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Synthesis of Allylic Amide Functionalized 2*H*-Chromenes and Coumarins Using a One-Pot Overman Rearrangement and Gold(I)-Catalyzed Hydroarylation

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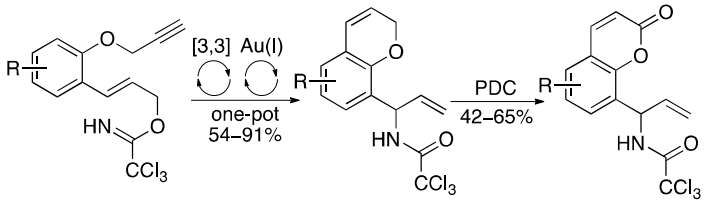


Abstract: A four-step synthesis of allylic trichloroacetimidates bearing a 2-proparyloxyaryl group has been developed from readily available 2-hydroxybenzaldehydes and these have been used for the preparation of allylic amide derived 2*H*-chromenes using an Overman rearrangement and a 6-*endo*-*dig* hydroarylation. High yields of the 2*H*-chromenes were achieved using a stepwise approach involving an Overman rearrangement under thermal conditions followed by a hydroarylation reaction with a gold(I) triflimide catalyst. An alternative method where both reactions were performed as a one-pot process was also developed and instead used a gold(I) chloride catalyst activated by silver(I) hexafluoroantimonate for the cycloisomerization step. The allylic amide derived 2*H*-chromenes were converted to the corresponding coumarin analogues by a PDC-mediated chemoselective allylic oxidation.

Keywords: 2*H*-chromenes, coumarins, Overman rearrangement, gold catalysis, hydroarylation.

INTRODUCTION

2*H*-1-Benzopyrans, commonly known as 2*H*-chromenes are an important class of heterocyclic compound found in a wide array of natural products.[1] These include the α-monomethyl 2*H*-chromene **1** from the leaf essential oil of *Calyptranthes tricona*[2] and tephrowatsin B (**2**), a flavonoid from *Tephrosia watsoniana* (Figure 1).[3] Many 2*H*-chromenes also display significant pharmacological activity such as the natural product, cannabichromene (**3**), which has analgesic, anti-inflammatory and antiviral properties.[4] Various synthetic 2*H*-chromenes have also been developed for medicinal applications and include iclaprim (**4**), an antibiotic used for skin infections,[5] and the 6-fluoro 2*H*-chromene **5** which, is a high affinity antagonist for the 5-HT_{1A} receptor.[6]

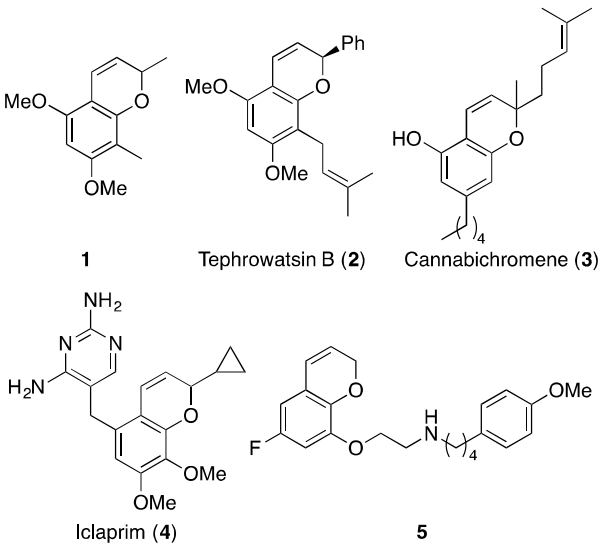


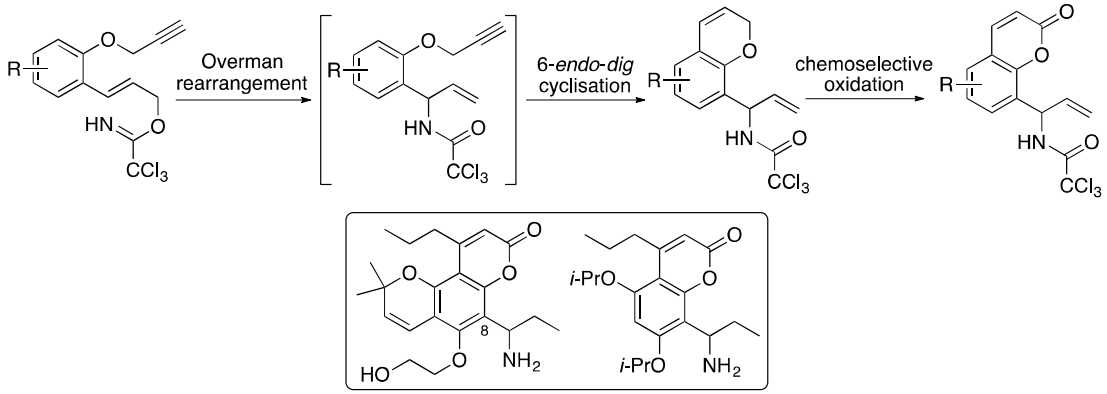
Figure 1. Structures of 2*H*-chromene natural products (**1**, **2** and **3**) and pharmacologically active compounds (**4** and **5**).

Due to their structural diversity and wide-ranging pharmacological activities, a variety of methods have been reported for the synthesis of 2*H*-chromenes.[7,8] One key approach has been formation of the pyran ring by intramolecular hydroarylation of aryl propargyl ethers. While this 6-*endo*-*dig* cycloisomerization can be performed under thermal conditions,[9] recent efforts have shown that this transformation can also be catalyzed using platinum(IV),[10] indium(III),[11] mercury(II),[12] palladium(II)[13]

and various gold(I) complexes.[14] This wide range of mild metal-catalyzed methods for the synthesis of 2*H*-chromenes has allowed the preparation of highly functional derivatives that have found use in various applications including laser dyes, organic light emitting devices and fluorescent probes.[15]

We have recently reported a series of one-pot multireaction processes using benzannulated alkene derived allylic alcohols for the rapid and efficient synthesis of amino-substituted indenes, dihydronaphthalenes, 1-benzoxepines and 1-benzoazepines.[16] We were interested in developing a novel one-pot multistep process involving an Overman rearrangement and 6-*endo*-*dig* cyclization process for the preparation of allylic amide derived 2*H*-chromenes (Scheme 1). It was proposed that these compounds could then be used in a chemoselective oxidation for the synthesis of coumarin analogues. Compounds with this coumarin core structure (see box, Scheme 1) have shown bactericidal effects against *Mycobacterium tuberculosis*.[17] However, previous routes to this class of coumarin derivatives installed the 8-aminopropyl group using low yielding Friedel–Crafts acylation (<20%) and reductive amination steps (23–47%).[17,18] It was proposed that use of allylic trichloroacetimidates bearing a 2-propargyloxyaryl group in combination with an optimized one-pot multibond forming process would allow access to these coumarin structures more efficiently.

Scheme 1. Proposed Approach to Allylic Amine Derived 2*H*-Chromenes and Coumarins



We now report the facile preparation of (*E*)-(2-propargyloxy)cinnamyl alcohols from readily available 2-hydroxybenzaldehydes and demonstrate that these compounds are effective substrates for the

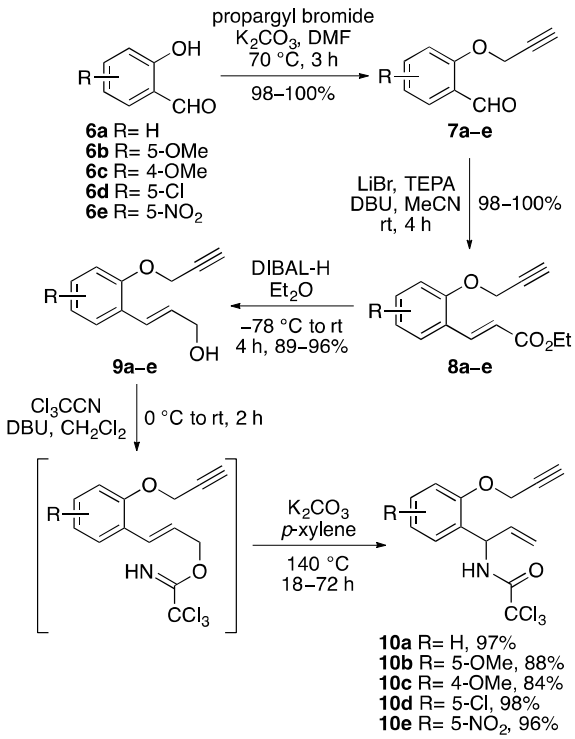
synthesis of allylic amide derived 2*H*-chromenes using either a stepwise approach or a one-pot two-step process. We also describe the preparation of the corresponding coumarin derivatives by the chemoselective oxidation of the allylic amine derived 2*H*-chromenes.

RESULTS AND DISCUSSION

Our studies began with the development of a short synthetic route for the preparation of cinnamyl alcohols bearing a 2-propargyloxy group (Scheme 2). Initially, a series of commercially available 2-hydroxybenzaldehydes **6a**–**e** were alkylated with propargyl bromide and potassium carbonate. This was followed by a Horner-Wadsworth-Emmons reaction with triethyl phosphonoacetate (TEPA) under Masamune-Roush conditions and gave (*E*)-propargyl derived cinnamic esters **8a**–**e** in essentially quantitative yields over the two steps.[19] Analysis of the ^{1}H NMR spectra of the crude reaction mixtures for this transformation showed exclusive *E*-alkene formation. DIBAL-H reduction under standard conditions then gave cinnamyl alcohols **9a**–**e** in 89–96% yield.

Before developing the one-pot process, the optimal reagents and conditions for the hydroarylation step needed to be established. Therefore, cinnamyl alcohols **9a**–**e** were converted to the corresponding allylic trichloroacetamides **10a**–**e** by first conversion to the allylic trichloroacetimidate using trichloroacetonitrile and catalytic DBU and then Overman rearrangement under thermal conditions.[20,21] In general, the rearrangements were complete after 18 hours and gave excellent yields over the two steps (84–98%). It should be noted that longer reaction times for the rearrangement step were required for the two substrates with electron-withdrawing substituents (R = 5-Cl, 48 h; R = 5-NO_2, 72 h).

Scheme 2. Synthesis of Allylic Trichloroacetamides 10a–e[a]

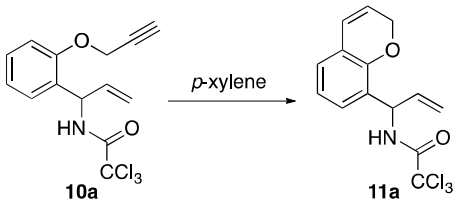


[a]Isolated yields are shown.

Having prepared a series of propargyloxy derived allylic trichloroacetamides, optimal conditions for the subsequent hydroarylation reaction were next investigated. During the development of the Overman rearrangement and using extended reaction times for some of the substrates, low amounts (<10%) of the 2*H*-chromenes were detected by ^{1}H NMR spectroscopy in the crude reaction mixtures. Based on this observation, initial attempts at converting allylic trichloroacetamide **10a** to the corresponding 2*H*-chromene **11a** focused on a thermally mediated 6-*endo*-*dig* cycloisomerization (Table 1). It was proposed that a successful hydroarylation reaction under these conditions would allow the development of a one-pot synthesis of the 2*H*-chromenes from the corresponding allylic trichloroacetimidate where both the rearrangement and cycloisomerization steps were performed simply by heating. As only small amounts of 2*H*-chromenes were observed at 140 ºC during the Overman rearrangement, the initial hydroarylation reaction was performed at a higher temperature of 160 ºC (entry 1). However, after heating for four days, only 35% conversion was observed. A higher temperature of 180 ºC was next

investigated but, after five days, this gave a modest conversion of 50%. It was proposed that microwave heating might allow a more efficient hydroarylation reaction with a shorter reaction time (entries 3 and 4). While a temperature of 200 ºC did show 91% conversion after two hours (entry 4), the 34% isolated yield of **11a** indicated that decomposition was an issue when using very high temperatures. Gold(I)-catalysts were next studied for the cycloisomerization reaction. Using chloro(triphenylphosphine)gold(I) (2.5 mol %),[14a] activated by silver(I) hexafluoroantimonate (2.5 mol %) at 80 ºC, gave 85% conversion after four hours (entry 5). However, using $Ph_3PAuNTf_2$ (2.5 mol %),[14b,e] which requires no activation, gave complete conversion after only four hours under similar conditions (entry 6).[22] Furthermore, the ^1H NMR spectrum of the crude reaction mixture indicated a clean transformation and the exclusive formation of 6-*endo*-*dig* product **11a**.

Table 1. Optimization of the Hydroarylation Reaction



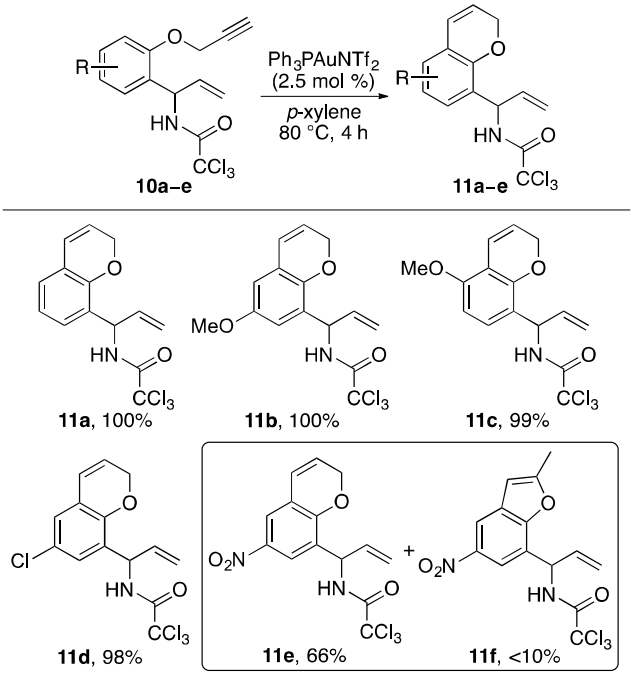
entry	reaction conditions	time (h)	conversion (%)[a]
1	160 ºC	96	35
2	180 ºC	120	50
3	MW, 180 ºC	3	66
4	MW, 200 ºC	2	91
5	Ph_3PAuCl (2.5 mol %), $AgSbF_6$ (2.5 mol %), 80 ºC	4	85
6	$Ph_3PAuNTf_2$ (2.5 mol %), 80 ºC	4	100

[a]Conversions were measured using ^1H NMR spectroscopy.

With conditions for an optimized hydroarylation reaction identified, the scope of this transformation for the preparation of a range of allylic amide substituted 2*H*-chromenes was explored (Scheme 3). For substrates **10a**–**d**, the reactions were complete after four hours, at 80 ºC and gave the products **11a**–**d** in essentially quantitative yields. The ability of this procedure for multigram synthesis of *2H*-chromenes was also studied using aryl propargyl ether **10a**. On scale-up (2–3 g), and using the same reaction time and temperature, it was found that the catalyst loading could be lowered to 1 mol % to give 2*H*-chromene **11a** in quantitative yield.

Under the same conditions as for substrates **10a**–**d**, nitro derivative **10e** gave 2*H*-chromene **11e** in 66% isolated yield (Scheme 3). Analysis of the ^{1}H NMR spectrum of the crude reaction mixture indicated a number of additional minor products, including 2-methylbenzofuran **11f**, which is formed via an *ortho*-allenyl phenolate intermediate and a subsequent 5-*exo*-*dig* cyclization.[14e] This propensity of aryl propargyl ethers with electron deficient substituents to undergo side-reactions during gold(I)-catalyzed cycloisomerization reactions has been observed in other studies.[14]

Scheme 3. Gold(I)-Catalyzed Synthesis of 2*H*-Chromenes 11a–e[a]

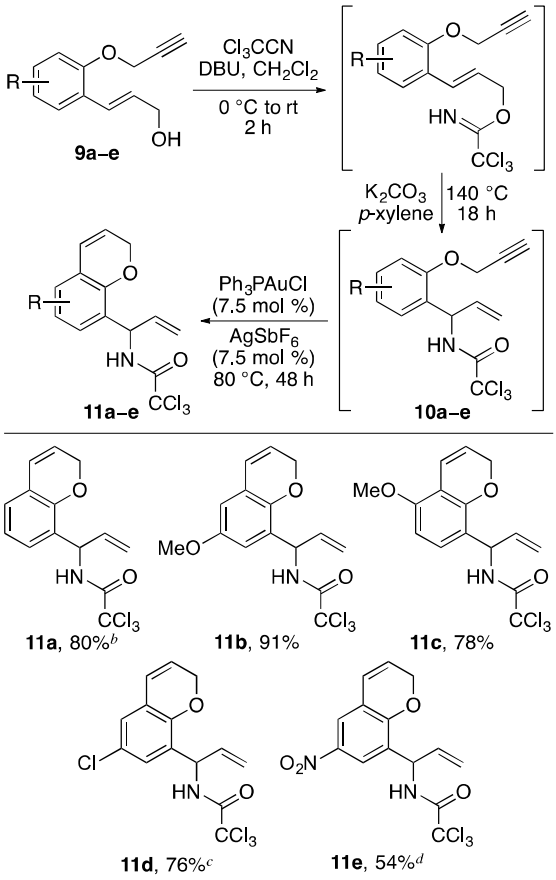


[a]Isolated yields are shown.

The next stage of this project investigated the combination of the optimized Overman rearrangement and gold(I)-catalyzed hydroarylation reaction for the one-pot synthesis of 2*H*-chromenes **11a**–**e** (Scheme 4).[23] Initially, the Overman rearrangement was performed for each substrate at 140 ºC and the same reaction time as previously described (Scheme 2). Surprisingly, addition of $Ph_3PAuNTf_2$ (2.5 mol %) to the completed Overman rearrangement reactions and heating of the mixtures to 80 ºC gave none of the hydroarylation product for any of the substrates. These results indicated that the highly active $Ph_3PAuNTf_2$ complex was not stable under the conditions of the one-pot process. To confirm this, the one-pot process for the formation of 2*H*-chromene **11a** was repeated using a combination of Ph_3PAuCl and $AgNTF_2$ (to form $Ph_3PAuNTf_2$ in situ) for the hydroarylation step. Again, no conversion to 2*H*-chromene **11a** was observed, providing further evidence that this issue is due to the active catalyst.

Instead, the use of Ph_3PAuCl, activated by $AgSbF_6$ was investigated for the hydroarylation step as part of the one-pot process. Initial trials showed that this catalytic system was compatible with the conditions of the Overman rearrangement and gave high conversions (>90%) to the 2*H*-chromenes. On optimization of the one-pot process, it was found for the majority of substrates, that a higher catalyst loading of both complexes (7.5 mol %) and a longer reaction (48 h) was required, compared to the single step cycloisomerization catalyzed by $Ph_3PAuNTf_2$ (2.5 mol %). Despite the longer reaction times for this stage, high yields (76–91%) were obtained for the one-pot synthesis of 2*H*-chromenes **11a**–**d** over the three steps (Scheme 4). As observed with the $Ph_3PAuNTf_2$ complex, the $Ph_3PAuCl/AgSbF_6$ catalyzed hydroarylation of electron-deficient 5-nitroaryl propargyloxy ether **10e** again produced a number of minor by-products. However, by increasing the catalyst loading (10 mol %), the one-pot synthesis of **11e** could be achieved in 54% overall yield.

Scheme 4. One-pot Synthesis of 2*H*-Chromenes 11a–e[a]

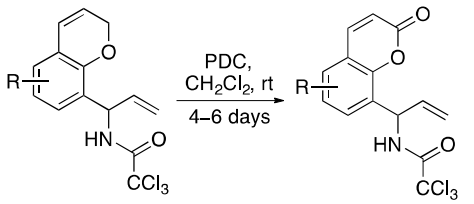


[a]Isolated yields are shown. [b]The hydroarylation step was complete after 4 h. [c]The Overman rearrangement was complete after 48 h. [d]The Overman rearrangement was complete after 72 h and the hydroarylation step was done using 10 mol % of both complexes and was complete after 65 h.

Following the development of the two approaches for the preparation of allylic amide derived 2*H*-chromenes **11a**–**e**, we wanted to demonstrate their potential as synthetic building blocks. A transformation that has been investigated in this study is the chemoselective allylic oxidation to give the corresponding coumarins, a structural motif found in many natural products and used as fluorescent probes to investigate various biological systems.[24] On searching the literature, there are relatively few reports of this transformation.[25–27] The only general method, reported by Schmidt and co-workers, showed that following ring closing metathesis of 2-allyoxystyrenes to give 2*H*-chromenes, subsequent addition of *tert*-butyl hydroperoxide as part of a one-pot process resulted in allylic oxidation and the

formation of coumarins in yields of 30–63%.[27] Therefore, our initial attempts at the chemoselective oxidation of 2*H*-chromene **11a** investigated the use of *tert*-butyl hydroperoxide as the oxidant. However, coumarin **12a** could only be isolated in 34% yield. While the allylic oxidation of 2*H*-chromenes to coumarins is rare, a similar transformation to convert 5,6-dihydropyrans to the corresponding 5,6-dihydropyran-2-ones using chromium(VI) reagents is known.[28,29] As such, the oxidation of **11a** was next investigated using pyridinium dichromate (PDC) (Scheme 5). On investigating various temperatures for this reaction, it was found that room temperature (20 °C) gave the cleanest, most selective transformation. While the reaction did take six days to go to completion, coumarin **12a** was isolated in 65% yield. Some of the other 2*H*-chromenes were then oxidized using this general procedure (room temperature, 4–6 days) and this gave the corresponding coumarins **12b–d** in 42–62% yields.

Scheme 5. Chemoselective Oxidation of 2*H*-Chromenes to Coumarins[a]



11a,b,d,e

12a R= H, 65%
12b R= 6-OMe, 62%
12c R= 6-Cl, 42%
12d R= 6-NO_2, 58%

[a]Isolated yields are shown.

CONCLUSIONS

In summary, a rapid and efficient approach has been developed for the synthesis of allylic amide functionalized 2*H*-chromenes from readily available 2-hydroxybenzaldehydes using an Overman rearrangement and a gold(I)-catalyzed cycloisomerization as the key steps. Two different approaches involving stepwise rearrangement and hydroarylation with a gold(I) triflimide complex or a one-pot two-step process using a more robust gold(I)-chloride catalyst activated by silver(I)

hexafluoroantimonate has been presented. A PDC oxidation was developed for the conversion of the 2*H*-chromenes to the corresponding 8-(2-amidopropenyl)coumarins, which are structurally related to compounds that are bactericidal against *M. tuberculosis*. Work is currently underway to investigate other applications of allylic amide functionalized 2*H*-chromenes and coumarins, as well as the development of new one-pot multistep reaction processes.

EXPERIMENTAL SECTION

All reagents and starting materials were obtained from commercial sources and used as received. All dry solvents were purified using a solvent purification system. All reactions were performed under an atmosphere of argon unless otherwise mentioned. Brine refers to a saturated solution of sodium chloride. Flash column chromatography was performed using silica gel 60 (35–70 μm). Aluminium-backed plates pre-coated with silica gel $60F_{254}$ were used for thin layer chromatography and were visualized with a UV lamp or by staining with potassium permanganate. ^{1}H NMR spectra were recorded on a NMR spectrometer at either 400 or 500 MHz and data are reported as follows: chemical shift in ppm relative to tetramethylsilane or the solvent as the internal standard ($CDCl_3$, δ 7.26 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances, integration). ^{13}C NMR spectra were recorded on a NMR spectrometer at either 101 or 126 MHz and data are reported as follows: chemical shift in ppm relative to tetramethylsilane or the solvent as internal standard ($CDCl_3$, δ 77.0 ppm), multiplicity with respect to hydrogen (deduced from DEPT experiments, C, CH, CH_2 or CH_3). Infrared spectra were recorded on a FTIR spectrometer; wavenumbers are indicated in cm^{-1}. Mass spectra were recorded using electron impact, chemical ionization or electrospray techniques. HRMS spectra were recorded using a dual-focusing magnetic analyzer mass spectrometer. Melting points are uncorrected.

2-Propargyloxybenzaldehyde (7a).[30] Propargyl bromide (3.34 mL, 30.0 mmol) was added to a stirred solution of 2-hydroxybenzaldehyde (**6a**) (3.00 g, 25.0 mmol) and potassium carbonate (7.00 g,

50.0 mmol) in *N,N*'-dimethylformamide (120 mL) and heated to 70 °C for 3 h. The reaction mixture was cooled to room temperature, diluted with 5% aqueous lithium chloride solution (20 mL) and extracted with diethyl ether (3 × 50 mL). The organic layer was washed with 5% aqueous lithium chloride solution (3 × 50 mL), brine (50 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by column chromatography (diethyl ether/petroleum ether, 1:4) gave 2-propargyloxybenzaldehyde (**7a**) (3.94 g, 100%) as a white solid. Mp 69–70 °C (lit.[30] 69–70 °C); R_f = 0.65 (diethyl ether/petroleum ether = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.57 (t, J = 2.5 Hz, 1H), 4.81 (d, J = 2.5 Hz, 2H), 7.06 (br t, J = 7.5 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 7.54 (ddd, J = 8.5, 7.5, 1.9 Hz, 1H), 7.83 (dd, J = 7.5, 1.9 Hz, 1H), 10.46 (br d, J = 0.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.4 (CH_2), 76.5 (CH), 77.7 (C), 113.2 (CH), 121.7 (CH), 125.4 (C), 128.5 (CH), 135.7 (CH), 159.7 (C), 189.5 (CH); MS (EI) *m/z* 160 (M^+, 30), 131 (100), 121 (49), 109 (40), 83 (47), 65 (30), 39 (34).

5-Methoxy-2-propargyloxybenzaldehyde (7b).[31] The reaction was carried out as described for the synthesis of 2-propargyloxybenzaldehyde (**7a**) using 2-hydroxy-5-methoxybenzaldehyde (**6b**) (0.152 g, 1.00 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:4) gave 5-methoxy-2-propargyloxybenzaldehyde (**7b**) (0.190 g, 100%) as a white solid. Mp 60–62 °C; R_f = 0.91 (diethyl ether/petroleum ether = 1:1); Spectroscopic data was consistent with the literature.[31] ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.55 (t, J = 2.4 Hz, 1H), 3.81 (s, 3H), 4.78 (d, J = 2.4 Hz, 2H), 7.08 (d, J = 9.1 Hz, 1H), 7.14 (dd, J = 9.1, 3.3 Hz, 1H), 7.34 (d, J = 3.3 Hz, 1H), 10.44 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.8 (CH_3), 57.4 (CH_2), 76.4 (CH), 77.9 (C), 110.4 (CH), 115.7 (CH), 123.2 (CH), 126.2 (C), 126.2 (C), 154.5 (C), 189.4 (CH); MS (ESI) *m/z* 213 (MNa^+, 100).

4-Methoxy-2-propargyloxybenzaldehyde (7c).[31] The reaction was carried out as described for the synthesis of 2-propargyloxybenzaldehyde (**7a**) using 2-hydroxy-4-methoxybenzaldehyde (**6c**) (0.152 g, 1.00 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:4) gave 4-methoxy-2-propargyloxybenzaldehyde (**7c**) (0.188 g, 99%) as a white solid. Mp 82–84 °C (lit.[31] 76–78 °C); R_f = 0.41 (diethyl ether/petroleum ether = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.58 (t, J = 2.4 Hz,

1H), 3.87 (s, 3H), 4.80 (d, J = 2.4 Hz, 2H), 6.58–6.61 (m, 2H), 7.81–7.84 (m, 1H), 10.29 (br d, J = 0.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.7 (CH_3), 56.4 (CH_2), 76.6 (CH), 77.6 (C), 99.5 (CH), 106.9 (CH), 119.6 (C), 130.6 (CH), 161.5 (C), 165.9 (C), 188.1 (CH); MS (ESI) *m/z* 213 (MNa^+, 100).

5-Chloro-2-propargyloxybenzaldehyde (7d).[31] The reaction was carried out as described for the synthesis of 2-propargyloxybenzaldehyde (**7a**) using 2-hydroxy-5-chlorobenzaldehyde (**6d**) (1.57 g, 10.0 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:4) gave 5-chloro-2-propargyloxybenzaldehyde (**7d**) (1.93 g, 99%) as a white solid. Mp 74–75 °C (lit.[31] 74–76 °C); R_f = 0.58 (diethyl ether/petroleum ether = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.59 (t, J = 2.4 Hz, 1H), 4.82 (d, J = 2.4 Hz, 2H), 7.08 (d, J = 8.9 Hz, 1H), 7.50 (dd, J = 8.9, 2.8 Hz, 1H), 7.80 (d, J = 2.8 Hz, 1H), 10.40 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.8 (CH_2), 76.9 (C), 77.2 (CH), 115.0 (CH), 126.5 (C), 127.5 (C), 128.1 (CH), 135.2 (CH), 158.1 (C), 188.2 (CH); MS (ESI) *m/z* 217 (MNa^+, 100).

5-Nitro-2-propargyloxybenzaldehyde (7e).[32] The reaction was carried out as described for the synthesis of 2-propargyloxybenzaldehyde (**7a**) using 2-hydroxy-5-nitrobenzaldehyde (**6e**) (2.75 g, 16.5 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:4) gave 5-nitro-2-propargyloxybenzaldehyde (**7e**) (3.31 g, 98%) as a white crystalline solid. Mp 90–91 °C (lit.[32] 91.5–93 °C); R_f = 0.32 (diethyl ether/petroleum ether = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (t, J = 2.4 Hz, 1H), 5.01 (d, J = 2.4 Hz, 2H), 7.32 (d, J = 9.2 Hz, 1H), 8.45 (dd, J = 9.2, 2.9 Hz, 1H), 8.69 (d, J = 2.9 Hz, 1H), 10.45 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 57.2 (CH_2), 76.3 (C), 77.9 (CH), 113.8 (CH), 124.5 (CH), 125.2 (C), 130.4 (CH), 142.2 (C), 163.4 (C), 187.3 (CH); MS (EI) *m/z* 205 (M^+, 16), 176 (53), 167 (100), 137 (34), 120 (36), 92 (27), 65 (46).

Ethyl (2*E*)-3-(2'-Propargyloxyphenyl)prop-2-enoate (8a). Lithium chloride (4.20 g, 98.4 mmol) was added to a solution of triethyl phosphonoacetate (16.6 mL, 83.6 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (12.5 mL, 83.6 mmol) in acetonitrile (100 mL) and stirred at room temperature for 0.5 h. 2-Propargyloxybenzaldehyde (**7a**) (3.94 g, 24.6 mmol) was added and the solution was stirred at room temperature for 3.5 h. The reaction was quenched by the addition of a

saturated solution of ammonium chloride (10 mL), concentrated to half volume *in vacuo* and extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with water (100 mL), brine (100 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by column chromatography (diethyl ether/petroleum ether, 1:10) yielded ethyl (2*E*)-3-(2'-propargyloxyphenyl)prop-2-enoate (**8a**) (5.67 g, 100%) as a colorless oil. R_f = 0.70 (diethyl ether/petroleum ether = 1:1); IR (neat) 2983, 1701, 1632, 1486, 1316, 1220, 1175, 1022, 750, 731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, J = 7.1 Hz, 3H), 2.53 (t, J = 2.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 4.78 (d, J = 2.4 Hz, 2H), 6.51 (d, J = 16.2 Hz, 1H), 7.01 (br t, J = 7.6 Hz, 1H), 7.05 (br d, J = 8.3 Hz, 1H), 7.35 (ddd, J = 8.3, 7.6, 1.6 Hz, 1H), 7.53 (dd, J = 7.6, 1.6 Hz, 1H), 8.00 (d, J = 16.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.4 (CH_3), 56.1 (CH_2), 60.4 (CH_2), 76.1 (CH), 78.2 (C), 112.7 (CH), 119.1 (CH), 121.6 (CH), 124.1 (C), 128.8 (CH), 131.2 (CH), 139.6 (CH), 156.1 (C), 167.3 (C); MS (EI) *m/z* 230 (M^+, 38), 201 (44), 185 (39), 157 (40), 147 (46), 118 (100), 103 (14), 91 (66); HRMS (EI) calcd for $C_{14}H_{14}O_3$ (M^+), 230.0943, found 230.0944.

Ethyl (2*E*)-3-(5'-Methoxy-2'-propargyloxyphenyl)prop-2-enoate (8b). The reaction was carried out as described for the synthesis of ethyl (2*E*)-3-(2'-propargyloxyphenyl)prop-2-enoate (**8a**) using 5-methoxy-2-propargyloxybenzaldehyde (**7b**) (0.167 g, 0.880 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:10) gave ethyl (2*E*)-3-(5'-methoxy-2'-propargyloxyphenyl)prop-2-enoate (**8b**) (0.225 g, 99%) as a colorless oil. R_f = 0.60 (diethyl ether/petroleum ether = 1:1); IR (neat) 3020, 1701, 1633, 1494, 1288, 1214, 1179, 1043, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, J = 7.1 Hz, 3H), 2.51 (t, J = 2.4 Hz, 1H), 3.80 (s, 3H), 4.27 (q, J = 7.1 Hz, 2H), 4.72 (d, J = 2.4 Hz, 2H), 6.48 (d, J = 16.2 Hz, 1H), 6.91 (dd, J = 9.0, 3.1 Hz, 1H), 7.01 (d, J = 9.0 Hz, 1H), 7.06 (d, J = 3.1 Hz, 1H), 7.98 (d, J = 16.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.4 (CH_3), 55.7 (CH_3), 57.0 (CH_2), 60.4 (CH_2), 75.8 (CH), 78.5 (C), 112.9 (CH), 114.7 (CH), 116.9 (CH), 119.3 (CH), 125.0 (C), 139.4 (CH), 150.5 (C), 154.3 (C), 167.2 (C); MS (ESI) *m/z* 283 (MNa^+, 100); HRMS (ESI) calcd for $C_{15}H_{16}NaO_4$ (MNa^+), 283.0941, found 283.0932.

Ethyl (2*E*)-3-(4'-Methoxy-2'-propargyloxyphenyl)prop-2-enoate (8c). The reaction was carried out as described for the synthesis of ethyl (2*E*)-3-(2'-propargyloxyphenyl)prop-2-enoate (**8a**) using 4-methoxy-2-propargyloxybenzaldehyde (**7c**) (1.73 g, 9.07 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:10) gave ethyl (2*E*)-3-(4'-methoxy-2'-propargyloxyphenyl)prop-2-noate (**8c**) (2.35 g, 100%) as a colorless oil. R_f = 0.46 (diethyl ether/petroleum ether = 1:1); IR (neat) 2984, 1704, 1605, 1258, 1161, 1021, 970 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, J = 7.1 Hz, 3H), 2.54 (t, J = 2.5 Hz, 1H), 3.83 (s, 3H), 4.24 (q, J = 7.1 Hz, 2H), 4.75 (d, J = 2.5 Hz, 2H), 6.40 (d, J = 16.1 Hz, 1H), 6.54 (dd, J = 8.6, 2.4 Hz, 1H), 6.60 (d, J = 2.4 Hz, 1H), 7.46 (d, J = 8.6 Hz, 1H), 7.90 (d, J = 16.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.4 (CH_3), 55.5 (CH_3), 56.4 (CH_2), 60.2 (CH_2), 76.2 (CH), 78.0 (C), 99.9 (CH), 106.4 (CH), 116.5 (CH), 117.1 (C), 130.2 (CH), 139.5 (CH), 157.6 (C), 162.4 (C), 167.7 (C); MS (ESI) *m/z* 283 (MNa^+, 100); HRMS (ESI) calcd for $C_{15}H_{16}NaO_4$ (MNa^+), 283.0941, found 283.0935.

Ethyl (2*E*)-3-(5'-Chloro-2'-propargyloxyphenyl)prop-2-enoate (8d). The reaction was carried out as described for the synthesis of ethyl (2*E*)-3-(2'-propargyloxyphenyl)prop-2-enoate (**8a**) using 5-chloro-2-propargyloxybenzaldehyde (**7d**) (0.120 g, 0.620 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:10) gave ethyl (2*E*)-3-(5'-chloro-2'-propargyloxyphenyl)prop-2-enoate (**8d**) (0.163 g, 100%) as a colorless oil. R_f = 0.60 (diethyl ether/petroleum ether = 1:1); IR (neat) 3020, 1705, 1635, 1480, 1216, 1181, 1024, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, J = 7.1 Hz, 3H), 2.54 (t, J = 2.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 4.76 (d, J = 2.4 Hz, 2H), 6.47 (d, J = 16.4 Hz, 1H), 6.99 (d, J = 8.9 Hz, 1H), 7.29 (dd, J = 8.9, 2.6 Hz, 1H), 7.49 (d, J = 2.6 Hz, 1H), 7.90 (d, J = 16.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.3 (CH_3), 56.4 (CH_2), 60.6 (CH_2), 76.4 (CH), 77.8 (C), 114.2 (CH), 120.4 (CH), 125.7 (C), 126.8 (C), 128.2 (CH), 130.6 (CH), 138.1 (CH), 154.6 (C), 166.9 (C); MS (ESI) *m/z* 287 (MNa^+, 100); HRMS (ESI) calcd for $C_{14}H_{13}{}^{35}ClNaO_3$ (MNa^+), 287.0445, found 287.0434.

Ethyl (2*E*)-3-(5'-Nitro-2'-propargyloxyphenyl)prop-2-enoate (8e). The reaction was carried out as described for the synthesis of ethyl (2*E*)-3-(2'-propargyloxyphenyl)prop-2-enoate (**8a**) using 5-nitro-2-propargyloxybenzaldehyde (**7e**) (0.140 g, 0.680 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:10) gave ethyl (2*E*)-3-(5'-nitro-2'-propargyloxyphenyl)prop-2-enoate (**8e**) (0.183 g, 98%) as a white solid. Mp 95–96 °C; R_f = 0.45 (diethyl ether/petroleum ether = 1:1); IR (neat) 2986, 1701, 1581, 1514, 1343, 1270, 1233, 1016, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, J = 7.1 Hz, 3H), 2.61 (t, J = 2.4 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 4.90 (d, J = 2.4 Hz, 2H), 6.60 (d, J = 16.4 Hz, 1H), 7.15 (d, J = 9.2 Hz, 1H), 7.93 (d, J = 16.4 Hz, 1H), 8.25 (dd, J = 9.2, 2.8 Hz, 1H), 8.43 (d, J = 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.3 (CH_3), 56.7 (CH_2), 60.8 (CH_2), 76.7 (CH), 77.4 (C), 112.5 (CH), 121.9 (CH), 124.0 (CH), 124.9 (C), 126.4 (CH), 137.1 (CH), 142.0 (C), 160.2 (C), 166.5 (C); MS (ESI) *m/z* 298 (MNa^+, 100); HRMS (ESI) calcd for $C_{14}H_{13}NNaO_5$ (MNa^+), 298.0686, found 298.0672.

(2*E*)-3-(2'-Propargyloxyphenyl)prop-2-en-1-ol (9a). Diisobutylaluminium hydride (54.0 mL, 54.0 mmol, 1 M in hexane) was added dropwise with stirring to a solution of ethyl (2*E*)-3-(2'-propargyloxyphenyl)prop-2-enoate (**8a**) (5.66 g, 24.6 mmol) in dichloromethane (100 mL) at −78 °C. The solution was stirred at −78 °C for 2 h and then allowed to return to room temperature over 2 h. The reaction was quenched with 10% aqueous potassium sodium tartrate solution (10 mL), extracted with diethyl ether (2 × 50 mL), washed with water (100 mL), brine (100 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by column chromatography (diethyl ether/petroleum ether, 1:2) gave (2*E*)-3-(2'-propargyloxyphenyl)prop-2-en-1-ol (**9a**) (4.30 g, 93%) as a colorless oil. R_f = 0.25 (diethyl ether/petroleum ether = 1:1); IR (neat) 3304, 2870, 1598, 1487, 1217, 1024, 974, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.02 (br s, 1H), 2.51 (t, J = 2.4 Hz, 1H), 4.30 (br d, J = 5.7 Hz, 2H), 4.70 (d, J = 2.4 Hz, 2H), 6.36 (dt, J = 16.2, 5.7 Hz, 1H), 6.92 (d, J = 16.2 Hz, 1H), 6.95–6.99 (m, 2H), 7.19–7.24 (m, 1H), 7.44 (dd, J = 8.0, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 56.2 (CH_2), 64.1 (CH_2), 75.7 (CH), 78.7 (C), 112.7 (CH), 121.7 (CH), 125.8 (CH), 126.5 (C), 127.1 (CH), 128.6 (CH), 129.7 (CH),

154.7 (C); MS (EI) *m/z* 188 (M^+, 38), 149 (46), 131 (100), 121 (55), 91 (84), 77 (43), 65 (13); HRMS (EI) calcd for $C_{12}H_{12}O_2$ (M^+), 188.0837, found 188.0838.

(2*E*)-3-(5'-Methoxy-2'-propargyloxyphenyl)prop-2-en-1-ol (9b). The reaction was carried out as described for the synthesis of (2*E*)-3-(2'-propargyloxyphenyl)prop-2-en-1-ol (**9a**) using ethyl (2*E*)-3-(5'-methoxy-2'-propargyloxyphenyl)prop-2-enoate (**8b**) (1.87 g, 7.17 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:2) gave (2*E*)-3-(5'-methoxy-2'-propargyloxyphenyl)prop-2-en-1-ol (**9b**) (1.39 g, 89%) as a colorless oil. R_f = 0.13 (diethyl ether/petroleum ether = 1:1); IR (neat) 3288, 2920, 1583, 1492, 1286, 1202, 1041, 1021, 970, 803, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (br s, 1H), 2.50 (t, J = 2.4 Hz, 1H), 3.79 (s, 3H), 4.34 (dd, J = 5.8, 1.6 Hz, 2H), 4.67 (d, J = 2.4 Hz, 2H), 6.37 (dt, J = 16.0, 5.8 Hz, 1H), 6.78 (dd, J = 8.9, 3.1 Hz, 1H), 6.92 (dt, J = 16.0, 1.6 Hz, 1H), 6.95 (d, J = 8.9 Hz, 1H), 7.02 (d, J = 3.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 55.7 (CH_3), 57.3 (CH_2), 64.1 (CH_2), 75.4 (CH), 78.9 (C), 112.1 (CH), 113.7 (CH), 114.9 (CH), 125.7 (CH), 127.7 (C), 129.9 (CH), 149.2 (C), 154.5 (C); MS (ESI) *m/z* 241 (MNa^+, 100); HRMS (ESI) calcd for $C_{13}H_{14}NaO_3$ (MNa^+), 241.0835, found 241.0829.

(2*E*)-3-(4'-Methoxy-2'-propargyloxyphenyl)prop-2-en-1-ol (9c). The reaction was carried out as described for the synthesis of (2*E*)-3-(2'-propargyloxyphenyl)prop-2-en-1-ol (**9a**) using ethyl (2*E*)-3-(4'-methoxy-2'-propargyloxyphenyl)prop-2-enoate (**8c**) (2.48 g, 9.40 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:2) gave (2*E*)-3-(4'-methoxy-2'-propargyloxyphenyl)prop-2-en-1-ol (**9c**) (1.99 g, 92%) as a white solid. Mp 66–68 °C; R_f = 0.16 (diethyl ether/petroleum ether = 1:1); IR (neat) 3302, 2929, 1608, 1503, 1258, 1194, 1161, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.86 (br s, 1H), 2.53 (t, J = 2.4 Hz, 1H), 3.80 (s, 3H), 4.28 (dd, J = 6.1, 1.1 Hz, 2H), 4.69 (d, J = 2.4 Hz, 2H), 6.26 (dt, J = 16.0, 6.1 Hz, 1H), 6.51 (dd, J = 8.5, 2.4 Hz, 1H), 6.56 (d, J = 2.4 Hz, 1H), 6.82 (br d, J = 16.0 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.4 (CH_3), 56.3 (CH_2), 64.3 (CH_2), 75.8 (CH), 78.5 (C), 100.0 (CH), 106.2 (CH), 119.3 (C), 125.8 (CH),

127.4, (CH), 127.9 (CH), 155.8 (C), 160.3 (C); MS (ESI) *m/z* 241 (MNa^+, 100); HRMS (ESI) calcd for $C_{13}H_{14}NaO_3$ (MNa^+), 241.0835, found 241.0830.

(2*E*)-3-(5'-Chloro-2'-propargyloxyphenyl)prop-2-en-1-ol (9d). The reaction was carried out as described for the synthesis of (2*E*)-3-(2'-propargyloxyphenyl)prop-2-en-1-ol (**9a**) using ethyl (2*E*)-3-(5'-chloro-2'-propargyloxyphenyl)prop-2-enoate (**8d**) (2.48 g, 9.40 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:2) gave (2*E*)-3-(5'-chloro-2'-propargyloxyphenyl)prop-2-en-1-ol (**9d**) (1.95 g, 93%) as a white solid. Mp 67–68 °C; R_f = 0.25 (diethyl ether/petroleum ether = 1:1); IR (neat) 3285, 2929, 1480, 1222, 1025, 963, 795 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.20 (br s, 1H), 2.53 (t, *J* = 2.5 Hz, 1H), 4.30 (br d, *J* = 5.4 Hz, 2H), 4.68 (d, *J* = 2.5 Hz, 2H), 6.34 (dt, *J* = 16.1, 5.4 Hz, 1H), 6.84 (dt, *J* = 16.1, 1.5 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 1H), 7.15 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.39 (d, *J* = 2.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.5 (CH_2), 63.7 (CH_2), 76.1 (CH), 78.2 (C), 114.0 (CH), 124.3 (CH), 126.8 (CH), 126.8 (C), 128.0, (CH), 128.2 (C), 131.0 (CH), 153.2 (C); MS (ESI) *m/z* 245 (MNa^+, 100); HRMS (ESI) calcd for $C_{12}H_{11}{}^{35}ClNaO_2$ (MNa^+), 245.0340, found 245.0333.

(2*E*)-3-(5'-Nitro-2'-propargyloxyphenyl)prop-2-en-1-ol (9e). The reaction was carried out as described for the synthesis of (2*E*)-3-(2'-propargyloxyphenyl)prop-2-en-1-ol (**9a**) using ethyl (2*E*)-3-(5'-nitro-2'-propargyloxyphenyl)prop-2-enoate (**8e**) (1.25 g, 4.54 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:2) gave (2*E*)-3-(5'-nitro-2'-propargyloxyphenyl)prop-2-en-1-ol (**9e**) (1.02 g, 96%) as a white solid. Mp 92–93 °C; R_f = 0.16 (diethyl ether/petroleum ether = 1:1); IR (neat) 3299, 2917, 1584, 1514, 1343, 1230, 1011, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.56 (t, *J* = 5.6 Hz, 1H), 2.59 (t, *J* = 2.4 Hz, 1H), 4.39 (td, *J* = 5.6, 1.7 Hz, 2H), 4.85 (d, *J* = 2.4 Hz, 2H), 6.51 (dt, *J* = 16.1, 5.6 Hz, 1H), 6.92 (dt, *J* = 16.1, 1.7 Hz, 1H), 7.08 (d, *J* = 9.1 Hz, 1H), 8.15 (dd, *J* = 9.1, 2.8 Hz, 1H), 8.36 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 56.5 (CH_2), 63.6 (CH_2), 76.9 (C), 77.1 (CH), 112.0 (CH), 122.6 (CH), 123.3 (CH), 124.2 (CH), 127.4 (C), 132.6 (CH), 142.1 (C),

159.0 (C); MS (ESI) *m/z* 256 (MNa^+, 100); HRMS (ESI) calcd for $C_{12}H_{11}NNaO_4$ (MNa^+), 256.0580, found 256.0570.

3-(2'-Propargyloxyphenyl)-3-(2'',2'',2''-trichloromethylcarbonylamino)prop-1-ene (10a). (2*E*)-3-(2'-Propargyloxyphenyl)prop-2-en-1-ol (**9a**) (0.20 g, 1.1 mmol) was dissolved in dichloromethane (16 mL) and cooled to 0 °C under argon with stirring. Trichloroacetonitrile (0.16 mL, 1.6 mmol) was added to the solution, followed by 1,8-diazabicyclo[5.4.0]undec-7-ene (0.08 mL, 0.54 mmol) and the reaction mixture was allowed to warm to room temperature over 2 h. The mixture was filtered through a short pad of alumina (neutral, Brockman V) with diethyl ether (150 mL) and concentrated *in vacuo* to yield the crude allylic trichloroacetimidate as a yellow oil which was used without further purification. The allylic trichloroacetimidate was transferred to a dry Schlenk tube containing a stirrer bar and potassium carbonate (15 mg, 3 mg/mL) to which *p*-xylene (5 mL) was then added. The tube was purged with argon, sealed and heated to 140 °C for 18 h. The reaction mixture was concentrated *in vacuo* and purified by column chromatography (diethyl ether/petroleum ether, 1:20) to give 3-(2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonylamino)prop-1-ene (**10a**) (0.33 g, 97%) as a white solid. Mp 46–48 °C; R_f = 0.72 (diethyl ether/petroleum ether = 1:1); IR (neat) 3410, 3297, 1707, 1502, 1489, 1223, 1020, 818, 751 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.53 (t, J = 2.4 Hz, 1H), 4.77 (d, J = 2.4 Hz, 2H), 5.16–5.26 (m, 2H), 5.56–5.65 (m, 1H), 6.06 (ddd, J = 17.1, 10.3, 5.4 Hz, 1H), 6.98–7.07 (m, 2H), 7.27 (dd, J = 7.7, 1.6 Hz, 1H), 7.30–7.37 (m, 1H), 7.93 (br d, J = 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 56.0 (CH), 56.0 (CH_2), 76.2 (CH), 77.8 (C), 92.9 (C), 112.6 (CH), 116.1 (CH_2), 122.1 (CH), 127.1 (C), 129.5 (CH), 129.7 (CH), 135.8 (CH), 155.1 (C), 160.8 (C); MS (EI) *m/z* 331 (M^+, 5), 296 (90), 260 (22), 186 (29), 171 (41), 131 (100), 114 (61), 103 (68), 77 (75); HRMS (EI) calcd for $C_{14}H_{12}{}^{35}Cl_3NO_2$ (M^+), 330.9934, found 330.9937.

3-(5'-Methoxy-2'-propargyloxyphenyl)-3-(2'',2'',2''-trichloromethylcarbonylamino)prop-1-ene (10b). The reaction was carried out as described for the synthesis of 3-(2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonylamino)prop-1-ene (**10a**) using (2*E*)-3-(5'-methoxy-2'-propargyloxyphenyl)prop-2-en-1-ol (**9b**) (0.302 g, 1.38 mmol). Flash column chromatography (diethyl

ether/petroleum ether, 1:10) gave 3-(5'-methoxy-2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonylamino)prop-1-ene (**10b**) (0.441 g, 88%) as a yellow oil. R_f = 0.43 (diethyl ether/petroleum ether = 1:1); IR (neat) 3404, 3298, 2917, 1707, 1493, 1205, 1041, 817, 709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.51 (t, J = 2.4 Hz, 1H), 3.78 (s, 3H), 4.71 (d, J = 2.4 Hz, 2H), 5.15–5.30 (m, 2H), 5.52–5.61 (m, 1H), 6.04 (ddd, J = 17.1, 10.3, 5.4 Hz, 1H), 6.78–6.87 (m, 2H), 6.92–6.99 (m, 1H), 7.95 (br d, J = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 55.9 (CH_3), 56.2 (CH), 56.8 (CH_2), 76.1 (CH), 78.2 (C), 93.1 (C), 113.9 (CH), 114.2 (CH), 115.7 (CH), 116.4 (CH_2), 128.4 (C), 135.9 (CH), 149.3 (C), 154.7 (C), 161.0 (C); MS (CI) *m/z* 362 (MH^+, 33), 328 (42), 292 (10), 236 (11), 201 (100), 163 (5); HRMS (CI) calcd for $C_{15}H_{15}{}^{35}Cl_3NO_3$ (MH^+), 362.0118, found 362.0116.

3-(4'-Methoxy-2'-propargyloxyphenyl)-3-(2'',2'',2''-trichloromethylcarbonylamino)prop-1-ene (10c). The reaction was carried out as described for the synthesis of 3-(2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonylamino)prop-1-ene (**10a**) using (2*E*)-3-(4'-methoxy-2'-propargyloxyphenyl)prop-2-en-1-ol (**9c**) (0.100 g, 0.459 mmol). Flash column chromatography (diethyl ether/petroleum ether, 1:10) gave 3-(4'-methoxy-2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonylamino)prop-1-ene (**10c**) (0.142 g, 84%) as a yellow oil. R_f = 0.46 (diethyl ether/petroleum ether = 1:1); IR (neat) 3416, 3305, 3018, 1709, 1614, 1500, 1197, 1162, 1025, 820, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.54 (t, J = 2.4 Hz, 1H), 3.81 (s, 3H), 4.73 (d, J = 2.4 Hz, 2H), 5.17–5.22 (m, 2H), 5.52–5.59 (m, 1H), 6.04 (ddd, J = 17.0, 10.4, 5.3 Hz, 1H), 6.53 (dd, J = 8.4, 2.4 Hz, 1H), 6.60 (d, J = 2.4 Hz, 1H), 7.17 (d, J = 8.4 Hz, 1H), 7.80 (br d, J = 8.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 55.4 (CH_3), 55.5 (CH), 56.1 (CH_2), 76.3 (CH), 77.7 (C), 93.0 (C), 100.6 (CH), 105.6 (CH), 115.8 (CH_2), 119.5 (C), 130.3 (CH), 136.1 (CH), 156.1 (C), 160.8 (C), 160.8 (C); MS (ESI) *m/z* 384 (MNa^+, 55); HRMS (ESI) calcd for $C_{15}H_{14}{}^{35}Cl_3NNaO_3$ (MNa^+), 383.9931, found 383.9914.

3-(5'-Chloro-2'-propargyloxyphenyl)-3-(2'',2'',2''-trichloromethylcarbonylamino)prop-1-ene (10d). The reaction was carried out as described for the synthesis of 3-(2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonylamino)prop-1-ene (**10a**) using (2*E*)-3-(5'-chloro-2'-

propargyloxyphenyl)prop-2-en-1-ol (**9d**) (0.10 g, 0.45 mmol). The Overman rearrangement was heated to 140 °C for 48 h. Flash column chromatography (diethyl ether/petroleum ether, 1:10) gave 3-(5'-chloro-2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonylamino)prop-1-ene (**10d**) (0.16 g, 98%) as a white solid. Mp 64–66 °C; R_f = 0.56 (diethyl ether/petroleum ether = 1:1); IR (neat) 3422, 3306, 2931, 1713, 1504, 1486, 1215, 1022, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.54 (t, J = 2.2 Hz, 1H), 4.75 (d, J = 2.2 Hz, 2H), 5.15–5.35 (m, 2H), 5.55–5.65 (m, 1H), 6.03 (ddd, J = 17.0, 10.4, 5.3 Hz, 1H), 6.96 (d, J = 8.6 Hz, 1H), 7.20–7.40 (m, 2H), 7.70 (br d, J = 8.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 55.1 (CH), 56.4 (CH_2), 76.6 (CH), 77.3 (C), 92.8 (C), 113.9 (CH), 116.8 (CH_2), 127.1 (C), 128.9 (C), 129.1 (CH), 129.5 (CH), 135.0 (CH), 153.6 (C), 160.9 (C); MS (ESI) *m/z* 388 (MNa^+, 45); HRMS (ESI) calcd for $C_{14}H_{11}{}^{35}Cl_4NNaO_2$ (MNa^+), 387.9436, found 387.9424.

3-(5'-Nitro-2'-propargyloxyphenyl)-3-(2'',2'',2''-trichloromethylcarbonylamino)prop-1-ene (10e). The reaction was carried out as described for the synthesis of 3-(2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonylamino)prop-1-ene (**10a**) using (2*E*)-3-(5'-nitro-2'-propargyloxyphenyl)prop-2-en-1-ol (**9e**) (0.100 g, 0.429 mmol). The Overman rearrangement was heated to 140 °C for 72 h. Flash column chromatography (diethyl ether/petroleum ether, 1:10) gave 3-(5'-nitro-2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonylamino)prop-1-ene (**10e**) (0.155 g, 96%) as a white crystalline solid. Mp 140–142 °C; R_f = 0.30 (diethyl ether/petroleum ether = 1:1); IR (neat) 3422, 3305, 2926, 1708, 1516, 1343, 1263, 1010, 821, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.60 (t, J = 2.3 Hz, 1H), 4.88 (d, J = 2.3 Hz, 2H), 5.30 (d, J = 17.1 Hz, 1H), 5.33 (d, J = 10.3 Hz, 1H), 5.71–5.82 (m, 1H), 6.05 (ddd, J = 17.1, 10.3, 5.4 Hz, 1H), 7.14 (d, J = 9.0 Hz, 1H), 7.44 (br d, J = 8.3 Hz, 1H), 8.22 (d, J = 2.7 Hz, 1H), 8.26 (dd, J = 9.0, 2.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 54.1 (CH), 56.8 (CH_2), 76.5 (CH), 77.4 (C), 92.5 (C), 112.5 (CH), 117.9 (CH_2), 124.7 (CH), 125.6 (CH), 128.6 (C), 134.2 (CH), 142.1 (C), 159.7 (C), 161.0 (C); MS (ESI) *m/z* 399 (MNa^+, 48); HRMS (ESI) calcd for $C_{14}H_{11}{}^{35}Cl_3N_2NaO_4$ (MNa^+) 398.9677, found 398.9662.

8-[1'-(2'',2'',2''-Trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (11a). 3-(2'-Propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonylamino)prop-1-ene (**10a**) (0.82 g, 2.5 mmol) was dissolved in *p*-xylene (10 mL) under argon followed by [bis(trifluoromethanesulfonyl)imidate](triphenylphosphine)gold(I) (2:1) toluene adduct (0.097 g, 0.062 mmol) and the mixture was heated to 80 °C for 4 h. The reaction mixture was concentrated *in vacuo* and purified by column chromatography (diethyl ether/petroleum ether, 1:15) to give 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11a**) (0.82 g, 100%) as a colorless oil. R_f = 0.67 (diethyl ether/petroleum ether = 1:1); IR (neat) 3418, 2930, 1707, 1700, 1507, 1215, 821, 747 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.86 (dd, J = 3.6, 1.9 Hz, 2H), 5.18–5.24 (m, 2H), 5.55 (ddt, J = 8.2, 5.4, 1.7 Hz, 1H), 5.82 (dt, J = 9.9, 3.6 Hz, 1H), 6.03 (ddd, J = 17.1, 10.4, 5.4 Hz, 1H), 6.45 (dt, J = 9.9, 1.9 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 6.96 (dd, J = 7.6, 1.7 Hz, 1H), 7.06 (dd, J = 7.6, 1.7 Hz, 1H), 7.94 (br d, J = 8.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.4 (CH), 65.7 (CH_2), 93.0 (C), 116.0 (CH_2), 121.8 (CH), 122.0 (CH), 123.1 (C), 124.5 (CH), 125.3 (C), 126.8 (CH), 128.9 (CH), 135.9 (CH), 151.4 (C), 160.8 (C); MS (EI) *m/z* 331 (M^+, 24), 296 (47), 260 (22), 224 (10), 196 (7), 170 (100), 128 (35), 115 (30), 77 (10); HRMS (EI) calcd for $C_{14}H_{12}{}^{35}Cl_3NO_2$ (M^+), 330.9934, found 330.9939.

6-Methoxy-8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (11b). The reaction was carried out as described for the synthesis of 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11a**) using 3-(5'-methoxy-2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonylamino)prop-1-ene (**10b**) (0.060 g, 0.17 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:15) gave 6-methoxy-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11b**) (0.060 g, 100%) as a colorless oil. R_f = 0.60 (diethyl ether/petroleum ether = 1:1); IR (neat) 3404, 2955, 1708, 1503, 1472, 1203, 818 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 4.78 (dd, J = 3.6, 1.9 Hz, 2H), 5.18–5.24 (m, 2H), 5.49 (ddt, J = 8.6, 5.4, 1.6 Hz, 1H), 5.86 (dt, J = 9.9, 3.6 Hz, 1H), 6.01 (ddd, J = 17.1, 10.3, 5.4 Hz, 1H), 6.41 (dt, J = 9.9, 1.9 Hz, 1H), 6.53 (d, J = 2.9 Hz, 1H), 6.62 (d, J = 2.9 Hz, 1H), 8.01 (br d, J =

8.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 55.7 (CH_3), 55.7 (CH), 65.5 (CH_2), 92.9 (C), 111.9 (CH), 113.9 (CH), 116.1 (CH_2), 123.1 (CH), 124.1 (C), 124.6 (CH), 126.0 (C), 135.7 (CH), 145.1 (C), 154.2 (C), 160.8 (C); MS (CI) *m/z* 362 (MH^+, 42), 328 (5), 290 (4), 243 (4), 201 (100), 85 (4); HRMS (CI) calcd for $C_{15}H_{15}{}^{35}Cl_3NO_3$ (MH^+), 362.0118, found 362.0113.

5-Methoxy-8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (11c). The reaction was carried out as described for the synthesis of 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11a**) using 3-(4'-methoxy-2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonyl-amino)prop-1-ene (**10c**) (0.025 g, 0.070 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:15) gave 5-methoxy-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11c**) (0.025 g, 99%) as a colorless oil. R_f = 0.53 (diethyl ether/petroleum ether = 1:1); IR (neat) 3421, 2928, 1707, 1492, 1215, 1109, 821, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 4.78 (dd, *J* = 3.6, 1.6 Hz, 2H), 5.16–5.22 (m, 2H), 5.49 (ddt, *J* = 8.4, 5.3, 1.6 Hz, 1H), 5.77 (dt, *J* = 10.0, 3.6 Hz, 1H), 6.02 (ddd, *J* = 17.0, 10.4, 5.3 Hz, 1H), 6.44 (d, *J* = 8.6 Hz, 1H), 6.77 (dt, *J* = 10.0, 1.6 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 7.85 (br d, *J* = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 55.3 (CH_3), 55.7 (CH), 65.2 (CH_2), 93.0 (C), 103.8 (CH), 112.5 (C), 115.7 (CH_2), 118.2 (C), 119.4 (CH), 119.9 (CH), 129.0 (CH), 136.2 (CH), 152.1 (C), 155.3 (C), 160.7 (C); MS (ESI) *m/z* 384 (MNa^+, 51); HRMS (ESI) calcd for $C_{15}H_{14}{}^{35}Cl_3NNaO_3$ (MNa^+), 383.9931, found 383.9916.

6-Chloro-8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (11d). The reaction was carried out as described for the synthesis of 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11a**) using 3-(5'-chloro-2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonyl-amino)prop-1-ene (**10d**) (0.062 g, 0.17 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:10) gave 6-chloro-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11d**) (0.061 g, 98%) as a white solid. Mp 62–64 °C; R_f = 0.68 (diethyl ether/petroleum ether = 1:1); IR (neat) 3418, 2927, 1713, 1504, 1466,

1214, 821, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.86 (dd, J = 3.6, 1.9 Hz, 2H), 5.20–5.26 (m, 2H), 5.52 (ddt, J = 8.6, 5.3, 1.6 Hz, 1H), 5.86 (dt, J = 9.9, 3.6 Hz, 1H), 6.00 (ddd, J = 17.0, 10.4, 5.3 Hz, 1H), 6.38 (dt, J = 9.9, 1.9 Hz, 1H), 6.94 (d, J = 2.5 Hz, 1H), 7.04 (d, J = 2.5 Hz, 1H), 7.72 (br d, J = 8.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 54.6 (CH), 65.9 (CH_2), 92.8 (C), 116.7 (CH_2), 123.4 (CH), 123.6 (CH), 124.4 (C), 126.3 (CH), 126.5 (C), 127.0 (C), 128.2 (CH), 135.1 (CH), 149.9 (C), 160.8 (C); MS (ESI) *m/z* 388 (MNa^+, 42); HRMS (ESI) calcd for $C_{14}H_{11}{}^{35}Cl_4NNaO_2$ (MNa^+), 387.9436, found 387.9419.

6-Nitro-8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (11e). The reaction was carried out as described for the synthesis of 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11a**) using 3-(5'-nitro-2'-propargyloxyphenyl)-3-(2",2",2"-trichloromethylcarbonyl-amino)prop-1-ene (**10e**) (0.15 g, 0.40 mmol). Purification by column chromatography (diethyl ether/petroleum ether, 1:10) gave 6-nitro-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11e**) (0.098 g, 66%) as a yellow solid. Mp 138–140 °C; R_f = 0.48 (diethyl ether/petroleum ether = 1:1); IR (neat) 3418, 2924, 1710, 1518, 1338, 1216, 837, 754 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.05 (dd, J = 3.4, 2.0 Hz, 2H), 5.28 (dd, J = 17.2, 1.7 Hz, 1H), 5.33 (dd, J = 10.4, 1.7 Hz, 1H), 5.68 (ddt, J = 8.3, 5.4, 1.7 Hz, 1H), 5.93 (dt, J = 10.1, 3.4 Hz, 1H), 6.03 (ddd, J = 17.2, 10.4, 5.4 Hz, 1H), 6.47 (dt, J = 10.1, 2.0 Hz, 1H), 7.41 (br d, J = 8.3 Hz, 1H), 7.83 (d, J = 2.7 Hz, 1H), 8.00 (d, J = 2.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 53.5 (CH), 67.1 (CH_2), 92.5 (C), 117.7 (CH_2), 122.0 (CH), 122.6 (C), 123.0 (CH), 123.8 (CH), 124.1 (CH), 126.5 (C), 134.3 (CH), 141.7 (C), 156.6 (C), 160.9 (C); MS (ESI) *m/z* 399 (MNa^+, 51); HRMS (ESI) calcd for $C_{14}H_{11}{}^{35}Cl_3N_2NaO_4$ (MNa^+), 398.9677, found 398.9665.

8-[1'-(2'',2'',2''-Trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (11a). (2*E*)-3-(2'-Propargyloxyphenyl)prop-2-en-1-ol (**9a**) (0.050 g, 0.27 mmol) was dissolved in dichloromethane (4.0 mL) and cooled to 0 °C under argon with stirring. Trichloroacetonitrile (0.040 mL, 0.040 mmol) was added to the solution, followed by 1,8-diazabicyclo[5.4.0]undec-7-ene (0.020 mL, 0.13 mmol) and the

mixture was allowed to warm to room temperature over 2 h. The reaction mixture was filtered through a short pad of alumina (neutral, Brockman V) with diethyl ether (100 mL) and concentrated *in vacuo* to yield the crude allylic trichloroacetimidate as a yellow oil which was used without further purification. The allylic trichloroacetimidate was transferred to a dry Schlenk tube containing a stirrer bar and potassium carbonate (12 mg, 3 mg/mL) to which toluene (4 mL) was then added. The tube was purged with argon, sealed and heated to 140 °C for 18 h. The reaction mixture was allowed to cool to room temperature and chloro(triphenylphosphine)gold(I) (0.012 g, 0.020 mmol) and silver(I) hexafluoroantimonate (0.006 g, 0.020 mmol) were added. The reaction mixture was heated to 80 °C for 4 h. The reaction mixture was concentrated *in vacuo* and purified by column chromatography (diethyl ether/petroleum ether, 1:15) to give 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11a**) (0.069 g, 80%) as a colorless oil. Spectroscopic data was as described above.

6-Methoxy-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (11b). The reaction was carried out as described for the synthesis of 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11a**) using (2*E*)-3-(5'-methoxy-2'-propargyloxyphenyl)prop-2-en-1-ol (**9b**) (0.10 g, 0.46 mmol), chloro(triphenylphosphine)gold(I) (0.017 g, 0.035 mmol) and silver(I) hexafluoroantimonate (0.008 g, 0.035 mmol). The hydroarylation step was heated to 80 °C for 48 h. Purification by column chromatography (diethyl ether/petroleum ether, 1:15) gave 6-methoxy-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11b**) (0.15 g, 91%) as a colorless oil. Spectroscopic data was as described above.

5-Methoxy-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (11c). The reaction was carried out as described for the synthesis of 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11a**) using (2*E*)-3-(4'-methoxy-2'-propargyloxyphenyl)prop-2-en-1-ol (**9c**) (0.10 g, 0.46 mmol), chloro(triphenylphosphine)gold(I) (0.017 g, 0.035 mmol) and silver(I) hexafluoroantimonate (0.008 g, 0.035 mmol). The hydroarylation step was heated to 80 °C for 48 h. Purification by column chromatography (diethyl ether/petroleum ether, 1:15)

gave 5-methoxy-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11c**) (0.13 g, 78%) as a colorless oil. Spectroscopic data was as described above.

6-Chloro-8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (11d). The reaction was carried out as described for the synthesis of 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11a**) using (2*E*)-3-(5'-chloro-2'-propargyloxyphenyl)prop-2-en-1-ol (**9d**) (0.11 g, 0.47 mmol), chloro(triphenylphosphine)gold(I) (0.018 g, 0.035 mmol) and silver(I) hexafluoroantimonate (0.009 g, 0.035 mmol). The Overman rearrangement was heated to 140 °C for 48 h. The hydroarylation step was heated to 80 °C for 48 h. Purification by column chromatography (diethyl ether/petroleum ether, 1:15) gave 6-chloro-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11d**) (0.13 g, 76%) as a white solid. Spectroscopic data was as described above.

6-Nitro-8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (11e). The reaction was carried out as described for the synthesis of 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11a**) using (2*E*)-3-(5'-nitro-2'-propargyloxyphenyl)prop-2-en-1-ol (**9e**) (0.085 g, 0.36 mmol), chloro(triphenylphosphine)gold(I) (0.018 g, 0.036 mmol) and silver(I) hexafluoroantimonate (0.009 g, 0.036 mmol). The Overman rearrangement was heated to 140 °C for 72 h. The isomerisation step was heated to 80 °C for 65 h. Purification by column chromatography (diethyl ether/petroleum ether, 1:10) gave 6-nitro-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11e**) (0.074 g, 54%) as a white solid. Spectroscopic data was as described above.

8-[1'-(2'',2'',2''-Trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromen-2-one (12a). Pyridinium dichromate (0.070 g, 0.19 mmol) was added to a stirred solution of 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11a**) (0.030 g, 0.090 mmol) in dichloromethane (1 mL) and stirred at room temperature for 6 days. The reaction mixture was concentrated *in vacuo* and purified by column chromatography (diethyl ether/petroleum ether, 1:1) to give 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromen-2-one (**12a**) (0.020 g, 65%) as a white solid. Mp 136–138 °C; R_f = 0.13 (diethyl ether/petroleum ether = 1:1); IR (neat) 3424,

2926, 1711, 1604, 1505, 1117, 907, 833, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.23–5.34 (m, 2H), 5.83 (ddt, J = 8.4, 5.7, 1.6 Hz, 1H), 6.16 (ddd, J = 17.1, 10.3, 5.7 Hz, 1H), 6.44 (d, J = 9.6 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 7.46 (dd, J = 7.7, 1.6 Hz, 1H), 7.52 (dd, J = 7.7, 1.6 Hz, 1H), 7.73 (d, J = 9.6 Hz, 1H), 7.80 (br d, J = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 54.9 (CH), 92.5 (C), 116.8 (CH), 117.9 (CH_2), 119.4 (C), 124.6 (CH), 126.6 (C), 128.2 (CH), 131.4 (CH), 134.6 (CH), 143.7 (CH), 151.8 (C), 159.2 (C), 161.1 (C); MS (ESI) *m/z* 368 (MNa^+, 51); HRMS (ESI) calcd for $C_{14}H_{10}{}^{35}Cl_3NNaO_3$ (MNa^+), 367.9618, found 367.9606.

6-Methoxy-8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromen-2-one (12b). The reaction was carried out as described for the synthesis of 8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromen-2-one (**12a**) using 6-methoxy-8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11b**) (0.066 g, 0.18 mmol). The reaction mixture was allowed to stir at room temperature for 4 days. Purification by column chromatography (diethyl ether/petroleum ether, 7:3) gave 6-methoxy-8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromen-2-one (**12b**) (0.042 g, 62%) as a white solid. Mp 135–138 °C; R_f = 0.15 (diethyl ether/petroleum ether = 2:1); IR (neat) 3247, 2967, 1714, 1702, 1584, 1537, 1462, 1303, 1175, 1117, 921, 827 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.85 (s, 3H), 5.24–5.35 (m, 2H), 5.72–5.81 (m, 1H), 6.14 (ddd, J = 16.5, 10.5, 6.0 Hz, 1H), 6.43 (d, J = 9.6 Hz, 1H), 6.89 (d, J = 2.8 Hz, 1H), 7.10 (d, J = 2.8 Hz, 1H), 7.66 (d, J = 9.6 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.0 (CH), 56.0 (CH_3), 92.6 (C), 110.3 (CH), 117.3 (CH), 118.2 (CH_2), 119.0 (CH), 120.0 (C), 127.9 (C), 134.6 (CH), 143.6 (CH), 146.1 (C), 156.1 (C), 159.6 (C), 161.2 (C); MS (ESI) *m/z* 398 (MNa^+, 51); HRMS (ESI) calcd for $C_{15}H_{12}{}^{35}Cl_3NNaO_4$ (MNa^+), 397.9724, found 397.9715.

6-Chloro-8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromen-2-one (12c). The reaction was carried out as described for the synthesis of 8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromen-2-one (**12a**) using 6-chloro-8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11d**) (0.036 g, 0.099 mmol). The reaction

mixture was allowed to stir at room temperature for 6 days. Purification by column chromatography (diethyl ether/petroleum ether, 1:1) gave 6-chloro-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromen-2-one (**12c**) (0.015 g, 42%) as a white solid. Mp 150–153 °C; R_f = 0.15 (diethyl ether/petroleum ether = 1:1); IR (neat) 3322, 2945, 1726, 1704, 1598, 1573, 1512, 1222, 1174, 1122, 1098, 823 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.31 (dd, J = 17.1, 1.6 Hz, 1H), 5.35 (dd, J = 10.3, 1.6 Hz, 1H), 5.78 (ddt, J = 7.5, 5.8, 1.6 Hz, 1H), 6.14 (ddd, J = 17.1, 10.3, 5.8 Hz, 1H), 6.48 (d, J = 9.6 Hz, 1H), 7.45 (d, J = 2.4 Hz, 1H), 7.49 (d, J = 2.4 Hz, 1H), 7.60–7.70 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 54.5 (CH), 92.4 (C), 118.1 (CH), 118.9 (CH_2), 120.6 (C), 127.4 (CH), 128.7 (C), 130.1 (C), 131.1 (CH), 134.0 (CH), 142.6 (CH), 150.3 (C), 158.7 (C), 161.3 (C); MS (ESI) *m/z* 402 (MNa^+, 49); HRMS (ESI) calcd for $C_{14}H_9{}^{35}Cl_4NNaO_3$ (MNa^+), 401.9229, found 401.9222.

6-Nitro-8-[1'-(2'',2'',2''-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromen-2-one (12d). The reaction was carried out as described for the synthesis of 8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromen-2-one (**12a**) using 6-nitro-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromene (**11e**) (0.038 g, 0.10 mmol). The reaction mixture was allowed to stir at room temperature for 4 days. Purification by column chromatography (diethyl ether/petroleum ether, 7:3) gave 6-nitro-8-[1'-(2",2",2"-trichloromethylcarbonylamino)-2'-propenyl]-2*H*-chromen-2-one (**12d**) (0.023 g, 58%) as a white solid. Mp 61–64 °C; R_f = 0.18 (diethyl ether/petroleum ether = 2:1); IR (neat) 3332, 3087, 1739, 1703, 1612, 1531, 1345, 1177, 1112, 908, 822 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.37 (dd, J = 17.1, 1.5 Hz, 1H), 5.43 (dd, J = 10.3, 1.5 Hz, 1H), 5.92 (ddt, J = 6.8, 6.0, 1.5 Hz, 1H), 6.16 (ddd, J = 17.1, 10.3, 6.0 Hz, 1H), 6.60 (d, J = 9.7 Hz, 1H), 7.49 (d, J = 6.8 Hz, 1H), 7.81 (d, J = 9.7 Hz, 1H), 8.39 (d, J = 2.6 Hz, 1H), 8.41 (d, J = 2.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 53.9 (CH), 92.2 (C), 118.9 (CH), 119.5 (C), 119.9 (CH_2), 123.6 (CH), 125.3 (CH), 129.1 (C), 133.3 (CH), 142.7 (CH), 144.0 (C), 155.3 (C), 157.8 (C), 161.4 (C); MS (ESI) *m/z* 413 (MNa^+, 51); HRMS (ESI) calcd for $C_{14}H_9{}^{35}Cl_3N_2NaO_5$ (MNa^+), 412.9469, found 412.9459.

SUPPORTING INFORMATION AVAILABLE. ^{1}H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) While hydroarylation reactions with $Ph_3PAuNTf_2$ in dichloromethane can be done at room temperature (see reference 14b), we observed very low conversion using these conditions in *p*-xylene after 4 hours. To be able to use *p*-xylene for the hydroarylation step of the one-pot process (which is necessary for the high temperature Overman rearrangement), we conducted a temperature screen for this transformation and found that 80 ºC allowed complete conversion after 4 h.

(23) During the development of an optimal one-pot process for the preparation of allylic amide functionalized 2*H*-chromenes, one-pot processes involving a palladium(II)-catalyzed Overman rearrangement, followed by a gold(I)-catalyzed hydroarylation, as well as a one-pot process where both steps are catalyzed by gold(I) were investigated. However, in both cases, the transition metal-catalyzed Overman rearrangements of the aryl substituted allylic trichloroacetimidates gave low conversions (<40%) to the corresponding allylic trichloroacetamides.

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