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Synthesis of methoxychalcone derivatives with isobornyl substituents

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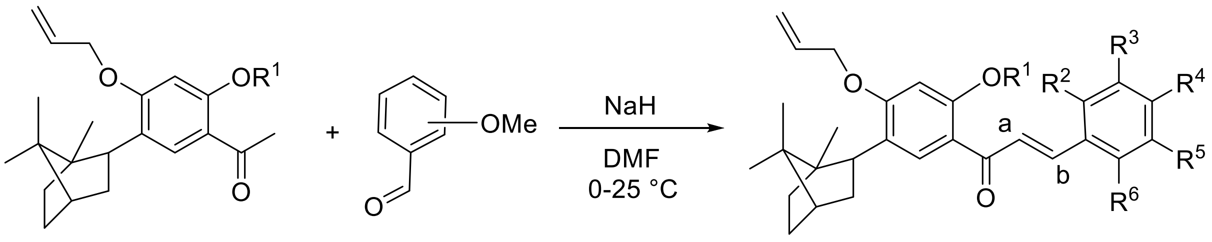
Abstract

A series of new methoxychalcone derivatives with an isobornyl fragment in ring A was synthesized *via* the Claisen-Schmidt condensation of O-allylated 2,4-dihydroxy-5-isobornylacetophenone with different methoxybenzaldehydes.



R^1=Allyl or H

14 examples
27-82 % Yeld

Keywords: Chalcones, Claisen-Schmidt condensation, allylation, methoxybenzaldehydes

Introduction

Chalcones are aromatic ketones with two phenyl rings form the basic structural core of many natural biologically active compounds.[1–4] The large structural diversity of chalcones is due to the number, position, and type of substituents in rings A and B. Varying the substituents in the chalcone structure, it is possible to provide directional interaction with certain biological targets. The important role of methoxy groups in the B ring for inhibiting the binding of *Plasmodium falciparum* enzymes has been described.[5–7] Mellado *et al*. demonstrated the high antiproliferative activity of a series of methoxy-substituted chalcones in comparison with the widely used anticancer drug 5-fluorouracil.[8] Chalcone synthesized from the 3,4,5-trimethoxybenzaldehyde and 4-methoxyacetophenone was shown to be able to prevent the progression of diabetic cardiomyopathy by inhibiting inflammatory reaction and leveling oxidative stress.[9] At the same time, modification of the α-position of 2′,3,4,4′-tetramethoxychalcone with electron-withdrawing substituents allowed to obtain compounds capable of modulating inflammatory reactions by means of influencing the activity of heme oxygenase-1 (HO-1), the inducible activity of nitric oxide synthase and levels of cytokine expression.[10] Chalcone which has 3,4,6-trimethoxy groups and 2-hydroxy groups in ring A demonstrated antimicrobial activity.[11]

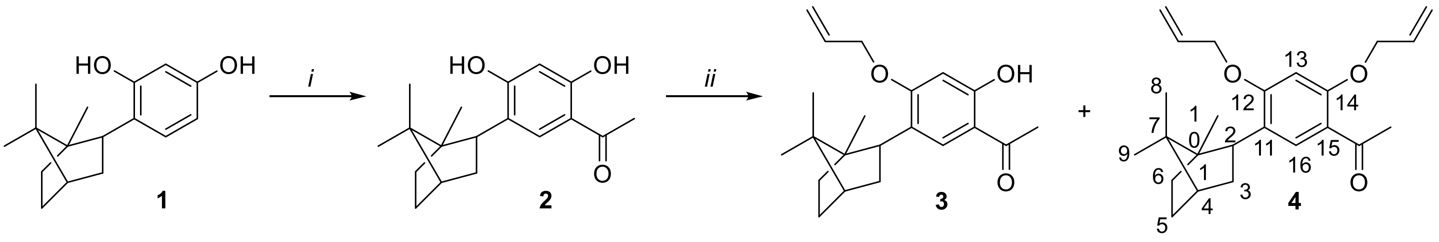
It should be noted that bicyclic monoterpenoids attract attention as a source of a key structural block as well as one of the pharmacophore group of biologically active molecules. There have been recorded instances of an extremely high potential of monoterpenes for the synthesis of antiviral and antibacterial agents.[12–15] As shown previously, chalcone combining in its structure the 2′,4′-dihydroxylated ring A with a lipophilic myrtenyl substituent in ring B, demonstrated high antibacterial activity against gram-positive pathogens (*S. aureus, E. faecalis*).[16]

Among the many methods available for the synthesis of chalcones, the Claisen-Schmidt condensation of acetophenone derivatives with benzaldehyde in the presence of a catalyst is most applicable. Besides the alkali metal hydroxides different heterogeneous catalysts can be used as catalysts in this reaction, such as nanoparticles ZnO[17,18] and MgO[19], silica-supported transition metal based heterogeneous catalysts,[20] piperidine-functionalized silica,[21] ionic liquids,[22] and cesium salts of 12-tungstophosphoric acid.[23]

The simplicity of synthesis, high reaction capacity and a wide spectrum of pharmacological activity caused the growing interest of researches to this group of compounds. Thus, the synthesis of natural bioregulator analogs is a promising direction for obtaining compounds with new or improved characteristics. In the present work we synthesized of a number of methoxy chalcone derivatives with an isobornyl substituent in ring A based on O-allylated 1,3-dihydroxy-4-isobornylacetophenone.

Results and Discussion

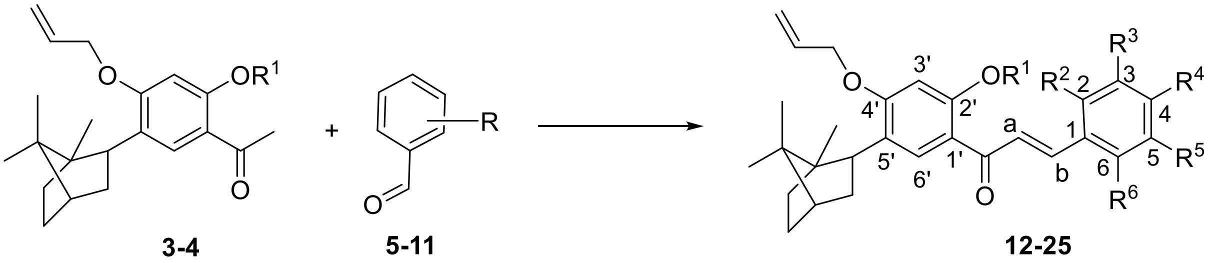
The initial 1,3-dihydroxy-4-isobornylbenzene **1** synthesized via the alkylation of resorcinol with camphene according to the known method[24] was racemic mixture, since the alkylation was carried out with racemic camphene. Following acetylation of compound **1** by acetic anhydride in BF_3 Et_2O at 60 °C leads to the formation of 2,4-dihydroxy-5-isobornylacetophenone **2** in 76% yield (Scheme 1). Since we synthesized chalcones using the strong base NaH, we preliminarily protected the OH groups of 1-acetyl-2,4-dihydroxy-5-isobornylbenzene **2** by *O*-allylation in the presence of K_2CO_3/KI.[25] Varying the temperature of the reaction mixture and the ratio of the starting reagents allowed the conditions for the selective preparation of mono- or diester **3** and **4**, respectively. Allylation at 40 °C predominantly leads to the formation of 1-acetyl-4-allyloxy-2-hydroxy-5-isobornylbenzene **3** with a yield of 66%. Compound **4** is formed in 72% yield at heating to 80 °C and using a twofold excess of allyl bromide. Mono- and di-*O*-allylation products **3** and **4** were isolated separately and used for further synthesis of methoxy derivatives of chalcones.



Reagents and conditions: i: Ac_2O, $BF_3{\cdot}Et_2O$, 60 °C, 3 h, 76%; ii: $(CH_3)_2CO$, AllylBr, K_2CO_3/KI, heat.

Scheme 1. Synthesis of allyloxy derivatives of 1,3-dihydroxy-4-isobornylbenzene

Chalcones **12–25** were synthesized by condensation of compounds **3** and **4** with methoxy-substituted benzaldehydes **5**-**11** in the presence of sodium hydride in dimethylformamide (DMF) (Scheme 2, Table 1).



R = 2-MeO (**5**); 3-MeO (**6**); 4-MeO (**7**);
2,3-MeO (**8**); 3,4-MeO (**9**);
2,4,6-MeO (**10**); 3.4.5-MeO (**11**)

Reagents and conditions: NaH, DMF, 0–25 °C

Scheme 2. Synthesis of chalcones

Table I. Structure and yield of the methoxy chalcone derivatives

Chalcone	R^1	R^2	R^3	R^4	R^5	R^6	Yield, %
12	H	$-OCH_3$	H	H	H	H	55
13	H	H	$-OCH_3$	H	H	H	48
14	H	H	H	$-OCH_3$	H	H	70
15	H	$-OCH_3$	$-OCH_3$	H	H	H	69
16	H	H	$-OCH_3$	$-OCH_3$	H	H	75
17	H	$-OCH_3$	H	$-OCH_3$	H	$-OCH_3$	78
18	H	H	$-OCH_3$	$-OCH_3$	$-OCH_3$	H	49
19	Allyl	$-OCH_3$	H	H	H	H	57
20	Allyl	H	$-OCH_3$	H	H	H	27
21	Allyl	H	H	$-OCH_3$	H	H	68
22	Allyl	$-OCH_3$	$-OCH_3$	H	H	H	61
23	Allyl	H	$-OCH_3$	$-OCH_3$	H	H	82
24	Allyl	$-OCH_3$	H	$-OCH_3$	H	$-OCH_3$	78
25	Allyl	H	$-OCH_3$	$-OCH_3$	$-OCH_3$	H	47

As can be seen from Table I, the yield of chalcones depends on the position of the methoxy groups in the aromatic ring of the starting benzaldehyde. Chalcones having a methoxy group in the *meta*-position were obtained in low yields. At the same time chalcones synthesized from the benzaldehydes with at least one methoxy groups in the *para*- or *ortho*-position were obtained in moderate or high yields. The methoxy group, which has the +M effect, in the *ortho*- and *para*-positions of the aromatic ring increases the rate of the reaction on account of further stabilizing the positive reaction center of the carbonyl group as a result of conjugation. In the case of *meta*-substituents, there is no mesomeric effect, in consequence of which the reaction rate and the yield of the target products decrease.

The structures of the new methoxy-substituted chalcones with an isobornyl fragment were determined on the basis of NMR spectroscopy and mass spectrometry data. All signals of the terpene substituent and allyloxy fragment are present in the ^{1}H and ^{13}C NMR spectra of chalcones **12–25**. In the high field region at 3.85–3.98 ppm in the ^{1}H NMR spectra, characteristic singlet of methoxy groups are observed, while the signal of the protons of the CH_3 group of the acetyl fragment is absent. In the ^{1}H NMR spectra, signals of α-, β-protons of the double bond are observed as doublets in the range of 7.44–8.39 ppm with the spin-spin interaction constant *J* 15.5–15.9 Hz, which indicates that the substituents at the double bond are in the *trans*-orientation. There are also signals of the protons of the aromatic ring, which correspond to the submitted structures. In the ^{13}C NMR spectra, there are no signals of the carbon atom of the CH_3 group of the acetyl substituent and signals of the methoxy groups appear in the region of 55 ppm. The signal of the carbon atom of the C=O group of the initial acetophenone shifts to the high field region from 202 to 192 ppm; moreover, signals of carbon atoms at a double bond in the α, β-position are observed.

Conclusions

By the condensation reaction of mono- and diallyloxy derivatives of 1,3-dihydroxy-4-isobornyl-acetophenone with mono-, di- and trimethoxy-substituted benzaldehydes, a number of methoxy-substituted chalcones with an isobornyl moiety were synthesized in 27–78% yields. The structures of all the obtained compounds were confirmed by NMR spectroscopy and mass spectrometry.

Experimental Section

Materials and methods

The ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance II 300 instrument (300 MHz and 75 MHz) in (D_6) DMSO and $CDCl_3$. The assignment of the atom signals of synthesized compounds was carried out using the ^{1}H and J-modulated ^{13}C NMR spectra, as well as using the HSQC, HMBC, NOESY, COSY techniques. The melting points were measured on a Sanyo Gallenkamp MPD 350 instrument. Mass spectra were recorded on a Thermo Finnigan LCQ Fleet instrument. The reaction progress was monitored by thin layer chromatography (TLC) on Sorbfil plates. Column chromatography was carried out on silica gel Alfa Aesar 70 / 230μ.

The spectral data were partially obtained using the equipment of the Center of Collective Usage 'Chemistry' (Institute of Chemistry, Komi Scientific Center, Ural Branch of the RAS).

Synthesis and spectral characteristics of compounds **2-4** were described previously.[26]

General procedure for the synthesis of chalcones

To a cooled and stirred solution of the acetophenone derivative **3** or **4** (0.3 mmol) and sodium hydride (0.3 mmol, 60% in mineral oil) in DMF (1 ml) was added dropwise the appropriate benzaldehyde **5-11** (0.3 mmol) in DMF (1 ml). The resulting mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with water, extracted with ethyl acetate and washed with 10% HCl solution (3×10 ml), and next with water until neutral reaction and dried over anhydrous Na_2SO_4. The sought chalcone was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent.

Spectral characteristics synthesized compounds

3-(2-Methoxyphenyl)-1’-(5’-isobornyl-4’-allyloxy-2’-hydroxyphenyl)-propenone (12). Orange powder; 0.074 g (55%), mp 111-113 °C. Column chromatography on silica gel, eluent PE/AcOEt, 10: 1; R_f = 0.34 (PE/AcOEt, 7:1). ^{1}H NMR (CDCl$_3$, δ ppm, *J*/Hz): isobornyl fragment 0.78 (s, 3 H, C(10)H$_3$); 0.90 (s, 3 H, C(8)H$_3$); 1.01(s, 3 H, C(9)H$_3$); 1.29—1.51 (m, 2 H, H(5), H(6)); 1.54—1.73 (m, 2 H, H(3), H(6)); 1.86—1.98 (m, 2 H, H(5), H(4)); 2.20—2.30 (m, 1 H, H(3)); 3.31 (t, 1 H, H(2), *J* 9 Hz); chalcone 3.98 (s, 3 H, C(2)-OC$\underline{H}_3$); 4.61 (d, 2 H,C(4’)–O-C$\underline{H}_2$-CH=CH$_2$, *J* 4.3 Hz); 5.37 (d, 1 H,C(4’)–O-CH$_2$-CH=C$\underline{H}_2$, H*cis*, *J* 10.6 Hz); 5.53 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H}_2$, H*trans*, *J* 16.7 Hz); 6.10—6.19 (m, 1 H, C(4’)–O-CH$_2$-C$\underline{H}$=CH$_2$); 6.46 (s, 1 H, H(3`)); 7.00 (d, 1 H, H(3), *J* 8.1 Hz); 7.06 (t, 1 H, H(4), *J* 8.2 Hz); 7.42 (t, 1 H, H(5), *J* 8.2 Hz); 7.61 (d, 1 H, H(6), *J* 8.1 Hz); 7.81 (d, 1 H, H(β), *J* 15.9 Hz); 7.86 (s, 1 H, H(6`)); 8.13 (d, 1 H, H(α), *J* 15.8 Hz); 13.44 (s, 1 H, C(2`) OH). ^{13}C NMR (CDCl$_3$, δ ppm): 12.5 (10”); 20.3 (8”); 21.6 (9”); 27.6 (5”); 34.3 (3”); 39.6 (6”); 44.3 (2”); 45.7 (4”); 48.1 (7”); 49.5 (1”); 55.5 (C(2)-O$\underline{C}$H$_3$); 68.8 (C(4’)–O-$\underline{C}$H$_2$-CH=CH$_2$); 100.2 (3’); 111.2 (3); 113.3 (5’); 117.2 (1’); 117.8 (C(4’)–O-CH$_2$-CH=$\underline{C}$H$_2$); 120.9 (4); 121.8 (β); 123.8 (1); 129.1 (6’); 130.4 (5); 131.7 (6); 132.4 (C(4’)–O-CH$_2$-$\underline{C}$H=CH$_2$); 140.1 (α); 159.1 (2); 164.1 (4’); 164.5 (2’); 192.8 (C=O). ESI-MS *m/z*: calcd. for $C_{29}H_{35}O_4$ $[M+H]^+$ 447.59, found 447.54.

3-(3-Methoxyphenyl)-1’-(5’-isobornyl-4’-allyloxy-2’-hydroxyphenyl)-propenone (13). Yellow powder; 0.065 g (48%), mp 128—131 °C. Column chromatography on silica gel, eluent PE/AcOEt, 50:1; R_f = 0.36 (PE/Me$_2$CO, 8:1). ^{1}H NMR (CDCl$_3$, δ ppm, *J*/Hz): isobornyl fragment 0.73 (s, 3 H, C(10)H$_3$); 0.86 (s, 3 H, C(8)H$_3$); 0.93 (s, 3 H, C(9)H$_3$); 1.29—1.47 (m, 2 H, H(5), H(6)); 1.54—1.65 (m, 2 H, H(3), H(6)); 1.78—1.96 (m, 2 H, H(5), H(4)); 2.24-2.31 (m, 1 H, H(3)); 3.28 (t, 1 H, H(2), *J* 9 Hz); chalcone 3.85 (s, 3 H, C(3)-OC$\underline{H}_3$); 4.64 (d, 2 H, C(4’)–O-C$\underline{H}_2$-CH=CH$_2$, *J* 4.3 Hz); 5.37 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H}_2$, H*cis*, *J* 10.6 Hz); 5.54 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H}_2$, H*trans*, *J* 16.6 Hz); 6.11—6.19 (m, 1 H, C(4’)–O-CH$_2$-C$\underline{H}$=CH$_2$); 6.46 (s, 1 H, H(3’)); 7.02 (d, 1 H, H(4), *J* 8.3 Hz); 7.17 (s, 1 H, H(2)); 7.28 (d, 1 H, H(6), *J* 8.2 Hz); 7.40 (t, 1 H, H(5), *J* 8.3 Hz); 7.57 (d, 1 H, H(β), *J* 16.1 Hz); 7.81 (s, 1 H, H(6’)); 7.87 (d, 1 H, H(α)), *J* 15.8 Hz); 13.29 (s, 1 H, OH). ^{13}C NMR (CDCl$_3$, δ ppm): 12.4 (10”); 20.2 (8”); 21.5 (9”); 27.4 (5”); 34.3 (3”); 39.5 (6”); 44.2 (2”); 45.5 (4”); 48.1 (7”); 49.5 (1”); 55.4 (C(3)-O$\underline{C}$H$_3$); 69 (C(4’)–O-$\underline{C}$H$_2$-CH=CH$_2$); 100 (3’); 112.9 (5’); 113.6 (2); 116.2 (4); 117.9 (C(4’)–O-CH$_2$-CH=$\underline{C}$H$_2$); 120.9 (6); 124.2 (1’); 125.9 (β); 127.5 (1); 128.9 (5); 130.1 (6’); 132.3 (C(4’)–O-CH$_2$-$\underline{C}$H=CH$_2$); 143.9 (α); 159.9 (3); 163.3 (4`); 164.9 (2`); 191.2 (C=O). ESI-MS *m/z*: calcd. for $C_{29}H_{35}O_4$ $[M+H]^+$ 447.59, found 447.51.

3-(4-Methoxyphenyl)-1’-(5’-isobornyl-4’-allyloxy-2’-hydroxyphenyl)-propenone (14). Yellow-orange powder; 0.094 g (70%), mp 146—148 °C (decomp.). Column chromatography on silica gel, eluent PE/Me$_2$CO, 30:1; R_f = 0.48 (PE/Me$_2$CO, 10:1). ^{1}H NMR (CDCl$_3$, δ ppm, *J*/Hz): isobornyl fragment 0.75 (s, 3 H, C(10)H$_3$); 0.89 (s, 3 H, C(8)H$_3$); 0.98 (s, 3 H, C(9)H$_3$); 1.12—1.53 (m, 2 H, H(5), H(6)); 1.63—1.71 (m, 2 H, H(3), H(6)); 1.94—1.98 (m, 2 H, H(5), H(4)); 2.18—2.25 (m, 1 H, H(3)); 3.30 (t, 1 H, H(2), *J* 9 Hz); chalcone 3.90 (s, 3 H, C(4)-OC$\underline{H}_3$); 4.60 (d, 2 H, C(4’)–O-C$\underline{H}_2$-CH=CH$_2$, *J* 4.3 Hz); 5.40 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H}_2$, H*cis*, *J* 10.5 Hz); 5.44 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H}_2$, H*trans*, *J* 17.2 Hz); 6.10—6.18 (m, 1 H, C(4’)–O-CH$_2$-C$\underline{H}$=CH$_2$); 6.46 (s, 1 H, H(3`)); 6.99—7.06 (m, 2 H, H(2), H(6)); 7.45 (d, 1 H, H(β), *J* 15.4 Hz); 7.63 (d, 2 H, H(3), H(5), *J* 8.4 Hz); 7.81 (s, 1 H, H(6’)); 7.87 (d, 1 H, H(α), *J* 14.3 Hz); 13.43 (s, 1 H, OH). ^{13}C NMR (CDCl$_3$, δ ppm): 12.4 (10”); 20.2 (8”); 21.5 (9”); 27.4 (5”); 34.2 (3”); 39.4 (6”); 44.2 (2”); 45.6 (4”); 48.1 (7”); 49.5 (1”); 55.4 (C(4)-O$\underline{C}$H$_3$); 68.9 (C(4’)–O-$\underline{C}$H$_2$-CH=CH$_2$); 100 (3’); 113.1 (5’);

117.8 (C(4’)–O-CH$_2$-CH=$\underline{C}$H$_2$); 118.1 (β); 123.7 (1`); 127.6 (1); 128.7 (6`); 130.2 (2,6); 131.9 (3,5); 132.3 (C(4’)–O-CH$_2$-$\underline{C}$H=CH$_2$); 143,9 (α); 161.7 (4); 164. (4’); 164.50 (2’); 192.2 (C=O). ESI-MS *m/z*: calcd. for $C_{29}H_{35}O_4$ $[M+H]^+$ 447.59, found 447.52.

3-(2,3-Dimethoxyphenyl)-1′-(5′-isobornyl-4’-allyloxy-2’-hydroxyphenyl)-propenone (15). Yellow powder; 0.099 g (69%), mp 117—119 °C. Column chromatography on silica gel, eluent PE/AcOEt, 20:1; R$_f$ = 0.23 (PE/AcOEt 10:1). ^{1}H NMR (CDCl$_3$, δ ppm, *J*/Hz): isobornyl fragment 0.76 (s, 3 H, C(10)H$_3$); 0.89 (s, 3 H, C(8)H$_3$); 0.97 (s, 3 H, C(9) H$_3$); 1.28—1.50 (m, 2 H, H(5), H(6)); 1.59—1.70 (m, 2 H, H(3), H(6)); 1.87—1.95 (m, 2 H, H(5), H(4)); 2.17—2.28 (m, 1 H, H(3)); 3.29 (t, 1 H, H(2), *J* 9 Hz); chalcone 3.94 (s, 6 H, C(2,3)-OC$\underline{H_3}$); 4.61 (d, 2 H, C(4’)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 4.2 Hz); 5.37 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis*, *J* 10.4 Hz); 5.53 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 16.8 Hz); 6.03—6.18 (m, 1 H, C(4’)–O-CH$_2$-C$\underline{H}$=CH$_2$); 6.46 (s, 1 H, H(3`)); 7.02 (d, 1 H, H(4), *J* 8.4 Hz); 7.16 (t, 1 H, H(5), *J* 8.3 Hz); 7.24 (d, 1 H, H(6), *J* 8.3 Hz); 7.77 (d, 1 H, H(β), *J* 15.6 Hz); 7.84 (s, 1 H, H(6’)); 8.12 (d, 1 H, H(α), *J* 16 Hz); 13.42 (s, 1 H, OH). ^{13}C NMR (CDCl$_3$, δ ppm): 12.4 (10”); 20.2 (8”); 21.6 (9”); 27.4 (5”); 34.2 (3”); 39.5 (6”); 44.3 (2”); 45.6 (4”); 48.1 (7”); 48.9 (1”); 55.8 (C(3)-O$\underline{C}$H$_3$); 61.1 (C(2)-O$\underline{C}$H$_3$); 68.8 (C(4’)–O-$\underline{C}$H$_2$-CH=CH$_2$); 100.3 (3’); 113.2 (5’); 114.2 (4); 117.8 (C(4’)–O-CH$_2$-CH=$\underline{C}$H$_2$); 120.8 (6); 122.5 (β); 123.9 (1’); 124.2 (5); 128.9 (6’); 129.1 (1); 132.4 (C(4’)–O-CH$_2$-$\underline{C}$H=CH$_2$); 139.2 (α); 153.3 (3); 164.4 (2); 164.6 (4`); 164.9 (2`); 192.5 (C=O). ESI-MS *m/z*: calcd. for $C_{30}H_{37}O_5$ $[M+H]^+$ 477.60, found 477.34.

3-(3,4-Dimethoxyphenyl)-1′-(5′-isobornyl-4’-allyloxy-2’-hydroxyphenyl)-propenone (16). Orange powder; 0.108 g (75%), mp 111—113 °C. Column chromatography on silica gel, eluent PE/AcOEt, 15:1; R$_f$ = 0.34 (PE/AcOEt, 10:1). ^{1}H NMR (CDCl$_3$, δ ppm, *J*/Hz): isobornyl fragment 0.77 (s, 3 H, C(10)H$_3$) 0.89 (s, 3 H, C(8)H$_3$); 0.99 (s, 3 H, C(9)H$_3$); 1.35—1.51 (m, 2 H, H(5), H(6)); 1.57—1.69 (m, 2 H, H(3), H(6)); 1.82—1.99 (m, 2 H, H(5), H(4)); 2.27—2.35 (m, 1 H, H(3)); 3.3 (t, 1 H, H(2), *J* 9 Hz); chalcone 3.97 (s, 6 H, C(3,4)-OC$\underline{H_3}$); 4.61 (d, 2 H, C(4’)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 4.2 Hz); 5.38 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis*, *J* 10.6 Hz); 5.55 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 16.8 Hz); 6.11—6.19 (m, 1 H, C(4’)–O-CH$_2$-C$\underline{H}$=CH$_2$); 6.45 (s, 1 H, H(3`)); 6.96 (d, 1 H, H(5), *J* 8.1 Hz); 7.17 (s, 1 H, H(2)); 7.27 (d, 1 H, H(6), *J* 8.2 Hz); 7.44 (d, 1 H, H(β), *J* 15.7 Hz); 7.81 (s, 1 H, H(6’)); 7.85 (d, 1 H, H(α), *J* 15.9 Hz); 13.34 (s, 1 H, OH). ^{13}C NMR (CDCl$_3$, δ ppm): 12.5 (10”); 20.3 (8”); 21.6 (9”); 27.4 (5”); 34.5 (3”); 39.6 (6”); 44.2 (2”); 45.6 (4”); 48.1 (7”); 49.5 (1”); 56 (C(3,4)-O$\underline{C}$H$_3$); 69 (C(4’)–O-$\underline{C}$H$_2$-CH=CH$_2$); 100 (3’); 111.04 (2); 111.30 (5); 113.1 (5’); 117.8 (C(4’)–O-CH$_2$-CH=$\underline{C}$H$_2$); 118.6 (β); 122.8 (6); 123.9 (1’); 128.8 (6’); 129.1 (1); 132.4 (C(4’)–O-CH$_2$-$\underline{C}$H=CH$_2$); 144,1 (α); 149.3 (3); 151.5 (4); 164.1 (4`); 164.4 (2`); 192.1 (C=O). ESI-MS *m/z*: calcd. for $C_{30}H_{37}O_5$ $[M+H]^+$ 477.60, found 477.34.

3-(2,4,6-Trimethoxyphenyl)-1′-(5′-isobornyl-4’-allyloxy-2’-hydroxyphenyl)-propenone (17). Orange powder; 0.118 g (78%), mp 184—187 °C. Column chromatography on silica gel, eluent PE/AcOEt, 15:1; R$_f$ = 0.31 (PE/Me$_2$CO, 5:1). ^{1}H NMR (CDCl$_3$, δ ppm, *J*/Hz): isobornyl fragment 0.77 (s, 3 H, C(10)H$_3$); 0.89 (s, 3 H, C(8)H$_3$); 0.99 (s, 3 H, C(9)H$_3$); 1.26—1.48 (m, 2 H, H(5), H(6)); 1.57—1.68 (m, 2 H, H(3), H(6)); 1.88—1.96 (m, 2 H, H(5), H(4)); 2.18—2.27 (m, 1 H, H(3)); 3.28 (t, 1 H, H(2), *J* 9 Hz); chalcone 3.93 (s, 3 H, C(4)-OC$\underline{H_3}$); 4.02 (s, 6 H, C(2,6)-OC$\underline{H_3}$); 4.61 (d, 2 H, C(4’)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 4.1 Hz); 5.35 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis, J* 10.6 Hz); 5.52 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 16.8 Hz); 6.05—6.14 (m, 1 H, C(4’)–O-CH$_2$-C$\underline{H}$=CH$_2$); 6.15 (s, 2 H, H(3), H(5)); 6.47 (s, 1 H, H(3`)); 7.88 (s, 1 H, H(6`)); 8.06 (d, 1 H, H(β), *J* 15.8 Hz); 8.39 (d, 1 H, H(α), *J* 15.9 Hz); 13.41 (s, 1 H, OH). ^{13}C NMR (CDCl$_3$, δ ppm): 12.5 (10”); 20.3 (8”); 21.5 (9”); 27.6 (5”); 33.9 (3”); 39.5 (6”); 44.4 (2”); 45.6 (4”); 47.9 (7”); 49.6 (1”); 55.3 (C(4)-O$\underline{C}$H$_3$); 55.6 (C(2,6)-O$\underline{C}$H$_3$); 68.8 (C(4)–O-$\underline{C}$H$_2$-CH=CH$_2$); 90.8 (3,5); 100.1 (3’); 106.1 (5’); 115.2 (1’); 117.8 (C(4’)–O-CH$_2$-CH=$\underline{C}$H$_2$); 121.6 (β); 123.9 (1); 129.1 (6’); 133.2 (C(4’)–O-CH$_2$-$\underline{C}$H=CH$_2$); 134.6 (α); 163.2 (4); 164.2 (2,6); 164.8 (4’); 165.1 (2’); 192.7 (C=O). ESI-MS *m/z*: calcd. for $C_{31}H_{39}O_6$ $[M+H]^+$ 507.63, found 507.49.

3-(3,4,5-Trimethoxyphenyl)-1′-(5′-isobornyl-4’-allyloxy-2’-hydroxyphenyl)-propenone (18). Yellow powder; 0.074 g (49%), mp 146—148 °C. Column chromatography on silica gel, eluent PE/AcOEt, 20:1; R$_f$ = 0.38

(PE/Me_2CO, 5:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*/Hz): isobornyl fragment 0.78 (s, 3 H, $C(10)H_3$); 0.89 (s, 3 H, $C(8)H_3$); 1.10 (s, 3 H, $C(9)H_3$); 1.29—1.47 (m, 2 H, H(5), H(6)); 1.59—1.65 (m, 2 H, H(3), H(6)); 1.85—1.92 (m, 2 H, H(5), H(4)); 2.14—2.22 (m, 1 H, H(3)); 3.31 (t, 1 H, H(2), *J* 9 Hz); chalcone 3.96 (s, 9 H, C(3,4,5)-OC$\underline{H_3}$); 4.61 (d, 2 H, C(4’)–O-C$\underline{H_2}$-CH=CH_2, *J* 4.3 Hz); 5.36 (d, 1 H, C(4’)–O-CH_2-CH=C$\underline{H_2}$, H*cis,* *J* 10.6 Hz); 5.53 (d, 1 H, C(4’)–O-CH_2-CH=C$\underline{H_2}$, H*trans*, *J* 16.8 Hz); 6.07—6.15 (m, 1 H, C(4’)–O-CH_2-C$\underline{H}$=CH_2); 6.46 (s, 1 H, H(3’)); 6.89 (s, 2 H, H(2), H(6)); 7.45 (d, 1 H, H(β), *J* 15.9 Hz); 7.76 (d, 1 H, H(α), *J* 15.7 Hz); 7.82 (s, 1 H, H(6’)); 13.34 (s, 1 H, OH). ^{13}C NMR ($CDCl_3$, δ ppm): 12.5 (10”); 20.4 (8”); 21.5 (9”); 27.4 (5”); 34.6 (3”); 39.7 (6”); 44.2 (2”); 45.7 (4”); 48.1 (7”); 49.4 (1”); 56.2 (C(4)-O$\underline{C}H_3$); 61.1 (C(3,5)-O$\underline{C}H_3$); 68.9 (C(4’)–O-$\underline{C}H_2$-CH=CH_2); 100.1 (3’); 105.7 (2,6); 112.4 (5`); 117.8 (C(4’)–O-CH_2-CH=$\underline{C}H_2$); 120.2 (β); 124.1 (1’); 128.9 (6’); 130.4 (1); 132.3 (C(4’)–O-CH_2-$\underline{C}$H=CH_2); 143.9 (α); 153.5 (4); 156.1 (3,5); 164.2 (4’); 164.4 (2’); 192 (C=O). ESI-MS *m/z*: calcd. for $C_{31}H_{39}O_6$ $[M+H]^+$ 507.63, found 507.52.

3-(2-Methoxyphenyl)-1′-(5′-isobornyl-2′,4′-diallyloxyphenyl)-propenone (19). Pale yellow oil; 0.083 g (57%). Column chromatography on silica gel, eluent PE/Me_2CO, 15:1; R_f = 0.25 (PE/Me_2CO 7: 1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*/Hz): isobornyl fragment 0.76 (s, 3 H, $C(10)H_3$); 0.86 (s, 3 H, $C(8)H_3$); 0.93 (s, 3 H, $C(9)H_3$); 1.26—1.49 (m, 2 H, H(5), H(6)); 1.57—1.64 (m, 2 H, H(3), H(6)); 1.80—1.97 (m, 2 H, H(5), H(4)); 2.27—2.34 (m, 1 H, H(3)); 3.29 (t, 1 H, H(2), *J* 9 Hz); chalcone; 3.90 (s, 3 H, C(2)-OC$\underline{H_3}$); 4.61 (d, 2 H, C(4’)–O-C$\underline{H_2}$-CH=CH_2, *J* 4.2 Hz); 4.67 (d, 2 H, C(2’)–O-C$\underline{H_2}$-CH=CH_2, *J* 5.3 Hz); 5.30 (d, 1 H, C(4’)–O-CH_2-CH=C$\underline{H_2}$, H*cis*, *J* 10.5 Hz); 5.37 (d, 1 H, C(2’)–O-CH_2-CH=C$\underline{H_2}$, H*cis*, *J* 10.6 Hz); 5.48 (d, 1 H, C(4’)–O-CH_2-CH=C$\underline{H_2}$, H*trans*, *J* 16.9 Hz); 5.54 (d, 1 H, C(2’)–O-CH_2-CH=C$\underline{H_2}$, H*trans*, *J* 15.5 Hz); 6.02—6.19 (m, 2 H, C(4’)–O-CH_2-C$\underline{H}$=CH_2 and C(2’)–O-CH_2-C$\underline{H}$=CH_2); 6.48 (s, 1 H, H(3’); 6.94 (d, 1 H, H(3), *J* 8.4 Hz); 6.98 (t, 1 H, H(4), *J* 8.4 Hz); 7.36 (t, 1 H, H(5), *J* 8.3 Hz); 7.63 (d, 1 H, H(6), *J* 8.3 Hz); 7.73 (d, 1 H, H(β), *J* 15.9 Hz); 7.86 (s, 1 H, H(6’)); 8.09 (d, 1 H, H(α), *J* 15.7 Hz). ^{13}C NMR ($CDCl_3$, δ ppm): 12.4 (10”; 20.3 (8”); 21.4 (9”); 27.5 (5”); 33.9 (3”); 39.6 (6”); 44.4 (2”); 45.7 (4”); 48.1 (7”); 49.6 (1”); 55.4 (C(2)-O$\underline{C}H_3$); 68.7 (C(4’)–O-$\underline{C}H_2$-CH=CH_2); 69.9 (C(2`)–O-$\underline{C}H_2$-CH=CH_2); 97.2 (3’); 111.2 (3); 117.5 (C(4’)–O-CH_2-CH=$\underline{C}H_2$); 117.7 (C(2’)–O-CH_2-CH=$\underline{C}H_2$); 120.6 (4); 121.3 (5’); 124.6 (1’); 125.3 (1); 128.1 (β); 128.4 (6’); 128.6 (5); 131.1 (6); 132.8 (C(4’)–O-CH_2-$\underline{C}$H=CH_2, C(2’)–O-CH_2-$\underline{C}$H=CH_2); 136.9 (α); 157.4 (2); 158.6 (4’); 161.7 (2`); 190.9 (C=O). ESI-MS *m/z*: calcd. for $C_{32}H_{39}O_4$ $[M+H]^+$ 487.65, found 487.44.

3-(3-Methoxyphenyl)-1′-(5′-isobornyl-2′,4′-diallyloxyphenyl)-propenone (20). Pale yellow oil; 0.039 g (27%). Column chromatography on silica gel, eluent PE/Me_2CO, 20:1; R_f = 0.39 (PE/Me_2CO, 5: 1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*/Hz): isobornyl fragment 0.74 (s, 3 H, $C(10)H_3$); 0.85 (s, 3 H, $C(8)H_3$); 0.92 (s, 3 H, $C(9)H_3$); 1.29—1.48 (m, 2 H, H(5), H(6)); 1.58—1.63 (m, 2 H, H(3), H(6)); 1.79—1.96 (m, 2 H, H(5), H(4)); 2.26—2.34 (m, 1 H, H(3)); 3.27 (t, 1 H, H(2), *J* 9 Hz); chalcone 3.86 (s, 3 H, C(3)-OC$\underline{H_3}$); 4.62 (d, 2 H, C(4’)–O-C$\underline{H_2}$-CH=CH_2, *J* 4.3 Hz); 4.66 (d, 2 H, C(2’)–O-C$\underline{H_2}$-CH=CH_2, *J* 5.5 Hz); 5.31 (d, 1 H, C(4’)–O-CH_2-CH=C$\underline{H_2}$, H*cis*, *J* 10.6 Hz); 5.37 (d, 1 H, C(2`)–O-$CH_2$-CH=C$\underline{H_2}$, H*cis*, *J* 10.5 Hz); 5.48 (d, 1 H, C(4`)–O-CH_2-CH=C$\underline{H_2}$, H*trans*, *J* 16.7 Hz); 5.54 (d, 1 H, C(2`)–O-CH_2-CH=C$\underline{H_2}$, H*trans*, *J* 15.5 Hz); 6.05—6.19 (m, 2 H, C(4’)–O-CH_2-C$\underline{H}$=CH_2 and C(2’)–O-CH_2-C$\underline{H}$=CH_2); 6.47 (s, 1 H, H(3’)); 6.95 (d, 1 H, H(4), *J* 8.2 Hz); 7.14 (s, 1 H, H(2)); 7.21 (d, 1 H, H(6), *J* 8.3 Hz); 7.32 (t, 1 H, H(5), *J* 8.2 Hz); 7.66—7.70 (m, 2 H, H(α, β)); 7.87 (s, 1 H, H(6`)). $^{13}$C NMR ($CDCl_3$, δ ppm): 12.4 (10”); 20.2 (8”); 21.5 (9”); 27.5 (5”); 33.9 (3”); 39.6 (6”); 44.4 (2”); 45.6 (4”); 48.1 (7”); 49.7 (1”); 55.3 (C(3)-O$\underline{C}H_3$); 68.9 (C(4`)–O-$\underline{C}H_2$-CH=CH_2); 69.9 (C(2`)–O-$\underline{C}H_2$-CH=CH_2); 97.1 (3’); 108.4 (5’); 112.9 (2); 115.8 (4); 117.5 (C(4’)–O-CH_2-CH=$\underline{C}H_2$); 117.9 (C(2’)–O-CH_2-CH=$\underline{C}H_2$); 120.8 (1’); 121.1 (6); 125.4 (1); 127.9 (β); 128.5 (5); 129.7 (6’); 132.8 (C(4’)–O-CH_2-$\underline{C}$H=CH_2, C(2’)–O-CH_2-$\underline{C}$H=CH_2); 137.1 (3); 141.3 (α); 157.6 (4’); 159.8 (2`); 191.6 (C=O). ESI-MS *m/z*: calcd. for $C_{32}H_{39}O_4$ $[M+H]^+$ 487.65, found 487.42.

3-(4-Methoxyphenyl)-1′-(5′-isobornyl-2′,4′-diallyloxyphenyl)-propenone (21). Light yellow solid; 0.099 g (68%), mp 105—107 °C. Column chromatography on silica gel, eluent PE/AcOEt, 20:1; R_f = 0.29 (PE/Me_2CO, 5: 1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*/Hz): isobornyl fragment 0.74 (s, 3 H, $C(10)H_3$); 0.85 (s, 3 H, $C(8)H_3$); 0.92 (s, 3 H, $C(9)H_3$); 1.29—1.48 (m, 2 H, H(5), H(6)); 1.56—1.66 (m, 2 H, H(3), H(6)); 1.79—1.96 (m, 2 H, H(5), H(4)); 2.26—

2.33 (m, 1 H, H(3)); 3.28 (t, 1 H, H(2), *J* 9 Hz); chalcone 3.87 (s, 3 H, C(4)-OC$\underline{H_3}$); 4.61 (d, 2 H, C(4’)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 4.2 Hz); 4.66 (d, 2 H, C(2’)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 5.4 Hz); 5.31 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis*, *J* 10.5 Hz); 5.48 (d, 1 H, C(2’)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis*, *J* 10.5 Hz); 5.52 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 16.8 Hz); 5.54 (d, 1 H, C(2’)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 15.3 Hz); 6.05—6.17 (m, 2 H, C(4’)–O-CH$_2$-C$\underline{H}$=CH$_2$, C(2`)–O-CH$_2$-C$\underline{H}$=CH$_2$); 6.47 (s, 1 H, H(3’)); 6.93 (d, 2 H, H(2), H(6), *J* 8.4 Hz); 7.50—7.59 (m, 3 H, H(β), H(3), H(5)); 7.70 (d, 1 H, H(α), *J* 15.6 Hz); 7.85 (s, 1 H, H(6’)). ^{13}C NMR (CDCl$_3$, δ ppm): 12.1 (10”); 20.2 (8”); 21.4 (9”); 27.5 (5”); 33.8 (3”); 39.5 (6”); 44.4 (2”); 45.6 (4”); 48.1 (7”); 49.6 (1”); 55.3 (C(4)-O$\underline{C}$H$_3$); 68.9 (C(4’)–O-$\underline{C}$H$_2$-CH=CH$_2$); 69.9 (C(2’)–O-$\underline{C}$H$_2$-CH=CH$_2$); 97.1 (3`); 114.2 (2,6); 117.1 (5`); 117.5 (C(4`)–O-CH$_2$-CH=$\underline{C}$H$_2$); 117.8 (C(2’)–O-CH$_2$-CH=$\underline{C}$H$_2$); 125.3 (1); 125.5 (β); 128.3 (1’); 129.9 (3,5); 130.9 (6’); 132.8 (C(4’)–O-CH$_2$-$\underline{C}$H=CH$_2$, C(2’)–O-CH$_2$-$\underline{C}$H=CH$_2$); 141.4 (α); 157.4 (4); 161.1 (4’); 161.7 (2’); 190.5 (C=O). ESI-MS *m/z*: calcd. for $C_{32}H_{39}O_4$ [M+H]$^+$ 487.65, found 487.44.

3-(2,3-Dimethoxyphenyl)-1′-(5′-isobornyl-2′,4′-diallyloxyphenyl)-propenone (22). Pale yellow oil; 0.094 g (61%). Column chromatography on silica gel, eluent PE/Me$_2$CO, 15:1; R$_f$ = 0.36 (PE/Me$_2$CO, 5:1). ^{1}H NMR (CDCl$_3$, δ ppm, *J*/Hz): isobornyl fragment 0.74 (s, 3 H, C(10)H$_3$); 0.85 (s, 3 H, C(8)H$_3$); 0.92 (s, 3 H, C(9)H$_3$); 1.29—1.51 (m, 2 H, H(5), H(6)); 1.56—1.63 (m, 2 H, H(3), H(6)); 1.84—1.90 (m, 2 H, H(5), H(4)); 2.26—2.33 (m, 1 H, H(3)); 3.27 (t, 1 H, H(2), *J* 9 Hz); chalcone 3.89 (s, 3 H, C(3)-OC$\underline{H_3}$); 3.91 (s, 3 H, C(2)-OC$\underline{H_3}$); 4.61 (d, 2 H, C(4’)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 4.4 Hz); 4.67 (d, 2 H, C(2’)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 5.6 Hz); 5.29 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis*, *J* 10.3 Hz); 5.38 (d, 1 H, C(2’)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis, J* 10.4 Hz); 5.46 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 17.1 Hz); 5.53 (d, 1 H, C(2`)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 15.4 Hz); 6.03—6.18 (m, 2 H, C(4`)–O-CH$_2$-C$\underline{H}$=CH$_2$ and C(2’)–O-CH$_2$-C$\underline{H}$=CH$_2$); 6.46 (s, 1 H, H(3’)); 6.95 (d, 1 H, H(4), *J* 8.3 Hz); 7.08 (t, 1 H, H(5), *J* 8.3 Hz); 7.27 (d, 1 H, H(6), *J* 8.3 Hz); 7.72 (d, 1 H, H(β), *J* 15.7 Hz); 7.88 (s, 1 H, H(6’)); 8.05 (d, 1 H, H(α), *J* 15.9 Hz). ^{13}C NMR (CDCl$_3$, δ ppm): 12.4 (10”); 20.3 (8”); 20.5 (9”); 27.5 (5”); 33.9 (3”); 39.6 (6”); 44.4 (2”); 45.6 (4”); 48 (7”); 49.6 (1”); 55.9 (C(3)-O$\underline{C}$H$_3$); 61.4 (C(2)-O$\underline{C}$H$_3$); 68.9 (C(4’)–O-$\underline{C}$H$_2$-CH=CH$_2$); 69.9 (C(2’)–O-$\underline{C}$H$_2$-CH=CH$_2$); 97.1 (3’); 113.5 (4); 117.5 (C(4`)–O-CH$_2$-CH=$\underline{C}$H$_2$); 117.9 (C(2’)–O-CH$_2$-CH=$\underline{C}$H$_2$); 119.3 (6); 121 (5’); 123.9 (5); 125.4 (1’); 128.8 (β); 129.9 (1); 131.1 (6’); 132.8 (C(4`)–O-CH$_2$-$\underline{C}$H=CH$_2$, C(2’)–O-CH$_2$-$\underline{C}$H=CH$_2$); 136 (α); 148.9 (3); 153.2 (2); 157.6 (4’); 161.9 (2’); 190.5 (C=O). ESI-MS *m/z*: calcd. for $C_{33}H_{41}O_5$ [M+H]$^+$ 517.67, found 517.36.

3-(3,4-Dimethoxyphenyl)-1′-(5′-isobornyl-2′,4′-diallyloxyphenyl)-propenone (23). Light yellow solid; 0.127 g (82%), mp 120—122 °C. Column chromatography on silica gel, eluent PE/Me$_2$CO, 15:1; R$_f$ = 0.19 (PE/Me$_2$CO, 5:1). ^{1}H NMR (CDCl$_3$, δ ppm, *J*/Hz): isobornyl fragment 0.70 (s, 3 H, C(10)H$_3$); 0.81 (s, 3 H, C(8)H$_3$); 0.88 (s, 3 H, C(9)H$_3$); 1.25—1.47 (m, 2 H, H(5), H(6)); 1.55—1.62 (m, 2 H, H(3), H(6)); 1.81—1.95 (m, 2 H, H(5), H(4)); 2.26—2.32 (m, 1 H, H(3)); 3.24 (t, 1 H, H(2), *J* 9 Hz); chalcone: 3.90 (s, 3 H, C(4)-OC$\underline{H_3}$); 3.91 (s, 3 H, C(3)-OC$\underline{H_3}$); 4.57 (d, 2 H, C(4’)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 4.1 Hz); 4.62 (d, 2 H, C(2’)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 5.3 Hz); 5.26 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis*, *J* 10.5 Hz); 5.33 (d, 1 H, C(2`)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis*, *J* 10.6 Hz); 5.45 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 16.9 Hz); 5.51 (d, 1 H, C(2’)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 15.5 Hz); 6.01—6.15 (m, 2 H, C(4’)–O-CH$_2$-C$\underline{H}$=CH$_2$ and C(2’)–O-CH$_2$-C$\underline{H}$=CH$_2$); 6.43 (s, 1 H, H(3’)); 6.86 (d, 1 H, H(5), *J* 8.2 Hz);7.12 (s, 1 H, H(2)); 7.15 (d, 1 H, H(6), *J* 8.3 Hz); 7.53 (d, 1 H, H(β), *J* 15.7 Hz); 7.64 (d, 1 H, H(α), *J* 15.9 Hz); 7.82 (s, 1 H, H(6’)). ^{13}C NMR (CDCl$_3$, δ ppm): 12.4 (10”); 18.2 (8”); 20.3 (9”); 27.5 (5”); 33.9 (3”); 39.6 (6”); 44.4 (2”); 45.6 (4”); 48 (7”); 49.6 (1”); 55.9 (C(3,4)-O$\underline{C}$H$_3$); 68.9 (C(4’)–O-$\underline{C}$H$_2$-CH=CH$_2$); 69.9 (C(2’)–O-$\underline{C}$H$_2$-CH=CH$_2$); 97.1 (3’); 109.8 (2); 111.1 (5); 117.5 (C(4’)–O-CH$_2$-CH=$\underline{C}$H$_2$); 117.7 (C(2’)–O-CH$_2$-CH=$\underline{C}$H$_2$); 121.1 (5’); 122.9 (6); 125.4 (1’); 125.6 (β); 128.6 (1); 131.1 (6’); 132.8 (C(4’)–O-CH$_2$-$\underline{C}$H=CH$_2$, C(2’) –O-CH$_2$-$\underline{C}$H=CH$_2$); 141.6 (α); 149.2 (4); 150.8 (3); 157.4 (4’); 161.7 (2`); 190.3 (C=O). ESI-MS *m/z*: calcd. for $C_{33}H_{41}O_5$ [M+H]$^+$ 517.67, found 517.33.

3-(2,4,6-Trimethoxyphenyl)-1′-(5′-isobornyl-2′,4′-diallyloxyphenyl)-propenone (24). Pale yellow oil; 0.128 g (78%). Column chromatography on silica gel, eluent PE/Me$_2$CO, 20:1; R$_f$ = 0.23 (PE/Me$_2$CO, 5: 1). ^{1}H NMR (CDCl$_3$, δ ppm, *J*/Hz): isobornyl fragment 0.74 (s, 3 H, C(10)H$_3$); 0.84 (s, 3 H, C(8)H$_3$); 0.91 (s, 3 H, C(9)H$_3$); 1.29—

1.48 (m, 2 H, H(5), H(6)); 1.55—1.62 (m, 2 H, H(3), H(6)); 1.78—1.89 (m, 2 H, H(5), H(4)); 2.24—2.31 (m, 1 H, H(3)); 3.28 (t, 1 H, H(2), *J* 9 Hz); chalcone 3.87 (s, 9 H, C(2,4,6)-OC$\underline{H_3}$); 4.58 (d, 2 H, C(4`)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 4.3 Hz); 4.65 (d, 2 H, C(2`)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 5.5 Hz); 5.26 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis, J* 10.5 Hz); 5.35 (d, 1 H, C(2’)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis, J* 10.6 Hz); 5.47 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 16.9 Hz); 5.53 (d, 1 H, C(2`)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 15.2 Hz); 6.01—6.11 (m, 2 H, C(4`)–O-CH$_2$-C$\underline{H}$=CH$_2$ and C(2`)–O-CH$_2$-C$\underline{H}$=CH$_2$); 6.14 (s, 2 H, H(3), H(5)); 6.46 (s, 1 H, H(3`)); 7.78 (s, 1 H, H(6`)); 7.91 (d, 1 H, H(β), *J* 15.6 Hz); 8.18 (d, 1 H, H(α), *J* 15.9 Hz). $^{13}$C NMR (CDCl$_3$, δ ppm): 12.4 (10”); 20.3 (8”); 20.5 (9”); 27.5 (5”); 33.9 (3”); 39.6 (6”); 44.4 (2”); 45.7 (4”); 48 (7”); 49.6 (1”); 55.3 (C(4)-O$\underline{C}$H$_3$); 55.6 (C(2,6)-O$\underline{C}$H$_3$); 68.8 (C(4`)–O-$\underline{C}$H$_2$-CH=CH$_2$); 70.1 (C(2`)–O-$\underline{C}$H$_2$-CH=CH$_2$); 90.5 (3,5); 97.6 (3`); 106.9 (5`); 117.1 (C(4`)–O-CH$_2$-CH=$\underline{C}$H$_2$); 117.3 (C(2`)–O-CH$_2$-CH=$\underline{C}$H$_2$); 122.3 (1`); 124.9 (1); 127.4 (β); 130.8 (6`); 133.1 (C(4`)–O-CH$_2$-$\underline{C}$H=CH$_2$, C(2`)–O-CH$_2$-$\underline{C}$H=CH$_2$); 133.5 (α); 157 (4); 160.9 (2,6); 161.5 (4’); 162.6 (2`); 192.7 (C=O). ESI-MS *m/z*: calcd. for C$_{34}$H$_{43}$O$_6$ [M+H]$^+$ 547.29, found 547.27.

3-(3,4,5-Trimethoxyphenyl)-1′-(5′-isobornyl-2′,4′-diallyloxyphenyl)propenone (25). ale yellow oil; 0.077 g (47%). Column chromatography on silica gel, eluent PE/Me$_2$CO, 15:1); R$_f$ = 0.28 (PE/Me$_2$CO, 5: 1). ^{1}H NMR (CDCl$_3$, δ ppm, *J*/Hz): isobornyl fragment 0.71 (s, 3 H, C(10)H$_3$); 0.88 (s, 3 H, C(8)H$_3$); 0.92 (s, 3 H, C(9)H$_3$); 1.28—1.45 (m, 2 H, H(5), H(6)); 1.59—1.63 (m, 2 H, H(3), H(6)); 1.77—1.88 (m, 2 H, H(5), H(4)); 2.23—2.32 (m, 1 H, H(3)); 3.28 (t, 1 H, H(2), *J* 9 Hz); chalcone 3.91 (s, 9 H, C(3,4,5)-OC$\underline{H_3}$); 4.62 (d, 2 H, C(4’)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 4.2 Hz); 4.66 (d, 2 H, C(2’)–O-C$\underline{H_2}$-CH=CH$_2$, *J* 5.4 Hz); 5.35 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis, J* 10.5 Hz); 5.39 (d, 1 H, C(2’)–O-CH$_2$-CH=C$\underline{H_2}$, H*cis, J* 10.6 Hz); 5.51 (d, 1 H, C(4’)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 16.8 Hz); 5.54 (d, 1 H, C(2’)–O-CH$_2$-CH=C$\underline{H_2}$, H*trans*, *J* 15.2 Hz); 6.07—6.13 (m, 2 H, C(4’)–O-CH$_2$-C$\underline{H}$=CH$_2$ and C(2`)–O-CH$_2$-C$\underline{H}$=CH$_2$); 6.47 (s, 1 H, H(3`)); 6.85 (s, 2 H, H(2), H(6)); 7.59 (d, 1 H, H(β), *J* 16 Hz); 7.68 (d, 1 H, H(α), *J* 15.7 Hz); 7.87 (s, 1 H, H(6’)). ^{13}C NMR (CDCl$_3$, δ ppm): 12.4 (10”); 20.2 (8”); 20.3 (9”); 27.5 (5”); 33.9 (3”); 39.5 (6”); 44.4 (2”); 45.5 (4”); 48 (7”); 49.7 (1”); 56.1 (C(4)-O$\underline{C}$H$_3$); 60.9 (C(3,5)-O$\underline{C}$H$_3$); 68.9 (C(4`)–O-$\underline{C}$H$_2$-CH=CH$_2$); 69.8 (C(2’)–O-$\underline{C}$H$_2$-CH=CH$_2$); 96.6 (3`); 105.5 (2,6); 117.6 (C(4`)–O-CH$_2$-CH=$\underline{C}$H$_2$); 117.9 (C(2`)–O-CH$_2$-CH=$\underline{C}$H$_2$); 120.3 (5’); 125.4 (1`); 126.9 (β); 131.1 (1); 131.2 (6`); 133.1 (C(4`)–O-CH$_2$-$\underline{C}$H=CH$_2$, C(2`)–O-CH$_2$-$\underline{C}$H=CH$_2$); 138.2 (4); 141.4 (α); 153.4 (3,5); 157.5 (4’); 161.9 (2’); 190 (C=O). ESI-MS *m/z*: calcd. for C$_{34}$H$_{43}$O$_6$ [M+H]$^+$ 547.29, found 547.69.

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