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Ring-closing metathesis for the synthesis of 2*H*- and 4*H*-chromenes

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Abstract—Six 4*H*-chromenes were synthesized from substituted phenols using vinylstannylation and ring-closing metathesis (RCM) as key steps. In addition, a different approach involving amongst other steps, an aryl allyl isomerization and RCM afforded a set of seven 2*H*-chromenes from phenolic precursors.

1. Introduction

Compounds in which a benzene and pyran ring are fused together with various levels of saturation and oxidation are very common in Nature.[1] The 1-benzopyrans include structural skeletons such as chromane **1**, 4*H*-chromene **2** and 2*H*-chromene **3** as depicted in Figure 1.

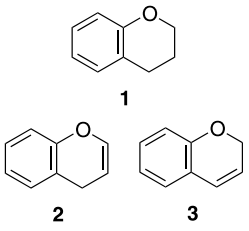

Figure 1.

As a class of compounds the 4*H*-chromenes **2** (also known as 4*H*-1-benzopyrans) are rather unusual and only a few examples of natural products containing this structure have been isolated.[2] An example of a naturally occurring 4*H*-chromene is 7-hydroxy-6-methoxy-4*H*-chromene **4**, which was efficiently synthesized by De Korte and co-workers (Fig. 2).[3] This natural product, which reportedly has interesting organoleptic properties, was isolated from the plant *Wisteria sinensis* along with the related compound, 6,7-dimethoxy-4*H*-chromene **5**.[2] In contrast to the paucity of 4*H*-chromene examples, the literature abounds with vast numbers of papers reporting the isolation and synthesis of naturally occurring 2*H*-chromenes **3**.[1] Examples reported recently include compounds **6** and **7**, both isolated from the leaf essential oil of *Calyptranthes tricona* (Fig. 2).[4]

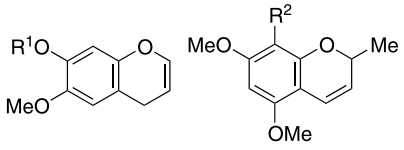

Figure 2.

The chromene skeletons have also elicited pharmaceutical interest as structural elements in drug-like compounds. Examples of artificial compounds bearing the 2*H*-chromene motif include 6-fluoro-2*H*-chromene **8**,[5] which exhibited the highest 5-HT_{1A} receptor affinity among a series of novel 6-fluorochromane derivatives; and 6-substituted 2*H*-chromenyl compound **9**,[6] which was tested for potential antidiabetic activity as a Na^+-glucose co-transporter inhibitor (Fig. 3). In addition, a series of hypoglycemic benzenesulfonylsemicarbazides with potential application in the treatment of diabetes mellitus included substituted 2*H*-chromene **10**.[7]

In recent years, the ring-closing metathesis (RCM) reaction[8] has been used to synthesize both the 2*H*-[9] and 4*H*-chromene[10] classes. Methodology for the synthesis of the 2*H*-chromenes normally involves the RCM of an

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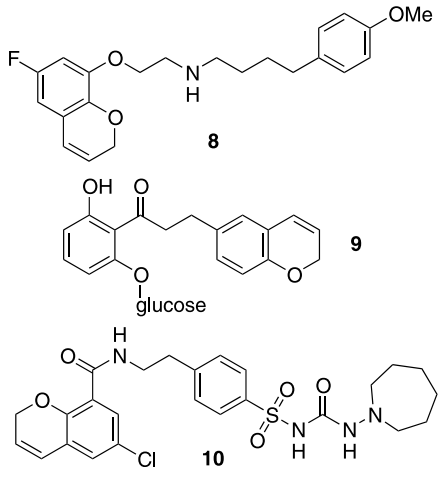


Figure 3.

o-allyloxystyrene [see disconnection (a) in Fig. 4]. On the other hand the synthesis of the 4*H*-chromenes using RCM, described only by ourselves in a communication[11] and by Lam and co-workers (one example),[10] has been accomplished by the RCM between a vinyloxy group and an arylallyl functionality (disconnection (b) in Fig. 4). In addition, our research group has been interested in the use of RCM and isomerization[12] methodology towards the synthesis of benzo-fused compounds.[11,13]

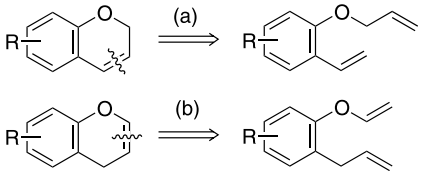


Figure 4.

In this publication we report in full novel syntheses to both the 4*H*- and 2*H*-chromene structures using RCM as the key step.[11] This paper describes in detail how the 4*H*-chromenes were synthesized by way of an *O*-vinylation followed by RCM using the second generation Grubbs catalyst **11** (Fig. 5). In addition, we disclose the synthesis of a small set of 2*H*-chromenes, which were obtained by first using a versatile aryl allyl isomerization step followed by the usual RCM reaction.[14]

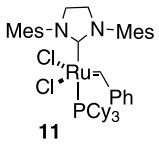
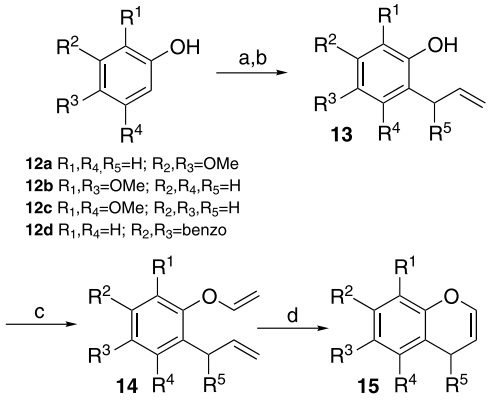


Figure 5.

2. Discussion: 4*H*-chromenes

Variably substituted phenols **12** were initially converted into their corresponding aryl allyl ethers. Subsequent thermal Claisen rearrangements then gave the substituted phenols **13** in acceptable yields over two steps (Scheme 1 and Table 1). The compounds were then converted into the respective aryl vinyl ethers **14**, also in excellent yield, using a copper-mediated procedure described in the literature.[15] The crucial ruthenium-mediated RCM reactions on compounds **14** were highly successful, affording the 4*H*-chromenes **15** in 63–98% yield. It is known that RCM using Grubbs' catalysts on substrates containing electron-rich vinylic olefins can be problematic[16] but that there are numerous literature examples demonstrating the application of RCM to alkyl vinyl ethers.[16b,17,18] However, our results are amongst the first describing the successful use of RCM on substrates bearing phenolic vinyl ethers.[9 g,h,10,19]

As mentioned in the introduction, 4*H*-chromene **15a** (=**5**) occurs naturally as a fragrance component from the plant *Wisteria sinensis* and the spectra of our synthesized product compared well to those obtained for the natural product.[2] The other substituted 4*H*-chromenes that were synthesized are described in Scheme 1 and Table 1 and it can be seen that most of the reaction yields were in an acceptable range. In addition, 4*H*-chromenes **15d** and **15e**, bearing a methyl functionality at position 5 of the pyran ring, were also obtained in good yields. Of interest was that relative to the 4-methyl-4*H*-chromenes **15b** and **15d**, the unsubstituted chromenes **15a**, **15c** and **15e** were much more prone to decomposition. This was evident by the rapid darkening of the oils, even within minutes under air, to afford deep green or blue oils after a number of weeks, which were difficult to characterize.



Scheme 1. (a) K_2CO_3, allyl bromide, acetone, 60 °C; (b) △ (180–240 °C), neat; (c) $Cu(OAc)_2$, $Sn(vinyl)_4$, acetonitrile, O_2, rt; (d) 5% catalyst **11**, toluene, 60 °C (for yields see Table 1 below).

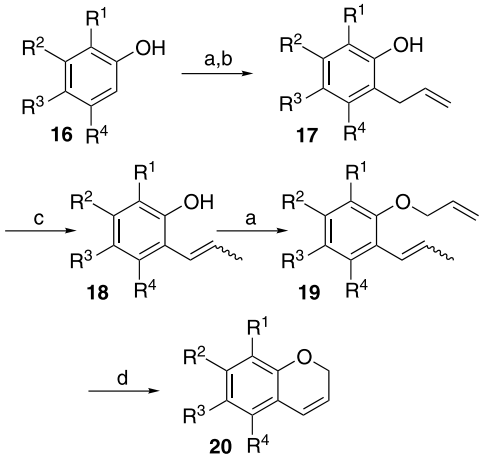
3. Discussion: 2*H*-chromenes

The synthesis of a small set of substituted 2*H*-chromenes required us to adopt a different approach. The 2-allylphenols **17** were synthesised as before, making use of the initial allylation of the substituted phenols **16** followed by a Claisen rearrangement (Scheme 2 and Table 2). The next step required the isomerization of the terminal alkene groups of **17** to the thermodynamically more favoured internal alkenes of the 2-(prop-1-enyl)phenols **18**. This was accomplished using the ruthenium-based catalyst, $[RuClH(CO)(PPh_3)_3]$, utilised by the group of Krompiec, and co-workers for a variety of isomerization applications.[20] For the most part, products **18** were obtained as a mixture of *E*- and *Z*-isomers with the *E*-isomers predominating. The only exception to this was that the isomerization of 1-allylnaphthalen-2-ol **17f** predominantly afforded the *Z*-isomer

Table 1. Yields for Scheme 1

	13[a]	13→14	14→15
a R^1,R^4,R^5=H; R^2,R^3=OMe	45%[b]	98%	90%
b R^1,R^4=H; R^2,R^3=OMe; R^5=Me	65%[b]	98%	98%
c R^1,R^3=OMe; R^2,R^4,R^5=H	91%[c]	99%	80%
d R^1,R^3=OMe; R^2,R^4=H; R^5=Me	42%[c]	98%	82%
e R^1,R^4=OMe; R^2,R^3,R^5=H	63%[d]	99%	85%
f R^1,R^2=H; R^3,R^4=benzo	90%[e]	74%	63%

[a] Yield over two steps.
[b] From compound **12a**.
[c] From compound **12b**.
[d] From compound **12c**.
[e] From compound **12d**.



Scheme 2. (a) K_2CO_3, allyl bromide, acetone, 60 °C; (b) Δ (180–240 °C) or microwave (150–200 °C), neat; (c) [$RuCl(CO)(PPh_3)_3$] (cat 1–4 mol%), toluene, 80 °C; (d) 5% catalyst **11**, toluene, rt −60 °C (for yields see Table 2 below).

of 1-(prop-1-enyl)naphthalen-2-ol **18f** after chromatography.[20b] A facile *O*-allylation on compounds **18a–g** then afforded the substituted 1-allyloxy-2-(prop-1-enyl)benzenes **19a–g** in acceptable yields. Compounds **19a–g** subsequently underwent RCM with Grubbs' second generation catalyst **11** to afford the desired 2*H*-chromenes **20a–g** in acceptable to good yields. The 2*H*-chromenes synthesized also contained a range of functional groups in varied positions on the aromatic portion, demonstrating the utility of this methodology. In particular the use of the nitro group, which can readily be reduced to an amine, and the versatile aldehyde substituents mean that subsequent modifications of the 2*H*-chromene skeletons should be readily attainable.

It is of interest to note that most of the previous RCM approaches to the 2*H*-chromene skeleton make use of an *O*-allyl group cyclizing onto a styrene. The presence of the styrene often necessitates an atom-inefficient Wittig reaction on the corresponding benzaldehyde,[9b,f] a transition metal-mediated vinylation of an aromatic halide[9d,j] or even a ketone to enol silyl ether transformation.[9g] Our methodology is thus different in that it enables the use of very simple precursors and reactions for the synthesis of the 2*H*-chromenes, utilizing the ruthenium-mediated isomerization as a key step.[21]

4. Conclusion

We have thus demonstrated a simple, versatile method of synthesizing the 4*H*-chromene skeleton using as key steps a copper-mediated aryl vinyl ether formation followed by a ruthenium-mediated RCM reaction. In addition this paper discloses our novel approach to the 2*H*-chromenes involving an aryl allyl isomerization and a RCM reaction. An advantage of both approaches is that they require substituted phenols as precursors. Since a wide variety of these compounds are commercially available or readily synthesized, it allows for a versatile approach to both classes of 1-benzopyrans.

5. Experimental

^1H and ^{13}C NMR spectra were recorded either on a Bruker

Table 2. Yields for Scheme 2

	16→17[a]	17→18	18→19	19→20
a $R^1=NO_2$; R^2,R^3,R^4=H	84%	96%	71%	90%
b R^1,R^2,R^4=H; $R^3=NO_2$	49%	96%	100%	100%
c R^1=OMe; R^2,R^3=H; R^4=CHO	68%	67%	81%	77%
d R^1=CHO; R^2,R^3,R^4=H	45%	89%	100%	80%
e R^1,R^2,R^4=H; R^3=CHO	41%	42%	64%	76%
f R^1,R^2=H; R^3,R^4=benzo[b]	90%	84%	65%	45%[c,d]
g R^1,R^2,R^3,R^4=H	[e]	90%	86%	80%[f,g]

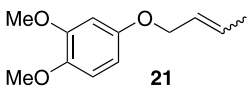
[a] Yields over two steps.
[b] For starting material **16a** R^1,R^4=H; R^2,R^3=benzo.
[c] Reaction on a 0.6 mmol scale.
[d] When reaction was repeated on a 0.3 mmol scale yield of **20f** obtained was 82%.
[e] 2-Allylphenol purchased from Aldrich.
[f] Yield >80% by ^1H NMR spectroscopy.
[g] Reaction performed on NMR spectroscopy scale as described in Ref. 13a.

AC-200, Bruker 300 or Bruker DRX 400 spectrometer at the frequency indicated. All ^{13}C signals in the aromatic/alkene region have been assigned as quaternary (C) or non-quaternary (CH). Infra-red spectra were recorded on either a Bruker IFS 25 Fourier Transform spectrometer or on a Bruker Vector 22 Fourier Transform spectrometer. Mass spectra were recorded on a Kratos MS 9/50, VG 70E MS or a VG 70 SEQ mass spectrometer. Macherey-Nagel kieselgel 60 (particle size 0.063–0.200 mm) was used for conventional silica gel chromatography. All solvents used for reactions and chromatography were distilled prior to use. All microwave reactions were performed in a CEM Corporation Discover Focused Microwave Synthesis system.

5.1. Experimental part A: 4*H*-chromenes

5.2. Known precursors for the synthesis of the 4*H*-chromenes 15a–f. 3,4-Dimethoxyphenol **12a** was allylated to afford 4-allyloxy-1,2-dimethoxybenzene.[22a] A Claisen rearrangement was performed on this compound to afford 2-allyl-4,5-dimethoxyphenol **13a**.[22b] Similarly, allylations on 3,4-dimethoxyphenol **12a** and 2,4-dimethoxyphenol **12b** with crotyl bromide afforded 4-(but-2-enyloxy)-1,2-dimethoxybenzene **21** (see below for experimental details and structure) and 1-(but-2-enyloxy)-2,4-dimethoxybenzene,[22c] respectively, which were converted to 4,5-dimethoxy-2-(1-methylallyl)phenol[22d] **13b** and 2,4-dimethoxy-6-(1-methylallyl)phenol[22c] **13d**, respectively, by way of the Claisen rearrangement. In a similar manner, 2-allyl-4,6-dimethoxyphenol **13c** (see below for experimental details) and 2-allyl-3,6-dimethoxyphenol[13e] **13e** were synthesized from 2,4-dimethoxyphenol **12b** and 2,5-dimethoxyphenol[13e] **12c**, respectively, by way of the intermediate allyl ethers; 1-allyloxy-2,4-dimethoxybenzene[22e] and 2-allyloxy-1,4-dimethoxybenzene.[13e] In a similar manner, 2-hydroxynaphthalene **12d** was converted into 2-allyloxynaphthalene[22f] and then into 1-allyl-naphthalen-2-ol[22f] **13f** by way of thermal Claisen rearrangement.

5.2.1. 4-(But-2-enyloxy)-1,2-dimethoxybenzene 21. Crotyl bromide (5.3 g, 39 mmol, 4.0 mL) and K_2CO_3 (8.1 g, 59 mmol) were added to 3,4-dimethoxyphenol **12a** (3.0 g, 18 mmol) dissolved in dry acetone (200 mL). The reaction mixture was then heated at reflux under nitrogen for 21 h. The K_2CO_3 was removed by filtration and the solvent was removed in vacuo. Purification by silica gel column chromatography (10% EtOAc/hexane) afforded the product 4-(but-2-enyloxy)-1,2-dimethoxybenzene **21** as a clear yellow oil (2.0 g, 53%, *E*:*Z* ratio 75:25). (Found: M^+, 208.1099, $C_{12}H_{16}O_3$ requires 208.1099); ^1H NMR (300 MHz, $CDCl_3$, only *E* isomer characterized): δ= 1.71–1.75 (3H, m, CH_3), 3.80 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 4.37 (2H, br d, J=5.8 Hz, OCH_2), 5.66–5.78 [1H, m, OCH_2=CHC*H*(CH_3)], 5.80–5.87 [1H, m OCH_2C*H*=CH(CH_3)], 6.37 (1H, dd, J=8.7, 2.5 Hz, 5-H), 6.52 (1H, d, J=2.5 Hz, 3-H), 6.73 (1H, d, J=8.7 Hz, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$, only *E* isomer characterized): δ=17.5 (CH_3), 55.4 (OCH_3), 56.1 (OCH_3), 68.8 (OCH_2), 100.8 (CH), 103.7 (CH), 111.6 (CH), 126.0 (CH), 129.9 (CH), 143.2 (C), 149.6 (C), 153.1 (C); ν_{max} ($CHCl_3$)/cm^{-1}: 1610, 1602, 1511, 1454; MS: m/z=208 (M^+, 51%), 196 (37), 182 (100), 165 (55), 154 (90), 139 (57), 79 (50), 55 (92), 39 (80), 27 (50).



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5.2.2. 2-Allyl-4,6-dimethoxyphenol 13c. 1-Allyloxy-2,4-dimethoxybenzene (1.1 g, 5.7 mmol) was heated without solvent at 220–236 °C for 45 min under a N_2 atmosphere. The resultant brown residue was then subjected to silica gel column chromatography (20% EtOAc/hexane) to afford 2-allyl-4,6-dimethoxyphenol **13c** (0.58 g, 53%) as a light yellow oily material. (Found: M^+, 194.0958, $C_{11}H_{14}O_3$ requires 194.0943); ^1H NMR (300 MHz, $CDCl_3$): δ=3.39–3.41 (2H, m, $ArCH_2$), 3.72 (3H, s, OCH_3), 3.77 (3H, s, OCH_3), 5.03–5.11 (2H, m, CH_2CH=CH_2), 5.50 (1H, s, OH), 5.92–6.06 (1H, m, CH_2CH=CH_2), 6.35 (1H, d, J=2.7 Hz, ArH), 6.46 (1H, d, J=2.7 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=33.9 ($ArCH_2$), 55.4 (OCH_3), 55.6 (OCH_3), 97.1 (CH), 105.4 (CH), 115.3 (CH), 125.7 (C), 136.4 (CH), 137.4 (C), 146.8 (C), 152.7 (C); ν_{max} ($CHCl_3$)/cm^{-1}: 3555 br, 1639, 1617, 1605, 1499, 1467, 1431; MS: m/z=194 (M^+, 100%), 179 (34), 161 (5), 151 (12), 137 (6), 133 (6), 119 (6), 91 (10), 69 (8), 65 (5).

5.3. General procedure for the vinylation of substituted 2-allyl-phenols 13 to 1-allyl-2-vinyloxy-benzenes 14

Anhydrous $Cu(OAc)_2$ (1.2 mol equiv) was added to a thoroughly degassed solution of substituted 2-allylphenol **13** (ca. 1.0 mmol) in CH_3CN (3.0 mL). The reaction vessel was then fitted with an O_2 balloon and tetravinyltin (1.2 mol equiv) was added through a septum. The mixture was left to react for 22 h at room temperature after, which aqueous NH_4OAc (0.3 M, 25 mL) was added. The aqueous layer was then extracted with EtOAc (5×20 mL). The combined organic extracts were dried with anhydrous $MgSO_4$, then filtered and the solvent removed in vacuo. The resultant residue was purified by column chromatography (2–30% EtOAc/hexane) to afford the product **14**. The following compounds were prepared using this procedure:

5.3.1. 1-Allyl-4,5-dimethoxy-2-(vinyloxy)benzene 14a. The product **14a** (0.23 g, quantitative) was isolated as a clear oil starting from substrate **13a** (0.20 g, 1.0 mmol). (Found: M^+, 220.1100, $C_{13}H_{16}O_3$ requires 220.1099); ^1H NMR (300 MHz, $CDCl_3$): δ=3.30–3.32 (2H, d m, J= 6.6 Hz, $ArCH_2$), 3.84 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 4.26 [1H, dd, J=6.2, 1.8 Hz, OCH=C(H)*H*], 4.47 [1H, dd, J=13.9, 1.8 Hz, OCH=C(*H*)H], 5.02–5.03 [1H, m, CH_2-CH=C(H)*H*], 5.06–5.08 [1H, m, CH_2CH=C(*H*)H], 5.86–5.97 (1H, m, CH_2CH=CH_2), 6.56 (1H, dd, J=13.9, 6.2 Hz, OC*H*=CH_2), 6.57 (1H, s, ArH), 6.69 (1H, s, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=33.5 (CH_2), 56.0 (OCH_3), 56.2 (OCH_3), 92.1 (CH), 103.7 (CH), 112.9 (CH), 115.5 (CH), 122.3 (C), 136.9 (CH), 145.5 (C), 147.1 (C), 147.9 (C), 150.4 (CH); IR ν_{max} ($CHCl_3$)/cm^{-1} 1635, 1609, 1510; MS: m/z=221 (M^++H, 18%), 220 (M^+, 100%), 205 (22), 194 (93), 191 (23), 179 (56), 91 (20), 69 (23).

5.3.2. 1-(But-3-en-2-yl)-4,5-dimethoxy-2-(vinyloxy)benzene 14b. The product **14b** (0.22 g, quantitative) was

isolated as a light yellow oil starting from substrate **13b** (0.20 g, 1.0 mmol). (Found: M^+, 234.1255, $C_{14}H_{18}O_3$ requires 234.1256); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.29 (3H, d, J=7.0 Hz, CH_3) 3.77–3.81 [1H, m, C*H*(CH_3)], 3.84 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 4.28 [1H, dd, J=6.2, 1.7 Hz, OCH=C(H)*H*], 4.50 [1H, dd, J=13.9, 1.7 Hz, OCH=C(*H*)H], 5.02–5.07 [2H, m, CH(CH_3)CH=CH_2], 5.94–6.05 [1H, m, CH(CH_3)C*H*=CH_2], 6.56 (1H, dd, J=13.9, 6.2 Hz, OC*H*=CH_2), 6.56 (1H, s, ArH), 6.69 (1H, s, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.6 (CH_3), 36.2 [*C*H(CH_3)], 56.9 (OCH_3), 57.1 (OCH_3), 93.2 (CH), 104.6 (CH), 111.6 (CH), 114.0 (CH), 128.7 (C), 143.3 (CH), 146.5 (C), 147.5 (C), 148.6 (C), 151.5 (CH); IR ν_{max} ($CHCl_3$)/cm^{-1} 1639, 1609, 1509; MS: m/z=235 (M^++H, 22%), 234 (M^+, 100%), 219 (20), 205 (41), 192 (21), 191 (77), 176 (19), 161 (17), 91 (18), 77 (19), 27 (22).

5.3.3. 1-Allyl-3,5-dimethoxy-2-(vinyloxy)benzene 14c. The product **14c** (0.22 g, quantitative) was obtained as a clear oil starting from substrate **13c** (0.19 g, 1.0 mmol). (Found: M^+, 220.1099, $C_{13}H_{16}O_3$ requires 220.1099); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.32 (2H, d m, J=6.7 Hz, CH_2), 3.77 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 4.12 [1H, dd, J=6.3, 1.9 Hz, OCH=C(H)*H*], 4.24 [1H, dd, J=13.9, 1.9 Hz, OCH=C(*H*)H] 5.04–5.11 (2H, m, CH_2CH=CH_2), 5.85–5.96 (1H, m, CH_2C*H*=CH_2), 6.32 (1H, d, J=2.8 Hz, ArH), 6.39 (1H, d, J=2.8 Hz, ArH), 6.53 (1H, dd, J=13.9, 6.3 Hz, OC*H*=CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ=34.2 (CH_2), 55.4 (OCH_3), 55.9 (OCH_3), 89.1 (CH), 98.3 (CH), 105.1 (CH), 116.1 (CH), 134.4 (C), 135.8 (C), 136.3 (CH), 151.5 (CH) 152.6 (C), 157.0 (C); IR ν_{max} ($CHCl_3$)/cm^{-1} 1633, 1610, 1594, 1486; MS: m/z=220 (M^+, 100%), 206 (48), 196 (38), 191 (60), 181 (71), 177 (32), 149 (34), 69 (30), 57 (77), 43 (45).

5.3.4. 1-(But-3-en-2-yl)-3,5-dimethoxy-2-(vinyloxy)benzene 14d. The product **14d** (0.21 g, quantitative) was isolated as a light yellow oil starting from substrate **13d** (0.20 g, 1.0 mmol). (Found: M^+, 234.1255, $C_{14}H_{18}O_3$ requires 234.1256); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.29 (3H, d, J=7.0 Hz, CH_3) 3.71–3.81 [1H, m under 2×OCH_3, C*H*(CH_3)], 3.78 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 4.13 [1H, dd, J=6.3, 1.8 Hz, OCH=C(H)*H*], 4.25 [1H, dd, J=13.9, 1.8 Hz, OCH=C(*H*)H], 5.02–5.09 [2H, m, CH(CH_3)-CH=CH_2], 5.92–6.03 [1H, m, CH(CH_3)C*H*=CH_2], 6.31 (1H, d, J=2.7 Hz, ArH), 6.38 (1H, d, J=2.7 Hz, ArH), 6.55 (1H, dd, J=13.9, 6.3, OC*H*=CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.9 (CH_3), 35.8 [*C*H(CH_3)], 55.5 (OCH_3), 56.0 (OCH_3), 89.3 (CH), 98.0 (CH), 103.1 (CH), 113.4 (CH), 135.3 (C), 139.9 (C), 142.2 (CH), 151.9 (CH), 152.5 (C), 157.1 (C); IR ν_{max} ($CHCl_3$)/cm^{-1} 1640, 1610, 1600, 1487; MS: m/z=235 (M^++H, 16%), 234 (M^+, 100%), 219 (20), 207 (29), 205 (77), 192 (28), 191 (54), 149 (32).

5.3.5. 2-Allyl-1,4-dimethoxy-3-(vinyloxy)benzene 14e. The product **14e** (0.22 g, quantitative) was isolated as a clear yellow oil starting from substrate **13e** (0.19 g, 1.0 mmol). (Found: M^+, 220.1099, $C_{13}H_{16}O_3$ requires 220.1099); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.37 (2H, d m, J=6.2 Hz, CH_2), 3.77 (6H, s, 2×OCH_3), 4.14 [1H, dd, J=6.3, 1.9 Hz, OCH=C(H)*H*], 4.30 [1H, dd, J=13.9, 1.9 Hz, OCH=C(*H*)H], 4.92–5.01 (2H, m, CH_2CH=CH_2), 5.86–5.99 (1H, m, CH_2C*H*=CH_2), 6.56 (1H, dd, J=13.9, 6.3 Hz, OC*H*=CH_2), 6.62 (1H, d, J=8.9 Hz, ArH), 6.76 (1H, d, J=8.9 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=28.1 (CH_2), 55.8 (OCH_3), 56.4 (OCH_3), 89.6 (CH), 106.8 (CH), 110.6 (CH), 114.8 (CH), 123.2 (C), 136.1 (CH), 143.1 (C), 146.2 (C), 151.2 (CH), 152.1 (C); IR ν_{max} ($CHCl_3$)/cm^{-1} 1639, 1490; MS: m/z=221 (M^++H, 15%), 220 (M^+, 100%), 205 (21), 192 (45), 191 (33), 177 (21), 149 (58), 91 (43), 57 (50), 41 (63).

5.3.6. 1-Allyl-2-(vinyloxy)naphthalene 14f. The product **14f** (0.15 g, 74%) was isolated as a clear oil starting from substrate **13f** (0.18 g, 1.0 mmol). (Found: M^+, 210.10445, $C_{15}H_{14}O$ requires 210.10447); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.84 (2H, br d, J=5.9 Hz, CH_2), 4.34 [1H, dd, J=6.2, 1.7 Hz, OC=C*H*(H)], 4.55 [1H, dd, J=13.9, 1.7 Hz, OC=CH(*H*)], 4.48 [1H, dd, J=9.1, 1.6 Hz, CH_2CH=CH(*H*)], 5.03 (1H, br s, CH_2CH=C*H*(H)], 5.95–6.09 (1H, m, CH_2C*H*=CH_2), 6.68 (1H, dd, J=13.9, 6.2 Hz, OC*H*=CH_2), 7.24 (1H, d, J=9.0 Hz, ArH), 7.38–7.43 (1H, m, ArH), 7.47–7.52 (1H, m, ArH), 7.72 (1H, d, J=8.9 Hz, ArH), 7.80 (1H, d, J=8.1 Hz, ArH), 7.98 (1H, d, J=8.5 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=29.5 (CH_2), 93.2 (OCH=*C*H_2), 115.5 (CH), 119.1 (CH), 124.1 (CH), 124.3 (ArC), 124.5 (CH), 126.4 (CH), 128.2 (CH), 128.5 (CH), 131.0 (ArC), 133.1 (ArC), 136.3 (CH), 150.1 (CH), 151.1 (ArC); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1641, 1549, 1463; MS: m/z=210 (M^+, 100%), 181 (99), 165 (94), 152 (63), 128 (49), 115 (38), 77 (15), 63 (16).

5.4. General RCM procedure for the synthesis of substituted 4*H*-chromenes 15 from 1-allyl-2-vinyloxybenzenes 14

Typically, Grubbs catalyst **11** (4 mol%) was added to a degassed solution of the substituted 1-allyl-2-vinyloxybenzene **14** (ca. 0.5–1.0 mmol) dissolved in degassed, distilled toluene (ca. 30 mL, ca. 0.020 M). The reaction mixture was then heated at 60 °C for 1 h under a N_2 atmosphere. After removal of the solvent under reduced pressure the residue was purified by silica gel column chromatography (5–20% EtOAc/hexane) to afford the desired product **15**. The following compounds were obtained using this procedure:

5.4.1. 6,7-Dimethoxy-4*H*-chromene 15a (=5).[2,3] The product **15a** (0.12 g, 97%) was isolated as a light yellow oil starting from substrate **14a** (0.14 g, 0.64 mmol) and Grubbs catalyst **11** (20 mg, 0.024 mmol, 4 mol%) in toluene (30 mL, 0.020 M); ^{1}H NMR (200 MHz, $CDCl_3$): δ=3.31–3.33 (2H, m, 4-H), 3.82 (6H, s, 2×OCH_3), 4.86–4.93 (1H, m, 3-H), 6.42 (1H, s, ArH), 6.46 (1H, s, ArH), 6.42–6.46 (1H, m, 2-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=22.7 (CH_2), 55.8 (OCH_3), 56.1 (OCH_3), 99.7 (CH), 100.5 (CH), 110.2 (C), 111.2 (CH), 140.4 (CH), 144.7 (C), 144.8 (C), 148.0 (C).

5.4.2. 6,7-Dimethoxy-4-methyl-4*H*-chromene 15b. The product **15b** (0.15 g, 90%) was isolated as a dark yellow oil (that rapidly turned green upon drying under vacuum) starting from substrate **14b** (0.19 g, 0.81 mmol) and Grubbs catalyst **11** (27 mg, 0.031 mmol, 4 mol%) in toluene (40 mL, 0.02 M). (Found: M^+, 206.0940, $C_{12}H_{14}O_3$ requires 206.0943); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.32

(3H, d, $J=6.9$ Hz, CH_3), 3.44–3.48 (1H, m, 4-H), 3.83 (3H, s, OCH_3), 3.84 (3H, s, OCH_3), 4.84 (1H, dd, $J=6.2$, 3.9 Hz, 3-H), 6.43 (1H, s, ArH), 6.43–6.46 (1H, m, 2-H), 6.58 (1H, s, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 2 quaternary carbons not observed in spectrum): $\delta=25.6$ (CH_3), 28.2 (4-C), 55.6 (OCH_3), 56.0 (OCH_3), 98.0 (CH), 102.8 (CH), 105.7 (CH), 126.4 (C), 139.3 (CH), 155.4 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1664, 1618, 1509, 1452, 1406; MS: $m/z=206$ (M^+, 17%), 192 (14), 191 (100), 181 (15), 175 (10), 147 (22).

5.4.3. 6,8-Dimethoxy-4*H*-chromene 15c. The product **15c** (0.12 g, 68%) was isolated as a yellow oil that darkened rapidly with time, starting from substrate **14c** (0.20 g, 0.91 mmol) and Grubbs catalyst **11** (30 mg, 0.035 mmol, 4 mol%) in toluene (30 mL, 0.030 M). (Found: M^+, 192.0780, $C_{11}H_{12}O_3$ requires 192.0786); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=3.36$ (2H, br s, 4-H), 3.75 (3H, s, OCH_3), 3.85 (3H, s, OCH_3) 4.87–4.91 (1H, m, 3-H), 6.09 (1H, d, $J=2.5$ Hz, ArH), 6.34 (1H, d, $J=2.5$ Hz, ArH), 6.56 (1H, br d, $J=6.2$ Hz, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=23.4$ (4-C), 55.5 (OCH_3), 55.9 (OCH_3), 98.3 (CH), 99.4 (CH), 103.3 (CH), 120.5 (C), 135.3 (C), 140.6 (CH), 148.5 (C), 155.2 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1664, 1601, 1491, 1457, 1428; MS: $m/z=192$ (M^+, 100%), 191 (83), 180 (10), 177 (25), 176 (14), 149 (42), 148 (11), 134 (10), 133 (11), 121 (12), 106 (11), 91 (11), 77 (13), 63 (10).

5.4.4. 6,8-Dimethoxy-4-methyl-4*H*-chromene 15d. The product **15d** (0.16 g, 91%) was isolated as a yellow oil (that rapidly turned green upon drying under vacuum) starting from substrate **14d** (0.20 g, 0.85 mmol) and Grubbs catalyst **11** (28 mg, 0.030 mmol, 4 mol%) in toluene (40 mL, 0.021 M). (Found: M^+, 206.0943, $C_{12}H_{14}O_3$ requires 206.0943); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.30$ (3H, d, $J=6.9$ Hz, CH_3), 3.42–3.48 (1H, m, 4-H), 3.73 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 4.80–4.86 (1H, m, 3-H), 6.18 (1H, d, $J=2.6$ Hz, ArH), 6.32 (1H, d, $J=2.6$ Hz, ArH), 6.53 (1H, dd, $J=6.2$, 0.8 Hz, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=26.0$ (CH_3), 28.5 (4-C), 55.8 (OCH_3), 56.2 (OCH_3), 98.4 (CH), 103.1 (CH), 106.1 (CH), 126.7 (C), 139.7 (CH), 140.9 (C), 148.7 (C), 155.8 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1665, 1598, 1489; MS: $m/z=206$ (M^+, 45%), 192 (25), 191 (100), 181 (16).

5.4.5. 5,8-Dimethoxy-4*H*-chromene 15e. The product **15e** (0.14 g, 80%) was isolated as a light yellow oil starting from substrate **14e** (0.20 g, 0.91 mmol) and Grubbs catalyst **11** (30 mg, 0.035 mmol, 4 mol%) in toluene (30 mL, 0.030 M). (Found: M^+, 192.0785, $C_{11}H_{12}O_3$ requires 192.0786); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=3.22$–3.24 (2H, m, 4-H), 3.74 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 4.92–4.97 (1H, m, 3-H), 6.39 (1H, d, $J=8.9$ Hz, ArH), 6.53 (1H, dt, $J=6.3$, 1.9 Hz, 2-H), 6.67 (1H, d, $J=8.9$ Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=18.5$ (4-C), 55.5 (OCH_3), 56.3 (OCH_3), 100.3 (CH), 102.9 (CH), 109.4 (CH), 110.4 (C), 139.9 (CH), 141.5 (C), 141.9 (C), 151.2 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1676, 1640, 1599, 1494, 1454. MS: $m/z=193$ ($M^+ + 1$, 12%), 192 (100), 191 (40), 177 (62), 162 (16), 161 (35), 149 (10), 86 (20), 84 (32).

5.4.6. 1*H*-Benzo[*f*]chromene 15f.[23] The product **15f** (0.060 g, 63%) was isolated as a light-coloured semi-solid, which darkened rapidly with time, starting from substrate **14f** (0.11 g, 0.50 mmol) and Grubbs catalyst **11** (18 mg, 0.021 mmol, 4 mol%) in toluene (35 mL, 0.014 M); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=3.68$ (2H, br d, $J=1.9$ Hz, 1-H), 5.11–5.16 (1H, m, 2-H), 6.60 (1H, dt, $J=6.3$, 1.9 Hz, 3-H), 7.07 (1H, d, $J=8.9$ Hz, ArH), 7.39–7.44 (1H, m, ArH), 7.50–7.61 (1H, m, ArH), 7.65–7.70 (2H, m, 2×ArH), 7.78 (1H, d, $J=8.0$ Hz, 6-H).

5.5. Experimental part B: 2*H*-chromenes

5.5.1. Known precursors for the synthesis of the 2*H*-chromenes 20a–g. 2-Nitrophenol **16a**, 4-Nitrophenol **16b**, 3-hydroxy-4-methoxybenzaldehyde **16c**, 2-hydroxybenzaldehyde **16d**, 4-hydroxybenzaldehyde **16e** and 2-hydroxynaphthalene **16f** (=**12d**) were all converted to their allyl derivatives: 1-allyloxy-2-nitrobenzene,[24a] 1-allyloxy-4-nitrobenzene,[24b] 3-allyloxy-4-methoxybenzaldehyde,[24c] 2-allyloxybenzaldehyde,[24d] 4-allyloxybenzaldehyde,[24e] and 2-allyloxynaphthalene,[22f] respectively. A Claisen rearrangement was performed on these compounds to afford the rearranged products: 2-allyl-6-nitrophenol **17a**,[15b] 2-allyl-4-nitrophenol **17b**,[13e] 2-allyl-3-hydroxy-4-methoxybenzaldehyde **17c**,[15b] 3-allyl-2-hydroxybenzaldehyde **17d**,[24f] 3-allyl-4-hydroxybenzaldehyde[13e] **17e** and 1-allyl-naphthalen-2-ol[22f] **17f** (=**13f**), respectively. 2-Allylphenol **17g** was purchased from Aldrich and used without further purification.

5.6. General procedure for the isomerization of substituted 2-allylphenols 17 to 2-(prop-1-enyl)phenols 18

Typically, substituted 2-allylphenol **17** (ca. 3 mmol) and [RuClH(CO)(PPh_3)$_3$] (1–4 mol%) were dissolved in distilled, degassed toluene (5 mL). The reaction was heated at 65–90 °C for 24 h and the completion of the reaction was confirmed by NMR spectroscopy of a crude sample. The reaction solution was purified by filtration through a short silica gel pad (5% EtOAc/hexane) to afford the product, **18** as a mixture of *E*/*Z* isomers (predominantly *E*, which were then characterized by NMR spectroscopy). The following compounds were prepared using this procedure:

5.6.1. 2-Nitro-6-(prop-1-enyl)phenol 18a. The product **18a** (0.48 g, 96%, *E*:*Z* ratio 88:12) was obtained as an yellow oil from **17a** (0.50 g, 2.8 mmol). Found: M^+, 179.0556, $C_9H_9NO_3$ requires 179.0582); ^{1}H NMR (300 MHz, C_6D_6, only *E* isomer characterized, OH not observed in spectrum): $\delta=1.63$ (3H, dd, $J=6.7$, 1.7 Hz, CH_3), 5.92–6.04 (1H, m, CH=C*H*CH$_3$), 6.21–6.26 (1H, m, ArH), 6.71 (1H, dd, $J=15.9$, 1.6 Hz, C*H*=CHCH$_3$), 7.10–7.15 (1H, m, ArH), 7.53 (1H, dd, $J=8.5$, 1.4 Hz, ArH), 11.02 (1H, s, OH); ^{13}C NMR (75 MHz, C_6D_6, only *E* isomer characterized, one quaternary carbon obscured in spectrum): $\delta=18.8$ (CH_3), 119.2 (CH), 123.1 (CH), 124.1 (CH), 129.0 (CH), 133.3 (CH), 137.1 (C), 152.4 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 3205 br, 1655, 1605, 1539, 1443, 1333; MS: $m/z=179$ (M^+, 21%), 162 (32), 149 (23), 132 (40), 131 (53), 103 (10), 81 (11), 77 (14), 69 (100), 55 (12), 43 (15), 41 (18).

5.6.2. 4-Nitro-2-(prop-1-enyl)phenol 18b. The product **18b** (0.17 g, 96%, *E*:*Z* ratio 87:13) was obtained as an

orange oil from **17b** (0.18 g, 1.0 mmol). Found: M^+, 179.0574, $C_9H_9NO_3$ requires 179.0582); ^1H NMR (300 MHz, $CDCl_3$, only *E* isomer characterized, OH not observed in spectrum): $\delta=1.95$ (3H, dd, $J=6.5$, 1.6 Hz, CH_3), 6.32–6.41 (1H, m, CH=C*H*CH_3), 6.57 (1H, dd, $J=$ 17.3, 1.4 Hz, C*H*=$CHCH_3$), 6.88 (1H, d, $J=8.9$ Hz, 6-H), 7.99 (1H, dd, $J=8.9$, 2.7 Hz, 5-H), 8.23 (1H, d, $J=2.7$ Hz, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$, only *E* isomer characterized): $\delta=18.9$ (CH_3), 115.8 (CH), 123.2 (CH), 123.4 (CH), 123.8 (CH), 125.8 (C), 131.2 (CH), 141.6 (C), 158.0 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 3384 br, 1655, 1614, 1583, 1519, 1493, 1434, 1338; MS: $m/z=179$ (M^+, 100%), 167 (18), 149 (14), 132 (11), 118 (12), 103 (10), 77 (18), 69 (15), 57 (20), 41 (13).

5.6.3. 3-Hydroxy-4-methoxy-2-(prop-1-enyl)benzaldehyde 18c. The product **18c** (0.38 g, 67%, *E*:*Z* ratio 66:34) was obtained as an orange oil from **17c** (0.57 g, 3.0 mmol). Found: M^+, 192.0787, $C_{11}H_{12}O_3$ requires 192.0786; ^1H NMR (300 MHz, $CDCl_3$): *E* isomer $\delta=1.99$ (3H, dd, $J=6.9$, 1.6 Hz, CH_3), 3.97 (3H, s, OCH_3), 5.95 (1H, s, OH), 6.05 (1H, dq, $J=15.9$, 6.6 Hz, CH=C*H*CH_3), 6.80 (1H, dd, $J=15.9$, 1.7 Hz, C*H*=$CHCH_3$), 6.86 (1H, d, $J=8.5$ Hz, 5-H), 7.48 (1H, d, $J=8.5$ Hz, 6-H), 10.08 (1H, s, CHO): *Z* isomer $\delta=1.59$ (3H, dd, $J=6.6$, 1.7 Hz, CH_3), 3.98 (3H, s, OCH_3), 5.81 (1H, s, OH), 6.17 (1H, dq, $J=11.3$, 6.9 Hz, CH=C*H*CH_3), 6.55 (1H, dd, $J=11.3$, 1.6 Hz, C*H*=$CHCH_3$), 6.91 (1H, d, $J=8.6$ Hz, 5-H), 7.54 (1H, d, $J=8.6$ Hz, 6-H), 10.02 (1H, s, CHO); ^{13}C NMR (75 MHz, $CDCl_3$, only *E* isomer characterized): $\delta=19.7$ (CH_3), 56.6 (OCH_3), 109.0 (CH), 122.2 (CH), 123.0 (CH), 128.6 (C), 132.7 (C), 136.4 (CH), 143.3 (C), 150.8 (C), 192.0 (CHO); IR ν_{max} ($CHCl_3$)/cm^{-1}: 3424 br, 1678, 1593, 1484, 1440; MS $m/z=192$ (M^+, 83%), 177 (100), 162 (20), 103 (21), 91 (18), 77 (21).

5.6.4. 2-Hydroxy-3-(prop-1-enyl)benzaldehyde 18d. The product **18d** (0.45 g, 89%, *E*:*Z* ratio 85:15) was obtained as an orange oil from **17d** (0.51 g, 3.5 mmol). Found: M^+, 162.0653, $C_{10}H_{10}O_2$ requires 162.0681); ^1H NMR (300 MHz, $CDCl_3$, only *E* isomer characterized): $\delta=1.93$ (3H, dd, $J=6.6$, 1.6 Hz, CH_3), 6.29–6.41 (1H, m, CH=C*H*CH_3), 6.70 (1H, dd, $J=15.9$, 1.6 Hz, C*H*=$CHCH_3$), 6.94–6.99 (1H, m, ArH), 7.41 (1H, dd, $J=$ 7.6, 1.5 Hz, ArH), 7.62 (1H, d, $J=7.6$ Hz, ArH), 9.87 (1H, s, CHO), 11.43 (1H, s, OH); ^{13}C NMR (75 MHz, $CDCl_3$, only *E* isomer characterized): $\delta=19.0$ (CH_3), 119.6 (CH), 120.6 (C), 123.9 (CH), 128.4 (CH), 132.2 (CH), 133.6 (CH), 137.1 (C), 158.4 (C), 196.8 (CHO); IR ν_{max} ($CHCl_3$)/cm^{-1}: 3250 br, 1951, 1654, 1608, 1486, 1431; MS: $m/z=162$ (M^+, 100%), 144 (14), 133 (12), 121 (14), 115 (17), 103 (7), 91 (10), 77 (15), 57 (12), 43 (14), 41 (14).

5.6.5. 4-Hydroxy-3-(prop-1-enyl)benzaldehyde 18e. The product **18e** (0.42 g, 42%, *E*:*Z* ratio 92:8) was obtained as a yellow solid (mp 88–91 °C, recrystalized from $CHCl_3$) from **17e** (1.0 g, 6.2 mmol). Found: M^+, 162.0680, $C_{10}H_{10}O_2$ requires 162.0681); ^1H NMR (300 MHz, $CDCl_3$, only *E* isomer characterized): $\delta=1.93$ (3H, dd, $J=6.6$, 1.7 Hz, CH_3), 6.27–6.37 (1H, m, CH=C*H*CH_3), 6.64 (1H, d, $J=$ 15.9 Hz, C*H*=$CHCH_3$), 6.96 (1H, d, $J=8.4$ Hz, 5-H), 7.17 (1H, br s, OH), 7.65 (1H, dd, $J=8.4$, 1.9 Hz, 6-H), 7.88 (1H, d, $J=1.9$ Hz, 2-H), 9.84 (1H, s, CHO); ^{13}C NMR (75 MHz, $CDCl_3$, only *E* isomer characterized): $\delta=18.9$ (CH_3), 116.2 (CH), 124.2 (CH), 126.1 (C), 129.5 (C), 129.7 (CH), 129.7 (CH), 130.4 (CH), 158.7 (C), 191.9 (CHO); IR ν_{max} ($CHCl_3$)/cm^{-1}: 3260 br, 1670, 1586, 1501, 1436; MS: $m/z=162$ (M^+, 100%), 133 (13), 115 (121), 105 (12), 91 (10), 77 (14), 65 (9), 51 (9), 39 (9).

5.6.6. 1-(Prop-1-enyl)naphthalen-2-ol 18f.[25] The product **18f** (0.42 g, 84%, *E*:*Z* ratio 33:67) was obtained as a clear oil from **17f** (0.5 g, 2.7 mmol). Found: M^+, 184.0886, $C_{13}H_{12}O$ requires 184.0888; ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer $\delta=1.61$ (3H, br d, $J=6.7$ Hz, CH_3), 5.44 (1H, s, OH), 6.24–6.35 (1H, m, CH=C*H*CH_3), 6.56 (1H, br d, $J=$ 11.0 Hz, C*H*=$CHCH_3$), 7.20 (1H, d, $J=8.9$ Hz, ArH), 7.30–7.35 (1H, m, ArH), 7.41–7.46 (1H, m, ArH), 7.70–7.82 (3H, m, 3×ArH): *E* isomer $\delta=2.05$ (3H, br d, $J=6.4$ Hz, CH_3), 5.86 (1H, s, OH), 6.06–6.18 (1H, m, CH=C*H*CH_3), 6.66 (1H, br d, $J=16.3$ Hz, C*H*=$CHCH_3$), 7.19 (1H, d, $J=$ 8.7 Hz, ArH), 7.30–7.35 (1H, m, ArH), 7.41–7.46 (1H, m, ArH), 7.66 (1H, d, $J=8.9$ Hz, ArH), 7.70–7.82 (2H, m, 2× ArH); ^{13}C NMR (75 MHz, $CDCl_3$): *Z* isomer $\delta=14.8$ (CH_3), 115.3 (C), 117.0 (CH), 122.6 (CH), 123.3 (CH), 124.0 (CH), 126.3 (CH and C), 128.2 (CH), 129.1 (CH), 132.6 (C), 133.7 (CH), 149.7 (C): *E* isomer (some signals under those of *Z* isomer) $\delta=19.0$ (CH_3), 117.4 (CH), 123.7 (CH), 124.4 (CH), 128.7 (CH), 132.7 (C), 133.8 (CH), 150.3 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 3350 br, 1689, 1641, 1588, 1569, 1550, 1515, 1463, 1431; MS $m/z=185$ ($M^+ + 1$, 18%), 184 (100), 183 (37), 181 (11), 173 (14), 172 (17), 170 (15), 169 (94), 168 (10), 167 (14), 165 (257), 155 (12), 153 (11), 152 (14), 141 (18), 139 (13), 128 (14), 127 (13), 115 (23), 83 (15).

5.6.7. 2-(Prop-1-enyl)-phenol 18g.[26] The product **18g** (0.90 g, 90%, *E*:*Z* ratio 89:11) was obtained as an orange oil from **17g** (1.0 g, 7.5 mmol); ^{1}NMR (300 MHz, $CDCl_3$, only *E* isomer characterized): $\delta=1.90$ (3H, dd, $J=6.6$, 1.7 Hz, CH_3), 5.06 (1H, br s, OH), 6.19 (1H, dq, $J=15.9$, 6.6 Hz, CH=C*H*CH_3), 6.58 (1H, br d, $J=15.9$ Hz, C*H*=$CHCH_3$), 6.77 (1H, d, $J=8.0$ Hz, ArH), 6.85–6.90 (1H, m, ArH), 7.05–7.11 (1H, m, ArH), 7.28 (1H, dd, $J=$ 7.6, 1.2 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, only *E* isomer characterized): $\delta=18.9$ (CH_3), 115.6 (CH), 120.9 (CH), 125.1 (C), 125.3 (CH), 127.4 (CH), 127.9 (CH), 128.3 (CH), 152.3 (C).

5.7. General procedure for the allylation of substituted 2-(prop-1-enyl)phenols 18 to afford 1-allyloxy-2-(prop-1-enyl)benzenes 19

Typically, substituted 2-(prop-1-enyl)phenol **18** (ca. 2.6 mmol) and allyl bromide (2 mol equiv) were dissolved in acetone (10 mL) (or DMF for substrates containing an aldehyde functionality) containing K_2CO_3 (2 mol equiv). The resulting reaction mixture was then heated at reflux for 12–24 h (at 60 °C for DMF solutions). The reaction mixture was then cooled and the solvent removed under reduced pressure. H_2O (50 cm^3) was then added to the residue and the organic material, extracted using CH_2Cl_2 (4×40 mL). The organic layer was then separated and dried using $MgSO_4$ and then concentrated in vacuo. The organic residue obtained was then purified by column chromatography (10–30% EtOAc/hexane) to afford **19** as a mixture of *E*/*Z*

isomers (predominantly *E*, which were then characterized by NMR spectroscopy). The following compounds were prepared using this procedure:

5.7.1. 2-Allyloxy-1-nitro-3-(prop-1-enyl)benzene 19a. The product **19a** (0.25 g, 71%, *E*:*Z* ratio 90:10) was obtained as an orange oil from **18a** (0.18 g, 0.96 mmol). (Found: M^+, 219.0893, $C_{12}H_{13}NO_3$ requires 219.0895); ^{1}H NMR (300 MHz, $CDCl_3$, only *E* isomer characterized): δ= 1.93 (3H, dd, J=6.6, 1.6 Hz, CH_3), 4.49 (2H, br d, J= 5.8 Hz, OCH_2), 5.29 (1H, dd, J=10.4, 1.2 Hz, CH=C(H)*H*), 5.39 (1H, dd, J=17.1, 1.5 Hz, CH=C(*H*)H), 6.01–6.14 (1H, m, CH_2CH=CH_2), 6.26–6.38 (1H, m, CH=C*H*CH_3), 6.66 (1H, dd, J=15.9, 1.5 Hz, C*H*=$CHCH_3$), 7.12–7.17 (1H, m, ArH), 7.60–7.66 (2H, m, 2×ArH); ^{13}C NMR (75 MHz, $CDCl_3$, only *E* isomer characterized): δ=18.9 (CH_3), 77.0 (OCH_2 under $CDCl_3$ signals), 105.3 (CH), 122.9 (CH), 123.5 (CH), 124.5 (CH), 130.4 (CH), 130.5 (CH), 134.1 (C), 143.6 (C). 144.0 (CH), 147.1 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1670, 1655, 1602, 1531, 1444, 1359; MS: m/z=220 (M^++H, 29%), 219 (M^+, 44%), 204 (47), 190 (68), 186 (213), 172 (28), 162 (47), 132 (100), 115 (46), 103 (48), 77 (48), 39 (47).

5.7.2. 1-Allyloxy-4-nitro-2-(prop-1-enyl)benzene 19b. The product **19b** (0.18 g, quantitative, *E*:*Z* ratio 70:30) was obtained as an orange oil from **18b** (0.15 g, 0.83 mmol). Found: M^+, 219.0905, $C_{12}H_{13}NO_3$ requires 219.0895); ^{1}H NMR (300 MHz, $CDCl_3$): *E* isomer δ=1.94 (3H, dd, J= 6.6, 1.7 Hz, CH_3), 4.66–4.68 (2H, m, OCH_2), 5.35 [1H, dd, J=10.5, 1.3 Hz, CH=C(H)*H*], 5.44 [1H, dd, J=17.3, 1.3 Hz, CH=C(*H*)H], 6.01–6.14 (1H, m, CH_2CH=CH_3), 6.38 (1H, dq, J=15.9, 6.6 Hz, CH=C*H*CH_3), 6.70 (1H, dd, J=15.9, 1.6 Hz, C*H*=$CHCH_3$), 6.87 (1H, d, J=9.1 Hz, 6-H), 8.05 (1H, dd, J=9.1, 2.8 Hz, 5-H), 8.29 (1H, d, J= 2.8 Hz, 3-H): *Z* isomer δ=1.87 (3H, dd, J=7.2, 1.9 Hz, CH_3), 4.66–4.68 (2H, m, OCH_2), 5.34 [1H, dd, J=10.5, 1.4 Hz, CH=C(H)*H*], 5.40–5.46 [1H, m, CH=C(*H*)H], 5.91–6.11 (2H, m, CH_2CH=CH_3 and CH=C*H*CH_3), 6.51 (1H, dd, J=11.6, 1.7 Hz, C*H*=$CHCH_3$), 6.91 (1H, d, J= 9.0 Hz, 6-H), 8.12 (1H, dd, J=9.0, 2.7 Hz, 5-H), 8.16 (1H, d, J=2.7 Hz, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$): *E* isomer δ=18.9 (CH_3), 69.6 (OCH_2), 111.4 (CH), 118.3 (CH), 121.9 (CH), 123.5 (CH), 123.8 (CH), 128.1 (C), 129.5 (CH), 132.0 (CH), 141.6 (C), 159.7 (C): *Z* isomer δ=14.6 (CH_3), 69.5 (OCH_2), 111.1 (CH), 118.2 (CH), 123.3 (CH), 124.0 (CH), 125.6 (CH), 127.2 (C), 129.3 (CH), 131.9 (CH), 141.0 (C), 160.9 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1676, 1585, 1565, 1511; MS: m/z=219 (M^+, 48%), 190 (10), 178 (67), 161 (14), 133 (11), 132 (100), 131 (64), 103 (23), 78 (12), 77 (22), 63 (11), 51 (13), 41 (71), 39 (25).

5.7.3. 3-Allyloxy-4-methoxy-2-(prop-1-enyl)benzaldehyde 19c. The product **19c** (0.13 g, 81%, *E*:*Z* ratio 74:26) was obtained as an orange oil from **18c** (0.13 g, 0.68 mmol). (Found: M^+, 232.1083, $C_{14}H_{16}O_3$ requires 232.1099); ^{1}H NMR (300 MHz, $CDCl_3$): *E* isomer δ=1.98 (3H, dd, J=6.6, 1.7 Hz, CH_3), 3.92 (3H, s, OCH_3), 4.41–4.46 (2H, m, OCH_2), 5.22 [1H, br d, J=10.1 Hz, CH=C(H)*H*], 5.34 [1H, dd, J=17.2, 1.5 Hz, CH=C(*H*)H], 5.86 (1H, dq, J=15.9, 6.6 Hz, CH=C*H*CH_3), 6.00–6.14 (1H, m, CH_2CH=CH_3), 6.73 (1H, dd, J=15.9, 1.7 Hz, C*H*=$CHCH_3$), 6.91 (1H, d, J=8.7 Hz, 5-H), 7.71 (1H, d, J=8.7 Hz, 6-H), 10.05 (1H, s, CHO): *Z* isomer δ=1.55 (3H, dd, J=6.8, 1.7 Hz, CH_3), 3.94 (3H, s, OCH_3), 4.41–4.46 (2H, m under *E*-isomer, OCH_2), 5.18–5.24 [1H, m under *E*-isomer, CH=C(H)*H*], 5.31 [1H, dd, J=17.2, 1.5 Hz, CH=C(*H*)H], 6.00–6.14 (2H, m under *E*-isomer, CH_2CH=CH_3 and CH=C*H*CH_3), 6.57 (1H, br d, J=11.4 Hz, C*H*=$CHCH_3$), 6.95 (1H, d, J= 8.8 Hz, 5-H), 7.75 (1H, d, J=8.7 Hz, 6-H), 9.99 (1H, s, CHO);^{13}C NMR (75 MHz, $CDCl_3$, only *E* isomer characterized): δ=19.1 (CH_3), 55.8 (OCH_3), 73.8 (OCH_2), 110.4 (CH), 117.7 (CH), 117.8 (CH), 122.2 (CH), 125.9 (CH), 128.3 (C), 133.9 (C), 136.5 (CH), 145.0 (C), 157.0 (C), 191.4 (CHO); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1676, 1585, 1565, 1511, 1483, 1464, 1440, 1420; MS: m/z=232 (M^+, 37%), 191 (100), 175 (11), 164 (12), 163 (16), 148 (18), 135 (48), 119 (9), 103 (23), 91 (25), 77 (17), 65 (14), 41 (20).

5.7.4. 2-Allyloxy-3-(prop-1-enyl)benzaldehyde 19d. The product **19d** (0.53 g, quantitative, *E*:*Z* ratio 85:15) was isolated as a yellow oil from **18d** (0.43 g, 2.7 mmol). Found: M^+, 202.0997, $C_{13}H_{14}O_2$ requires 202.0994); ^{1}H NMR (300 MHz, $CDCl_3$, only *E* isomer characterized): δ=1.94 (3H, dd, J=6.6, 1.7 Hz, CH_3), 4.44–4.47 (2H, m, OCH_2), 5.29–5.37 [1H, m, CH=C(H)*H*], 5.38–5.44 [1H, m, CH=C(H)*H*], 6.07–6.15 (1H, m, OCH_2CHCH_2), 6.29–6.36 (1H, m, ArCH=C*H*), 6.67 (1H, dd, J=15.9, 1.5 Hz, ArC*H*=CH), 7.15–7.20 (1H, m, ArH), 7.67–7.72 (2H, m, 2×ArH), 10.39 (1H, s, CHO); ^{13}C NMR (75 MHz, $CDCl_3$, only *E* isomer characterized): δ=18.9 (CH_3), 77.0 (OCH_2), 118.7 (CH), 124.4 (CH), 124.5 (CH), 126.7 (CH), 128.6 (CH), 129.8 (C), 132.6 (CH), 132.7 (CH), 136.7 (C), 158.8 (C), 190.3 (CHO); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1684, 1590, 1445; MS: m/z=202 (M^+, 16%), 178 (16), 177 (84), 176 (15), 161 (39), 159 (21), 149 (100), 145 (18), 133 (27), 132 (24), 120 (37), 115 (17), 105 (38), 103 (16), 77 (35), 65 (21), 63 (15), 51 (27), 41 (54), 38 (34).

5.7.5. 4-Allyloxy-3-(prop-1-enyl)benzaldehyde 19e. The product **19e** (0.81 g, 64%, *E*:*Z* ratio 93:7) was obtained as an orange oil from **18e** (1.0 g, 6.2 mmol). Found: M^+, 202.0993, $C_{13}H_{14}O_2$ requires 202.0994); ^{1}H NMR (300 MHz, $CDCl_3$, only *E* isomer characterized): δ=1.92 (3H, br d, J=6.6 Hz, CH_3), 4.65 (2H, br d, J=5.1 Hz, OCH_2), 5.33 [1H, br d, J=10.6 Hz, CH=C(H)*H*], 5.44 [1H, br d, J=17.3 Hz, CH=C(H)*H*], 6.01–6.15 (1H, m, OCH_2-C*H*CH_2), 6.36 (1H, dq, J=15.8, 6.6 Hz, ArCH=C*H*), 6.73 (1H, br d, J=15.8 Hz, ArC*H*=CH), 6.94 (1H, d, J=8.5 Hz, 5-H), 7.69 (1H, dd, J=8.5, 1.7 Hz, 6-H), 7.93 (1H, d, J= 1.7 Hz, 2-H), 9.88 (1H, s, CHO); ^{13}C NMR (75 MHz, $CDCl_3$, only *E* isomer characterized): δ=18.9 (CH_3), 69.2 (OCH_2), 111.7 (CH), 118.1 (CH), 124.5 (CH), 127.9 (CH), 128.1 (C), 128.4 (CH), 129.8 (C), 130.3 (CH), 132.4 (CH), 159.9 (C), 191.1 (CHO); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1686, 1595, 1492; MS: m/z=202 (M^+, 58%), 173 (13), 161 (34), 159 (11), 133 (27), 115 (11), 106 (9), 105 (100), 103 (16), 79 (16), 77 (26), 51 (11), 41 (32), 39 (19).

5.7.6. 2-(Allyloxy)-1-(prop-1-enyl)naphthalene 19f.[25] The product **19f** (0.37 g, 65%, >95% *Z* isomer) was obtained as a clear oil from **18f** (0.30 g, 2.6 mmol). (Found: M^+, 224.1204, $C_{16}H_{16}O$ requires 224.1201); ^{1}H NMR (300 MHz, $CDCl_3$, only *Z* isomer characterized): δ=1.52 (3H, dd, J=6.8, 1.7 Hz, CH_3), 4.65–4.68 (2H, m, OCH_2), 5.23–5.27 (1H, m, CH=C(H)*H*), 5.38–5.45 [1H, m,

CH=C(*H*)H], 6.01–6.16 (2H, m, C*H*CH_3 and CH_2-C*H*=CH_2), 6.60 (1H, dd, J=11.2, 1.1 Hz, C*H*=$CHCH_3$), 7.26 (1H, d, J=9.0 Hz, ArH), 7.31–7.36 (1H, m, ArH), 7.41–7.47 (1H, m, ArH), 7.74–7.79 (2H, m, 2×ArH), 7.86 (1H, d, J=8.5 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, only *Z* isomer characterized): δ=15.4 (CH_3), 70.2 (OCH_2), 115.2 (CH), 117.1 (CH), 121.1 (C), 123.6 (CH), 125.1 (CH), 126.1 (CH), 128.0 (CH), 128.4 (CH), 129.1 (C), 129.7 (CH), 129.8 (CH), 132.7 (C), 133.9 (CH), 153.0 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1672, 1623, 1596, 1511, 1465, 1435; MS: *m*/*z*=224 (M^+, 85%), 183 (100), 165 (49), 155 (93), 139 (31), 115 (33), 41 (35).

5.7.7. 1-Allyloxy-2-(prop-1-enyl)benzene 19g. The product **19g** (0.45 g, 86%, *E*:*Z* ratio 90:10) was obtained as a clear oil from **18g** (0.40 g, 3.0 mmol). Found: M^+, 174.1043, $C_{12}H_{14}O$ requires 174.1045); ^{1}H NMR (300 MHz, $CDCl_3$, only *E* isomer characterized): δ=1.89 (3H, dd, J=6.7, 1.5 Hz, CH_3), 4.54–4.55 (2H, m, OCH_2), 5.27 [1H, dd, J=10.5, 1.3 Hz, CH=C(H)*H*], 5.41 [1H, dd, J=17.3, 1.3 Hz, CH=C(H)*H*], 6.01–6.14 (1H, m, C*H*=CH_2), 6.16–6.29 (1H, m, CH=C*H*), 6.75 (1H, d, J=15.9 Hz, ArC*H*=CH), 6.81–6.92 (2H, m, 2×ArH), 7.11–7.16 (1H, m, ArH), 7.39 (1H, d, J=7.6 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, only *E* isomer characterized): δ=19.3 (CH_3), 69.6 (OCH_2), 112.8 (CH), 117.6 (CH), 121.3 (CH), 126.1 (CH), 126.7 (CH), 126.8 (CH), 128.0 (CH), 130.6 (C), 134.0 (CH), 155.6 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1601; MS: *m*/*z*=174 (M^+, 51%), 145 (24), 133 (71), 121 (20), 105 (100), 91 (11), 77 (28), 65 (10), 51 (15), 41 (34), 39 (25).

5.8. General RCM procedure for the synthesis of substituted 2*H*-chromenes 20 from 1-allyloxy-2-(prop-1-enyl)benzenes 19

Typically, Grubbs catalyst **11** (4–6 mol%) was added to a degassed solution of the substituted 1-allyl-2-vinyloxybenzene **19** (ca. 0.5–1.0 mmol) dissolved in degassed, distilled toluene (ca. 30 mL, ca. 0.020 M). The reaction mixture was then heated at 60 °C for 1 h under a N_2 atmosphere. After removal of the solvent under reduced pressure the residue was purified by silica gel column chromatography (5–20% EtOAc/hexane) to afford the desired product **20**. The following compounds were obtained using this procedure:

5.8.1. 8-Nitro-2*H*-chromene 20a.[27] The product **20a** (0.14 g, 88%) was obtained as a light yellow oil from **19a** (0.20 g, 0.91 mmol). (Found: M^+, 177.0431, $C_9H_7O_3N$ requires 177.0426); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.00 (2H, dd, J=3.4, 1.9 Hz, 2-H), 5.90 (1H, dt, J=10.0, 3.4 Hz, 3-H), 6.45 (1H, dt, J=10.0, 1.9 Hz, 4-H), 6.87–6.93 (1H, m, ArH), 7.14 (1H, dd, J=7.4, 1.4 Hz, ArH), 7.67 (1H, dd, J=8.3, 1.4 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, one quaternary carbon not observed in spectrum): δ=66.5 (2-C), 120.4 (CH), 123.3 (CH), 123.4 (CH), 124.5 (C), 124.8 (CH), 130.9 (CH), 148.2 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1609, 1527, 1477, 1343; MS: *m*/*z*=177 (M^+, 100%), 176 (81), 130 (41), 103 (24), 102 (20), 77 (14), 51 (6).

5.8.2. 6-Nitro-2*H*-chromene 20b. The product **20b** (0.12 g, quantitative) was obtained as a fluffy yellow solid from **19b** (0.15 g, 0.68 mmol). This yellow solid (mp decomposition >210 °C with sweating at ca. 116 °C) decomposed rapidly (hours at room temperature) to a dark brown solid in air. (Found: M^+, 177.0434, $C_9H_7O_3N$ requires 177.0426); ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.99–5.00 (2H, m, 2-H), 5.88 (1H, dt, J=10.0, 3.3 Hz, 3-H), 6.43 (1H, d, J=10.0 Hz, 4-H), 6.78 (1H, d, J=8.9 Hz, 8-H), 7.83 (1H, d, J=2.5 Hz, 5-H), 7.99 (1H, dd, J=8.9, 2.5 Hz, 7-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=66.7 (2-C), 116.0 (CH), 121.7 (C), 122.1 (CH), 122.9 (CH), 123.6 (CH), 125.3 (CH), 141.8 (C), 159.5 (C); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1650, 1613, 1578, 1506, 1488, 1435; MS: *m*/*z*=177 (M^+, 99%), 176 (100), 131 (24), 130 (57), 103 (25), 102 (23), 77 (44), 74 (10), 69 (10), 63 (10), 51 (26).

5.8.3. 8-Methoxy-2*H*-chromene-5-carbaldehyde 20c. The product **20c** (0.32 g, 77%) was obtained as an orange oil from **19c** (0.50 g, 2.2 mmol). (Found: M^+, 190.0639, $C_{11}H_{10}O_3$ requires 190.0630); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.95 (3H, s, OCH_3), 4.86 (2H, dd, J=3.8, 1.8 Hz, 2-H), 6.00 (1H, dt, J=10.2, 3.8 Hz, 3-H), 6.89 (1H, d, J=8.5 Hz, ArH), 7.34 (1H, d, J=8.5 Hz, ArH), 7.53 (1H, dt, J=10.2, 1.8 Hz, 4-H), 9.97 (1H, s, CHO); ^{13}C NMR (75 MHz, $CDCl_3$): δ=56.0 (OCH_3), 65.1 (2-C), 110.4 (CH), 121.4 (CH), 122.9 (C), 124.4 (CH), 124.4 (C), 128.8 (CH), 143.2 (C), 152.5 (C), 191.7 (CHO); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1686, 1592, 1565, 1493, 1460, 1439, 1412; MS: *m*/*z*=190 (M^+, 100%), 189 (53), 175 (61), 161 (19), 147 (26), 119 (17), 91 (28), 65 (19).

5.8.4. 2*H*-Chromene-8-carbaldehyde 20d.[28] The product **20d** (0.21 g, 80%) was obtained as a light yellow oil from **19d** (0.34 g, 1.67 mmol). (Found: M^+, 160.0521, $C_{10}H_8O_2$ requires 160.0524); ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.96 (2H, br s, 2-H), 5.81–5.86 (1H, m, 3-H), 6.42 (1H, br d, J=10.0 Hz, 4-H), 6.87–6.92 (1H, m, ArH), 7.13 (1H, d, J=7.2 Hz, ArH), 7.61 (1H, d, J=7.8 Hz, ArH), 10.36 (1H, s, CHO); ^{13}C NMR (75 MHz, $CDCl_3$): δ=66.0 (2-C), 120.9 (CH), 122.4 (CH), 123.0 (C), 123.5 (CH), 123.6 (C), 127.2 (CH), 132.2 (CH), 156.9 (C), 189.1 (CHO); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1684, 1593, 1448, 1400; MS: *m*/*z*=160 (M^+, 80%), 159 (100), 148 (52), 120 (22), 118 (40), 103 (30), 102 (28), 91 (37), 89 (25), 77 (35), 63 (30), 57 (30), 55 (38), 51 (34), 41 (43), 39 (34).

5.8.5. 2*H*-Chromene-6-carbaldehyde 20e. The product **20e** (0.19 g, 76%) was obtained as an unstable orange oil from **19e** (0.31 g, 1.5 mmol). Found: M^+, 160.0531, $C_{10}H_8O_2$ requires 160.0524); ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.97 (2H, dd, J=3.3, 2.0 Hz, 2-H), 5.83 (1H, dt, J=10.0, 3.3 Hz, 3-H), 6.45 (1H, br d, J=10.0 Hz, 4-H), 6.84 (1H, d, J=8.3 Hz, 8-H), 7.47 (1H, d, J=1.9 Hz, 5-H), 7.62 (1H, dd, J=8.3, 1.9 Hz, 7-H), 9.82 (1H, s, CHO); ^{13}C NMR (75 MHz, $CDCl_3$): δ=66.4 (2-C), 116.2 (CH), 117.8 (C), 122.1 (C), 122.7 (CH), 123.5 (CH), 127.8 (CH), 132.1 (CH), 159.0 (C), 190.7 (CHO); IR ν_{max} ($CHCl_3$)/cm^{-1}: 1686, 1595, 1578; MS: *m*/*z*=160 (M^+, 73%), 159 (100), 131 (33), 103 (19), 77 (25), 51 (18), 40 (10).

5.8.6. 3*H*-Benzo[*f*]chromene 20f.[23,29] The product **20f** (0.086 g, 45%) was obtained as a yellow oil from **19f** (0.13 g, 0.58 mmol). The reaction was repeated on a smaller scale (**19f**, 0.067 g, 0.30 mmol) to afford the product **20f**

(0.055 g, 82%) in a better yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.86 (2H, dd, J=3.8, 1.7 Hz, 3-H), 5.91 (1H, dt, J=9.8, 3.8 Hz, 2-H), 7.06 (1H, d, J=8.9 Hz, ArH), 7.13 (1H, d, J=9.8 Hz, 1-H), 7.31–7.36 (1H, m, ArH), 7.44–7.50 (1H, m, ArH), 7.64 (1H, d, J=8.9 Hz, ArH), 7.74 (1H, d, J=8.2 Hz, ArH), 7.92 (1H, d, J=8.5 Hz, ArH).

5.8.7. 2*H*-Chromene 20g.[29] This reaction was performed on **19g** (~20 mg) on a NMR spectroscopy scale in an NMR tube using $CDCl_3$ as solvent.[13a] The formation of product **20g** (conversion >80%) was confirmed by ^{1}H and ^{13}C NMR spectroscopy and the spectra compared well with that reported in the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.80 (2H, dd, J=3.5, 1.9 Hz, 2-H), 5.75 (1H, dt, J=9.8, 3.5 Hz, 3-H), 6.40 (1H, br d, J=9.8 Hz, 4-H), 6.76 (1H, d, J=8.0 Hz, ArH), 6.82–6.87 (1H, m, ArH), 6.93–6.96 (1H, m, ArH), 7.05–7.11 (1H, m, ArH).

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