Having access to dienes **30**, **32**, and **34**, we then focused our attention on their Diels–Alder cycloaddition reaction with a suitable dienophile, which would secure formation of a benzene ring in our projected benzannulation reaction. We observed that prolonged heating of diene **30** with diethyl acetylenedicarboxylate (Scheme 6) in toluene at reflux led to the formation of a single product in 71% yield, which was identified as **39**. The formation of the latter may be explained by initial formation of the cycloadduct **38** (not isolated) followed by its aerial oxidation in situ.

Similarly, diene **32**, on reaction with dimethyl acetylenedicarboxylate under analogous conditions, provided benzannulated product **41** in comparable yield. The same sequence of reactions was then repeated with diene **34** to obtain the angularly fused benzopyranocoumarin derivative **43**. It is interesting to note that the angular- and linearly fused pyranocoumarin formed with similar facility and rate.

In conclusion, we have demonstrated that combined Claisen rearrangement, olefin isomerisation and olefin metathesis is an efficacious strategy for the preparation of several linearly and angularly architectured pyranocoumarin derivatives. This consecutive ruthenium-catalysed



Scheme 6 One-pot Diels–Alder cycloaddition and aromatisation

reaction protocol has been extended to the preparation of three hitherto unknown benzannulated pyranocoumarins by following the inclusion in the sequence of a Diels–Alder reaction as another atom-economic process. It is interesting to note that the ring-closing enyne metathesis of the internal olefins proceeded with *E*-stereoselectivity, which is not often documented. The advantage of the methodology lies in its true atom-economic nature, operational simplicity (only heat in most steps), catalytic use of reagents, predetermined mode of cyclisation, and high level of stereocontrol in the isomerisation as well as in the RCEYM steps. Moreover, the sequence proceeds with good overall yields. The methodology developed may complement the existing methodologies[26] for the preparation of pyrano- and benzopyrano-coumarin derivatives and it may also find use in the preparation of related compounds.

Melting points were recorded in open capillaries and are uncorrected. Infrared spectra were recorded with a Perkin–Elmer Spectrum 1 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 400 spectrometer purchased through a DST-FIST grant. Chemical shifts are recorded relative to residual solvent peak. Mass spectra were recorded with a JEOL-JMS 600 instrument from I. I. C. B., Kolkata or IACS, Kolkata. Petroleum ether (PE) refers to the fraction boiling in the range 60–80 °C. Silica gel (120–200 mesh) for column chromatography was purchased from Spectrochem, India.

Allylation of Hydroxycoumarins; General Procedure
A mixture of the appropriate hydroxycoumarin (10.0 mmol), allyl bromide (15.0 mmol, 1.3 mL) and anhydrous K_2CO_3 (30.0 mmol, 4.2 g) in anhydrous acetone (25 mL) was heated to reflux for 12 h. The mixture was then cooled, filtered and the filtrate was concentrated under reduced pressure. The residue was diluted with H_2O (20 mL) and then extracted with EtOAc (2 × 20 mL). The combined extract was washed successively with sat. aq $NaHCO_3$ (2 × 20 mL), H_2O (2 × 20 mL) and brine (30 mL), then dried (Na_2SO_4), filtered and the filtrate was concentrated under reduced pressure to leave a crude product, which was purified by column chromatography over silica gel using EtOAc–PE as eluent.

7-Allyloxy-4-methyl-2*H*-chromen-2-one (4)
The product was purified by column chromatography (EtOAc–PE, 10%).

Yield: 1.77 g (82%); colourless solid; mp 104–106 °C (EtOAc–PE) (Lit.[16] 103–104 °C).

IR (KBr): 2953, 2400, 1885, 1725, 1610, 1391, 1284, 1262, 1155, 1069, 994 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.8 Hz, 1 H), 6.88 (dd, *J* = 2.4, 8.8 Hz, 1 H), 6.82 (d, *J* = 2.4 Hz, 1 H), 6.13 (s, 1 H), 6.08–6.01 (m, 1 H), 5.45 (d, *J* = 17.2 Hz, 1 H), 5.34 (d, *J* = 10.8 Hz, 1 H), 4.60 (dd, *J* = 1.2, 5.2 Hz, 2 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 161.2, 155.1, 152.6, 132.2, 125.6, 118.4, 113.6, 112.7, 111.9, 101.7, 69.2, 18.6.

7-Allyloxy-4,8-dimethyl-2*H*-chromen-2-one (15)
The product was purified by column chromatography (EtOAc–PE, 15%).

Yield: 1.80 g (78%); colourless needles; mp 105–106 °C (EtOAc–PE) (Lit.[27] 108 °C).

IR (KBr): 3404, 2755, 1878, 1709, 1605, 1373, 1286, 1129 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.8 Hz, 1 H), 6.82 (d, *J* = 8.8 Hz, 1 H), 6.13 (s, 1 H), 6.12–6.03 (m, 1 H), 5.45 (td, *J* = 1.2, 19.2 Hz, 1 H), 5.32 (td, *J* = 1.2, 10.8 Hz, 1 H), 4.65–4.64 (m, 2 H), 2.39 (s, 3 H), 2.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4, 159.2, 152.8, 152.5, 132.7, 122.4, 117.5, 114.1, 113.6, 111.7, 107.8, 69.1, 18.6, 8.2.

6-Allyloxy-2*H*-chromen-2-one (22)
The product was purified by column chromatography (EtOAc–PE, 25%).

Yield: 1.67 g (84%); colourless solid; mp 92–93 °C (EtOAc–PE) (Lit.[28] 92 °C).

IR (KBr): 3419, 2983, 2912, 2864, 1726, 1573, 1489, 1429, 1341, 1259, 1180, 1098, 1010, 959 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 9.6 Hz, 1 H), 7.27 (d, *J* = 8.8 Hz, 1 H), 7.13 (dd, *J* = 2.8, 8.8 Hz, 1 H). 6.94 (d, *J* = 2.8 Hz, 1 H), 6.43 (d, *J* = 9.6 Hz, 1 H), 6.11–6.01 (m, 1 H), 5.44 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.33 (dd, *J* = 1.2, 10.8 Hz, 1 H), 4.58 (dd, *J* = 0.8, 4.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9, 154.9, 148.4, 143.3, 132.7, 120.0, 119.1, 118.0, 117.6, 116.9, 111.2, 69.3.

Claisen Rearrangement of Allyloxycoumarins; General Procedure
A solution of allyl ether **4**, **15**, or **22** (5 mmol) in diphenyl ether (12.5 mL) was heated at reflux for 2 h under a nitrogen atmosphere. The mixture was allowed to cool to r.t., then diluted with PE (50 mL). The precipitated solid was filtered off and then purified by chromatography over silica gel (PE–EtOAc) to give the product **5**, **16** or **23**.

8-Allyl-7-hydroxy-4-methyl-2*H*-chromen-2-one (5)
The product was purified by column chromatography (EtOAc–PE, 25%).

Yield: 864 mg (80%); colourless solid; mp 206–207 °C (EtOAc–PE) (Lit.[16] 198–199 °C).

IR (KBr): 3214, 1888, 1687, 1569, 1387, 1366, 1318, 1054, 995 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.4 Hz, 1 H), 6.86 (d, *J* = 8.8 Hz, 1 H), 6.15 (s, 1 H), 6.05–5.97 (m, 1 H), 5.21–5.13 (m, 2 H), 3.68 (d, *J* = 6.0 Hz, 2 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 159.2, 154.2, 153.0, 135.9, 124.3, 115.4, 113.1, 112.5, 112.4, 110.4, 27.0, 18.6.

6-Allyl-7-hydroxy-4,8-dimethyl-2*H*-chromen-2-one (16)
The product was purified by column chromatography (EtOAc–PE, 15%).

Yield: 955 mg (83%); colourless solid; mp 172–174 °C (EtOAc–PE) (Lit.[27] 168–170 °C).

IR (KBr): 3362, 2855, 1707, 1611, 1400, 1191, 1114, 902 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (s, 1 H), 6.14 (s, 1 H), 6.08–6.00 (m, 1 H), 5.64 (s, 1 H,), 5.25–5.20 (m, 2 H,), 3.49 (d, *J* = 6.0 Hz, 2 H), 2.40 (s, 3 H), 2.34 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9, 155.8, 153.1, 151.9, 135.8, 122.8, 121.8, 117.4, 113.4, 112.1, 111.7, 35.4, 18.8, 8.3.

5-Allyl-6-hydroxy-2*H*-chromen-2-one (23)
The product was purified by column chromatography (EtOAc–PE, 30%).

Yield: 798 mg (79%); colourless solid; mp 164–165 °C (EtOAc–PE) (Lit.[28] 159 °C).

IR (KBr): 3159, 1902, 1858, 1682, 1612, 1567, 1471, 1403, 1273, 1190, 825 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.69 (s, 1 H), 8.08 (d, J = 10 Hz, 1 H), 7.13–7.08 (m, 2 H), 6.32 (d, J = 10.0 Hz, 1 H), 5.93–5.85 (m, 1 H), 5.00–4.89 (m, 2 H), 3.57 (d, J = 5.6 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.4, 151.8, 147.8, 141.9, 136.9, 122.4, 119.8, 118.4, 116.2, 115.8, 115.4, 29.0.

Isomerisation of the 2-Allyl Hydroxycoumarins; General Procedure

To a stirred solution of the appropriate rearranged phenol **5**, **16** or **23** (2.5 mmol) in benzene (20 mL), was added $Ru(CO)ClH(PPh_3)_3$ (40 mg, 2 mol%) under a nitrogen atmosphere and the mixture was heated to reflux for 24 h. The solvent was removed under vacuum and the resulting crude residue was subjected to column chromatography on silica gel (EtOAc–PE). The product **6**, **17** or **24** was obtained as a colourless solid.

7-Hydroxy-4-methyl-8-(prop-1-enyl)-2*H*-chromen-2-one (6)

The product was purified by column chromatography (EtOAc–PE, 25%).

Yield: 448 mg (83%); colourless solid; mp 208–210 °C (EtOAc–PE).

IR (KBr): 3256, 2913, 1698, 1595, 1563, 1438, 1367, 1356, 1388, 1312, 1286, 1058, 977 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.72 (s, 1 H), 7.46 (d, J = 8.4 Hz, 1 H), 6.89 (d, J = 8.8 Hz, 1 H), 6.80–6.71 (m, 1 H), 6.62 (d, J = 16.0 Hz, 1 H), 6.16 (s, 1 H), 2.37 (s, 3 H), 1.92 (d, J = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.6, 159.0, 154.3, 152.2, 131.6, 124.3, 120.4, 112.9, 112.5, 111.7, 110.5, 20.3, 18.8.

HRMS (TOF, ES+): m/z [M + H]$^+$ calcd for $C_{13}H_{12}O_3$: 217.0865; found: 217.0867.

7-Hydroxy-4,8-dimethyl-6-(prop-1-enyl)-2*H*-chromen-2-one (17)

The product was purified by column chromatography (EtOAc–PE, 15%).

Yield: 489 mg (85%); colourless solid; mp 142–144 °C (EtOAc–PE).

IR (KBr): 3368, 2957, 1723, 1610, 1398, 1192, 1112 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 1 H), 6.57 (d, J = 16.0 Hz, 1 H), 6.24–6.17 (m, 1 H), 6.14 (s, 1 H), 5.65 (s, 1 H), 2.41 (s, 3 H), 2.34 (s, 3 H), 1.96 (dd, J = 1.6, 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 154.1, 153.0, 151.8, 130.3, 124.8, 121.9, 120.3, 113.5, 111.8, 111.5, 18.9, 18.8, 8.4.

HRMS (TOF, ES+): m/z [M + Na]$^+$ calcd for $C_{14}H_{14}O_3$: 253.0841; found: 253.0864.

6-Hydroxy-5-(prop-1-enyl)-2*H*-chromen-2-one (24)

The product was purified by column chromatography (EtOAc–PE, 30%).

Yield: 384 mg (76%); colourless solid; mp 126–130 °C (EtOAc–PE).

IR (KBr): 3181, 1893, 1678, 1599, 1567, 1468, 1400, 1293, 1267, 1191, 947, 826 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.81 (s, 1 H), 8.23 (d, J = 9.6 Hz, 1 H), 7.14–7.08 (m, 2 H), 6.59 (dd, J = 1.2, 15.6 Hz, 1 H), 6.41 (d, J = 10.0 Hz, 1 H), 6.16 (qd, J = 6.8, 16.0 Hz, 1 H), 1.93 (d, J = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.4, 151.7, 148.0, 142.4, 133.9, 123.2, 122.1, 119.8, 117.2, 115.9, 115.5, 19.7.

HRMS (TOF, ES+): m/z [M + H]$^+$ calcd for $C_{12}H_{10}O_3$: 203.0708; found: 203.0710.

Preparation of the Dienes 7, 18, 25, 8, 19 and 26

The title dienes were prepared by following the general procedure described for the preparation of **4**, **15** and **22** by using allyl bromide as alkylating agent to obtain **7**, **18** and **25**, but using methallyl chloride in place of allyl bromide in case of compounds **8**, **19** and **26**.

7-Allyloxy-4-methyl-8-(prop-1-enyl)-*2H*-chromen-2-one (7)

The product was purified by column chromatography (EtOAc–PE, 15%).

Yield: 768 mg (75%); colourless solid; mp 80–85 °C (EtOAc–PE).

IR (KBr): 3402, 2917, 1854, 1716, 1591, 1384, 1272, 1107, 1068 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, J = 8.8 Hz, 1 H), 7.08 (d, J = 9.2 Hz, 1 H), 6.75–6.69 (m, 1 H), 6.62 (d, J = 16.4 Hz, 1 H), 6.23 (s, 1 H,), 6.13–6.06 (m, 1 H,), 5.42 (dd, J = 1.6, 17.6 Hz, 1 H), 5.31 (d, J = 10.8 Hz, 1 H), 4.74–4.73 (m, 2 H), 2.39 (s, 3 H), 1.93 (d, J = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 158.7, 152.8, 151.8, 133.4, 132.6, 122.8, 119.4, 118.0, 114.8, 114.0, 112.0, 108.5, 69.6, 20.2, 18.9.

HRMS (TOF, ES+): m/z [M + H]$^+$ calcd for $C_{16}H_{16}O_3$: 257.1178; found: 257.1184.

4-Methyl-7-(2-methylallyloxy)-8-(prop-1-enyl)-2*H*-chromen-2-one (8)

The product was purified by column chromatography (EtOAc–PE, 20%).

Yield: 416 mg (77%); colourless solid; mp 78–80 °C (EtOAc–PE).

IR (KBr): 3404, 3062, 2850, 2911, 2762, 1888, 1728, 1699, 1595, 1558, 1448, 1431, 1370, 1386, 1284, 1083, 1118, 966 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.8 Hz, 1 H), 6.87–6.75 (m, 3 H), 6.16 (s, 1 H), 5.08 (d, J = 8.4 Hz, 2 H), 4.57 (s, 2 H), 2.40 (d, J = 0.8 Hz, 3 H), 1.98 (d, J = 6.0 Hz, 3 H), 1.87 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 158.7, 152.8, 151.7, 140.1, 133.3, 122.8, 119.4, 114.7, 113.9, 113.2, 111.9, 108.5, 72.5, 20.2, 19.5, 18.9.

HRMS (TOF, ES+): m/z [M + H]$^+$ calcd for $C_{17}H_{18}O_3$: 271.1334; found: 271.1339.

7-Allyloxy-4,8-dimethyl-6-(prop-1-enyl)-2*H*-chromen-2-one (18)

The product was purified by column chromatography (EtOAc–PE, 10%).

Yield: 400 mg (74%); colourless solid; mp 114–116 °C (EtOAc–PE).

IR (KBr): 3403, 3057, 2977, 2852, 2341, 1716, 1652, 1603, 1422 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (s, 1 H), 6.64 (dd, J = 1.2, 15.6 Hz, 1 H), 6.31–6.23 (m, 1 H), 6.21 (s, 1 H), 6.13–6.05 (m, 1 H), 5.43 (dd, J = 1.2, 16.8 Hz, 1 H), 5.30 (d, J = 10.4 Hz, 1 H), 4.35 (d, J = 5.6 Hz, 2 H), 2.43 (s, 3 H), 2.36 (s, 3 H), 1.94 (dd, J = 1.2, 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 157.2, 152.6, 151.7, 133.2, 128.2, 127.8, 125.2, 119.8, 119.1, 118.0, 116.4, 113.5, 74.5, 18.9 (two signals), 9.3.

HRMS (TOF, ES+): m/z [M + Na]$^+$ calcd for $C_{17}H_{18}O_3$: 293.1154; found: 293.1161.

4,8-Dimethyl-7-(2-methylallyloxy)-6-(prop-1-enyl)-2*H*-chromen-2-one (19)

The product was purified by column chromatography (EtOAc–PE, 15%).

Yield: 466 mg (82%); colourless solid; mp 98–99 °C (EtOAc–PE).

IR (KBr): 3413, 3020, 2919, 1714, 1216, 1108, 761 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (s, 1 H), 6.66 (d, *J* = 16.0 Hz, 1 H), 6.31–6.23 (m, 1 H), 6.21 (s, 1 H), 5.18 (s, 1 H), 5.04 (s, 1 H), 4.20 (s, 2 H), 2.44 (s, 3 H), 2.37 (s, 3 H), 1.94 (d, *J* = 1.6 Hz, 3 H), 1.92 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 157.3, 152.6, 151.7, 140.9, 128.2, 127.7, 125.1, 119.8, 119.1, 116.4, 113.5, 113.1, 77.1, 19.7, 18.9 (two signals), 9.1.

HRMS (TOF, ES+): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{20}O_3$: 285.1491; found: 285.1495.

6-Allyloxy-5-(prop-1-enyl)-2*H*-chromen-2-one (25)
The product was purified by column chromatography (EtOAc–PE, 25%).

Yield: 387 mg (80%); colourless solid; mp 70–75 °C (EtOAc–PE).

IR (KBr): 3085, 2970, 1863, 1725, 1592, 1565, 1450, 1442, 1278, 1267, 1109, 917 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 9.6 Hz, 1 H), 7.15 (d, *J* = 8.8 Hz, 1 H), 7.06 (d, *J* = 9.2 Hz, 1 H), 6.56 (dd, *J* = 1.2, 16.0 Hz, 1 H), 6.38 (d, *J* = 10.0 Hz, 1 H), 6.10–5.95 (m, 2 H), 5.41 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.30 (dd, *J* = 0.8, 10.4 Hz, 1 H), 4.59–4.57 (m, 2 H), 2.00 (dd, *J* = 1.6, 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9, 152.1, 149.0, 141.8, 134.7, 133.0, 126.0, 122.6, 117.7, 117.5, 116.3, 116.1, 115.2, 70.0, 19.3.

HRMS (TOF, ES+): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{14}O_3$: 243.1021; found: 243.1027.

6-(2-Methylallyloxy)-5-(prop-1-enyl)-2*H*-chromen-2-one (26)
The product was purified by column chromatography (EtOAc–PE, 20%).

Yield: 400 mg (78%); colourless gummy liquid.

IR ($CHCl_3$): 3083, 2916, 1730, 1567, 1448, 1266, 1085 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 9.6 Hz, 1 H), [7.76 (d, *J* = 9.6 Hz, 0.3 H)], 7.15 (d, *J* = 0.8 Hz, 1 H), [7.20 (d, *J* = 8.8 Hz, 0.3 H)], 7.09–7.04 (m, 1.3 H), 6.57 (d, *J* = 16.0 Hz, 1 H), 6.44–6.37 (m, 1.6 H), 6.03–5.96 (m, 1.3 H), 5.05–5.00 (two singlets, 2.6 H), 4.47 (s, 2.6 H), 2.00 (d, *J* = 6.0 Hz, 3 H), [1.53 (d, *J* = 6.4 Hz, 0.99 H)], 1.82 (d, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 152.2, 152.1, 148.9, 148.4, 142.0, 141.7, 140.5, 134.5, 131.0, 125.7, 124.3, 122.5, 122.0, 117.7, 117.3, 116.3, 116.1, 116.0, 115.6, 115.1, 112.7, 112.6, 72.7, 72.6, 19.4, 19.3, 15.0.

HRMS (TOF, ES+): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{16}O_3$: 257.1178; found: 257.1187.

Preparation of Pyranocoumarins 10, 12, 20, 21, 27 and 28 by RCM Reaction; General Procedure
Grubbs' catalyst **9** (5 mol%) was added to a stirred solution of the appropriate diene **7**, **18** or **25** (0.9 mmol) in anhydrous, degassed benzene (35 mL) under argon and the mixture was heated to reflux for 24 h until the disappearance of starting material was observed. The reaction mixture was then concentrated under reduced pressure and the residual mass was purified by chromatography over silica gel (EtOAc–PE) to afford the desired cyclic compound **10**, **20** or **27**. Compounds **12**, **21** and **28** were prepared similarly by following the above procedure but using the Grubbs second-generation catalyst **11**.

4-Methyl-8*H*-pyrano[2,3-*h*]chromen-2-one (10)
The product was purified by column chromatography (EtOAc–PE, 15%).

Yield: 163 mg (85%); colourless solid; mp 180–182 °C (EtOAc–PE) (Lit.[29] 184 °C).

IR (KBr): 3403, 3055, 2924, 2854, 1714, 1598, 1398, 1380, 1240, 1268, 1099, 997 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.8 Hz, 1 H), 6.99 (d, *J* = 10.0 Hz, 1 H), 6.74 (d, *J* = 8.4 Hz, 1 H), 6.14 (s, 1 H), 5.89–5.85 (m, 1 H), 4.94 (dd, *J* = 2.0, 3.2 Hz, 2 H), 2.39 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9, 156.9, 152.9, 149.3, 124.6, 121.8, 117.6, 114.0, 112.5, 111.8, 110.2, 66.0, 18.8.

HRMS (TOF, ES+): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{10}O_3$: 237.0528; found: 237.0529.

4,9-Dimethyl-8*H*-pyrano[2,3-*h*]chromen-2-one (12)
The product was purified by column chromatography (EtOAc–PE, 15%).

Yield: 172 mg (84%); colourless solid; mp 128–130 °C (EtOAc–PE).

IR (KBr): 3402, 3058, 2852, 2920, 1844, 1728, 1596, 1496, 1450, 1366, 1380, 1261, 1162, 1074, 999 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.4 Hz, 1 H), 6.74 (d, *J* = 3.2 Hz, 1 H), 6.71 (s, 1 H), 6.12 (s, 1 H), 4.78 (s, 2 H), 2.37 (s, 3 H), 1.85 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 155.5, 153.0, 148.7, 131.5, 123.4, 114.0, 112.3, 112.1, 111.7, 110.7, 69.5, 19.2, 18.8.

HRMS (TOF, ES+): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{12}O_3$: 251.0684; found: 251.0685.

4,10-Dimethylpyrano[3,2-*g*]chromen-2-(8*H*)-one (20)
The product was purified by column chromatography (EtOAc–PE, 10%).

Yield: 178 mg (87%); colourless solid; mp 178–180 °C (EtOAc–PE) (Lit.[29] 176–179 °C).

IR (KBr): 3393, 2925, 2864, 2328, 1704, 1654, 1616, 1574 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01 (s, 1 H), 6.45 (dt, *J* = 1.6, 10.0 Hz, 1 H), 6.11 (d, *J* = 1.0 Hz, 1 H), 5.82 (dt, *J* = 3.6, 10.0 Hz, 1 H), 4.95 (dd, *J* = 2.0, 3.2 Hz, 2 H), 2.37 (s, 3 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4, 155.1, 152.9, 152.7, 123.6, 121.8, 119.2, 118.2, 113.6, 113.1, 111.7, 66.2, 18.8, 7.9.

HRMS (TOF, ES$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{12}O_3$: 229.0865; found: 229.0870.

4,7,10-Trimethylpyrano[3,2-*g*]chromen-2-(8*H*)-one (21)
The product was purified by column chromatography (EtOAc–PE, 20%).

Yield: 181 mg (83%); colourless solid; mp 106–107 °C (EtOAc–PE).

IR (KBr): 3394, 3279, 2921, 2346, 1714, 1610, 1575, 1405, 1381, 1190, 1113 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94 (s, 1 H), 6.18 (s, 1 H), 6.10 (s, 1 H), 4.80 (s, 2 H), 2.36 (s, 3 H), 2.24 (s, 3 H), 1.82 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 153.8, 152.8, 152.4, 131.0, 118.8, 118.5, 118.0, 113.5, 112.6, 111.6, 69.6, 18.8 (two signals), 8.0.

HRMS (TOF, ES+): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{14}O_3$: 243.1021; found: 243.1026.

Pyrano[3,2-*f*]chromen-3(8*H*)-one (27)
The product was purified by column chromatography (EtOAc–PE, 30%).

Yield: 147 mg (82%); colourless solid; mp 138–140 °C (EtOAc–PE) (Lit.[30] 140 °C).

IR (KBr): 3386, 3079, 2924, 2854, 1719, 1588, 1569, 1462, 1254, 1184 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 9.6 Hz, 1 H), 7.10 (d, *J* = 8.8 Hz, 1 H), 6.99 (d, *J* = 9.2 Hz, 1 H), 6.80 (d, *J* = 9.6 Hz, 1 H),

6.44 (d, J = 10.0 Hz, 1 H), 6.05–6.01 (m, 1 H), 4.83 (dd, J = 2.0, 3.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.7, 150.3, 149.0, 138.5, 124.8, 120.0, 119.1, 118.3, 116.8, 116.7, 114.4, 65.2.

HRMS (TOF, ES+): m/z $[M + Na]^+$ calcd for $C_{12}H_8O_3$: 223.0371; found: 223.0371.

9-Methylpyrano[3,2-*f*]chromen-3(8*H*)-one (28)
The product was purified by column chromatography (EtOAc–PE, 20%).

Yield: 156 mg (81%); light-yellow solid; mp 84–85 °C (EtOAc–PE).

IR (KBr): 3371, 3086, 2965, 2921, 2851, 1713, 1593, 1567, 1464, 1348, 1248, 1120, 826 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 10.0 Hz, 1 H), 7.05 (d, J = 8.8 Hz, 1 H), 6.97 (d, J = 8.8 Hz, 1 H), 6.53 (s, 1 H), 6.42 (d, J = 10.0 Hz, 1 H), 4.70 (d, J = 0.4 Hz, 2 H), 1.92 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 149.1, 148.7, 138.6, 135.0, 119.5, 119.0, 116.3, 115.6, 113.9, 113.8, 68.9, 19.6.

HRMS (TOF, ES+): m/z $[M^+]$ calcd for $C_{13}H_{10}O_3$: 214.0630; found: 214.0651.

Preparation of Propargyl Ethers 29, 31 and 33
Prepared by following the general procedure described for the preparation of **4**, **15** and **22**, but using propargyl bromide in place of allyl bromide.

4-Methyl-8-(prop-1-enyl)-7-(prop-2-ynyloxy)-2*H*-chromen-2-one (29)
The product was purified by column chromatography (EtOAc–PE, 20%).

Yield: 404 mg (79%); colourless solid; mp 140–142 °C (EtOAc–PE).

IR (KBr): 3381, 3231, 2931, 2122, 1867, 1695, 1591, 1382, 1368, 1273, 1250, 1117, 1075, 984 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.8 Hz, 1 H), 6.99 (d, J = 8.8 Hz, 1 H), 6.85–6.78 (m, 1 H), 6.72 (d, J = 16.0 Hz, 1 H), 6.16 (s, 1 H), 4.83 (d, J = 2.0 Hz, 2 H), 2.57 (t, J = 2.0 Hz, 1 H), 2.40 (s, 3 H), 1.98 (d, J = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 157.5, 152.7, 151.7, 133.8, 122.7, 119.1, 115.2, 114.6, 112.4, 108.7, 77.9, 76.3, 56.5, 20.2, 18.9.

HRMS (TOF, ES+): m/z $[M + H]^+$ calcd for $C_{16}H_{14}O_3$: 255.1021; found: 255.1027.

4,8-Dimethyl-6-(prop-1-enyl)-7-(prop-2-ynyloxy)-2*H*-chromen-2-one (31)
The product was purified by column chromatography (EtOAc–PE, 10%).

Yield: 348 mg (65%); colourless solid; mp 125–127 °C (EtOAc–PE).

IR (KBr): 3738, 3236, 2966, 2325, 2122, 1706, 1621, 1571, 1603 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (s, 1 H), 6.67 (d, J = 15.6 Hz, 1 H), 6.30–6.23 (m, 2 H), 4.57 (d, J = 2.4 Hz, 2 H), 2.52 (t, J = 2.4 Hz, 1 H), 2.43 (s, 3 H), 2.41 (s, 3 H), 1.95 (dd, J = 1.6, 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 156.2, 152.5, 151.6, 128.3, 128.2, 125.1, 120.4, 119.4, 116.8, 113.8, 78.4, 75.8, 60.9, 18.9 (two signals), 9.6.

HRMS (TOF, ES+): m/z $[M + Na]^+$ calcd for $C_{17}H_{16}O_3$: 291.0997; found: 291.0986.

5-(Prop-1-enyl)-6-(prop-2-ynyloxy)-2*H*-chromen-2-one (33)
The product was purified by column chromatography (EtOAc–PE, 25%).

Yield: 374 mg (78%); colourless solid; mp 88–90 °C (EtOAc–PE).

IR (KBr): 3434, 3246, 2119, 1737, 1565, 1450, 1269, 1119, 1071, 802 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 9.6 Hz, 1 H), 7.26–7.18 (m, 2 H), 6.55 (d, J = 16.0 Hz, 1 H), 6.43–6.38 (m, 1 H), 6.03–5.96 (m, 1 H), 4.74 (d, J = 2.0 Hz, 2 H), 2.53–2.51 (m, 1 H), 2.00 (dd, J = 1.6, 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 151.0, 149.6, 141.7, 135.1, 122.3, 117.6, 117.1, 116.6, 116.2, 115.2, 78.3, 76.1, 57.1, 19.3.

HRMS (TOF, ES+): m/z $[M + Na]^+$ calcd for $C_{15}H_{12}O_3$: 263.0684; found: 263.0698.

RCEYM Reaction of 29, 31 and 33; General Procedure
Grubbs' catalyst **11** (5 mol%) was added to a stirred solution of the appropriate enyne derivative **29**, **31** or **33** (1 mmol), in anhydrous degassed benzene (30 mL) under an argon atmosphere, and the reaction mixture was heated at reflux for 24 h. After removal of the solvent in vacuo, the crude product was purified by column chromatography over silica gel (EtOAc–PE) to afford diene **30**, **32** or **34**.

(*E*,*Z*)-4-Methyl-9-(prop-1-enyl)-pyrano[2,3-*h*]chromen-2(8*H*)-one (30)
The product was purified by column chromatography (EtOAc–PE, 20%). The product was obtained as a mixture of two geometric isomers in which the *E*-isomer was enriched. NMR data for the major isomer is given below.

Yield: 178 mg (70%); colourless solid; mp 132–134 °C (EtOAc–PE).

IR (KBr): 3423, 2925, 2853, 1717, 1598, 1373, 1174, 1083 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.26 (m, 1 H), 6.86–6.72 (m, 2 H), 6.20 (d, J = 16.0 Hz, 1 H), 6.12 (s, 1 H), 5.78–5.63 (m, 1 H), 5.01 (d, J = 5.2 Hz, 2 H), 2.37 (s, 3 H), 1.86 (d, J = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 156.1, 153.0, 149.3, 130.7, 129.3, 127.0, 123.7, 114.0, 113.5, 112.1, 111.8, 110.9, 66.2, 18.8 (two signals).

HRMS (TOF, ES+): m/z $[M + H]^+$ calcd for $C_{16}H_{14}O_3$: 255.1021; found: 255.1026.

(*E*)-4,10-Dimethyl-6-(prop-1-enyl)-pyrano[3,2-*g*]chromen-2(8*H*)-one (32)
The product was purified by column chromatography (EtOAc–PE, 6%).

Yield: 192 mg (72%); colourless solid; mp 128–129 °C (EtOAc–PE).

IR (KBr): 2964, 2350, 1714, 1614, 1574, 1408, 1388 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (s, 1 H), 7.02 (s, 1 H), 6.28 (s, 1 H), 6.11 (s, 1 H), 5.65 (m, 1 H), 5.04 (s, 2 H), 2.37 (s, 3 H), 2.26 (s, 3 H), 1.86 (d, J = 6.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4, 154.4, 152.7, 152.6, 130.6, 128.9, 126.4, 121.7, 119.8, 118.8, 113.8, 112.7, 111.7, 66.2, 18.8 (two signals), 8.0.

HRMS (TOF, ES+): m/z $[M + Na]^+$ calcd for $C_{17}H_{16}O_3$: 291.0997; found: 291.0986.

(*E*)-9-(Prop-1-enyl)pyrano[3,2-*f*]chromen-3(8*H*)-one (34)
The product was purified by column chromatography (EtOAc–PE, 20%).

Yield: 180 mg (75%); colourless solid; mp 126–127 °C (EtOAc–PE).

IR (KBr): 3402, 3075, 2923, 2851, 1727, 1564, 1464, 1443, 1251, 1023 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 9.6 Hz, 1 H), 7.06 (d, *J* = 8.8 Hz, 1 H), 7.00 (d, *J* = 9.2 Hz, 1 H), 6.60 (s, 1 H), 6.44 (d, *J* = 10.0 Hz, 1 H), 6.24 (d, *J* = 16.0 Hz, 1 H), 5.84–5.77 (m, 1 H), 4.95 (s, 2 H), 1.90 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 149.6, 149.2, 138.5, 133.8, 129.2, 128.4, 119.5, 119.2, 116.3, 115.9, 114.8, 114.2, 65.4, 18.8.

HRMS (TOF, ES+): *m/z* $[M + Na]^+$ calcd for $C_{15}H_{12}O_3$: 263.0684; found: 263.0683.

Diels–Alder Reaction of Dienes 30, 32 and 34; General Procedure

To a stirred solution of the appropriate diene **30**, **32** or **34** (0.3 mmol) in anhydrous toluene (5 mL), dimethyl acetylenedicarboxylate or diethyl acetylenedicarboxylate (0.75 mmol, 2.5 equiv) was added and the mixture was heated to reflux for 48 h. The solvent was evaporated under reduced pressure and the residual mass was purified by column chromatography over silica gel (EtOAc–PE) to give the corresponding aromatised cycloadduct **39**, **41** or **43**.

Compound 39

The product was purified by column chromatography (EtOAc–PE, 30%).

Yield: 90 mg (71%); colourless solid; mp 150–152 °C (EtOAc–PE).

IR (KBr): 3431, 2923, 2986, 1736, 1594, 1376, 1316, 1206, 1078 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.4 Hz, 1 H), 7.21 (s, 1 H), 7.05 (d, *J* = 8.8 Hz, 1 H), 6.15 (s, 1 H), 4.95 (s, 2 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 4.15 (q, *J* = 7.0 Hz, 2 H), 2.42 (d, *J* = 4.0 Hz, 6 H), 1.38 (t, *J* =7.2 Hz, 3 H), 1.29 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 167.5, 165.9, 159.9, 159.7, 152.8, 151.2, 136.6, 135.5, 134.8, 129.5, 128.5, 125.4, 114.9, 114.0, 112.3, 111.9, 69.8, 61.9, 61.5, 19.7, 19.1, 14.1, 13.5.

HRMS (TOF, ES+): *m/z* $[M + Na]^+$ calcd for $C_{24}H_{22}O_7$: 445.1263; found: 445.1262

Compound 41

The product was purified by column chromatography (EtOAc–PE, 10%).

Yield: 75 mg (61%); colourless solid; mp 115–116 °C (EtOAc–PE).

IR (KBr): 3438, 3006, 2957, 1724, 1611, 1578 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 1 H), 7.18 (s, 1 H), 6.19 (s, 1 H), 5.05 (s, 2 H), 3.92 (s, 3 H), 3.84 (s, 3 H), 2.45 (s, 3 H), 2.38 (s, 3 H), 2.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.0, 167.9, 160.9, 152.8, 152.3, 136.5, 136.3, 132.3, 129.2, 128.6, 128.3, 125.5, 119.1, 117.9, 115.3, 114.6, 113.0, 69.0, 52.8, 52.6, 20.1, 18.7, 8.4.

HRMS (TOF, ES+): *m/z* $[M + Na]^+$ calcd for $C_{23}H_{20}O_7$: 431.1107; found: 431.1114.

Compound 43

The product was purified by column chromatography (EtOAc–PE, 25%).

Yield: 92 mg (75%); colourless solid; mp 120–122 °C (EtOAc–PE).

IR (KBr): 3431, 2927, 1731, 1570, 1466, 1231, 1103, 1029, 757 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 9.6 Hz, 1 H), 7.31–7.26 (m, 3 H), 6.37 (d, *J* = 9.6 Hz, 1 H), 5.10 (d, *J* = 12.8 Hz, 1 H), 4.76 (d, *J* = 12.8 Hz, 1 H), 4.40–4.36 (m, 2 H), 4.08–4.04 (m, 1 H), 3.94 (d, *J* = 6.8 Hz, 1 H), 2.45 (s, 3 H), 1.37 (t, *J* = 6.8 Hz, 3 H), 1.03 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 167.3, 160.3, 153.5, 149.8, 140.9, 138.4, 136.0, 135.3, 129.3, 129.1, 125.0, 121.2, 120.4, 118.1, 116.5, 116.0, 69.8, 62.3, 61.9, 19.5, 14.0, 13.5.

HRMS (TOF, ES+): *m/z* $[M + Na]^+$ calcd for $C_{23}H_{20}O_7$: 431.1107; found: 431.1107.

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