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$Yb(OTf)_3$-catalyzed propargylation and allenylation of 1,3-dicarbonyl derivatives with propargylic alcohols: one-pot synthesis of multi-substituted furocoumarin

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Abstract—A highly efficient and mild Lewis acid-catalyzed coupling reaction of 1,3-dicarbonyl compounds with propargylic alcohols has been established. Selective propargylation or allenylation products are obtained depending on the nature of propargylic alcohols. In addition, catalytic quantities of $Yb(OTf)_3$ can also effectively promote the propargylation and allylation of 4-hydroxycoumarins at the 3-position. By applying this reaction as the key step, a multi-substituted furocoumarin can easily be synthesized in a one-pot procedure. The advantages of this method are broad scope, mild conditions, and easy handling since water is the only side product.

1. Introduction

Propargyl- and allenyl-substituted carbonyl compounds are important building blocks in organic synthesis due to various transformations of the alkyne/allene and carbonyl into different functional groups. Among the numerous works devoted to these compounds, those on new synthetic methods are very topical. The major goal is to prepare complex compounds with required structures and/or to meet several desirable features including the cheap and readily available starting materials, atom-economy, mild reaction conditions, simple manipulation, and environmentally friendly catalysts. On the other hand, the alkylation of 1,3-dicarbonyl compounds is an important strategy for the formation of C–C bonds in organic synthesis. Recently, considerable interest has been focused on alkylation of 1,3-dicarbonyl compounds using alcohols as electrophiles,[1–3] since it offers several potential advantages, such as the wide availability of the starting materials and the generation of H_2O as the only side product. Such strategy has been elegantly applied to synthesis of allyl and benzyl-substituted 1,3-dicarbonyl compounds. However, to our surprise, analogous propargylation reaction remains little explored.

Very recently, Cadierno et al.[4] and Sanz et al.[5] found that Brønsted acids were effective as catalysts for the direct substitution of the hydroxyl group in propargylic alcohols with 1,3-dicarbonyl compounds. Nevertheless, alkyl-substituted propargylic alcohols are ineffective substrates therein; further, these reactions are generally performed under the refluxing reaction conditions. Although some catalytic methodologies for the direct hydroxyl substitution of propargylic alcohols in the presence of Lewis acid or other catalysts have been reported recently, the use of 1,3-dicarbonyl compounds as nucleophiles has not been well established in any of these works.[6–8] Given that $Yb(OTf)_3$ was an efficient catalyst for alkylation and allylation of 1,3-dicarbonyl compounds using alcohols as electrophiles directly, we are interested in further revealing the possibility of direct propargylation of 1,3-dicarbonyl compounds with alcohols catalyzed by $Yb(OTf)_3$ and examining the versatility of the propargyl-substituted 1,3-dicarbonyl compounds.[9] Herein we report an efficient $Yb(OTf)_3$-catalyzed propargylation or allenylation of 1,3-dicarbonyl compounds and 4-hydroxycoumarins with propargylic alcohols, allowing the easy preparation of useful synthetic intermediates for various applications and representing the first example of Lewis acid-catalyzed propargylation and allenylation of 1,3-dicarbonyl derivatives with propargylic alcohols.

2. Results and discussion

Firstly, we investigated the $Yb(OTf)_3$-catalyzed direct substitution of the hydroxyl group of secondary propargylic

Keywords: Propargylic alcohols; 1,3-Dicarbonyl compounds; Coumarins; Lewis acid catalysis; Substitution.
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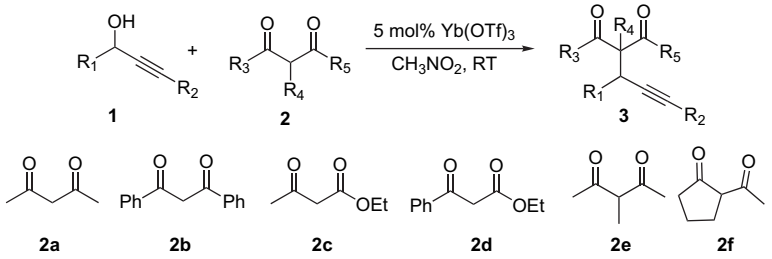
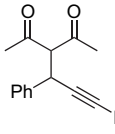
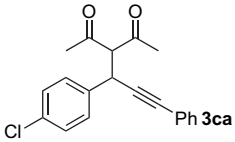
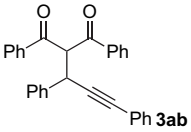
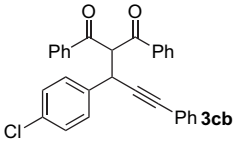
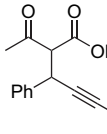
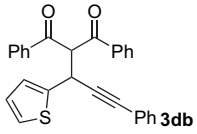
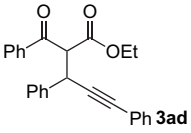
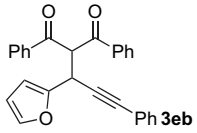
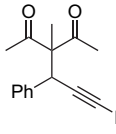
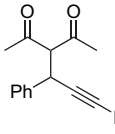
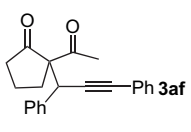
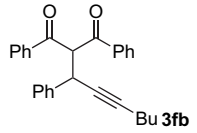
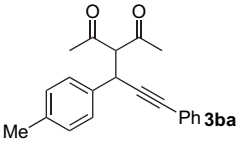
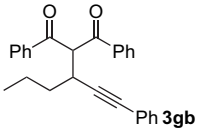
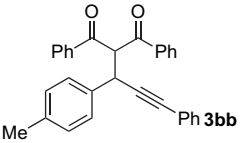
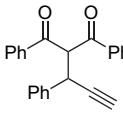
alcohols **1** with various 1,3-dicarbonyl compounds **2**. The results are summarized in Table 1. In the presence of 5 mol % $Yb(OTf)_3$ in nitromethane at room temperature, the reaction of 1,3-dicarbonyl compounds with propargylic alcohols **1a** smoothly proceeded to give the corresponding coupling products in high yields with complete regioselectivities in the propargylic position (Table 1, entries 1, 2, 5 and 6). The reaction of **1a** with low acidity keto-ester compounds

Table 1. $Yb(OTf)_3$-catalyzed propargylation of various 1,3-dicarbonyl compounds with propargylic alcohols[a]



Entry	1 R_1	R_2 2	Time (h)	Product	Yield[b] (%)	Entry	1 R_1	R_2 2	Time (h)	Product	Yield[b] (%)
1	**1a** Ph	Ph **2a**	0.5	 **3aa**	92	9	**1c** 4-Cl–C_6H_4	Ph **2a**	1	 **3ca**	85
2	**1a** Ph	Ph **2b**	0.5	 **3ab**	96	10	**1c** 4-Cl–C_6H_4	Ph **2b**	1	 **3cb**	92
3[c]	**1a** Ph	Ph **2c**	2	 **3ac**	84	11	**1d** 2-Thienyl	Ph **2b**	0.5	 **3db**	75
4[c]	**1a** Ph	Ph **2d**	1	 **3ad**	86	12	**1e** 2-Furyl	Ph **2b**	1	 **3eb**	51
5	**1a** Ph	Ph **2e**	0.5	 **3ae**	90	13	**1f** Ph	Bu **2a**	1	 **3fa**	90
6[c]	**1a** Ph	Ph **2f**	1	 **3af**	86	14	**1f** Ph	Bu **2b**	0.5	 **3fb**	92
7	**1b** 4-Me–C_6H_4	Ph **2a**	1	 **3ba**	87	15[d]	**1g** Pr	Ph **2b**	2	 **3gb**	55
8	**1b** 4-Me–C_6H_4	Ph **2b**	1	 **3bb**	90	16[d]	**1h** Ph	H **2b**	2	 **3hb**	82

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), $Yb(OTf)_3$ (0.025 mmol) in 2 mL CH_3NO_2 at room temperature.
[b] Isolated yields.
[c] Around 1:1 mixture of diastereoisomers.
[d] The reaction was carried out at 50 °C.

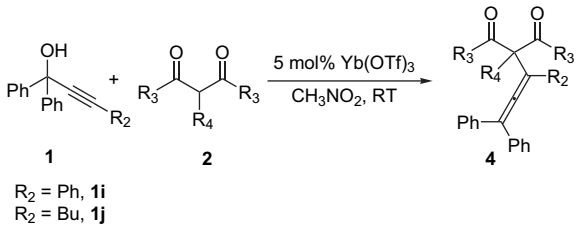
can also give quickly the desired product in high yields (Table 1, entries 3 and 4). However, treatment of **1a** with lower acidic diethyl malonate compounds under the same reaction conditions failed to get the desired product. To explore the scope of the $Yb(OTf)_3$-catalyzed propargylation of 1,3-dicarbonyl compounds, the reaction was also carried out with other propargylic alcohols. Various aryl-substituted propargylic alcohols smoothly reacted with 1,3-dicarbonyl compounds to give the propargylation products in high yields and complete regioselectivities (Table 1, entries 7–10), while heteroaromatic-substituted propargylic alcohols regioselectively afforded the desired products only in moderate yields (Table 1, entries 11 and 12). Variation of the alkyne substituents from aryl to alkyl did not affect the yields (Table 1, entries 1 vs 13 and 2 vs 14).

In contrast to the previous observation in the Brønsted acid catalytic system, where the secondary alkyl-substituted propargylic alcohols did not react with 1,3-dicarbonyl compounds,[5] the propyl-substituted propargylic alcohol afforded the desired product in moderate yield in the present Lewis acid catalytic system. However, the yield was lower than those of the corresponding aryl-substituted propargylic alcohols, possibly due to the absence of the additional delocalization of the aromatic ring leading to the low stability of the resulting propargylic cationic intermediate (Table 1, entry 15). The structure of **3gb** was confirmed by X-ray diffraction analysis, which was in good agreement with the proposed structure (Fig. 1). To the best of our knowledge, this represents the first example of the coupling of alkyl-substituted propargylic alcohols with 1,3-dicarbonyl compounds. In addition, the reaction of terminal propargylic alcohol **1h** with **2b** also gave the coupling product **3hb** in high yield and complete regioselectivity by increasing the reaction temperature (Table 1, entry 16).

Carbonyl-functionalized allenes are important building blocks in organic synthesis. There has been a growing effort in the past to develop new methods for synthesis of such highly valuable but challenging compounds under mild conditions from simple and readily available starting materials.[10] After having established that $Yb(OTf)_3$ is an efficient catalyst for the coupling of secondary propargylic alcohols with 1,3-dicarbonyl compounds, we were interested in studying the reactivity of tertiary propargylic alcohols toward 1,3-dicarbonyl compounds. Table 2 shows the typical results. Significantly, in these cases a regioselective allenylation instead of propargylation took place affording allene derivatives **4** in moderate to good yields. These results seem to indicate that all these reactions proceed through the formation of a cationic species, and the regioselectivity of nucleophilic trapping depends on the structure of propargylic alcohol (**1**). The large steric hindrance around the hydroxyl group (e.g., tertiary alkynols) favors nucleophiles attacking an allenyl-type cation, forming the allenylation products. Based on the X-ray crystallographic analysis of **4ie** as depicted in Figure 2, the isomerization of propargyl to allenyl was unambiguously confirmed.

Examples of allenylation of 1,3-dicarbonyl compounds are very rare. Notably, under the previously reported *p*-toluenesulfonic acid monohydrate catalysis, treatment of propargylic alcohol **1i** with **2b** gave the conjugated diene–dione in a good yield due to Meyer–Schuster rearrangement that is different to the present observation.[5]

Table 2. $Yb(OTf)_3$-catalyzed allenylation of 1,3-dicarbonyl compounds with tertiary propargylic alcohols[a]



1 **2** **4**

R_2 = Ph, **1i**
R_2 = Bu, **1j**

Entry	1	2	Time (h)	Product	Yield[b] (%)
1	**1i**	**2a**	0.5	**4ia**	53
2	**1i**	**2b**	0.5	**4ib**	75
3	**1i**	**2e**	0.5	**4ie**	80
4	**1j**	**2b**	1	**4jb**	86
5	**1j**	**2e**	1	**4je**	82

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), $Yb(OTf)_3$ (0.025 mmol) in 2 mL CH_3NO_2 at room temperature.
[b] Isolated yields.

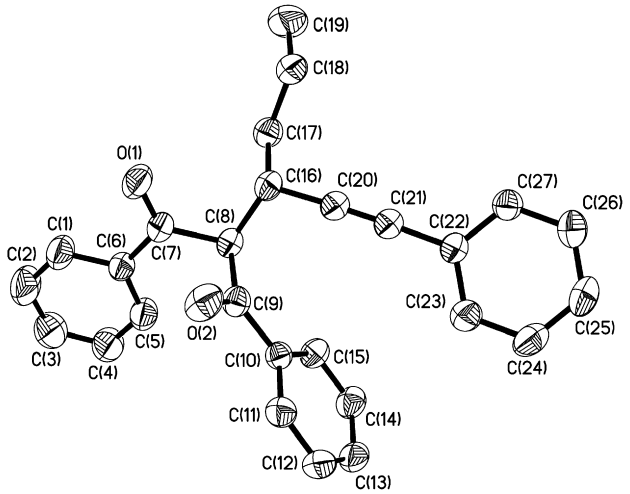


Figure 1. Molecular structure of compound **3gb**.

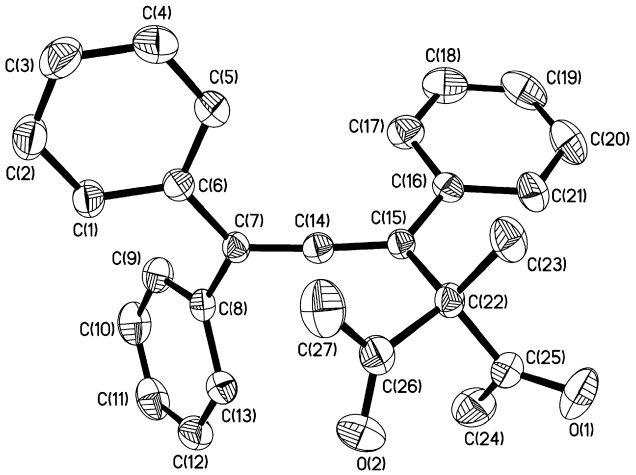
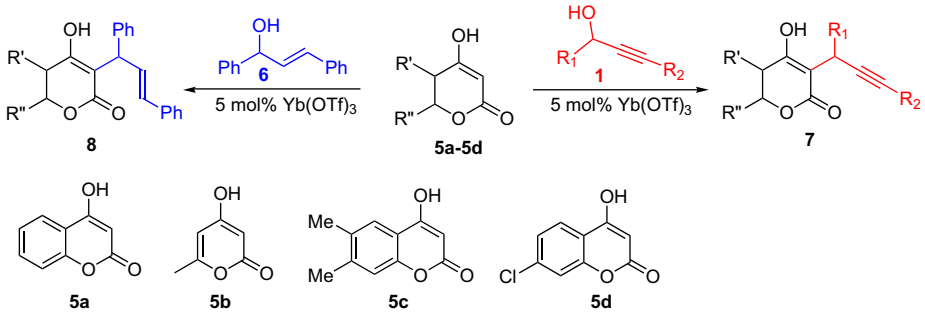


Figure 2. Molecular structure of compound **4ie**.

Table 3. Syntheses of coumarin analog by $Yb(OTf)_3$-catalyzed allylation/propargylation reaction[a]



Entry	5	1	Time (h)	Product	Isolated yield (%)	Entry	6	5	1	Time (h)	Product	Isolated yield (%)
1	**5a**	**1a**	2	**7aa**	85	6		**5b**	**1a**	1	**7ba**	85
2	**5a**	**1d**	2	**7ad**	62	7	**6**	**5a**		0.5	**8a**	95
3	**5a**	**1f**	2	**7af**	75	8	**6**	**5c**		1	**8c**	89
4	**5c**	**1a**	12	**7ca**	76	9	**6**	**5d**		1	**8d**	92
5	**5d**	**1a**	12	**7da**	71	10	**6**	**5b**		0.5	**8b**	90

[a] Reaction conditions: **5** (0.5 mmol), alcohols **1** or **6** (0.75 mmol), $Yb(OTf)_3$ (0.025 mmol) in a mixture of 1 mL CH_3NO_2 and 1 mL dioxane at 50 °C.

The development of new methods for the efficient and selective preparation of highly substituted coumarins is of great interest in organic chemistry because of the frequent existence of such structures in biologically active compounds and their role as valuable synthetic intermediates for potential new pharmaceuticals, especially anticoagulants.[11] Although there are several reports in the literatures about the allylation of coumarins, most of them need organic halides as substrates.[12] Encouraged by the above results, we subsequently explored the reaction of 4-hydroxycoumarins with propargylic and allylic alcohols. As shown in Table 3, 4-hydroxycoumarins reacted with alkynols **1a** and a catalytic amount of $Yb(OTf)_3$ to give propargyl-substituted coumarins **7aa** in good yields (Table 3, entry 1). The reaction is general for different propargylic alcohols and the selected coumarins (Table 3, entries 2–6). Similarly, reaction of 1,3-diphenyl allylic alcohol **6** with 4-hydroxycoumarin derivatives **5** in the presence of 5 mol % $Yb(OTf)_3$ allows the synthesis of allylated products **8** in good to excellent yields (Table 3, entries 7–10). Thus, a new method for the synthesis of 3-propargyl/allyl-substituted 4-hydroxycoumarins has been developed from simple alcohol starting materials, using only a catalytic amount of a Lewis acid with water being the only side product of the process.

Having successfully developed an efficient propargylation of 4-hydroxycoumarins with propargylic alcohols, we finally turned our attention to the application of this method to a one-pot synthesis of furocoumarin, which is a key structural unit in many natural compounds such as wedelolactone and medicagol.[13] Treatment of 4-hrdroxycoumarin with propargylic alcohol **1a** in the presence of 5 mol % $Yb(OTf)_3$ followed by addition of K_2CO_3 allowed the isolation of multi-substituted furocoumarin **9** in 37% yield. This method provides a mild and straightforward route to multi-substituted furocoumarin (Scheme 1). The structure of **9** has been determined by X-ray analysis (Fig. 3).

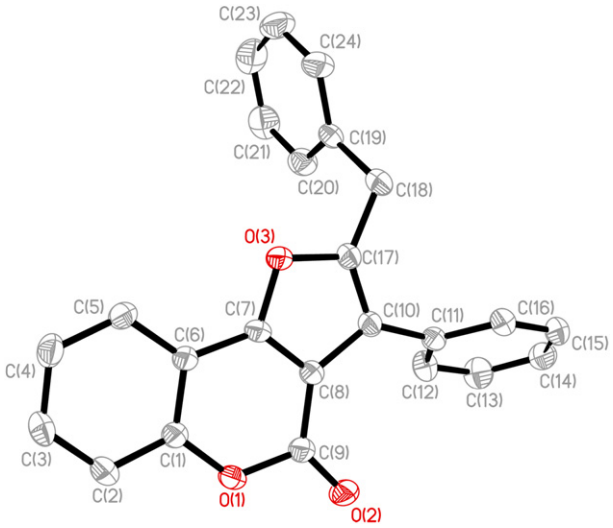
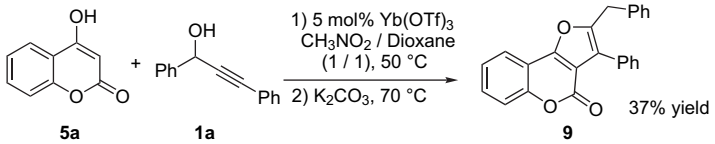


Figure 3. Molecular structure of compound **9**.

3. Conclusion

In summary, we have presented the first example of Lewis acid-catalyzed propargylation of 1,3-dicarbonyl compounds



Scheme 1.

with propargylic alcohols. Selective propargylation or allenylation products can be obtained depending on the structures of propargylic alcohols. In addition, $Yb(OTf)_3$ can also effectively promote the propargylation and allylation of 4-hydroxycoumarins at the 3-position. Moreover, we have developed a simple strategy for the synthesis of multi-substituted furocoumarins by using the Lewis acid-catalyzed nucleophilic substitution of propargylic alcohols as the key step. The advantages of this method are mild conditions, broad scope, and easy handling; further, some different selectivities from the Brønsted acid catalytic system are observed.

4. Experimental

4.1. General

All manipulations were performed in air. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer using the residue of deuterated solvents as the internal standard. Mass spectra were recorded on a Philips Agilent MS5973N instrument operating in EI mode. GC–MS analysis was performed using a Hewlett Packard Model HP 6890 Series with HP-5 column. High-resolution mass spectra were obtained with a JEOL JMS-700 (EI) or JEOL JMS-HX110A (FAB+) spectrometer. The reactions were monitored by TLC with Huanghai GF254 silica gel. Flash column chromatography was carried out using 300–400 mesh silica gel using ethyl acetate and hexane as eluents.

4.2. General experimental procedure for the $Yb(OTf)_3$-catalyzed propargylation and allenylation of 1,3-dicarbonyl compounds with propargylic alcohols

To a mixture of alcohols **1** (0.5 mmol) and 1.5 equiv of nucleophiles in 2 mL of nitromethane was added 5 mol % $Yb(OTf)_3$ (16 mg, 0.025 mmol). The reaction mixture was stirred at room temperature or the corresponding conditions mentioned in the text. After completion of the reaction monitored by GC–MS or TLC, solvent was removed under reduced pressure. The residue was purified by a short column chromatography using hexane/ethyl acetate as eluents.

4.3. General experimental procedure for the $Yb(OTf)_3$-catalyzed propargylation and allenylation of 4-hydroxycoumarin with propargylic alcohols

To a mixture of 1 mL nitromethane and 1 mL dioxane were added 4-hydroxycoumarin (0.5 mmol), alcohol **1** or **6** (0.75 mmol) and 5 mol % $Yb(OTf)_3$ (16 mg, 0.025 mmol) and the reaction mixture was stirred at 50 °C. After completion of the reaction monitored by GC–MS or TLC, solvent was removed under reduced pressure. The residue was purified by a short column chromatography using hexane/ethyl acetate as eluents.

4.4. Characterization data

4.4.1. 3-(1,3-Diphenyl-2-propynyl)pentane-2,4-dione (3aa). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.92 (s, 3H), 2.38 (s, 3H), 4.22 (d, J=11 Hz, 1H), 4.68 (d, J=11 Hz, 1H), 7.24–7.28 (m, 4H), 7.31–7.37 (m, 4H), 7.38–7.41 (m, 2H). EI-MS: m/z (relative intensity) 290 (M^+, 10%), 247 (100).

4.4.2. 2-(1,3-Diphenyl-2-propynyl)-1,3-diphenylpropane-1,3-dione (3ab). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 5.16 (d, J=10 Hz, 1H), 5.90 (d, J=10 Hz, 1H), 7.02 (d, J=7.1 Hz, 2H), 7.14–7.18 (m, 4H), 7.25–7.30 (m, 4H), 7.36–7.48 (m, 3H), 7.51–7.55 (m, 3H), 7.76 (d, J=7.6 Hz, 2H), 8.12 (d, J=7.6 Hz, 2H). EI-MS: m/z (relative intensity): 414 (M^+, 2%), 309 (5), 191 (100).

4.4.3. Ethyl 3-oxo-[2-(1,3-diphenyl-2-propynyl)]butanoate (3ac). Mixture of two diastereoisomers (ca. 1:1): ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.05 (t, J=6.8 Hz, 3H), 1.26 (t, J=6.8 Hz, 3H), 2.00 (s, 3H), 2.42 (s, 3H), 3.92–4.07 (m, 4H), 4.24 (m, 2H), 4.60–4.66 (m, 2H), 7.18–7.47 (m, 20H). EI-MS: m/z (relative intensity): 320 (M^+, 2%), 277 (70), 247 (95), 191 (100).

4.4.4. Ethyl 3-oxo-[2-(1,3-diphenyl-2-propynyl)]-3-phenylpropionate (3ad). Mixture of two diastereoisomers (ca. 1:1). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 0.96 (t, J=7.2 Hz, 3H), 1.22 (t, J=7.2 Hz, 3H), 3.92 (m, 2H), 4.19–4.25 (m, 2H), 4.86 (d, J=10.7 Hz, 1H), 4.91–4.98 (m, 3H), 7.10–7.52 (m, 26H), 7.88 (d, J=7.5 Hz, 2H), 8.12 (d, J=7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 192.64, 191.76, 167.26, 166.72, 138.65, 138.61, 136.25, 136.37, 133.57, 131.59, 131.44, 128.88, 128.69, 128.58, 128.54, 128.48, 128.45, 128.13, 128.01, 127.92, 127.87, 127.61, 127.35, 125.82, 122.86, 122.78, 88.95, 88.88, 84.25, 84.22, 61.87, 61.75, 61.52, 61.09, 38.34, 37.94, 14.02, 13.67. EI-MS: m/z (relative intensity): 382 (M^+, 2%), 309 (100), 277 (85).

4.4.5. 3-(1,3-Diphenyl-2-propynyl)-3-methylpentane-2,4-dione (3ae). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.46 (s, 3H), 1.92 (s, 3H), 2.39 (s, 3H), 5.22 (s, 1H), 7.27–7.30 (m, 6H), 7.37–7.43 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 205.99, 203.70, 136.53, 131.58, 129.68, 128.40, 128.22, 128.19, 127.57, 122.75, 88.09, 85.35, 72.11, 41.91, 27.95, 26.37, 14.80. EI-MS: m/z (relative intensity): 304 (M^+, 2%), 261 (100).

4.4.6. 2-Acetyl-2-(1,3-diphenyl-2-propynyl)cyclopentanone (3af). Mixture of two diastereoisomers (ca. 1:1). Diastereoisomer 1: ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.27–1.29 (m, 1H), 1.65–1.67 (m, 2H), 1.79–1.88 (m, 1H), 2.12–2.20 (m, 1H), 2.52 (s, 3H), 2.76–2.81 (m, 1H), 5.04 (s, 1H), 7.28–7.32 (m, 6H), 7.38–7.42 (m, 4H). EI-MS: m/z (relative intensity): 316 (M^+, 2%), 273 (100), 191 (80).

Diastereoisomer 2: ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.77–1.82 (m, 1H), 2.01–2.13 (m, 1H), 2.20 (s, 3H), 2.26–2.38 (m, 2H), 2.42–2.49 (m, 1H), 2.67–2.73 (m, 1H), 4.92 (s, 1H), 7.25–7.33 (m, 8H), 7.36–7.38 (m, 2H). EI-MS: m/z (relative intensity): 316 (M^+, 3%), 273 (100), 191 (80).

4.4.7. 3-[1-(4-Methylphenyl)-3-phenyl-2-propynyl]pentane-2,4-dione (3ba). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.93 (s, 3H), 2.31 (s, 3H), 2.37 (s, 3H), 4.20 (d, J=10.9 Hz, 1H), 4.64 (d, J=10.9 Hz, 1H), 7.12 (d, J=7.9 Hz, 2H), 7.24–7.29 (m, 5H), 7.34–7.36 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 201.68, 201.58,

137.42, 135.13, 131.60, 129.53, 128.20, 127.93, 126.59, 122.75, 88.29, 84.72, 75.67, 29.65, 29.33, 28.67, 21.02. EI-MS: *m*/*z* (relative intensity): 304 (M^+, 5%), 261 (100).

4.4.8. 2-[1-(4-Methylphenyl)-3-phenyl-2-propynyl]-1,3-diphenylpropane-1,3-dione (3bb). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.23 (s, 3H), 5.16 (d, J=10.0 Hz, 1H), 5.90 (d, J=10.0 Hz, 1H), 6.98 (d, J=6.9 Hz, 2H), 7.06 (d, J=6.9 Hz, 2H), 7.11–7.27 (m, 5H), 7.42–7.46 (m, 5H), 7.52–7.54 (m, 1H), 7.76 (d, J=7.3 Hz, 2H), 8.12 (d, J=7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 193.49, 192.49, 137.02, 136.98, 136.48, 136.26, 133.42, 133.28, 131.34, 129.25, 129.06, 128.80, 128.56, 128.45, 128.36, 127.88, 127.82, 122.93, 89.58, 84.95, 63.20, 38.29, 20.95. EI-MS: *m*/*z* (relative intensity): 324 (M^+−COPh, 30%), 219 (100).

4.4.9. 3-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl]pentane-2,4-dione (3ca). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.96 (s, 3H), 2.37 (s, 3H), 4.16 (d, J=10.9 Hz, 1H), 4.66 (d, J=10.9 Hz, 1H), 7.17–7.30 (m, 8H), 7.34–7.36 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 201.06, 200.89, 136.80, 133.60, 131.59, 129.52, 128.98, 128.45, 128.26, 122.39, 87.49, 85.20, 75.55, 37.17, 29.65, 28.60. EI-MS: *m*/*z* (relative intensity): 324 (M^+, 5%), 281 (100).

4.4.10. 2-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl]-1,3-diphenylpropane-1,3-dione (3cb). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 5.16 (d, J=10.0 Hz, 1H), 5.86 (d, J=10.0 Hz, 1H), 7.00 (d, J=7.6 Hz, 2H), 7.13–7.30 (m, 7H), 7.46–7.50 (m, 5H), 7.53–7.55 (m, 1H), 7.76 (d, J=7.9 Hz, 2H), 8.12 (d, J=7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 193.12, 192.29, 137.80, 136.82, 136.24, 133.57, 133.25, 131.35, 129.96, 129.04, 128.87, 128.69, 128.44, 128.06, 127.93, 122.58, 88.76, 85.43, 62.95, 38.05. EI-MS: *m*/*z* (relative intensity): 343 (M^+−COPh, 35%), 239 (50), 105 (100).

4.4.11. 1,3-Diphenyl-2-[3-phenyl-1-(2-thienyl)-2-propynyl]propane-1,3-dione (3db). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 5.52 (d, J=10.0 Hz, 1H), 5.94 (d, J=10.0 Hz, 1H), 6.84 (m, 1H), 7.01–7.06 (m, 2H), 7.08–7.12 (d, J=2.7 Hz, 1H), 7.15–7.23 (m, 4H), 7.32–7.35 (m, 2H), 7.42–7.51 (m, 3H), 7.57–7.61 (m, 1H), 7.84 (d, J=8.7 Hz, 2H), 8.12 (d, J=8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 193.05, 192.57, 142.27, 136.86, 136.45, 134.56, 132.98, 132.32, 130.74, 130.17, 129.62, 128.95, 128.20, 127.72, 127.38, 126.07, 124.16, 122.64, 88.69, 85.40, 62.79, 33.38. EI-MS: *m*/*z* (relative intensity) 315 (M^+−COPh, 100).

4.4.12. 1,3-Diphenyl-2-[3-phenyl-1-(2-furanyl)-2-propynyl]propane-1,3-dione (3eb). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 5.30 (d, J=10.0 Hz, 1H), 6.08 (d, J=10.0 Hz, 1H), 6.22 (m, 1H), 6.28 (d, J=2.7 Hz, 1H), 7.05–7.52 (m, 12H), 7.88 (d, J=7.3 Hz, 2H), 8.10 (d, J=7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 193.08, 192.47, 150.97, 142.27, 136.83, 136.14, 133.77, 133.69, 131.63, 129.16, 129.00, 128.88, 128.64, 128.32, 128.11, 122.71, 110.67, 108.10, 86.37, 84.74, 59.63, 32.65. EI-MS: *m*/*z* (relative intensity) 299 (M^+−COPh, 30%).

4.4.13. 3-(1-Phenyl-2-heptynyl)pentane-2,4-dione (3fa). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 0.88 (t, J=7.3 Hz, 3H), 1.35–1.38 (m, 2H), 1.43–1.46 (m, 2H), 1.87 (s, 3H), 2.16 (t, J=7.2 Hz, 2H), 2.33 (s, 3H), 4.06 (d, J=11.0 Hz, 1H), 4.40 (d, J=11.0 Hz, 1H), 7.23–7.32 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): 202.06, 202.03, 138.96, 128.81, 128.07, 127.59, 85.45, 78.72, 76.15, 37.82, 31.21, 30.85, 28.55, 21.95, 18.45, 13.63. EI-MS: *m*/*z* (relative intensity) 270 (M^+, 2%), 227 (100).

4.4.14. 1,3-Diphenyl-2-(1-phenyl-2-heptynyl)propane-1,3-dione (3fb). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 0.74 (t, J=3.5 Hz, 3H), 1.13–1.17 (m, 4H), 1.92–1.94 (m, 2H), 4.92 (dt, J=2.2, 10.1 Hz, 1H), 5.78 (d, J=12 Hz, 1H), 7.12–7.14 (m, 1H), 7.21–7.26 (m, 4H), 7.36–7.48 (m, 5H), 7.53–7.55 (m, 1H), 7.70 (d, J=7.3 Hz, 2H), 8.08 (d, J=7.3 Hz, 2H). EI-MS: *m*/*z* (relative intensity) 394 (M^+, 3%), 289 (100).

4.4.15. 1,3-Diphenyl-2-(1-propyl-3-phenyl-2-propynyl)-propane-1,3-dione (3gb). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 0.96 (t, J=6.8 Hz, 3H), 1.53–1.64 (m, 4H), 3.88–3.90 (m, 1H), 5.56 (d, J=9.6 Hz, 1H), 6.83–6.96 (m, 2H), 7.02–7.20 (m, 3H), 7.33–7.56 (m, 6H), 7.98 (d, J=7.8 Hz, 2H), 8.08 (d, J=7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 194.49, 193.50, 137.04, 136.67, 133.79, 133.53, 131.42, 129.19, 128.99, 128.91, 128.79, 128.06, 127.83, 123.25, 90.41, 84.58, 60.56, 35.89, 33.14, 20.79, 13.89. EI-MS: *m*/*z* (relative intensity) 380 (M^+, 10%). Anal. Calcd for $C_{27}H_{24}O_2$: C, 85.23; H, 6.36. Found: C, 84.81; H, 6.15.

4.4.16. 1,3-Diphenyl-2-(1-phenyl-2-propynyl)propane-1,3-dione (3hb). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.18 (d, J=1.8 Hz, 1H), 4.99 (dd, J=10.0, 2.3 Hz, 1H), 5.88 (d, J=10.0 Hz, 1H), 7.10–7.14 (m, 1H), 7.19–7.30 (m, 3H), 7.37–7.56 (m, 7H), 7.69 (d, J=7.8 Hz, 2H), 8.02 (d, J=7.8 Hz, 2H). EI-MS: *m*/*z* (relative intensity) 338 (M^+, 20%), 233 (100).

4.4.17. 3-(Triphenyl-1,2-propadienyl)pentane-2,4-dione (4ia). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.03 (s, 6H), 7.236–7.51 (m, 16H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 208.58, 192.14, 135.88, 135.54, 129.19, 128.74, 128.68, 127.95, 127.83, 126.16, 112.28, 108.01, 105.49, 31.71, 24.09. EI-MS: *m*/*z* (relative intensity) 366 (M^+, 5%).

4.4.18. 2-[(Triphenyl-1,2-propadienyl)]-1,3-diphenylpropane-1,3-dione (4ib). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 6.59 (s, 1H), 7.13–7.35 (m, 12H), 7.42 (d, J=7.3 Hz, 4H), 7.90 (d, J=7.3 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 210.19, 193.97, 135.73, 134.94, 133.41, 129.07, 128.76, 128.69, 128.51, 128.33, 127.76, 127.63, 126.68, 125.81, 115.92, 104.96, 58.43.

4.4.19. 3-Methyl-3-(triphenyl-1,2-propadienyl)pentane-2,4-dione (4ie). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.65 (s, 3H), 2.18 (s, 6H), 7.21–7.42 (m, 15H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 207.55, 207.28, 135.48, 134.17, 129.61, 129.18, 128.31, 128.05, 127.61, 127.28, 126.81, 114.15, 110.00, 68.78, 28.66, 27.40, 20.35. EI-MS: *m*/*z* (relative intensity) 380 (M^+, 2%), 337 (100).

Anal. Calcd for $C_{27}H_{24}O_2$: C, 85.23; H, 6.36. Found: C, 84.98; H, 6.24.

4.4.20. 3-Methyl-3-(3,3-diphenyl-1-butyl-1,2-propadienyl)pentane-2,4-dione (4je). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 0.84 (t, J=7.3 Hz, 3H), 1.28–1.32 (m, 2H), 1.51–1.56 (m, 5H), 2.00–2.10 (m, 8H), 7.23–7.36 (m, 10 H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 207.31, 203.39, 136.40, 128.60, 128.28, 127.59, 113.91, 108.37, 69.71, 29.99, 29.26, 27.55, 22.59, 18.96, 14.04. EI-MS: *m*/*z* (relative intensity) 360 (M^+, 2%), 318 (100).

4.4.21. 2-[(3,3-Diphenyl-1-butyl-1,2-propadienyl)]-1,3-diphenylpropane-1,3-dione (4jb). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 0.84 (t, J=7.6 Hz, 3H), 1.31–1.36 (m, 2H), 1.54–1.59 (m, 2H), 2.29 (t, J=7.8 Hz, 2H), 5.99 (s, 1H), 7.13–7.26 (m, 14H), 7.41 (t, J=7.3 Hz, 2H), 7.86 (d, J=7.3 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 206.19, 194.59, 136.13, 136.01, 133.43, 128.78, 128.71, 128.47, 128.33, 127.27, 113.15, 104.35, 61.35, 32.35, 30.03, 22.66, 14.13. EI-MS: *m*/*z* (relative intensity) 470 (M^+, 2%). Anal. Calcd for $C_{34}H_{30}O_2$: C, 86.77; H, 6.43. Found: C, 86.81; H, 6.41. HRMS (EI) calcd for $C_{34}H_{30}O_2$: 470.2246; found: 470.2241.

4.4.22. 3-[1,3-Diphenyl-2-propynyl]-4-hydroxy-1-benzopyran-2(*H*)-one (7aa). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 5.80 (s, 1H), 7.25–7.38 (m, 8H), 7.50–7.56 (m, 3H), 7.62 (dd, J=1.4, 7.8 Hz, 2H), 8.42 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 162.74, 161.26, 152.75, 138.64, 132.49, 131.95, 129.31, 129.13, 128.67, 127.86, 127.23, 124.19, 123.55, 121.49, 116.61, 116.05, 105.06, 87.95, 86.58, 33.49. EI-MS: *m*/*z* (relative intensity) 352 (M^+, 100%), 275 (30). Anal. Calcd for $C_{24}H_{16}O_3$: C 81.80; H 4.58. Found: C, 81.87; H, 4.59.

4.4.23. 3-[3-Phenyl-1-(2-thienyl)-2-propynyl]-4-hydroxy-1-benzopyran-2(*H*)-one (7ad). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 5.99 (s, 1H), 6.96 (t, J=4.5 Hz, 1H), 7.22–7.38 (m, 7H), 7.51–7.57 (m, 3H), 7.86 (dd, J=1.8, 8.2 Hz, 1H), 8.27 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 162.40, 161.35, 152.79, 141.84, 132.67, 131.97, 129.45, 128.67, 127.12, 125.55, 125.35, 124.26, 123.64, 121.25, 116.66, 115.95, 104.82, 87.32, 85.97, 29.28. EI-MS: *m*/*z* (relative intensity) 358 (M^+, 100%), 275 (30).

4.4.24. 3-[3-Butyl-1-phenyl-2-propynyl]-4-hydroxy-1-benzopyran-2(*H*)-one (7af). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 0.93 (t, J=7.3 Hz, 3H), 1.41–1.48 (m, 2H), 1.53–1.61 (m, 2H), 2.32–2.36 (m, 2H), 5.48 (t, J=2.3 Hz, 1H), 7.22–7.36 (m, 5H), 7.49–7.56 (m, 3H), 7.84 (dd, J=1.4, 8.2 Hz, 1H), 8.78 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 162.65, 161.22, 152.71, 139.38, 132.28, 128.91, 127.58, 127.15, 124.07, 123.46, 116.53, 116.15, 105.11, 89.30, 78.16, 33.10, 30.64, 22.13, 18.61, 13.65. EI-MS: *m*/*z* (relative intensity) 332 (M^+, 100%), 275 (35). Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06. Found: C, 79.24; H, 5.89.

4.4.25. 6,7-Dimethyl-3-[1,3-diphenyl-2-propynyl]-4-hydroxy-1-benzopyran-2(*H*)-one (7ca). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.28 (s, 3H), 2.32 (s, 3H), 5.79 (s, 1H), 7.06 (s, 1H), 7.25–7.37 (m, 6H), 7.50–7.53 (dd, J=2.5, 7.8 Hz, 2H), 7.58 (s, 1H), 7.62 (d, J=7.3 Hz, 2H), 8.37 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 163.16, 161.56, 151.22, 142.66, 138.88, 133.05, 131.93, 129.21, 129.06, 128.64, 127.74, 127.23, 123.39, 121.64, 117.07, 113.53, 104.09, 87.67, 86.89, 33.43, 20.41, 19.43. Anal. Calcd for $C_{26}H_{20}O_3$: C, 82.08; H, 5.30. Found: C, 81.59; H, 5.04. HRMS (EI) calcd for $C_{26}H_{20}O_3$: 380.1412; found: 380.1414.

4.4.26. 7-Chloro-3-[1,3-diphenyl-2-propynyl]-4-hydroxy-1-benzopyran-2(*H*)-one (7da). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 5.76 (s, 1H), 7.22–7.52 (m, 10H), 7.60 (d, J=7.8 Hz, 2H), 7.82 (d, J=2.3 Hz, 1H), 8.53 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 162.15, 160.08, 151.07, 138.35, 132.43, 131.93, 129.76, 129.41, 129.19, 128.69, 128.00, 127.24, 123.17, 121.31, 118.07, 117.21, 105.90, 88.18, 86.28, 33.63. Anal. Calcd for $C_{24}H_{15}ClO_3$: C, 74.52; H 3.91. Found: C, 74.89; H, 3.49. HRMS (EI) calcd for $C_{24}H_{15}ClO_3$: 386.0710; found: 386.0718.

4.4.27. 3-[1,3-Diphenyl-2-propynyl]-4-hydroxy-6-methyl-pyran-2-one (7ba). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.08 (s, 3H), 5.65 (s, 1H), 6.05 (s, 1H), 7.21–7.34 (m, 6H), 7.48 (dd, J=1.8, 7.8 Hz, 2H), 7.60 (d, J=7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 167.10, 165.62, 161.64, 139.31, 137.21, 131.88, 128.57, 128.43, 127.44, 127.16, 122.91, 102.75, 101.68, 87.77, 84.73, 32.20, 19.77. Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.93; H, 4.95.

4.4.28. 3-[1,3-Diphenyl-2-allyl]-4-hydroxy-1-benzopyran-2(*H*)-one (8a). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 5.50 (d, J=6.5 Hz, 1H), 6.55 (d, J=16.0 Hz, 1H), 6.81 (dd, J=6.0, 16.0 Hz, 1H), 7.22–7.44 (m, 12H), 7.50–7.55 (m, 1H), 7.86 (dd, J=1.5, 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 163.59, 161.26, 152.78, 140.00, 136.42, 133.83, 132.29, 129.29, 128.77, 128.43, 128.14, 128.11, 127.63, 126.67, 124.18, 123.33, 116.65, 116.09, 106.75, 44.14. EI-MS: *m*/*z* (relative intensity) 354 (M^+, 10%). Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.72; H, 5.22.

4.4.29. 6,7-Dimethyl-3-[1,3-diphenyl-2-allyl]-4-hydroxy-1-benzopyran-2(*H*)-one (8c). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.12 (s, 3H), 2.14 (s, 3H), 5.28 (d, J=8.7 Hz, 1H), 6.51 (d, J=15.6 Hz, 1H), 6.89 (s, 1H), 6.94 (dd, J=8.7, 15.6 Hz, 1H), 7.02 (m, 2H), 7.08–7.15 (m, 4H), 7.25–7.28 (m, 4H), 7.61 (s, 1H), 10.41 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 163.42, 161.27, 151.17, 142.61, 141.58, 137.47, 132.44, 131.78, 129.98, 128.54, 128.21, 127.54, 127.28, 126.35, 126.14, 123.47, 116.91, 114.09, 106.73, 43.93, 20.16, 19.42. Anal. Calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C, 80.91; H, 5.56. HRMS (EI) calcd for $C_{26}H_{22}O_3$: 382.1569; found: 382.1565.

4.4.30. 7-Chloro-3-[1,3-diphenyl-2-allyl]-4-hydroxy-1-benzopyran-2(*H*)-one (8d). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 5.48 (d, J=6.8 Hz, 1H), 6.57 (d, J=15.6 Hz, 1H), 6.86 (dd, J=6.8, 15.6 Hz, 1H), 7.18–7.43 (m, 12H), 7.86 (d, J=2.2 Hz, 1H), 8.01 (br s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 163.32, 160.28, 151.06, 139.95,

136.41, 133.92, 132.21, 129.76, 129.25, 128.78, 128.13, 128.09, 128.05, 127.62, 126.67, 123.08, 118.13, 117.36, 107.82, 44.20. Anal. Calcd for $C_{24}H_{17}ClO_3$: C, 74.13; H 4.41. Found: C, 74.38; H, 4.38. HRMS (EI) calcd for $C_{24}H_{17}ClO_3$: 388.0866; found: 388.0856.

4.4.31. 3-[1,3-Diphenyl-2-allyl]-4-hydroxy-6-methyl-pyran-2-one (8b). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.08 (s, 3H), 5.18 (d, J=8.7 Hz, 1H), 6.00 (s, 1H), 6.56 (d, J=15.6 Hz, 1H), 7.02 (dd, J=8.7, 15.6 Hz, 1H), 7.12–7.18 (m, 2H), 7.22–7.27 (m, 4H), 7.37–7.39 (m, 4H), 10.81 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 166.82, 166.09, 160.87, 142.89, 137.75, 131.32, 130.11, 128.61, 128.22, 127.76, 127.27, 126.44, 126.14, 104.28, 101.34, 43.43, 19.81. Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 78.77; H, 5.50.

4.4.32. 2-Benzyl-3-phenylfuro[3,2-*c*]coumarin (9). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 4.18 (s, 2H), 7.23–7.56 (m, 13H), 7.86 (d, J=7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 157.81, 157.03, 153.24, 152.60, 137.32, 130.62, 129.97, 129.84, 128.91, 128.48, 128.47, 128.23, 126.99, 124.38, 121.88, 120.98, 117.23, 112.88, 109.77, 32.58. EI-MS: m/z (relative intensity) 352(M^+, 10%). Anal. Calcd for $C_{24}H_{16}O_3$: C, 81.80; H, 4.58. Found: C, 81.43; H, 4.51.

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