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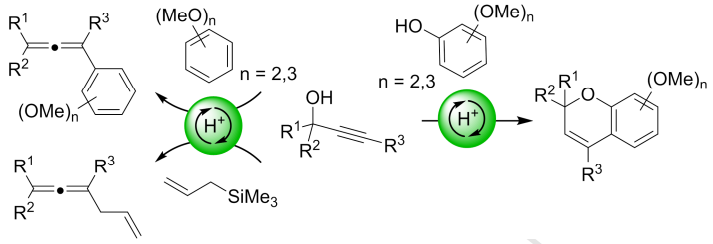

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ABSTRACT

A practical and environmentally benign Brønsted acid−catalyzed protocol for the preparation of all-carbon tetrasubstituted allenes, consisting in the direct S_N' addition of tri- or dimethoxy arenes or allyltrimethylsilane to tertiary propargylic alcohols, has been developed. In addition, a straightforward synthesis of densely substituted 2*H*-chromenes by metal-free tandem allenylation/heterocyclization reaction of methoxyphenols and tertiary alkynols is presented.

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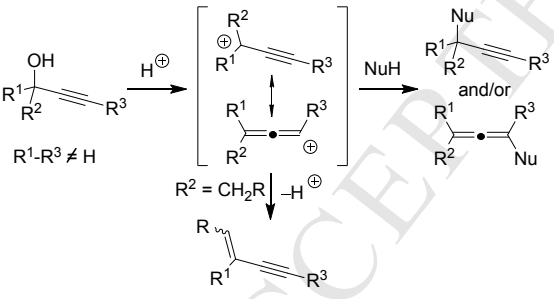
1. Introduction

Allenes are valuable building blocks with abundant applications in synthetic organic chemistry[1] or advanced material science[2] and commonly found in natural products and pharmacological active molecules.[3] So, the development of simple and efficient methods for the synthesis of allenes is an extremely active field in organic chemistry.[4] Among all the strategies described for the formation of the allene unit, the most extended and convenient method involves the nucleophilic substitution by organometallic species of acetylene derivatives bearing a leaving group at the propargylic carbon. This route turns to be almost unique for the synthesis of all-carbon tetrasubstituted allenes using metal catalysts derived from Cu, Rh, Pd, Mn, Ni or Fe and leaving groups such as halides, epoxides, sulfonates, phosphates, acetates or carbonates.[5] Moreover, the direct use of tertiary propargylic alcohols as substrates has been also extensively reported in the presence as catalysts of both Lewis acids[6] and late transition metals.[7] This route has the evident advantages of the wide availability and environmentally benign character of alcohols as well as the formation of water as the only byproduct of the process. However, these methods are limited by the precious, toxic, and/or moisture-sensitive nature of some of the catalysts employed.

In this scenario, the development of allenylation protocols using simple Brønsted acids as catalysts would be highly convenient. This approach implies the initial formation of an allenic-propargylic cation intermediate followed either by the nucleophilic substitution that could occur at both active positions or, alternatively, by a competitive elimination (Figure 1). Thus, selective addition of the carbon nucleophile through a S_N' mechanism is a key issue for the success of this strategy. Few efficient and general Brønsted acid-catalyzed syntheses of all-carbon tetrasubstituted allenes have been reported and they are restricted to the employment of 2-substituted indoles or 1,3-dicarbonyl compounds or related activated methylenes as nucleophiles.[8,9]

Figure 1. Possible evolutions of tertiary propargylic cations.

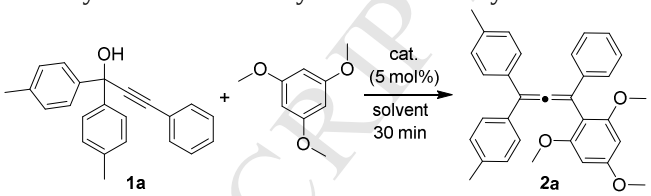


Based in our experience in the metal-free Brønsted acid-catalyzed direct nucleophilic substitutions of varied π-activated alcohols,[8a-c,9a,10] we envisioned that the combination of tertiary propargylic alcohols with bulky substituted electron-rich arenes would favored the S_N' nucleophilic addition, thus allowing the synthesis of all-carbon tetrasubstituted allenes.

2. Results and discussion

To test the viability of the proposed synthesis of allenes, we first investigated the reaction between highly activated tertiary alkynol **1a** and 1,3,5-trimethoxybenzene using *p*-toluenesulfonic acid (PTSA) as ready available and easily handled Brønsted acid catalyst. Pleasantly, the corresponding desired allene **2a** was exclusively obtained in good yield and in short reaction time (30 min) when performing the reaction in MeCN at room temperature in an open vessel (Table 1, entry 1). As would be expected, the substitution reaction did not take place in the absence of catalyst. Once we probed the feasibility and determined the selectivity of our strategy, the catalytic activity observed with PTSA was compared with several common Lewis acids (Table 1, entries 2–6). These essays revealed that none of the metal-based catalyst tested afforded better results than simple Brønsted acid and, therefore, PTSA should be the catalyst of choice for this kind of transformation. Additional experiments modifying the solvent employed were conducted showing that this Brønsted acid-catalyzed allene formation was also efficient in nitromethane or trifluoroethanol (Table 1, entries 7–9).

Table 1. Evaluation of Brønsted and Lewis acid catalysts for the allenylation of trimethoxybenzene with alkynol **1a**



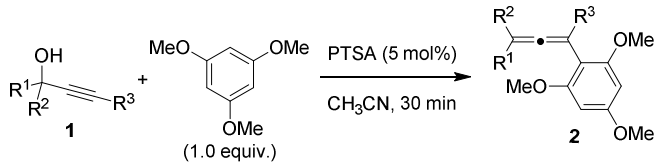
Entry	Catalyst	Solvent	Yield (%)[a]
1	PTSA	CH_3CN	79
2	$FeCl_3$	CH_3CN	79
3	$Cu(OTf)_2$	CH_3CN	81
4	$Sc(OTf)_3$	CH_3CN	80
5	AgOTf	CH_3CN	–
6	$In(OTf)_3$	CH_3CN	–
7	PTSA	CH_2Cl_2	33
8	PTSA	CH_3NO_2	79
9	PTSA	CF_3CH_2OH	69

[a] Isolated yield of **2a** after column chromatography.

After establishing PTSA as catalyst and MeCN as solvent at room temperature as the best reaction conditions, the scope of the process was examined using a collection of tertiary alkynols **1** having varied substitution at both the α and γ positions. The results have been summarized in Table 2. The developed method proved to be very efficient for the synthesis of tetraaryl allenes **2a-e**, regardless of the electronic nature of the arenes (Table 2, entries 1–6), and a triaryl cyclohexenyl allene **2g** (Table 2, entry 8). Next, we explored the reaction with less activated alkynols **1h-l** possessing an alkyl substituent at the propargylic position and we were pleased to find that the desired allenes **2h-l** were also produced in high yields (Table 2, entries 9–13). Remarkably, in all these examples the corresponding tetrasubstituted allenes **2** are exclusively obtained, generally in high yields, without the formation of significant amounts of the regioisomeric S_N acetylenic adduct or the elimination subproduct when possible. In addition, both electron rich and electron-deficient arenes as well as linear or branched alkyl groups are tolerated at the propargylic positions of the starting alkynol. Only in the case of alkynol **1f** bearing a 3-thienyl group at the γ position, the initially produced allene could not be isolated as it evolves under the acidic reaction conditions to a cyclopentene-fused thiophene **3f** (Table 2, entry 7). However, this is not a general limitation as reaction with less activated alkynol **1l** demonstrates the possibility of accessing 3-thienyl substituted allenes (Table 2, entry 13). To further test the scope of the allene synthesis, reaction of trimethoxybenzene with more challenging substrate **1m** bearing two aliphatic substituents at the propargylic position were surveyed under the optimal reaction conditions. Not surprisingly, due to the inferior

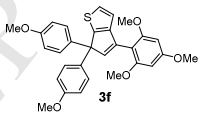
stabilities of the positively charged intermediates proposed (Figure 1) as a result of the replacement of both aryls groups by alkyls groups at the propargylic position, the reaction failed. Gratifyingly, changing the catalyst to a more acidic Brønsted acid such as TFESA (1,1,2,2-tetrafluoroethanesulfonic acid) and increasing the loading to a 10 mol%, dialkyl substituted allene **2m** could be obtained using an excess of nucleophile (Table 2, entry 14). Under these reaction conditions the allene formation was not the only observed product as appreciable amounts of a 1,3-enyne, formed by dehydration of the starting alkynol, were detected and accounted for the reduced isolated yield of the desired allene **2m**.

Table 2. Acid-catalyzed reaction of 1,3,5-trimethoxybenzene with tertiary alkynols **1**. Synthesis of tetrasubstituted allenes **2**

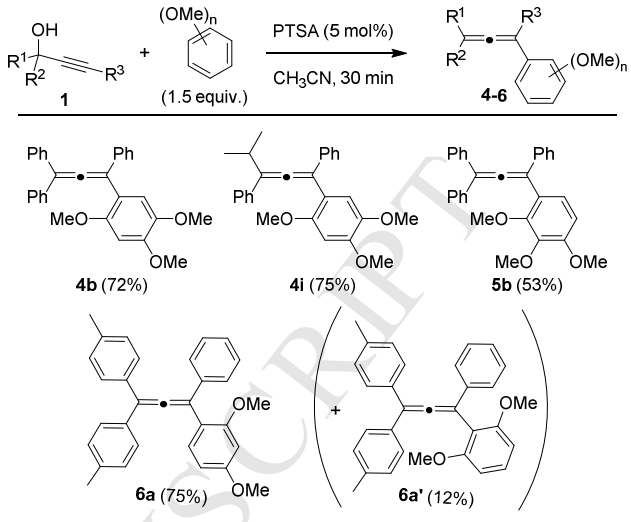


Entry	1	R^1	R^2	R^3	2	Yield (%)[a]
1	**1a**	*p*-MeC_6H_4	*p*-MeC_6H_4	Ph	**2a**	79
2	**1b**	Ph	Ph	Ph	**2b**	91
3[b]	**1b**	Ph	Ph	Ph	**2b**	85
4	**1c**	*p*-ClC_6H_4	*p*-ClC_6H_4	Ph	**2c**	99
5	**1d**	*p*-ClC_6H_4	*p*-ClC_6H_4	*p*-MeC_6H_4	**2d**	71
6	**1e**	*p*-$OMeC_6H_4$	*p*-$OMeC_6H_4$	Ph	**2e**	94
7	**1f**	*p*-$OMeC_6H_4$	*p*-$OMeC_6H_4$	3-Th[c]	–[d]	62
8	**1g**	Ph	Ph	*c*-C_6H_9[e]	**2g**	75
9	**1h**	*c*-C_3H_5	Ph	Ph	**2h**	61
10	**1i**	*i*-Pr	Ph	Ph	**2i**	78
11	**1j**	Pr	Ph	Ph	**2j**	91
12	**1k**	Et	*p*-ClC_6H_4	Ph	**2k**	81
13[f]	**1l**	Me	Ph	3-Th[c]	**2l**	78
14	**1m**	*i*-Pr	*i*-Pr	Ph	**2m**	58[g]

[a] Isolated yield of **2** after column chromatography.
[b] Reaction performed at a 4 mmol scale (1.14 g of **1b**)
[c] 3-Th = 3-Thienyl.
[d] A cyclopenta[*b*]thiophene **3f** was exclusively obtained.
[e] *c*-C_6H_9 = Cyclohexenyl.
[f] Reaction conduted with 3 equiv. of trimethoxybenzene.
and 10 mol% of TFESA (1,1,2,2-tetrafluoroethanesulfonic acid).
[g] 27% of the dehydration product from the alkynol was also detected.



The scope of the process was then explored using other trimethoxybenzenes such as 1,2,4-trimethoxybenzene and 1,2,3-trimethoxybenzene (Scheme 1). In contrast to 1,3,5-trimethoxybenzene, these isomeric arenes present different nucleophilic positions that add an extra regiocontrol issue. Notably, reactions of 1,2,4-trimethoxybenzene with representative alkynols **1b** and **1i** occurred selectively to form tetrasubstituted allenes **4b** and **4i** in good yields. Similarly, allene **5b** was obtained as major product in a synthetically useful yield from 1,2,3-trimethoxybenzene and tertiary alkynol **1b**. Less nucleophilic 1,3-dimethoxyarene also reacted with model substrate **1a** to afford a 6:1 mixture of regiosomeric allenes **6a** and **6a'** (Scheme 1), whereas the analogous reaction with even less nucleophilic anisole did not occur under the optimized reaction conditions.

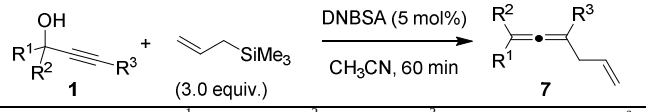


Scheme 1. Acid-catalyzed reaction tertiary alkynols **1** with other tri- and dimethoxyarenes.

At this point we were intrigued by the possibility of expanding this developed metal-free methodology to more challenging nucleophiles such as less sterically demanding allyltrimethylsilane. An initial experiment with the model tertiary alkynol **1a**, under the reaction conditions established for trimethoxybenzene, regioselectively gave the desired allene **7a** in a moderate 34% yield. After an optimization, we found that using the stronger 2,4-dinitrobenzensulfonic acid (DNBSA) as catalyst and an excess of allyltrimethylsilane (3 equiv.) enabled the exclusive formation of allene **7a** at room temperature in high yield and in less than 1 hour (Table 3, entry 1). The scope of the synthesis of allyl allenes **7** was then analyzed using representative tertiary propargylic alcohols **1**. As in the case of trimethoxybenzene, highly activated α,α,γ-triarylsubstituted substrates **1b-e** afforded the corresponding allenes **7b-e** in high yields (Table 3, entries 2–6) with the exception of **7e** that decomposed under the reaction conditions and during the purification process. Moreover, the process tolerates the presence of an alkenyl group at γ-position and an heteroaryl group at the α-position, as demonstrated by the preparation of allenes **7g** and **7n** (Table 3, entries 7 and 10). However, reaction of less reactive alkynol **1i**, bearing an *iso*-propyl and a phenyl groups at the propargylic position, was not selective and the corresponding allene **7i** was formed accompanied with almost equimolecular amounts of the propargylic adduct **8** and small amounts of the dehydration subproduct **9** (Table 3, entry 8). Not surprisingly, no reaction occurred with even less activated propargylic alcohol **1m** (Table 3, entry 9).

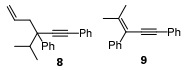
It should be noted the complete regioselective substitution at the γ-position of the propargylic alkynol determined in all the reactions with trimethoxybenzenes and in most of the experiments with allyltrimethylsilane. The absence of formation of propargylic substitution products is significant because analogous Brønsted acid-catalyzed reactions with secondary propargylic alcohols exclusively occurred at the α-position.[10a,c] In the same way, related reactions of tertiary propargylic alkynols with 2-unsubstituted indoles took place selectively at the propargylic position.[8c,10d]

On the other hand, gram scale reactions with both nucleophiles, trimethoxybenzene and allyltrimethylsilane, were assessed using 1.14 grams (4 mmol) of alkynol **1b** as substrate producing 1.47 g of **2b** (Table 2, entry 3) and 1.12 g of **7b** (Table 3, entry 3), respectively. These results further prove the practicality of the developed Brønsted acid-catalyzed allene synthesis.**Table 3.** Acid-catalyzed reaction of allylsilane with tertiary alkynols **1**. Synthesis of tetrasubstituted allenes **7**



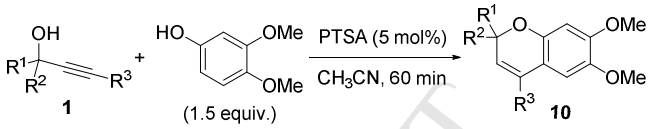
Entry	**1**	R^1	R^2	R^3	**7**	Yield (%)[a]
1	**1a**	*p*-MeC_6H_4	*p*-MeC_6H_4	Ph	**7a**	80
2	**1b**	Ph	Ph	Ph	**7b**	77
3[b]	**1b**	Ph	Ph	Ph	**7b**	87
4	**1c**	*p*-ClC_6H_4	*p*-ClC_6H_4	Ph	**7c**	77
5	**1d**	*p*-ClC_6H_4	*p*-ClC_6H_4	*p*-MeC_6H_4	**7d**	65
6	**1e**	*p*-$OMeC_6H_4$	*p*-$OMeC_6H_4$	Ph	**7e**	15[c]
7	**1g**	Ph	Ph	*c*-C_6H_9[d]	**7g**	61
8	**1i**	*i*-Pr	Ph	Ph	**7i**	38[e]
9	**1m**	*i*-Pr	*i*-Pr	Ph	**7m**	–
10	**1n**	Ph	3-Th[f]	Ph	**7n**	79

[a] Isolated yield of **7** after column chromatography.
[b] Reaction performed at a 4 mmol scale (1.14 g of **1b**)
[c] The product decomposed in the reaction media and during purification.
[d] *c*-C_6H_9 = Cyclohexenyl.
[e] The allene was obtained accompanied with the S_N adduct **8** (32%) and the dehydration product **9** (5%).
[f] 2-Th = 2-Thienyl.



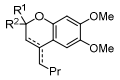
Having demonstrated the feasibility of the synthesis of all-carbon tetrasusbstituted allenes from tertiary propargylic alcohols under simple Brønsted acid catalysis, and the wide scope founded when trimethoxyarenes are used as nucleophiles, we turned our attention to dimethoxyphenols that would initially produce allenes that could evolve in cascade reaction to highly valuable products. To this aim, we selected 3,4-dimethoxyphenol that we envisaged that would furnish polysubstituted 2*H*-chromenes in a cascade fashion through an initial S_N' attack, of the more nucleophilic 6 position of the phenol, followed by heterocyclization of the acid-activated allene.[11,12] As we anticipated, reaction of a slight excess of the selected phenol (1.5 equiv.) with the model tertiary alkynol **1a**, under the conditions developed for trimethoxyarenes, exclusively produced 2*H*-chromene **10a** in very high yield (Table 4, entry 1). The scope of the cascade process was then examined. As depicted in Table 4, triaryl as well as diaryl-heteroaryl substituted substrates **1a-e,o** efficiently react with 3,4-dimethoxyphenol affording the corresponding chromenes **10a-e,o** in high yields (entries 1–4 and 10), including an example at gram scale (entry 3). Moreover, most of the reactions of less reactive alkynols **1h-k,p-t**, containing one aromatic and one alkyl group at the propargylic position, also occurred with total selection to form the cascade products **10h-j,p-r** in good yields (Table 4, entries 5–7, 11–13). Only 2*H*-chromene **10k**, derived from a propargylic alcohol bearing a linear alkyl group and an electron-poor arene at the α-position, was obtained in moderate yield due to the formation of competitive S_N adduct (Table 4, entry 8). Notably, reaction of more demanding α-di-*iso*-propyl substituted propargylic alcohol **1m** occurred selectively to form a 2,2-dialkyl substituted chromene derivative **10m** in good yield with formation of less than 10% of the elimination subproduct (Table 4, entry 9). In addition, this methodology is also useful for the preparation of 4-alkyl substituted chromenes **10s-u** from γ-alkyl substituted propargylic alcohols **1s-u** (Table 4, entries 14–16).

Table 4. Acid-catalyzed synthesis of polysubstituted 2*H*-chromenes **10** from tertiary alkynols **1** and 3,4-dimethoxyphenol.

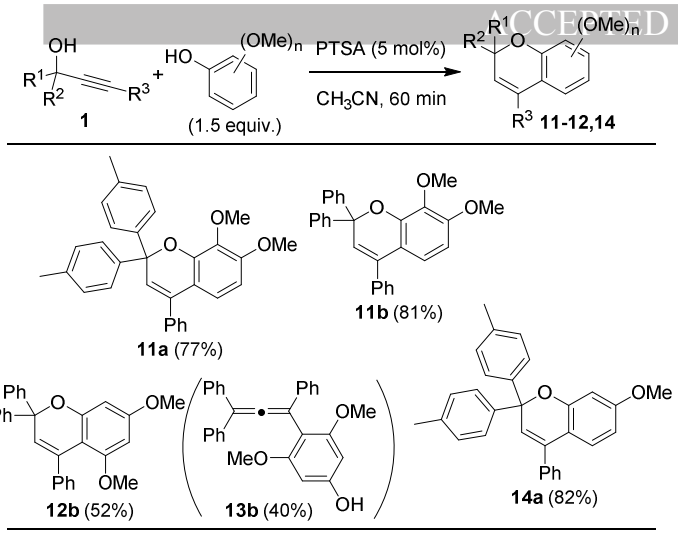


Entry	**1**	R^1	R^2	R^3	**10**	Yield (%)[a]
1	**1a**	*p*-MeC_6H_4	*p*-MeC_6H_4	Ph	**10a**	89
2	**1b**	Ph	Ph	Ph	**10b**	86
3	**1b**	Ph	Ph	Ph	**10b**	76
4	**1c**	*p*-ClC_6H_4	*p*-ClC_6H_4	Ph	**10c**	76
5	**1e**	*p*-$OMeC_6H_4$	*p*-$OMeC_6H_4$	Ph	**10e**	88
6	**1h**	*c*-C_3H_5	Ph	Ph	**10h**	86
7	**1i**	*i*-Pr	Ph	Ph	**10i**	81
8	**1j**	Pr	Ph	Ph	**10j**	90
9	**1k**	Et	*p*-ClC_6H_4	Ph	**10k**	62[c]
10	**1m**	*i*-Pr	*i*-Pr	Ph	**10m**	72[d]
11	**1o**	Ph	2-Th[e]	Ph	**10o**	70
12	**1p**	*c*-C_3H_5	2-Th[e]	Ph	**10p**	71
13	**1q**	Me	Ph	Ph	**10q**	75
14	**1r**	*c*-C_3H_5	*p*-ClC_6H_4	Ph	**10r**	77
15	**1s**	*p*-MeC_6H_4	*p*-MeC_6H_4	Bu	**10s**	70[f]
16	**1t**	Pr	Ph	Bu	**10t**	67[f]
17	**1u**	Ph	Ph	*c*-C_3H_5	**10u**	63

[a] Isolated yield of **10** after column chromatography.
[b] Reaction performed at a 4 mmol scale (1.14 g of **1b**)
[c] Formation of S_N adduct was also observed (16%).
[d] < 10% of elimination product was also detected.
[e] 2-Th = 2-Thienyl.
[f] Obtained as a mixture (1.2:1 entry 15, 1.9:1 entry 16) of two isomers as a result of olefin isomerization.



The range of the accessible 2,2,4-trisubstituted 2*H*-chromenes using our metal-free methodology was extended to other isomers **11** and **12** by switching the nucleophile to 2,3-dimethoxyphenol or 3,5-dimethoxyphenol (Scheme 2). As expected, reaction with the later phenol produced a mixture of the corresponding 2*H*-chromene **12b** and the allene derivative **13b** as a result of the initial competitive nucleophilic S_N' addition. Finally, 2*H*-chromene **14a** has been synthesized in high yield from less nucleophilic 3-methoxyphenol, thus enhancing the usefulness of the developed methodology.



Scheme 2. Acid-catalyzed reaction of tertiary alkynols **1** with other methoxyphenols.

3. Conclusions

In conclusion, we have developed a clean, simple and effective metal-free methodology for the preparation of functionalized all-carbon tetrasubstituted allenes by direct nucleophilic substitution reaction of tertiary propargylic alcohols with tri- or dimethoxyarenes and allyltrimethylsilane. While the scope of the reaction with allyltrimethylsilane seems to be limited, a wide variety of allenes have been prepared employing rich aromatic compounds as nucleophiles. In addition, the employment of methoxyphenols as the nucleophilic partners lead to the formation of 2*H*-chromenes in a cascade process that involves the heterocyclization of the initially formed allene in the reaction medium giving functionalized chromenes as final products of the process.

4. Experimental section

4.1. General methods

All common reagents, catalysts and solvents were obtained from commercial suppliers and used without any further purification. The starting alkynols **1** were synthesized by well established procedures consisting in the nucleophilic addition of the appropriate lithium acetylide to the corresponding ketone. All reactions were assembled under air atmosphere in oven-dried glassware with magnetic stirring. TLC analysis was performed on aluminium-backed plates coated with silica gel 60 (230-240 mesh) with F_{254} indicator (Merck). Flash column chromatography was carried out on silica gel 60, 230-240 mesh. R_f values are reported on silica gel. ^{1}H NMR spectra were recorded recorded on Varian Mercury-Plus 300 MHz and Varian Inova-400 MHz in $CDCl_3$. Chemical shifts are reported in ppm using the residual solvent peak as reference ($CHCl_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, hept: heptet; m: multiplet, dd: doublet of doublets, dt: doublet of triplets, dq: doublet of quartets, ddt: doublet of doublet of triplets, bs: broad singlet), coupling constant (*J* in Hz), and integration. ^{13}C NMR spectra were recorded at 75.4 or 100.6 MHz using broadband proton decoupling, and chemical shifts are reported in ppm using residual solvent peaks as reference ($CDCl_3$: δ 77.16). Carbon multiplicities were assigned by DEPT techniques. High-resolution mass spectra (HRMS) were recorded on a Micromass Autospec spectrometer using EI at 70 eV. Melting points were measured on a Gallenkamp apparatus using open capillary tubes and are uncorrected. GC-MS and low-resolution mass spectra (LRMS) measurements were recorded on Agilent 6890N/5973 Network GC System equipped with a HP-5MS column.

*4.2 General procedure for the synthesis of tetrasubstituted allenes **2**,**4-7** from propargylic alcohols **1***

To a mixture of the corresponding alkynol **1** (1 mmol) and the appropriate trimethoxyarene (1 mmol, 168 mg), 1,3-dimethoxybenzene (1 mmol, 138 mg) or allyltrimethylsilane (3 mmol, 0.5 mL) in MeCN (2 mL) was added *p*-toluenesulfonic acid monohydrate (PTSA) (5 mol %, 9 mg) for reactions with arenes or 2,4-dinitrobenzenesulfonic acid hydrate (DNBSA) (5 mol %, 15 mg) for reactions with allyltrimethylsilane. The resulted reaction mixture was stirred at room temperature until the reactants had been consumed, as determined by GC–MS and/or TLC. The crude mixture was neutralized by the addition of NaOH 0.5 M (5 mL), and EtOAc (15 mL) was added. The separated aqueous phase was extracted with EtOAc (3 x 15 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: mixtures of hexane/AcOEt) to afford the corresponding allenes **2**,**4-7** in the yields reported in Tables 2-3 and Scheme 1.

*1-(2,4,6-Trimethoxyphenyl)-1-phenyl-3,3-di-p-tolylpropa-1,2-diene (**2a**)*. 365 mg (79% yield). White solid; mp: 159–161 °C; R_f (Hexane/AcOEt 6:1) 0.21. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 6H), 3.67 (s, 6H), 3.86 (s, 3H), 6.23 (s, 2H), 7.13–7.21 (m, 5H), 7.24–7.29 (m, 2H), 7.30–7.36 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 3H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.3 (2 × CH_3), 55.4 (CH_3), 55.9 (2 × CH_3), 91.1 (2 × CH), 103.3 (C), 106.3 (C), 111.2 (C), 126.2 (2 × CH), 126.6 (CH), 128.4 (2 × CH), 128.7 (4 × CH), 129.0 (4 × CH), 133.5 (2 × C), 136.6 (C), 136.8 (2 × C), 159.3 (2 × C), 161.1 (C), 208.5 (C) ppm. LRMS (EI) *m/z* (%): 462 (M^+, 100); HRMS (EI) calcd for $C_{32}H_{30}O_3^+$ 462.2189 found 462.2181.

*1-(2,4,6-Trimethoxyphenyl)-1,3,3-triphenylpropa-1,2-diene (**2b**)*. 1 mmol scale rection: 395 mg (91% yield); 4 mmol scale reaction: 1.47 g (85% yield). White solid; mp: 170–172 °C; R_f (Hexane/AcOEt 10:1) 0.32. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 6H), 3.87 (s, 3H), 6.24 (s, 2H), 7.18–7.41 (m, 11H), 7.52–7.57 (m, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.5 (CH_3), 55.9 (2 × CH_3), 91.2 (2 × CH), 103.7 (C), 106.1 (C), 111.5 (C), 126.2 (2 × CH), 126.8 (CH), 127.2 (2 × CH), 128.3 (4 × CH), 128.4 (2 × CH), 128.9 (4 × CH), 136.5 (2 × C), 136.4 (C), 136.8 (2 × C), 159.3 (2 × C), 161.1 (C), 208.8 (C) ppm. LRMS (EI) *m/z* (%): 434 (M^+, 100); HRMS (EI) calcd for $C_{30}H_{26}O_3^+$ 434.1876 found 434.1877.

*3,3-Di-p-Chlorophenyl-1-(2,4,6-trimethoxyphenyl)-1-phenylpropa-1,2-diene (**2c**)*. 496 mg (99% yield). White solid; mp: 204–206 °C; R_f (Hexane/AcOEt 6:1) 0.23. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 6H), 3.85 (s, 3H), 6.22 (s, 2H), 7.19–7.32 (m, 9H), 7.40–7.42 (m, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.5 (CH_3), 55.9 (2 × CH_3), 91.1 (2 × CH), 104.4 (C), 105.4 (C), 109.7 (C), 126.2 (2 × CH), 127.1 (CH), 128.6 (6 × CH), 130.0 (4 × CH), 133.1 (2 × C), 134.7 (2 × C), 135.8 (C), 159.2 (2 × C), 161.4 (C), 208.8 (C) ppm. LRMS (EI) *m/z* (%): 502 (M^+, 100); HRMS (EI) calcd for $C_{30}H_{24}Cl_2O_3^+$ 502.1097 found 502.1098.

*3,3-Di-p-Chlorophenyl-1-(2,4,6-trimethoxyphenyl)-1-di-p-tolylpropa-1,2-diene (**2d**)*. 367 mg (71% yield). White solid; mp: 188–190 °C; R_f (Hexane/AcOEt 8:1) 0.47. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 3.66 (s, 6H), 3.86 (s, 3H), 6.22 (s, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.5

Hz, 4H), 7.41 (d, *J* = 8.5 Hz, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.3 (CH_3), 55.5 (CH_3), 55.9 (2 × CH_3), 91.0 (2 × CH), 104.3 (C), 105.5 (C), 109.6 (C), 126.1 (2 × CH), 128.5 (4 × CH), 129.4 (2 × CH), 130.0 (4 × CH), 132.7 (C), 133.0 (C), 134.8 (C), 136.9 (C), 159.2 (2 × C), 161.3 (C), 208.6 (C) ppm. LRMS (EI) *m/z* (%): 516 (M^+, 100); HRMS (EI) calcd for $C_{31}H_{26}Cl_2O_3^+$ 516.1254 found 516.1257.

3,3-Di-p-Methoxyphenyl-1-(2,4,6-trimethoxyphenyl)-1-phenyl-1,2-diene ***(2e)***. 465 mg (94% yield). White solid; mp: 184–186 °C; R_f (Hexane/AcOEt 3:1) 0.12. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 6H), 3.82 (s, 6H), 3.86 (s, 3H), 6.23 (s, 2H), 6.88 (d, *J* = 7.8 Hz, 4H), 7.13–7.20 (m, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.30–7.34 (m, 2H), 7.44 (d, *J* = 7.8 Hz, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.4 (2 × CH_3), 55.5 (CH_3), 56.0 (2 × CH_3), 91.1 (2 × CH), 103.2 (C), 106.5 (C), 110.6 (C), 113.7 (4 × CH), 126.2 (2 × CH), 126.6 (CH), 128.4 (2 × CH), 128.9 (2 × C), 129.9 (4 × CH), 136.8 (C), 158.9 (2 × C), 159.3 (2 × C), 161.1 (C), 208.2 (C) ppm. LRMS (EI) *m/z* (%): 494 (M^+, 100); HRMS (EI) calcd for $C_{32}H_{30}O_5^+$ 494.2088 found 494.2092.

6,6-bis(4-Methoxyphenyl)-4-(2,4,6-trimethoxyphenyl)-6H-cyclopenta[b]thiophene ***(3f)***. 310 mg (62% yield). Yellow solid; mp: 87–89 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 12H), 3.88 (s, 3H), 6.26 (s, 2H), 6.75–6.96 (m, 6H), 7.28 (bs, 1H), 7.40 (d, *J* = 7.8 Hz, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.2 (2 × CH_3), 55.3 (CH_3), 55.9 (2 × CH_3), 63.3 (C), 91.0 (2 × CH), 106.3 (C), 113.6 (4 × CH), 120.8 (CH), 127.6 (CH), 128.9 (4 × CH), 130.2 (C), 136.2 (CH), 146.5 (2 × C), 149.2 (C), 150.6 (C), 158.2 (2 × C), 159.2 (2 × C), 160.8 (C) ppm. LRMS (EI) *m/z* (%): 500 (M^+, 100); HRMS (EI) calcd for $C_{30}H_{28}O_5S^+$ 500.1652 found 500.1655.

1-Cyclohexenyl-1-(2,4,6-trimethoxyphenyl)-3,3-diphenylpropa-1,2-diene ***(2g)***. 329 mg (75% yield). White solid; mp: 139–141 °C; R_f (Hexane/AcOEt 15:1) 0.23. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.60–1.63 (m, 2H), 1.70–1.73 (m, 2H), 2.05–2.08 (m, 2H), 2.33–2.36 (m, 2H), 3.69 (s, 6H), 3.82 (s, 3H), 5.36 (bs, 1H), 6.19 (s, 2H), 7.22–7.26 (m, 2H), 7.31–7.33 (m, 4H), 7.45–7.47 (m, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 22.5 (CH_2), 23.0 (CH_2), 26.0 (CH_2), 26.8 (CH_2), 55.4 (CH_3), 56.1 (2 × CH_3), 91.4 (2 × CH), 106.2 (C), 107.2 (C), 110.3 (C), 124.2 (CH), 126.7 (2 × CH), 128.1 (4 × CH), 128.8 (4 × CH), 132.8 (C), 137.3 (2 × C), 159.1 (2 × C), 160.7 (C), 207.5 (C) ppm. LRMS (EI) *m/z* (%): 438 (M^+, 100), 270 (66), 181 (43); HRMS (EI) calcd for $C_{30}H_{30}O_3^+$ 438.2189 found 438.2193.

3-Cyclopropyl-1-(2,4,6-trimethoxyphenyl)-1,3-diphenylpropa-1,2-diene ***(2h)***. 242 mg (61% yield). Yellow oil; R_f (Hexane/AcOEt 10:1) 0.30. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.63–0.67 (m, 1H), 0.83–0.90 (m, 3H), 1.65–1.71 (m, 1H), 3.75 (s, 6H), 3.86 (s, 3H), 6.21 (s, 2H), 7.14–7.37 (m, 8H), 7.76–7.81 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 6.88 (CH_2), 6.93 (CH_2), 10.9 (CH), 55.5 (CH_3), 55.8 (2 × CH_3), 90.9 (2 × CH), 104.8 (C), 106.6 (c), 111.1 (C), 126.0 (2 × CH), 126.6 (CH), 126.7 (CH), 126.8 (2 × CH), 128.3 (2 × CH), 128.4 (2 × CH), 136.8 (C), 137.2 (C), 159.1 (2 × C), 161.0 (C), 205.6 (C) ppm. LRMS (EI) *m/z* (%): 398 (M^+, 100), 229 (37), 181 (76); HRMS (EI) calcd for $C_{27}H_{26}O_3^+$ 398.1876 found 398.1881.

3-Isopropyl-1-(2,4,6-trimethoxyphenyl)-1,3-diphenylpropa-1,2-diene ***(2i)***. 313 mg (78% yield). White solid; mp: 115–117 °C; R_f (Hexane/AcOEt 15:1) 0.19. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (d, *J* = 6.7 Hz, 3H), 1.41 (d, *J* = 6.7 Hz, 3H), 3.03 (hept, *J* = 6.7 Hz, 1H), 3.76 (s, 6H), 3.89 (s, 3H), 6.26 (s, 2H), 7.15–7.40 (m, 8H), 7.62–7.70 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 22.3 (CH_3), 22.5 (CH_3), 28.8 (CH), 55.4 (CH_3), 55.7 (2 × CH_3), 90.8 (2 × CH), 104.9 (C), 106.7 (C), 114.9 (C), 125.9 (2 × CH), 126.4 (CH), 126.5 (CH), 127.0 (2 × CH), 128.3 (2 × CH), 128.4 (2 × CH), 136.3 (C), 137.1 (C), 159.2 (2 × C), 161.0 (C), 205.9 (C) ppm. LRMS (EI) *m/z* (%): 400 (M^+, 22), 357 (100); HRMS (EI) calcd for $C_{27}H_{28}O_3^+$ 400.2033 found 400.2035.

1-(2,4,6-Trimethoxyphenyl)-1,3-diphenyl-3-propylpropa-1,2-diene ***(2j)***. 365 mg (91% yield). Colourless oil; R_f (Hexane/AcOEt 15:1) 0.22. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.3, 3H), 1.76–1.96 (m, 2H), 2.58–2.78 (m, 2H), 3.82 (s, 6H), 3.93 (s, 3H), 6.33 (s, 2H), 7.22–7.50 (m, 8H), 7.74 (d, *J* = 8.4, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.4 (CH_3), 21.0 (CH_2), 32.2 (CH_2), 55.4 (CH_3), 55.7 (2 × CH_3), 90.9 (2 × CH), 103.8 (C), 106.7 (C), 107.7 (C), 126.0 (2 × CH), 126.4 (CH), 126.5 (3 × CH), 128.2 (2 × CH), 128.3 (2 × CH), 136.8 (C), 137.2 (C), 159.2 (2 × C), 161.0 (C), 206.9 (C) ppm. LRMS (EI) *m/z* (%): 400 (M^+, 54), 371 (100); HRMS (EI) calcd for $C_{27}H_{28}O_3^+$ 400.2033 found 400.2036.

3-p-Chlorophenyl-3-ethyl-1-(2,4,6-trimethoxyphenyl)-1-phenylpropa-1,2-diene ***(2k)***. 340 mg (81% yield). Colourless oil; R_f (Hexane/AcOEt 10:1) 0.37. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.3 Hz, 3H), 2.40–2.67 (m, 2H), 3.72 (s, 6H), 3.85 (s, 3H), 6.21 (s, 2H), 7.12–7.30 (m, 7H), 7.50–7.58 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 12.1 (CH_3), 23.1 (CH_2), 55.5 (CH_3), 55.7 (2 × CH_3), 90.8 (2 × CH), 104.9 (C), 106.3 (C), 108.8 (C), 126.0 (2 × CH), 126.6 (CH), 127.7 (2 × CH), 128.3 (2 × CH), 128.4 (2 × CH), 132.1 (C), 135.4 (C), 136.9 (C), 159.1 (2 × C), 161.1 (C), 206.6 (C) ppm. LRMS (EI) *m/z* (%): 420 (M^+, 100); HRMS (EI) calcd for $C_{26}H_{25}ClO_3^+$ 420.1487 found 420.1492.

3-Methyl-1-(2,4,6-trimethoxyphenyl)-3-phenyl-1-(3-thienyl)propa-1,2-diene ***(2l)***. 295 mg (78% yield). Orange solid; mp: 120–122 °C; R_f (Hexane/AcOEt 10:1) 0.33. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 3H), 3.80 (s, 6H), 3.88 (s, 3H), 6.26 (s, 2H), 6.82–6.87 (m, 1H), 7.14–7.43 (m, 5H), 7.63–7.68 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 16.5 (CH_3), 55.4 (CH_3), 55.9 (2 × CH_3), 91.0 (2 × CH), 98.1 (C), 101.7 (C), 107.0 (C), 120.1 (CH), 125.1 (CH), 126.4 (2 × CH), 126.6 (CH), 126.8 (CH), 128.2 (2 × CH), 137.9 (C), 139.0 (C), 159.2 (2 × C), 161.0 (C), 207.0 (C) ppm. LRMS (EI) *m/z* (%): 378 (M^+, 100); HRMS (EI) calcd for $C_{23}H_{22}O_3S^+$ 378.1284 found 378.1288.

3,3-Diiso-propyl-1-(2,4,6-trimethoxyphenyl)-1-phenylpropa-1,2-diene ***(2m)***. 212 mg (58% yield). White solid; mp: 102–104 °C; R_f (Hexane/AcOEt 15:1) 0.19. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (d, *J* = 6.8 Hz, 6H), 1.21 (d, *J* = 6.8 Hz, 6H), 2.30 (hept, *J* = 6.8 Hz, 2H), 3.71 (s, 6H), 3.87 (s, 3H), 6.21 (s, 2H), 7.07–7.14 (m, 1H), 7.17–7.30 (m, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 22.4 (2 × CH_3), 22.6 (2 × CH_3), 31.1 (2 × CH), 55.4 (CH_3), 55.6 (2 × CH_3), 90.7 (2 × CH), 103.2 (C), 108.3 (C), 120.2 (C), 125.4 (2 × CH), 125.7 (CH), 128.1 (2 × CH), 138.7 (C), 159.2 (2 × C), 160.7 (C), 201.0 (C) ppm. LRMS (EI) *m/z* (%): 366 (M^+, 100); HRMS (EI) calcd for $C_{24}H_{30}O_3^+$ 366.2189 found 366.2194.

1-(2,3,5-Trimethoxyphenyl)-1,3,3-triphenylpropa-1,2-diene ***(4b)***. 313 mg (72% yield). White solid; mp: 181–183 °C; R_f (Hexane/AcOEt 10:1) 0.35. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3H), 3.81 (s, 3H), 3.95 (s, 3H), 6.65 (s, 1H), 6.86 (s, 1H), 7.22–7.41 (m, 11H), 7.48–7.53 (m, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 56.2 (CH_3), 56.6 (CH_3), 57.0 (CH_3), 98.8 (CH), 108.0 (C), 111.8 (C), 114.7 (CH), 116.6 (C), 127.0 (2 × CH), 127.1 (CH), 127.4 (2 × CH), 128.46 (4 × CH), 128.51 (2 × CH), 128.7 (4 × CH), 136.57 (2 × C), 136.59 (C), 143.3 (C), 149.4 (C), 152.1 (C), 208.5 (C) ppm. LRMS (EI) *m/z* (%): 434 (M^+, 100); HRMS (EI) calcd for $C_{30}H_{26}O_3^+$ 434.1876 found 434.1879.

*3-Isopropyl-1-(2,3,5-trimethoxyphenyl)-1,3-diphenylpropa-1,2-diene (**4i**)*. 300 mg (75% yield). Colourless oil; R_f (Hexane/AcOEt 15:1) 0.24. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (d, *J* = 6.7 Hz, 1H), 1.32 (d, *J* = 6.7 Hz, 1H), 3.01 (hept, *J* = 6.7 Hz, 1H), 3.68 (s, 1H), 3.81 (s, 1H), 3.93 (s, 1H), 6.61 (s, 1H), 6.86 (s, 1H), 7.37–7.14 (m, 8H), 7.58–7.49 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 22.5 (CH_3), 22.7 (CH_3), 29.0 (CH), 56.2 (CH_3), 56.6 (CH_3), 56.9 (CH_3), 98.5 (CH), 109.4 (C), 114.8 (CH), 115.5 (C), 117.4 (C), 126.5 (2 × CH), 126.7 (CH), 126.8 (3 × CH), 128.4 (2 × CH), 128.5 (2 × CH), 136.3 (C), 137.2 (C), 143.1 (C), 149.2 (C), 151.9 (C), 205.5 (C) ppm. LRMS (EI) *m/z* (%): 400 (M^+, 100); HRMS (EI) calcd for $C_{27}H_{28}O_3^+$ 400.2033 found 400.2036.

*1-(2,3,4-Trimethoxyphenyl)-1,3,3-triphenylpropa-1,2-diene (**5b**)*. The product could not be completely isolated from 1,2,3-trimethoxybenzene. The yield and the following spectroscopic data were estimated from the mixture. 230 mg (53% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H), 3.91 (s, 3H), 3.93 (s, 3H), 6.74 (d, *J* = 8.6 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 7.18–7.41 (m, 11H), 7.43–7.52 (m, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 56.1 (CH_3), 61.0 (CH_3), 61.1 (CH_3), 107.3 (CH), 108.2 (C), 111.9 (C), 123.0 (C), 125.5 (CH), 127.0 (2 × CH), 127.2 (CH), 127.5 (2 × CH), 128.5 (6 × CH), 128.6 (4 × CH), 136.6 (2 × C), 136.9 (C), 142.7 (C), 152.2 (C), 153.6 (C), 208.2 (C) ppm. LRMS (EI) *m/z* (%): 434 (M^+, 100).

*1-(2,4-Dimethoxyphenyl)-1-phenyl-3,3-di-p-tolylpropa-1,2-diene (**6a**)*. The product was isolated together with the regioisomeric allene **6a'**. The yield and the following spectroscopic data were estimated from the mixture. 324 mg (75% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 6H), 3.69 (s, 3H), 3.87 (s, 3H), 6.54–6.59 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 4H), 7.22–7.40 (m, 10H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.3 (2 × CH_3), 55.5 (CH_3), 55.7 (CH_3), 99.3 (CH), 104.6 (CH), 107.8 (C), 111.3 (C), 118.1 (C), 126.8 (CH), 126.9 (2 × CH), 128.4 (2 × CH), 128.6 (4 × CH), 129.2 (4 × CH), 131.8 (C), 133.8 (2 × C), 137.0 (2 × C + CH), 158.7 (C), 160.7 (C), 208.3 (C) ppm. LRMS (EI) *m/z* (%): 432 (M^+, 100), 293 (12).

*3-Allyl-1,1-di-p-tolyl-3-phenylpropa-1,2-diene (**7a**)*. 269 mg (80% yield). Yellow oil; R_f (Hexane/AcOEt 30:1) 0.22. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 6H), 3.42–3.48 (m, 2H), 5.14–5.19 (m, 1H), 5.25–5.32 (m, 1H), 6.02–6.15 (m, 1H), 7.18–7.29 (m, 5H), 7.33–7.43 (m, 6H), 7.53–7.58 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.3 (2 × CH_3), 35.2 (CH_2), 107.2 (C), 113.0 (C), 116.7 (CH_2), 126.2 (2 × CH), 127.1(CH), 128.0 (4 × CH), 128.6 (2 × CH), 129.2 (4 × CH), 134.0 (2 × C), 135.7 (CH), 136.1 (C), 137.2 (2 × C), 207.3 (C) ppm. LRMS (EI) *m/z* (%): 336 (M^+, 100), 295 (87), 195 (77); HRMS (EI) calcd for $C_{26}H_{24}^+$ 336.1873 found 336.1878.

*3-Allyl-1,1,3-triphenylpropa-1,2-diene (**7b**)*. 1 mmol scale rection: 237 mg (77% yield); 4 mmol scale reaction: 1.05 g (85% yield). White solid; mp: 71–73 °C; R_f (Hexane/AcOEt 6:1) 0.59. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.44 (dt, *J* = 6.5, 1.4 Hz, 2H), 5.15 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.27 (dq, *J* = 17.0, 1.6 Hz, 1H), 6.06 (ddt, *J* = 16.6, 10.1, 6.5 Hz, 1H), 7.21–7.40 (m, 9H), 7.49–7.58 (m, 4H), 7.62–7.67 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 35.1 (CH_2), 107.5 (C), 113.3 (C), 116.9 (CH_2), 126.2 (2 × CH), 127.3 (CH), 127.5 (2 × CH), 128.48 (4 × CH), 128.54 (4 × CH), 128.7 (4 × CH), 135.5 (CH), 135.8 (C), 136.9 (2 × C), 207.6 (C) ppm. LRMS (EI) *m/z* (%): 308 (M^+, 24), 267 (100); HRMS (EI) calcd for $C_{24}H_{20}^+$ 308.1560 found 308.1569.

*3-Allyl-1,1-di-p-chlorophenyl-3-phenylpropa-1,2-diene (**7c**)*. 290 mg (77% yield). Yellow solid; mp: 104–106 °C; R_f (Hexane/AcOEt 30:1) 0.64. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.48 (d, *J* = 6.5 Hz, 2H), 5.21 (dd, *J* = 10.1, 1.7 Hz, 1H), 5.31 (dd, *J* = 16.8, 1.6 Hz, 1H), 6.07 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 1H), 7.21–7.42 (m, 11H), 7.55 (d, *J* = 7.5 Hz, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 35.0 (CH_2), 108.4 (C), 111.6 (C), 117.2 (CH_2), 126.1 (2 × CH), 127.6 (CH), 128.8 (6 × CH), 129.6 (4 × CH), 133.5 (CH), 135.0 (2 × C), 135.13 (C), 135.15 (C), 135.2 (C), 207.5 (C) ppm. LRMS (EI) *m/z* (%): 376 (M^+, 74), 335 (100), 299 (43); HRMS (EI) calcd for $C_{24}H_{18}Cl_2^+$ 376.0780 found 376.0787.

*3-Allyl-1,1-di-p-chlorophenyl-3-p-tolylpropa-1,2-diene (**7d**)*. 254 mg (65% yield). Yellow oil; R_f (Hexane/AcOEt 30:1) 0.60. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 3.40 (dt, *J* = 6.5, 1.4 Hz, 2H), 5.13 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.24 (dq, *J* = 17.1, 1.6 Hz, 1H), 6.00 (ddt, *J* = 16.7, 10.1, 6.5 Hz, 1H), 7.13–7.21 (m, 2H), 7.23–7.44 (m, 11H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.3 (CH_3), 35.0 (CH_2), 108.3 (C), 111.5 (C), 117.1 (CH_2), 126.1 (2 × CH), 128.8 (4 × CH), 129.5 (2 × CH), 129.6 (4 × CH), 132.2 (C), 133.4 (CH), 135.1 (2 × C), 135.3 (2 × C), 137.5 (C), 207.4 (C) ppm. LRMS (EI) *m/z* (%): 390 (M^+, 100); HRMS (EI) calcd for $C_{25}H_{20}Cl_2^+$ 390.0937 found 390.0946.

*3-Allyl-1,1-di-p-methoxyphenyl-3-phenylpropa-1,2-diene (**7e**)*. 55 mg (15% yield). Brown oil; R_f (Hexane/AcOEt 6:1) 0.29. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.39 (dq, *J* = 6.5, 1.5 Hz, 2H), 3.81 (s, 6H), 5.11 (dt, *J* = 10.1, 1.5 Hz, 1H), 5.22 (dt, *J* = 17.0, 1.6 Hz, 1H), 5.93–6.11 (m, 1H), 6.87 (d, *J* = 8.4 Hz, 4H), 7.15–7.38 (m, 7H), 7.42–7.58 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 35.2 (CH_2), 55.4 (2 × CH_3), 107.0 (C), 112.4 (C), 113.4 (4 × CH), 116.7 (CH_2), 126.1 (2 × CH), 127.1 (CH), 128.6 (2 × CH), 129.3 (2 × C), 129.6 (4 × CH), 135.8 (CH), 136.2 (C), 159.1 (2 × C), 207.0 (C) ppm. LRMS (EI) *m/z* (%): 368 (M^+, 100), 327 (72); HRMS (EI) calcd for $C_{26}H_{24}O_2^+$ 368.1171 found 368.1175.

*3-Allyl-3-cyclohexenyl-1,1-diphenylpropa-1,2-diene (**7g**)*. 190 mg (61% yield). Yellow oil; R_f (Hexane/AcOEt 20:1) 0.61. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.57–1.76 (m, 4H), 2.13–2.30 (m, 4H), 3.17 (dt, *J* = 6.7, 1.5 Hz, 2H), 5.03–5.14 (m, 1H), 5.18 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.83–5.92 (m, 1H), 5.98 (ddt, *J* = 16.7, 10.1, 6.7 Hz, 1H), 7.22–7.47 (m, 10H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 22.5 (CH_2), 23.0 (CH_2), 26.2 (CH_2), 27.4 (CH_2), 34.3 (CH_2), 109.8 (C), 112.2 (C), 116.1 (CH_2), 123.7 (CH), 127.1 (2 × CH), 128.38 (4 × CH), 128.42 (4 × CH), 132.6 (C), 136.3 (CH), 137.6 (2 × C), 206.8 (C) ppm. LRMS (EI) *m/z* (%): 368 (M^+, 100), 327 (72); HRMS (EI) calcd for $C_{24}H_{20}^+$ 312.1873 found 312.1881.

*3-Allyl-1,1-dipheny-3-(2-thienyl)lpropa-1,2-diene (**7n**)*. 248 mg (79% yield). Orange oil; R_f (Hexane/AcOEt 15:1) 0.46. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.39–3.42 (m, 2H), 5.01–5.17 (m, 1H), 5.20–5.30 (m, 1H), 5.95–6.14 (m, 1H), 6.96–7.04 (m, 2H), 7.10–7.44 (m, 8H), 7.45–7.60 (m, 3H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 35.3 (CH_2), 108.2 (C), 117.1 (C), 125.1 (CH_2), 126.0 (CH), 126.4 (2 × CH), 127.46 (CH), 127.51 (CH), 127.9 (CH), 128.3 (2 × CH), 128.6 (2 × CH), 128.7 (2 × CH), 128.8 (CH), 131.7 (CH), 135.2 (C), 135.6 (C), 136.5 (C), 207.3 (C) ppm. LRMS (EI) *m/z* (%): 314 (M^+, 100), 173 (54); HRMS (EI) calcd for $C_{22}H_{18}S^+$ 314.1124 found 314.1129.

*4.3 General procedure for the synthesis of 2H-Chromenes **10-12,14** from propargylic alcohols **1** and methoxyphenols*

PTSA (5 mol %, 9 mg) was added to a mixture of the corresponding alkynol **1** (1 mmol) and the appropriate dimethoxyphenol (1.5 mmol, 231 mg) or 3-methoxyphenol (1.5 mmol, 186 mg) in MeCN (2 mL). The reaction mixture was stirred at room temperature until the reactants had been consumed, as determined by GC–MS and/or TLC. The crude mixture was neutralized by the addition of NaOH 0.5 M (5 mL),

and EtOAc (15 mL) was added. The separated aqueous phase was extracted with EtOAc (3 x 15 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: mixtures of hexane/AcOEt) to afford the corresponding 2*H*-chromenes **10-12,14** in the yields reported in Table 4 and Scheme 2.

6,7-Dimethoxy-4-phenyl-2,2-di-p-tolyl-2H-chromene ***(10a)***. 399 mg (89% yield). White solid; mp: 61–63 °C; R_f (Hexane/AcOEt 5:1) 0.21. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 6H), 3.67 (s, 3H), 3.88 (s, 3H), 6.05 (s, 1H), 6.59 (s, 1H), 6.66 (s, 1H), 7.15–7.17 (m, 4H), 7.41–7.50 (m, 9H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.2 (2 × CH_3), 56.1 (CH_3), 56.5 (CH_3), 82.4 (C), 101.5 (CH), 109.4 (CH), 114.3 (C), 125.5 (CH), 127.1 (4 × CH), 128.0 (CH), 128.5 (2 × CH), 128.8 (2 × CH), 128.9 (4 × CH), 135.8 (C), 137.2 (2 × C), 138.5 (C), 142.3 (2 × C), 143.1 (C), 147.8 (C), 150.2 (C) ppm. LRMS (EI) *m/z* (%): 448 (M^+, 22), 357 (100); HRMS (EI) calcd for $C_{31}H_{28}O_3^+$ 448.2033 found 448.2036.

6,7-Dimethoxy-2,2,4-triphenyl-2H-chromene ***(10b)***. 1 mmol scale rection: 361 mg (86% yield); 4 mmol scale reaction: 1.26 g (76% yield). White solid; mp: 142–144 °C; R_f (Hexane/AcOEt 5:1) 0.19. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3H), 3.87 (s, 3H), 6.03 (s, 1H), 6.56 (s, 1H), 6.63 (s, 1H), 7.25–7.52 (m, 15H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 56.1 (CH_3), 56.5 (CH_3), 82.5 (C), 101.5 (CH), 109.4 (CH), 114.3 (C), 125.2 (CH), 127.1 (4 × CH), 127.6 (2 × CH), 128.1 (CH), 128.2 (4 × CH), 128.5 (2 × CH), 128.8 (2 × CH), 136.1 (C), 138.4 (C), 143.2 (C), 145.1 (2 × C), 147.7 (C), 150.3 (C) ppm. LRMS (EI) *m/z* (%): 420 (M^+, 24), 343 (100); HRMS (EI) calcd for $C_{29}H_{24}O_3^+$ 420.1720 found 420.1729.

2,2-Di-p-Chlorophenyl-6,7-dimethoxy-4-phenyl-2H-chromene ***(10c)***. 371 mg (76% yield). White solid; mp: 168–170 °C; R_f (Hexane/AcOEt 5:1) 0.22. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 3H), 3.88 (s, 3H), 5.92 (s, 1H), 6.59 (s, 1H), 6.62 (s, 1H), 7.29–7.32 (m, 4H), 7.41–7.48 (m, 9H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 56.1 (CH_3), 56.5 (CH_3), 81.6 (C), 101.4 (CH), 109.4 (CH), 114.2 (C), 123.9 (CH), 128.3 (CH), 128.46 (4 × CH), 128.50 (4 × CH), 128.6 (2 × CH), 128.7 (2 × CH), 133.7 (2 × C), 136.9 (C), 138.0 (C), 143.2 (2 × C), 143.5 (C), 147.3 (C), 150.5 (C) ppm. LRMS (EI) *m/z* (%): 488 (M^+, 22), 377 (100); HRMS (EI) calcd for $C_{29}H_{22}Cl_2O_3^+$ 488.0941 found 488.0945.

6,7-dimethoxy-2,2-di-p-methoxyphenyl-4-phenyl-2H-chromene ***(10e)***. 422 mg (88% yield). Yellow solid; mp: 65–67 °C; R_f (Hexane/AcOEt 3:1) 0.27. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.65 (s, 3H), 3.79 (s, 6H), 3.86 (s, 3H), 5.98 (s, 1H), 6.57 (s, 1H), 6.61 (s, 1H), 6.86 (d, *J* = 8.9 Hz, 4H), 7.39–7.51 (m, 9H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.3 (2 × CH_3), 56.1 (CH_3), 56.6 (CH_3), 82.2 (C), 101.5 (CH), 109.4 (CH), 113.5 (4 × CH), 114.3 (C), 125.6 (CH), 128.1 (CH), 128.48 (4 × CH), 128.53 (2 × CH), 128.8 (2 × CH), 135.7 (C), 137.4 (2 × C), 138.5 (C), 143.1 (C), 147.8 (C), 150.3 (C), 158.9 (2 × C) ppm. LRMS (EI) *m/z* (%): 480 (M^+, 39), 373 (100); HRMS (EI) calcd for $C_{31}H_{28}O_5^+$ 480.1931 found 480.1939.

2-Cyclopropyl-6,7-dimethoxy-2,4-diphenyl-2H-chromene ***(10h)***. 330 mg (86% yield). White solid; mp: 158–160 °C; R_f (Hexane/AcOEt 5:1) 0.25. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50–0.69 (m, 4H), 1.45–1.54 (m, 1H), 3.65 (s, 3H), 3.90 (s, 3H), 5.74 (s, 1H), 6.52 (s, 1H), 6.64 (s, 1H), 7.23–7.28 (m, 1H), 7.32–7.44 (m, 7H), 7.61–7.65 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 1.4 (CH_2), 1.6 (CH_2), 21.7 (CH), 56.1 (CH_3), 56.6 (CH_3), 80.6 (C), 101.3 (CH), 109.5 (CH), 114.2 (C), 122.9 (CH), 126.2 (2 × CH), 127.4 (CH), 128.0 (3 × CH), 128.5 (2 × CH), 128.8 (2 × CH), 136.4 (C), 138.6 (C), 142.9 (C), 144.9 (C), 148.3 (C) 150.1 (C) ppm. LRMS (EI) *m/z* (%): 384 (M^+, 48), 343 (100); HRMS (EI) calcd for $C_{26}H_{24}O_3^+$ 384.1720 found 384.1721.

2-Isopropyl-6,7-dimethoxy-2,4-diphenyl-2H-chromene ***(10i)***. 313 mg (81% yield). White solid; mp: 161–163 °C; R_f (Hexane/AcOEt 5:1) 0.30. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 2.28 (hept, *J* = 6.8 Hz, 1H), 3.62 (s, 3H), 3.91 (s, 3H), 5.95 (s, 1H), 6.49 (s, 1H), 6.64 (s, 1H), 7.19–7.34 (m, 3H), 7.38–7.51 (m, 7H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 17.5 (CH_3), 17.7 (CH_3), 39.0 (CH), 56.1 (CH_3), 56.6 (CH_3), 83.6 (C), 101.2 (CH), 109.6 (CH), 114.5 (C), 123.1 (CH), 126.1 (2 × CH), 127.0 (CH), 127.8 (2 × CH), 127.9 (CH), 128.5 (2 × CH), 128.8 (2 × CH), 136.5 (C), 138.9 (C), 142.8 (C), 144.9 (C), 148.6 (C), 150.1 (C) ppm. LRMS (EI) *m/z* (%): 386 (M^+, 1), 343 (100); HRMS (EI) calcd for $C_{26}H_{26}O_3^+$ 386.1876 found 386.1889.

6,7-Dimethoxy-2,4-diphenyl-2-propyl-2H-chromene ***(10j)***. 347 mg (90% yield). White solid; mp: 84–87 °C; R_f (Hexane/AcOEt 5:1) 0.27. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.1 Hz, 3H), 1.40–1.56 (m, 2H), 1.98–2.12 (m, 2H), 3.65 (s, 3H), 3.91 (s, 3H), 5.91 (s, 1H), 6.53 (s, 1H), 6.66 (s, 1H), 7.20–7.27 (m, 1H), 7.29–7.48 (m, 7H), 7.52–7.58 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.4 (CH_3), 17.7 (CH_2), 45.3 (CH_2), 56.1 (CH_3), 56.6 (CH_3), 81.1 (C), 101.3 (CH), 109.6 (CH), 114.4 (C), 124.8 (CH), 125.5 (2 × CH), 127.1 (CH), 127.9 (CH), 128.1 (2 × CH), 128.5 (2 × CH), 128.8 (2 × CH), 136.0 (C), 138.7 (C), 143.0 (C), 145.6 (2 × C), 148.4 (C), 150.1 (C) ppm. LRMS (EI) *m/z* (%): 386 (M^+, 32), 343 (100); HRMS (EI) calcd for $C_{26}H_{26}O_3^+$ 386.1876 found 386.1881.

2-p-Chlorophenyl-6,7-Dimethoxy-2-methyl-4-phenyl-2H-chromene ***(9k)***. 252 mg (62% yield). Yellow oil; R_f (Hexane/AcOEt 5:1) 0.32. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (t, *J* = 7.4 Hz, 3H), 2.08 (q, *J* = 7.4 Hz, 2H), 3.66 (s, 3H), 3.91 (s, 3H), 5.87 (s, 1H), 6.55 (s, 1H), 6.66 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.36–7.46 (m, 5H), 7.49 (d, *J* = 8.4 Hz, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.4 (CH_3), 17.7 (CH_2), 45.3 (CH_2), 56.1 (CH_3), 56.6 (CH_3), 81.1 (C), 101.3 (CH), 109.6 (CH), 114.4 (C), 124.8 (CH), 125.5 (2 × CH), 127.1 (CH), 127.9 (CH), 128.1 (2 × CH), 128.5 (2 × CH), 128.8 (2 × CH), 136.0 (C), 138.7 (C), 143.0 (C), 145.6 (2 × C), 148.4 (C), 150.1 (C) ppm. LRMS (EI) *m/z* (%): 406 (M^+, 3), 377 (100); HRMS (EI) calcd for $C_{25}H_{23}ClO_3^+$ 406.1330 found 406.1336.

2,2-Di-isopropyl-6,7-Dimethoxy-4-phenyl-2H-chromene ***(10m)***. 253 mg (72% yield). Yellow oil; R_f (Hexane/AcOEt 5:1) 0.37. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.8 Hz, 6H), 1.06 (d, *J* = 6.8 Hz, 6H), 2.04 (hept, *J* = 6.8 Hz, 2H), 3.65 (s, 3H), 3.86 (s, 3H), 5.20 (s, 1H), 6.42 (s, 1H), 6.48 (s, 1H), 7.29–7.45 (m, 5H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 16.7 (2 × CH_3), 17.4 (2 × CH_3), 35.8 (2 × CH), 56.0 (CH_3), 56.8 (CH_3), 86.3 (C), 99.6 (CH), 109.6 (CH), 112.3 (C), 120.8 (CH), 127.6 (CH), 128.5 (2 × CH), 128.6 (2 × CH), 136.6 (C), 139.2 (C), 141.7 (C), 150.1 (C), 150.7 (C) ppm. LRMS (EI) *m/z* (%): 352 (M^+, 2), 309 (100); HRMS (EI) calcd for $C_{23}H_{28}O_3^+$ 352.2033 found 352.2038.

6,7-Dimethoxy-2,4-diphenyl-2-thienyl-2H-chromene ***(10o)***. 298 mg (70% yield). Red solid; mp: 58–60 °C; R_f (Hexane/AcOEt 5:1) 0.28. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 3H), 3.88 (s, 3H), 6.07 (s, 1H), 6.60 (s, 1H), 6.68 (s, 1H), 6.92–6.98 (m, 2H), 7.26–7.50 (m, 9H), 7.57–7.61 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 56.1 (CH_3), 56.5 (CH_3), 80.4 (C), 101.6 (CH), 109.4 (CH), 114.1 (C), 124.7 (CH), 126.2 (CH), 126.43 (CH), 126.44 (CH), 126.5 (2 × CH), 127.8 (CH), 128.2 (3 × CH), 128.6 (2 × CH), 128.8 (2 × CH), 136.3 (C), 138.1 (C),

143.4 (C), 144.7 (C), 147.5 (C), 149.6 (C), 150.4 (C) ppm. LRMS (EI) *m/z* (%): 426 (M^+, 58), 349 (100); HRMS (EI) calcd for $C_{27}H_{22}O_3S^+$ 426.1284 found 426.1301.

2-Cyclopropyl-6,7-Dimethoxy-4-phenyl-2-thienyl-2H-chromene ***(10p)***. 277 mg (58% yield). Brown oil; R_f (Hexane/AcOEt 5:1) 0.24. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.60–0.65 (m, 3H), 0.77–0.82 (m, 1H), 1.53–1.62 (m, 1H), 3.65 (s, 3H), 3.85 (s, 3H), 5.65 (s, 1H), 6.53 (s, 1H), 6.53 (s, 1H), 6.94 (dd, *J* = 5.0, 3.6 Hz, 1H), 7.14 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.24 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.38–7.47 (m, 5H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 1.9 (CH_2), 2.0 (CH_2), 22.1 (CH), 56.1 (CH_3), 56.6 (CH_3), 78.6 (C), 101.5 (CH), 109.5 (CH), 114.0 (C), 122.3 (CH), 124.8 (CH), 125.3 (CH), 126.4 (CH), 128.1 (CH), 128.6 (2 × CH), 128.8 (2 × CH), 136.8 (C), 138.4 (C), 143.2 (C), 147.9 (C), 149.1 (C), 150.3 (C) ppm. LRMS (EI) *m/z* (%): 390 (M^+, 82), 349 (100); HRMS (EI) calcd for $C_{24}H_{22}O_3S^+$ 390.1284 found 390.1286.

6,7-Dimethoxy-2-methyl-2,4-diphenyl-2H-chromene ***(10q)***. 268 mg (75% yield). White solid; mp: 144–146 °C; R_f (Hexane/AcOEt 5:1) 0.30. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.84 (s, 3H), 3.66 (s, 3H), 3.90 (s, 3H), 5.88 (s, 1H), 6.56 (s, 1H), 6.64 (s, 1H), 7.23–7.25 (m, 1H), 7.33–7.45 (m, 7H), 7.59–7.62 (m, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 29.6 (CH_3), 56.1 (CH_3), 56.5 (CH_3), 78.5 (C), 101.4 (CH), 109.5 (CH), 114.3 (C), 125.4 (2 × CH), 125.6 (CH), 127.3 (CH), 128.0 (CH), 128.3 (2 × CH), 128.5 (2 × CH), 128.8 (2 × CH), 135.6 (C), 138.5 (C), 143.1 (C), 146.0 (C), 148.1 (C), 150.1 (C) ppm. LRMS (EI) *m/z* (%): 358 (M^+, 10), 343 (100); HRMS (EI) calcd for $C_{24}H_{22}O_3^+$ 358.1563 found 358.1560.

2-p-Chlorophenyl-2-Cyclopropyl-6,7-Dimethoxy-4-phenyl-2H-chromene ***(10r)***. 322 mg (77% yield). Colourless oil; R_f (Hexane/AcOEt 5:1) 0.30. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.54–0.63 (m, 3H), 0.86–0.91 (m, 1H), 1.41–1.50 (m, 1H), 3.65 (s, 3H), 3.90 (s, 3H), 5.71 (s, 1H), 6.53 (s, 1H), 6.63 (s, 1H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.41–7.43 (m, 5H), 7.57 (d, *J* = 8.7 Hz, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 1.4 (CH_2), 1.6 (CH_2), 21.6 (CH), 56.0 (CH_3), 56.5 (CH_3), 80.1 (C), 101.2 (CH), 109.5 (CH), 114.1 (C), 122.3 (CH), 127.6 (2 × CH), 128.05 (CH), 128.11 (2 × CH), 128.5 (2 × CH), 128.7 (2 × CH), 133.1 (C), 136.7 (C), 138.3 (C), 143.1 (C), 143.5 (C), 148.1 (C), 150.2 (C) ppm. LRMS (EI) *m/z* (%): 418 (M^+, 52), 377 (100); HRMS (EI) calcd for $C_{26}H_{23}ClO_3^+$ 418.1330 found 418.1334.

4-Cyclopropyl-6,7-Dimethoxy-2,2-diphenyl-2H-chromene ***(10u)***. 242 mg (63% yield). Colourless oil; R_f (Hexane/AcOEt 5:1) 0.21. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.65–0.70 (m, 2H), 0.88–0.94 (m, 2H), 1.70–1.80 (m, 1H), 3.86 (s, 3H), 3.88 (s, 3H), 5.78 (d, *J* = 1.4 Hz, 1H), 6.61 (s, 1H), 7.11 (s, 1H), 7.23–7.36 (m, 6H), 7.41–7.45 (m, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 5.3 (2 × CH_2), 12.1 (CH), 55.9 (CH_3), 56.7 (CH_3), 82.5 (C), 101.0 (CH), 107.8 (CH), 115.2 (C), 121.0 (CH), 127.0 (4 × CH), 127.3 (2 × CH), 128.0 (4 × CH), 134.6 (C), 143.3 (C), 145.4 (2 × C), 147.0 (C), 150.1 (C) ppm. LRMS (EI) *m/z* (%): 384 (M^+, 22), 307 (100); HRMS (EI) calcd for $C_{26}H_{24}O_3^+$ 384.1720 found 384.1725.

7,8-Dimethoxy-4-phenyl-2,2-di-p-tolyl-2H-chromene ***(11a)***. 345 mg (77% yield). Colourless oil; R_f (Hexane/AcOEt 5:1) 0.23. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 6H), 3.81 (s, 3H), 3.88 (s, 3H), 6.05 (s, 1H), 6.36 (d, *J* = 8.6 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 4H), 7.33–7.51 (m, 9H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.2 (2 × CH_3), 56.0 (CH_3), 61.4 (CH_3), 82.7 (C), 104.1 (CH), 117.7 (C), 120.6 (CH), 126.1 (CH), 127.1 (4 × CH), 128.0 (CH), 128.4 (2 × CH), 128.9 (4 × CH), 129.0 (2 × CH), 135.9 (C), 137.1 (2 × C), 138.0 (C), 138.6 (C), 142.2 (2 × C), 145.0 (C), 153.8 (C) ppm. LRMS (EI) *m/z* (%): 448 (M^+, 100); HRMS (EI) calcd for $C_{31}H_{28}O_3^+$ 448.2033 found 448.2037.

7,8-Dimethoxy-2,2,4-triphenyl-2H-chromene ***(11b)***. 340 mg (81% yield). Colourless oil; R_f (Hexane/AcOEt 5:1) 0.50. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3H), 3.89 (s, 3H), 6.08 (s, 1H), 6.37 (d, *J* = 8.6 Hz, 1H), 6.71 (d, *J* = 8.6 Hz, 1H), 7.21–7.36 (m, 6H), 7.37–7.50 (m, 5H), 7.52–7.62 (m, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 56.0 (CH_3), 61.4 (CH_3), 82.8 (C), 104.2 (CH), 117.6 (C), 120.7 (CH), 125.7 (CH), 127.1 (4 × CH), 127.6 (2 × CH), 128.1 (CH), 128.2 (4 × CH), 128.5 (2 × CH), 129.0 (2 × CH), 136.2 (C), 138.0 (C), 138.5 (C), 145.0 (2 × C), 146.9 (C), 153.9 (C) ppm. LRMS (EI) *m/z* (%): 420 (M^+, 100); HRMS (EI) calcd for $C_{29}H_{24}O_3^+$ 420.1720 found 420.1727.

7,8-Dimethoxy-2,2,4-triphenyl-2H-chromene ***(12b)***. 231 mg (55% yield). White solid; mp: 62–65 °C; R_f (Hexane/AcOEt 5:1) 0.47. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.40 (s, 3H), 3.82 (s, 3H), 6.00 (s, 1H), 6.04 (d, *J* = 2.4 Hz, 1H), 6.40 (d, *J* = 2.4 Hz, 1H), 7.25–7.48 (m, 10H), 7.54–7.60 (m, 5H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.2 (CH_3), 55.4 (CH_3), 82.6 (C), 93.4 (CH), 95.2 (CH), 106.1 (C), 126.4 (CH), 126.8 (CH), 127.2 (4 × CH), 127.4 (2 × CH), 128.47 (2 × CH), 127.50 (2 × CH), 128.1 (4 × CH), 135.5 (C), 141.2 (C), 144.7 (2 × C), 155.8 (C), 157.5 (C), 161.6 (C) ppm. LRMS (EI) *m/z* (%): 420 (M^+, 32), 343 (100); HRMS (EI) calcd for $C_{29}H_{24}O_3^+$ 420.1720 found 420.1729.

1-(4-Hydroxy-2,6-dimethoxyphenyl)-1,3,3-triphenylpropa-1,2-diene ***(13b)***. 168 mg (58% yield). White solid; mp: 155–157 °C; R_f (Hexane/AcOEt 10:1) 0.33. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.62 (s, 6H), 5.26 (bs, 1H), 6.15 (s, 2H), 7.15–7.39 (m, 11H), 7.48–7.57 (m, 4H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.8 (2 × CH_3), 92.6 (2 × CH), 103.6 (C), 105.6 (C), 111.5 (C), 126.2 (2 × CH), 126.8 (CH), 127.2 (2 × CH), 128.3 (4 × CH), 128.5 (2 × CH), 128.8 (4 × CH), 136.38 (C), 136.42 (2 × C), 157.3 (C), 159.4 (2 × C), 208.9 (C) ppm. LRMS (EI) *m/z* (%): 420 (M^+, 32), 343 (100); HRMS (EI) calcd for $C_{29}H_{24}O_3^+$ 420.1720 found 420.1724.

7-Methoxy-4-phenyl-2,2-di-p-tolyl-2H-chromene ***(14a)***. 338 mg (82% yield). Colourless oil; R_f (Hexane/AcOEt 10:1) 0.50. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 6H), 3.83 (s, 3H), 6.11 (s, 1H), 6.45 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.70 (d, *J* = 2.5 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 4H), 7.43–7.57 (m, 9H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.2 (2 × CH_3), 51.4 (CH_3), 82.7 (C), 102.8 (CH), 106.9 (CH), 115.8 (C), 125.2 (CH), 126.7 (CH), 127.1 (4 × CH), 128.0 (CH), 128.3 (2 × CH), 128.9 (6 × CH), 135.7 (C), 137.2 (2 × C), 138.6 (C), 142.4 (2 × C), 154.5 (C), 161.0 (C) ppm. LRMS (EI) *m/z* (%): 418 (M^+, 96), 327 (100); HRMS (EI) calcd for $C_{30}H_{26}O_2^+$ 418.1927 found 418.1932.

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Supplementary Material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.XXXXXX

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