



# Synthesis and antibacterial activity of chalcones bearing prenyl or geranyl groups from *Angelica keiskei*

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## ABSTRACT

Chalcones bearing prenyl or geranyl groups from *Angelica keiskei*, such as 4-hydroxyderricin (**1a**), xanthoangelol (**1e**), xanthoangelol F (**1f**), xanthoangelol H (**2**), deoxyxanthoangelol H (**3**), and deoxydihydroxanthoangelol H (**4**) and their derivatives were synthesized. From the evaluation of antibacterial activity of the synthesized chalcones, **1a**, isobavachalcone (**1b**), **1e**, **1f**, bavachalcone (**5a**), and broussonchalcone B (**5b**) were found to inhibit Gram-positive bacteria.

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## 1. Introduction

Chalcones bearing prenyl or geranyl groups are an abundant subclass of natural flavonoids and have exhibited a variety of biological activities. 4-Hydroxyderricin (**1a**),<sup>1</sup> xanthoangelol (**1e**),<sup>1</sup> xanthoangelol F (**1f**),<sup>2</sup> xanthoangelol H (**2**),<sup>2</sup> deoxyxanthoangelol H (**3**),<sup>3</sup> and deoxydihydroxanthoangelol H (**4**)<sup>3</sup> were recently reported to be isolated from *Angelica keiskei* as biologically active chalcones (Fig. 1). For example, **1a** showed hypotensive and lipid-regulatory activity in hypertensive rats,<sup>4</sup> as well as antimetastatic activity;<sup>5</sup> **1a** and **1e** showed antibacterial activity against Gram-positive pathogenic bacteria,<sup>6</sup> and antitumor-promoting activity in mouse skin carcinogenesis using DMBA plus TPA;<sup>7</sup> **1a**, **1e**, and **1f** showed phenylephrine-induced vasoconstriction in vivo;<sup>8</sup> **1a**, **1e**, **1f**, and **2** showed cytotoxicity against neuroblastoma cells;<sup>9</sup> **1f** showed an inhibitory effect on the induction of EBV-EA by TPS in Raji cells.<sup>10</sup>

Recently, **1e** was synthesized by Jung et al.<sup>11</sup> However, no work has been done on the synthesis of **1a**, **1b**, **1f**, **2**, **3**, and **4**. It seems to be important to develop synthetic routes for these chalcones and related derivatives for the elucidation of the relationship between their structures and potential activities. We preliminarily reported the first synthesis of prenylated chalcone **1a** and its derivatives **2**, **3**, and **4**.<sup>12</sup> In this paper, synthesis of these chalcones and their related

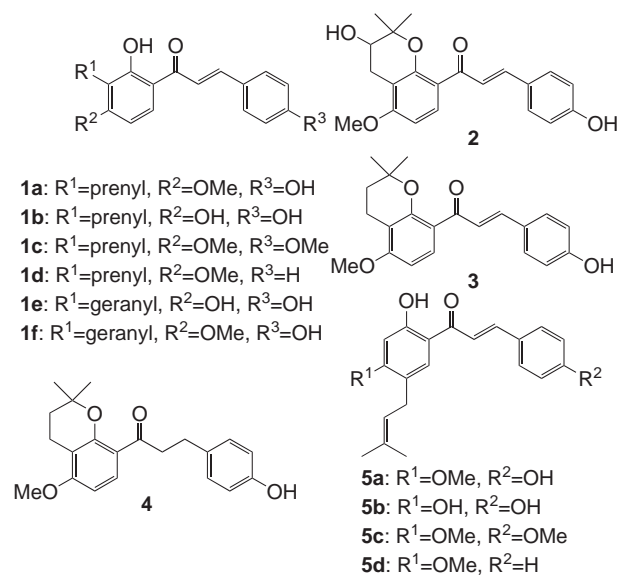


Fig. 1. Selected naturally occurring chalcones bearing prenyl or geranyl groups.

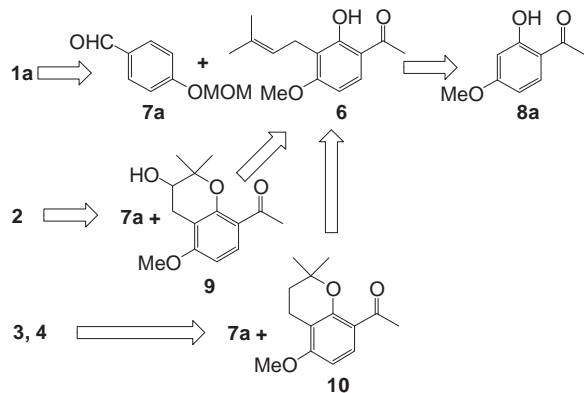
derivatives **1b–d**, **5a–d**, and additional synthesis of geranylated chalcones **1e**, **1f** are reported in details. Furthermore, evaluation of the antibacterial activity of these synthesized chalcones is also reported.

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## 2. Results and discussion

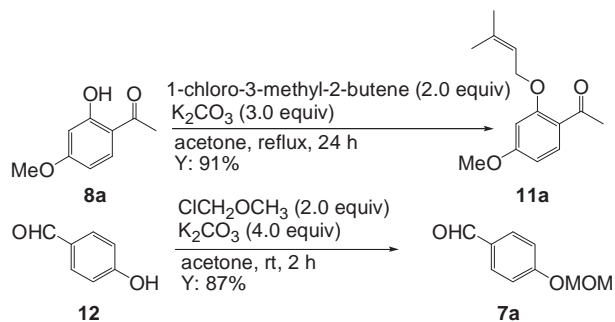
### 2.1. Synthesis of prenylated chalcones **1a**, **2**, **3**, and **4**

Scheme 1 shows our synthetic strategy for synthesis of prenylated chalcones **1a**, **2**, **3**, and **4**. As illustrated, Claisen–Schmidt condensation of the key intermediate **6** with 4-methoxymethoxybenzaldehyde (**7a**) would give **1a**. The key compound **6** could be obtained from accessible 2'-hydroxy-4'-methoxyacetophenone (**8a**). Chromanochalcones **2**, **3**, and **4** also would be prepared via **6**.



Scheme 1.

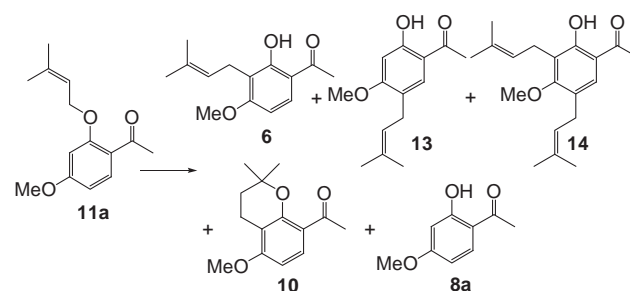
Synthesis of **1a** via [1,3]-sigmatropic rearrangement of 2'-prenyloxyacetophenone or 2'-prenyloxychalcone was first studied. 2'-Prenyloxyacetophenone (**11a**) was prepared from **8a** by treatment with 1-chloro-3-methyl-2-butene in the presence of  $K_2CO_3$  in 91% yield and methoxymethyl (MOM)-protected 4-hydroxybenzaldehyde (**7a**) was prepared from 4-hydroxybenzaldehyde (**12**) in 87% yield (Scheme 2).



Scheme 2.

Dauben et al. reported a [1,3]-sigmatropic rearrangement catalyzed by montmorillonite KSF clay of prenyl phenyl ethers to *ortho*- and *para*-prenyated phenols.<sup>13</sup> Montmorillonite K10 was reported to be more effective than montmorillonite KSF as the catalyst on the [1,3]-sigmatropic rearrangement by Dintzner et al.<sup>15</sup> Florisil<sup>®</sup> was also reported to promote the [1,3]-sigmatropic rearrangement effectively by Talamás et al.<sup>14</sup> Therefore, we first tried to compare montmorillonite K10 with Florisil<sup>®</sup> as the catalyst for the rearrangement reaction of **11a** (Table 1). The reaction of **11a** with montmorillonite K10 in  $CH_2Cl_2$  at 0 °C gave desired compound **6** in 53% yield, along with **13** (25%), **14** (7%), and **8a** (4%). In contrast, the reaction of **11a** using Florisil<sup>®</sup> in toluene at 110 °C provided **6** in 27% yield, along with **13** (32%), **10** (8%), and chroman **8a** (10%). Rearrangement with montmorillonite K10 provided a better yield of **6** than that with Florisil<sup>®</sup>.

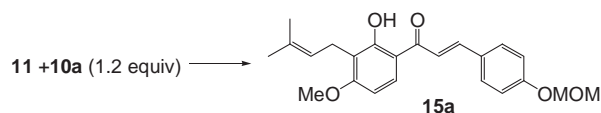
Table 1  
Rearrangement of **11a** in the presence of solid acid catalyst



Entry	Conditions	Yield/%				
		<b>6</b>	<b>13</b>	<b>14</b>	<b>10</b>	<b>8a</b>
1	Montmorillonite K10 (1 wt equiv), $CH_2Cl_2$ , 0 °C, 0.5 h	53	25	7	0	4
2	Florisil (10 wt equiv), toluene, reflux, 2 h	27	32	0	8	10

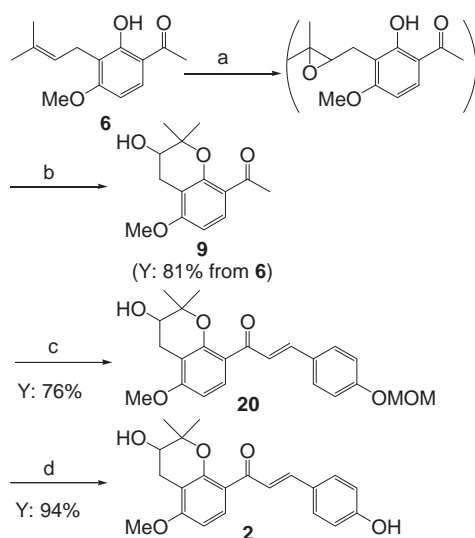
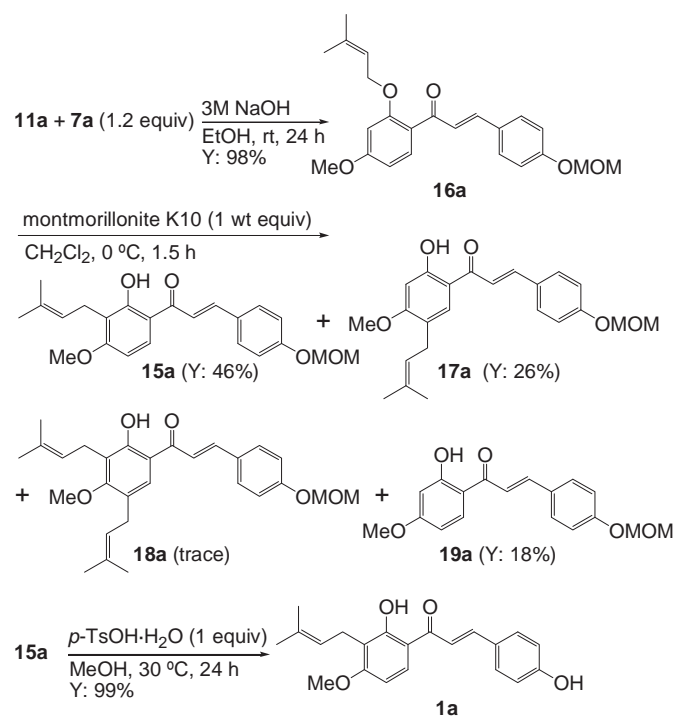
The Claisen–Schmidt condensation of **6** with **7a** was attempted under several conditions as shown in Table 2, but the desired chalcone **15a** was obtained in unsatisfactory yields in all cases. The low yield of **15a** is presumably caused by secondary cyclization of 2'-hydroxychalcone to flavanone as reported in the literature.<sup>16</sup> In contrast, **11a** was allowed to react directly with **7a** prepared from **12** to afford 2'-prenyloxychalcone **16a** in very high yield (Scheme 3). The [1,3]-sigmatropic rearrangement of **16a** using montmorillonite K10 at 0 °C gave the desired 3'-prenylchalcone **15a** in 46% yield as a main product, along with 5'-prenylchalcone **17a** (26%), 3',5'-diprenylchalcone **18a** (0.9%), and chalcone with no prenyl group **19a** (18%). Romano and Casillas were previously reported that a 3'-prenylchalcone was only obtained in low yield on a similar [1,3]-sigmatropic rearrangement of 2'-prenyloxychalcone with montmorillonite KSF in toluene at 100 °C.<sup>17</sup> Since 3'-prenylchalcone **15a** was obtained in moderate yield in the present conditions, montmorillonite K10 was ascertained to be more appropriate than montmorillonite KSF on the rearrangement of 2'-prenyloxychalcones. Deprotection of **15a** using *p*-toluenesulfonic acid at 30 °C in methanol gave **1a** in high yield. Thus **1a** could be prepared from **8a** in 41% yield over four steps.

Table 2  
Claisen–Schmidt condensation of **11** with **10a**



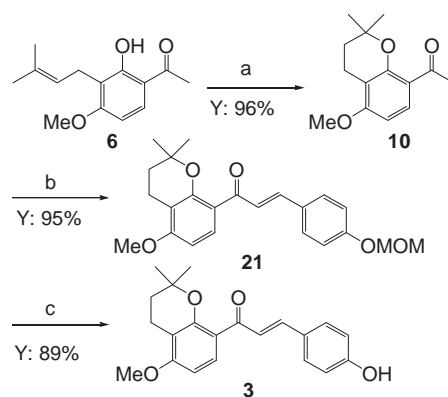
Entry	Conditions	Yield of <b>15a</b> /%
1	3 M NaOH, EtOH, rt, 24 h	38
2	50% KOH, EtOH, rt, 35 h	33
3	Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O (2.5 equiv), EtOH, 50 °C, rt, 1–72 h	23

Scheme 4 shows the synthetic route for chromanochalcone **2** from **6**. Oxidation of **6** with *m*-CPBA proceeded at room temperature to afford epoxide as an intermediate, which was immediately converted in situ into chroman **9** by subsequent cyclization with montmorillonite K10. The Claisen–Schmidt condensation of **9** with **7a** gave chalcone **20** in 76% yield. Deprotection of **20** using *p*-toluenesulfonic acid in refluxing methanol afforded **2** in 94% yield (28% total yield over six steps from **8a**).



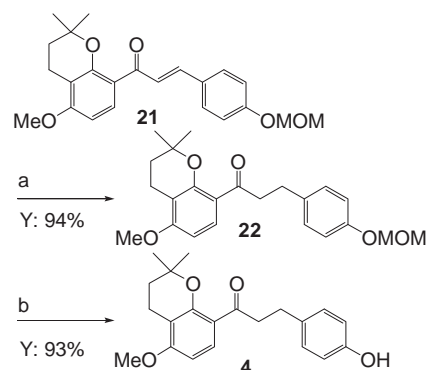
**Scheme 4.** Reagents and conditions: (a) *m*-CPBA (1.2 equiv), CH<sub>2</sub>Cl<sub>2</sub>, rt, 0.5 h; (b) montmorillonite K10 (1 wt equiv), CH<sub>2</sub>Cl<sub>2</sub>, rt, 1 h; (c) **7a** (1.2 equiv), 3 M NaOH, EtOH, rt, 20 h; (d) *p*-TsOH·H<sub>2</sub>O (1 equiv), MeOH, reflux, 2 h.

Synthetic route for chromanochalcone **3** from **6** is depicted in **Scheme 5**. Dauben et al. reported that short reaction times or low temperatures permitted the isolation of *ortho*-prenyl phenols on the [1,3]-sigmatropic rearrangement of prenyl phenyl ethers with montmorillonite KSF clay, while longer reaction times or higher temperatures provided the corresponding chromans in moderate yields.<sup>13</sup> Since the chromans probably produced from the intermediary *o*-prenylphenols under the reported conditions, cyclization of **6** into **10** was tried on similar conditions using montmorillonite K10. Treatment of **6** with montmorillonite K10 at 50 °C in toluene provided chroman **10** in 96% yield. The Claisen–Schmidt condensation of **10** with **7a** gave chalcone **21** in 95% yield. Deprotection of **21** under the same conditions as described above afforded **3** in 89% yield (39% total yield over five steps from **8a**).



**Scheme 5.** Reagents and conditions: (a) montmorillonite K10 (1 wt equiv), toluene, 50 °C, under N<sub>2</sub>, 40 h; (b) **7a** (1.2 equiv), 3 M NaOH, EtOH, rt, 20 h; (c) *p*-TsOH·H<sub>2</sub>O (1 equiv), MeOH, reflux, 1 h.

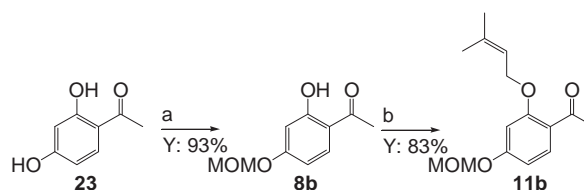
**Scheme 6** shows synthesis of **4**. Hydrogenation of **21** in the presence of Pd/C catalyst gave **22**, which was deprotected under the same conditions as described above to yield **4** in 38% total yield over six steps from **8a**.



**Scheme 6.** Reagents and conditions: (a) Pd/C (0.1 wt equiv), under H<sub>2</sub> (1 atm), EtOH, rt, 0.5 h; (b) *p*-TsOH·H<sub>2</sub>O (1 equiv), MeOH, reflux, 1 h.

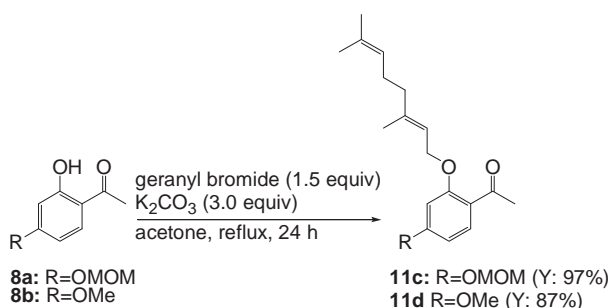
## 2.2. Synthesis of chalcones **1b–d** and **5a–d** and geranylated chalcones **1e, f**

Synthesis of prenylated chalcones **1b–d** and **5a–d** and geranylated chalcones **1e, f** was next performed. Synthetic route for these chalcones is similar to that described in the synthesis of 4-hydroxyderricin (**1a**). 4'-Methoxymethoxy-2'-prenyloxyacetophenone (**11b**) was prepared from **23** by methoxymethylation followed by prenylation (**Scheme 7**). Geranylation of **8a, b** with geranyl bromide

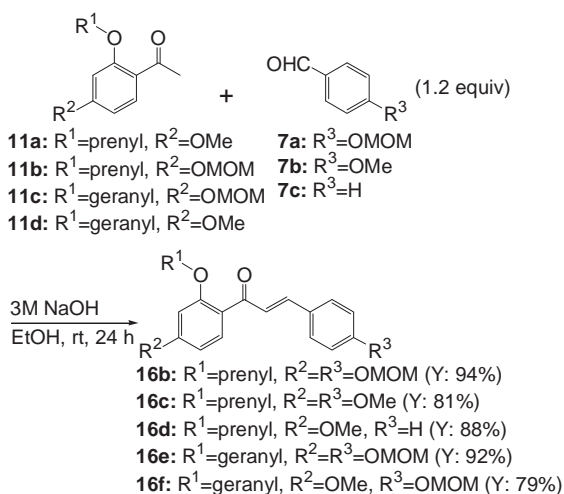


**Scheme 7.** Reagents and conditions: (a) chloromethyl methyl ether (1.2 equiv), K<sub>2</sub>CO<sub>3</sub> (3.0 equiv), acetone, 0 °C, 3 h; (b) 1-chloro-3-methyl-2-butene (2.0 equiv), K<sub>2</sub>CO<sub>3</sub> (3.0 equiv), acetone, reflux, 24 h.

in the presence of K<sub>2</sub>CO<sub>3</sub> afforded the corresponding 2'-geranyloxyacetophenone **11c, 11d** in good yields (**Scheme 8**). Claisen–Schmidt condensation of **11a–d** with **7a–c** in the presence of 3 M NaOH afforded the corresponding chalcones **16b–f** in good yields (**Scheme 9**). The rearrangement of **16b–f** using

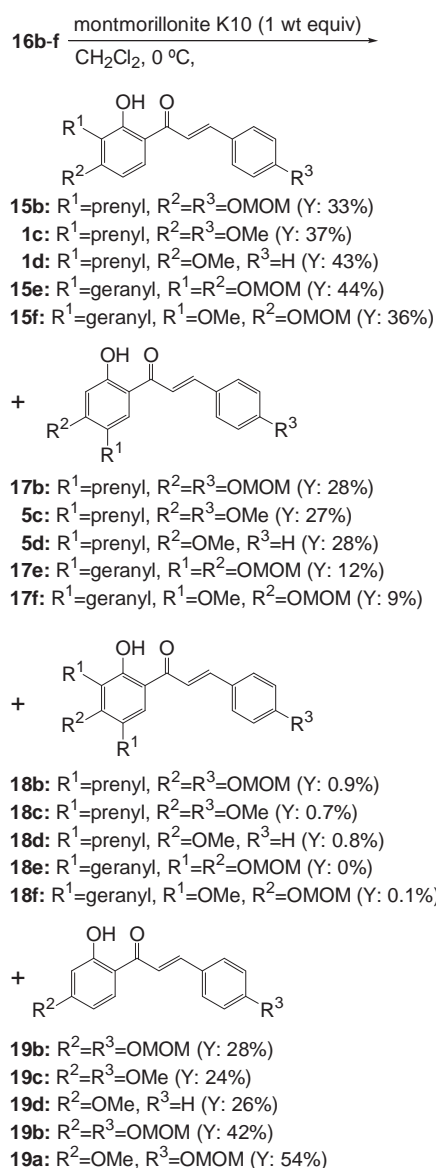


Scheme 8.



Scheme 9.

montmorillonite K10 at 0 °C gave: 3'-prenylated or 3'-geranylated chalcones **15b**, **1c**, **d**, and **15e**, **15f**; 5'-prenylated or 5'-geranylated chalcones **17b**, **2c**, **d**, and **17e**, **17f**; trace amounts of diprenylated or digeranylated chalcones **18b–f**; and non-substituted chalcones **19a–d**, respectively (Scheme 10). Thus we achieved first geranyl rearrangement of **16e** and **16f** using montmorillonite K10. Derricin (**1d**) could be prepared over three steps from **8a** in 27% yield: **1d** was reported to be isolated from *Derris sericea*,<sup>18</sup> *Lonchocarpus neuroscapha*,<sup>19</sup> *Lonchocarpus sericeus*,<sup>20</sup> and *Erythroxylum barbatum*;<sup>21</sup> it exhibited inhibitory effects on platelet aggregation,<sup>22</sup> and had already been prepared by Khanna et al.<sup>22</sup> Deprotection of **15b**, **15e**, **15f**, and **17a**, **b** gave naturally occurring chalcones (Scheme 11). Isobavachalcone (**1b**) was first synthesized by deprotection of **15b** with 3 M HCl in MeOH under reflux in 72% yield. Compound **1b** was reported to be isolated from *A. keiskei*<sup>3</sup> and the other plants;<sup>23–29</sup> it exhibited inhibitory effects on the induction of EBV-EA by TPS in Raji cells,<sup>3</sup> and exhibited antimycobacterial activity.<sup>28</sup> 5'-Prenylchalcone **17b** was deprotected with 3 M HCl to give broussonchalcone B (**5b**) in 35% yield along with bavachin (42%) as a by-product. On the other hand, the yield of **5b** could be improved by deprotection with a catalytic amount of carbon tetrabromide in refluxing 2-propanol according to the procedure reported by Lee et al.<sup>30</sup> **5b** was reported to be isolated from *Broussonetia papyrifera*<sup>31</sup> and had already been prepared by Nougoué-Tchamo et al.<sup>32</sup> Deprotection of **17a** by the same conditions gave bava-chalcone (**5a**) in 84% yield, which was reported to be isolated from *Psoralea corylifolia*;<sup>33</sup> it exhibited antibacterial activities<sup>24</sup> as well as inhibitory effects on osteoclast differentiation through suppression of NFATc1 induction by RANKL.<sup>34</sup> Although synthesis of **5a** had already been prepared from **8a** in only 1.5% yield by Jain et al.,<sup>35</sup> the

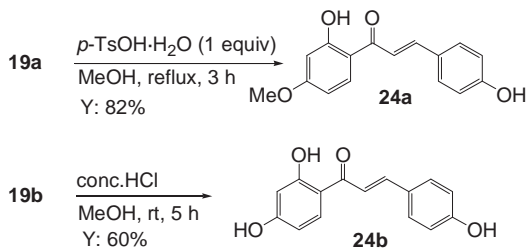
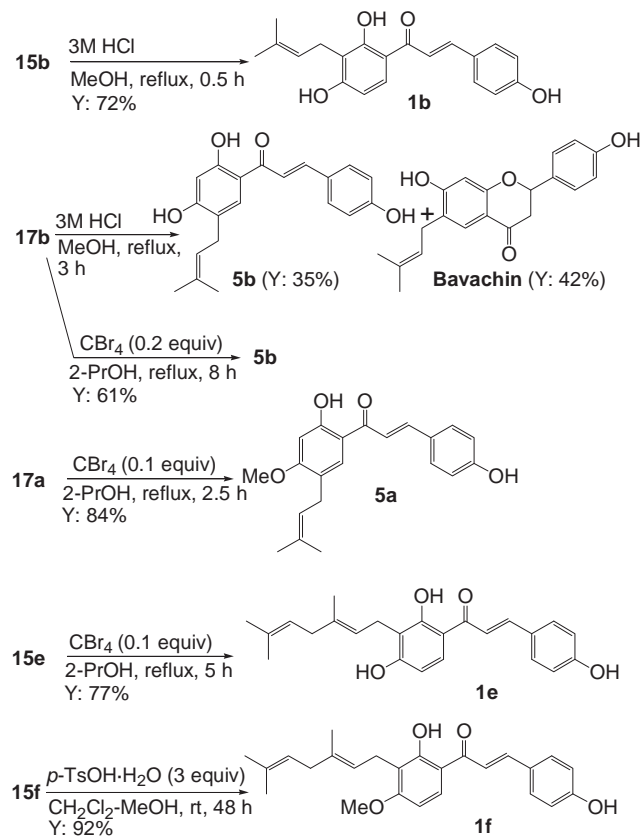


Scheme 10.

yield of **5a** from **8a** could be increased up to 20% in the present study. Xanthoangelol (**1e**) was synthesized in 77% yield from geranylated chalcone **15e** by the deprotection using carbon tetrabromide: **1e** could be prepared from **23** in 28% yield over five steps. Jung et al. previously reported that another method for synthesis of **1e** was via direct geranylation of **23** in 17% yield from **23**.<sup>11</sup> The yield of **1e** on our synthesis is somewhat high. Deprotection of **15f** with *p*-toluenesulfonic acid in CH<sub>2</sub>Cl<sub>2</sub>/MeOH at room temperature afforded Xanthoangelol F (**1f**) in 92% yield. Thus **1f** could be first synthesized from **8a** in 23% yield over four steps. Moreover 4'-methylisoliquiritigenin (**24a**) and isoliquiritigenin (**24b**) were prepared from **19a** and **19b**, respectively (Scheme 12).

### 2.3. Antibacterial activity

Antibacterial activity of synthesized chalcones **1a–f**, **2–4**, **5a–d**, **24a–b**, and **19c–d** was examined against both Gram-negative (*Escherichia coli*, *Proteus mirabilis*, *Pseudomonas fluorescens*) and Gram-positive bacteria (*Bacillus subtilis*, *Staphylococcus epidermidis*, *Micrococcus luteus*). The MIC values are summarized in Table 3. All chalcones had no effect against Gram-negative bacteria.



**Table 3**  
Antibacterial activity of chalcones

Chalcone	MIC ( $\mu\text{g/ml}$ )					
	<i>E. coli</i>	<i>P. mirabilis</i>	<i>P. fluorescens</i>	<i>B. subtilis</i>	<i>S. epidermidis</i>	<i>M. luteus</i>
<b>1a</b>	>256	>256	>256	2	2	2
<b>1b</b>	>256	>256	>256	4	4	4
<b>1c</b>	>256	>256	>256	>256	>256	>256
<b>1d</b>	>256	>256	>256	>256	>256	>256
<b>1e</b>	>256	>256	>256	4	4	4
<b>1f</b>	>256	>256	>256	64	64	64
<b>2</b>	>256	>256	>256	>256	>256	>256
<b>3</b>	>256	>256	>256	>256	>256	>256
<b>4</b>	>256	>256	>256	>256	>256	>256
<b>5a</b>	>256	>256	>256	4	4	4
<b>5b</b>	>256	>256	>256	8	8	16
<b>5c</b>	>256	>256	>256	>256	>256	>256
<b>5d</b>	>256	>256	>256	>256	>256	>256
<b>24a</b>	>256	>256	>256	>256	>256	>256
<b>24b</b>	>256	>256	>256	128	128	128
<b>19c</b>	>256	>256	>256	>256	>256	>256
<b>19d</b>	>256	>256	>256	>256	>256	>256
Streptomycin	<2	<2	<2	2	2	2

4-Hydroxyderricin (**1a**), isobavachalcone (**1b**), xanthoangelol (**1e**), xanthoangelol F (**1f**), bavavachalcone (**5a**), and brousochalcone B (**5b**) were active compounds against Gram-positive bacteria. From comparison of antibacterial activity against Gram-positive bacteria between prenylated chalcones, such as 4-hydroxyl analogs **1a**, **1b**, **5a**, and **5b**, 4-methoxy analogs **1c** and **5c**, and non-substituted analogs **1d** and **5d**, the hydroxyl group on the B-ring is found to enhance antibacterial activity. The 3'-prenylchalcones **1a** and **5a** and 5'-prenylchalcones **1b** and **5c** showed significant activity, but chalcones with no prenyl group, such as **24a**, **24b**, **2**, **3**, and **4** showed very weak activity. The prenyl moiety on the A-ring is revealed to contribute an increase in bacterial activity. The methoxy group at 4'-position on the A-ring slightly influence on the activity. On the other hand, 3'-geranylchalcone with 4'-hydroxy group **1e** showed stronger activity than that with 4'-hydroxy group **1f**. Yin et al.<sup>33</sup> and Ávila et al.<sup>36</sup> previously reported antibacterial activities of **1b**, **5a** and **1a–e**, **24b**, respectively. The present tendency for the activity of the synthesized chalcones is in agreement with their reports.

### 3. Conclusion

Total synthesis of prenylated chalcones, such as 4-hydroxyderricin (**1a**), isobavachalcone (**1b**), derricin (**1d**), xanthoangelol H (**2**), deoxyxanthoangelol H (**3**), deoxydihydroxanthoangelol H (**4**), bavavachalcone (**5a**), and brousochalcone B (**5b**) and geranylated chalcones, such as xanthoangelol (**1e**), xanthoangelol F (**1f**) has been accomplished via the [1,3]-sigmatropic rearrangement of 2'-prenyloxyacetophenone, 2'-prenyloxychalcones or 2'-geranyloxychalcones using montmorillonite K10 as a catalyst. 3'-Prenylchalcones **1a**, **1b**, 5'-prenylchalcones **5a**, **5b**, and 3'-geranylchalcone **1e** strongly inhibited Gram-positive bacteria.

### 4. Experimental

#### 4.1. General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker AV400 M spectrometer in CDCl<sub>3</sub>, MeOD-*d*<sub>4</sub>, acetone-*d*<sub>6</sub>, or DMSO-*d*<sub>6</sub> solution with TMS ( $\delta$  0.00) as an internal standard. IR spectra were recorded with a Jasco FT/IR-4100 spectrometer in Nujol mull, CHCl<sub>3</sub> or using KBr pellets. Melting points were measured on a Buchi melting point M565 (uncorrected). High resolution mass spectrometry (HRMS) was performed on a Hitachi M-2000AM mass spectrometer in electron impact mode at 70 eV. Silica gel 60 N purchased from Fuji Silysia Co. Ltd. was used for column chromatography. TLC plates silica gel 60 F<sub>254</sub> (layer thickness 0.25 mm) and PLC plate silica gel 60 F<sub>254</sub> (20×20 cm, layer thickness 1 mm) were purchased from Kanto Chemical Co., Inc. All commercial chemicals were analytical grade quality.

#### 4.2. 2'-Prenyloxy-4'-methoxyacetophenone (**11a**)

A mixture of 2'-hydroxy-4'-methoxyacetophenone **8a** (167 mg, 1 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (415 mg, 3 mmol), and 80% 1-chloro-3-methyl-2-butene (261 mg, 2 mmol) was stirred in dry acetone (5 cm<sup>3</sup>) under reflux for 24 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **11a** (214 mg, 91%) as colorless oil; *R*<sub>f</sub> (10% EtOAc/hexane) 0.18;  $\nu_{\text{max}}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3050, 3000, 2950, 1675, 1620, 1600, 1500, 1450, 1390, 1360, 1260, 1170, 1140, 1000;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.76 (3H, s, CH<sub>3</sub>), 1.81 (3H, s, CH<sub>3</sub>), 2.60 (3H, s, COCH<sub>3</sub>), 3.84 (3H, s, OCH<sub>3</sub>), 4.58 (2H, d, *J*=6.6 Hz, OCH<sub>2</sub>CH), 5.47–5.54 (1H, m, CH<sub>2</sub>CH=C), 6.45 (1H, d, *J*=2.3 Hz, C<sub>3</sub>H), 6.50 (1H, dd, *J*=2.3 and 8.8 Hz,

$C_5H$ ), 7.83 (1H, d,  $J=8.8$  Hz,  $C_6H$ );  $\delta_C$  (CDCl<sub>3</sub>) 18.21, 25.68, 31.98, 55.43, 65.35, 99.23, 105.02, 119.00, 121.44, 132.55, 138.29, 160.39, 164.32, 197.89; HRMS:  $M^+$ , found 234.1291.  $C_{14}H_{18}O_3$  requires 234.1256.

#### 4.3. 4-Methoxymethoxybenzaldehyde (7a)

To a stirred solution of 4-hydroxybenzaldehyde (**12**) (122 mg, 1 mmol) and anhydrous  $K_2CO_3$  (553 mg, 4 mmol) in dry acetone (5 cm<sup>3</sup>) was slowly added chloromethyl methyl ether (161 mg, 1.2 mmol) at room temperature and stirred for 2 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **7a** (145 mg, 87%) as colorless oil;  $R_f$  (10% EtOAc/hexane) 0.24;  $\nu_{max}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3050, 3000, 2980, 2950, 2850, 2780, 1700, 1620, 1600, 1520, 1440, 1400, 1320, 1260, 1160, 1120, 1100, 1000;  $\delta_H$  (CDCl<sub>3</sub>) 3.50 (3H, s, OCH<sub>3</sub>), 5.26 (2H, s, OCH<sub>2</sub>O), 7.17 (2H, d,  $J=8.8$  Hz,  $C_3H$  and  $C_5H$ ), 7.89 (2H, d,  $J=8.8$  Hz,  $C_2H$  and  $C_4H$ ), 9.90 (1H, s, OH);  $\delta_C$  (CDCl<sub>3</sub>) 56.3, 94.09, 116.26, 130.74, 131.84, 162.19, 190.85.

#### 4.4. Rearrangement of compound 11a with montmorillonite K10

To a stirred solution of **11a** (2812 mg, 12 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (12 cm<sup>3</sup>) was added montmorillonite K10 (2810 mg) at 0 °C and stirred for 0.5 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **6** (1482 mg, 53%), **13** (447 mg, 17%), **14** (236 mg, 7%), and **8a** (70 mg, 4%).

4.4.1. 2'-Hydroxy-4'-methoxy-3'-prenylacetophenone (**6**). Compound (**6**) as colorless oil;  $R_f$  (10% EtOAc/hexane) 0.20;  $\nu_{max}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3300, 3050, 2980, 2930, 2850, 1630, 1500, 1420, 1370, 1340, 1270, 1090;  $\delta_H$  (CDCl<sub>3</sub>) 1.67 (3H, d,  $J=0.9$  Hz,  $CH_3$ ), 1.78 (3H, s,  $CH_3$ ), 2.56 (3H, s, COCH<sub>3</sub>), 3.35 (2H, d,  $J=7.1$  Hz, Ph-CH<sub>2</sub>CH), 3.89 (3H, s, OCH<sub>3</sub>), 5.16–5.23 (1H, m, C=CHCH<sub>2</sub>), 7.45 (1H, d,  $J=9.0$  Hz,  $C_5H$ ), 7.60 (1H, d,  $J=9.0$  Hz,  $C_6H$ ), 12.7 (1H, s, OH);  $\delta_C$  (CDCl<sub>3</sub>) 17.75, 21.59, 25.76, 26.21, 55.72, 102.06, 114.36, 117.33, 121.93, 130.17, 131.85, 161.74, 163.21, 202.83; HRMS:  $M^+$ , found 234.1246.  $C_{14}H_{18}O_3$  requires 234.1256.

4.4.2. 2'-Hydroxy-4'-methoxy-5'-prenylacetophenone (**13**). Compound (**13**) as colorless oil;  $R_f$  (10% EtOAc/hexane) 0.32;  $\nu_{max}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3050, 2980, 2930, 2850, 1630, 1500, 1440, 1380, 1340, 1270, 1080;  $\delta_H$  (CDCl<sub>3</sub>) 1.71 (3H, s,  $CH_3$ ), 1.75 (3H, s,  $CH_3$ ), 2.54 (3H, s, COCH<sub>3</sub>), 3.22 (2H, d,  $J=7.1$  Hz, Ph-CH<sub>2</sub>CH), 3.86 (3H, s, OCH<sub>3</sub>), 5.22–5.29 (1H, m, C=CHCH<sub>2</sub>), 6.39 (1H, s,  $C_3H$ ), 7.40 (1H, s,  $C_6H$ ), 12.71 (1H, s, OH);  $\delta_C$  (CDCl<sub>3</sub>) 17.74, 25.74, 26.15, 27.75, 55.95, 99.00, 113.13, 121.63, 121.99, 130.69, 133.01, 163.85, 164.03, 202.50; HRMS:  $M^+$ , found 234.1240.  $C_{14}H_{18}O_3$  requires 234.1256.

4.4.3. 3',5'-Diprenyl-2'-hydroxy-4'-methoxyacetophenone (**14**). Compound (**14**) as colorless oil;  $R_f$  (10% EtOAc/hexane) 0.44;  $\delta_H$  (CDCl<sub>3</sub>) 1.68 (3H, d,  $J=1.1$  Hz,  $CH_3$ ), 1.73 (3H, s,  $CH_3$ ), 1.76 (3H, d,  $J=1.0$  Hz,  $CH_3$ ), 1.79 (3H, s,  $CH_3$ ), 1.75 (3H, s,  $CH_3$ ), 2.57 (3H, s, COCH<sub>3</sub>), 3.30 (2H, d,  $J=7.1$  Hz, Ph-CH<sub>2</sub>CH), 3.38 (2H, d,  $J=6.7$  Hz, Ph-CH<sub>2</sub>CH), 3.76 (3H, s, OCH<sub>3</sub>), 5.20–5.29 (2H, m, C=CHCH<sub>2</sub> × 2), 7.40 (1H, s,  $C_6H$ ), 12.60 (1H, s, OH);  $\delta_C$  (CDCl<sub>3</sub>) 17.90, 22.84, 25.74, 26.55, 27.99, 61.19, 116.31, 122.40, 122.72, 123.51, 125.59, 129.34, 131.89, 133.02, 160.96, 162.91, 203.55.

#### 4.5. 2'-Hydroxyl-4'-methoxy-4-methoxymethoxy-3'-prenyl-chalcone (**15a**)

To a stirred solution of **6** (118 mg, 0.5 mmol) and **7a** (100 mg, 0.6 mmol) in ethanol (5 cm<sup>3</sup>) was slowly added 3 M NaOH (5 cm<sup>3</sup>) at 0 °C, after which the reaction mixture was stirred at room temperature for 24 h. After completion of reaction (TLC), the solution was extracted with ethyl acetate (3 × 20 cm<sup>3</sup>). The organic layers were combined, washed with saturated sodium chloride solution, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **15a** (73 mg, 38%) as yellow needle crystal; mp (EtOAc/hexane) 109.1–110.0 °C;  $R_f$  (20% EtOAc/hexane) 0.34;  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 3050, 3000, 2950, 2900, 1640, 1620, 1590, 1460, 1430, 1380, 1320, 1290, 1220, 1180, 1160, 1120, 1080, 1000;  $\delta_H$  (CDCl<sub>3</sub>) 1.68 (3H, d,  $J=1.7$  Hz,  $CH_3$ ), 1.80 (3H, s,  $CH_3$ ), 3.39 (2H, d,  $J=7.1$  Hz, Ph-CH<sub>2</sub>CH), 3.49 (3H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 3.90 (3H, s, OCH<sub>3</sub>), 5.21 (2H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 5.21–5.26 (1H, m, C=CHCH<sub>2</sub>), 6.49 (1H, d,  $J=9.0$  Hz,  $C_5H$ ), 7.07 (2H, d,  $J=8.8$  Hz,  $C_3H$  and  $C_5H$ ), 7.48 (1H, d,  $J=15.4$  Hz,  $C_6H$ ), 7.59 (2H, d,  $J=8.8$  Hz,  $C_2H$  and  $C_6H$ ), 7.79 (1H, d,  $J=9.0$  Hz,  $C_6H$ ), 7.84 (1H, d,  $J=15.4$  Hz,  $C_6H$ ), 13.44 (1H, s, OH);  $\delta_C$  (CDCl<sub>3</sub>) 17.80, 21.72, 25.79, 55.75, 56.17, 94.20, 102.04, 114.67, 116.53, 117.58, 118.65, 122.05, 128.67, 129.09, 130.16, 131.85, 143.77, 159.24, 163.01, 163.21, 192.23; HRMS:  $M^+$ , found 382.1826.  $C_{23}H_{26}O_5$  requires 382.1780.

#### 4.6. 4'-Methoxy-4-methoxymethoxy-2'-prenylloxychalcone (**16a**)

To a stirred solution of **11a** (118 mg, 0.5 mmol) and **7a** (100 mg, 0.6 mmol) in ethanol (5 cm<sup>3</sup>) was slowly added 3 M NaOH (5 cm<sup>3</sup>) at 0 °C, after which the reaction mixture was stirred at room temperature for 12 h. After completion of reaction (TLC), the solution was extracted with ethyl acetate (3 × 20 cm<sup>3</sup>). The organic layers were combined, washed with saturated sodium chloride solution, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **16a** (187 mg, 98%) as yellow needle crystal; mp (EtOAc/hexane) 78.6–79.6;  $R_f$  (20% EtOAc/hexane) 0.22;  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 3100, 3032, 3013, 2960, 2937, 2905, 2865, 2837, 2905, 2866, 2838, 2360, 1646, 1604, 1589, 1567, 1509, 1460, 1442, 1432, 1384, 1316, 1282, 1245, 12,004, 1171, 1151, 1120, 1078, 1024;  $\delta_H$  (CDCl<sub>3</sub>) 1.74 (3H, s,  $CH_3$ ), 1.79 (3H, s,  $CH_3$ ), 3.48 (3H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 3.85 (3H, s, OCH<sub>3</sub>), 4.58 (2H, d,  $J=6.8$  Hz, Ph-CH<sub>2</sub>CH), 5.20 (2H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 5.52–5.56 (1H, m, C=CHCH<sub>2</sub>), 6.49 (1H, d,  $J=2.0$  Hz,  $C_3H$ ), 6.55 (1H, dd,  $J=2.0$  and 8.8 Hz,  $C_5H$ ), 7.03 (2H, d,  $J=8.8$  Hz,  $C_3H$  and  $C_5H$ ), 7.52 (2H, d,  $J=8.8$  Hz,  $C_2H$  and  $C_6H$ ), 7.59 (1H, d,  $J=15.9$  Hz,  $C_6H$ ), 7.65 (1H, d,  $J=15.9$  Hz,  $C_6H$ ), 7.83 (1H, d,  $J=8.8$  Hz,  $C_6H$ );  $\delta_C$  (CDCl<sub>3</sub>) 18.28, 25.26, 55.51, 56.11, 65.56, 94.24, 99.770, 105.44, 116.37, 119.16, 122.40, 125.94, 129.55, 129.76, 133.09, 138.77, 141.13, 158.61, 159.99, 164.11, 189.99; HRMS:  $M^+$ , found 382.1789.  $C_{23}H_{26}O_5$  requires 382.1780.

#### 4.7. Rearrangement of compound 16a

To a stirred solution of **16a** (3825 mg, 10 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was added montmorillonite K10 (3830 mg) at 0 °C and stirred for 1.5 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **15a** (1748 mg, 46%), **17a** (1010 mg, 26%), **18a** (22 mg, 0.9%), and **19a** (575 mg, 18%).

**4.7.1. 2'-Hydroxyl-4'-methoxy-4-methoxymethoxy-5'-prenylchalcone (17a).** Compound (17a) as yellow needle crystal; mp (EtOAc/hexane) 82.8–83.8 °C;  $R_f$  (20% EtOAc/hexane) 0.38;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3004, 2980, 2959, 2911, 2897, 2853, 2784, 2730, 2687, 2657, 1633, 1602, 1562, 1506, 1440, 1422, 1404, 1381, 1321, 1297, 1278, 1233, 1206, 1171, 1155, 1135, 1112, 1096, 1085;  $\delta_H$  (CDCl<sub>3</sub>) 1.74 (3H, d,  $J=0.5$  Hz, CH<sub>3</sub>), 1.78 (3H, d,  $J=1.0$  Hz, CH<sub>3</sub>), 3.26 (2H, d,  $J=7.1$  Hz, Ph-CH<sub>2</sub>CH), 3.49 (3H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 3.87 (3H, s, OCH<sub>3</sub>), 5.23 (2H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 5.26–5.31 (1H, m, C=CHCH<sub>2</sub>), 6.43 (1H, s, C<sub>3</sub>H), 7.09 (2H, d,  $J=8.7$  Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.45 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 7.59 (1H, s, C<sub>6</sub>H), 7.60 (2H, d,  $J=8.7$  Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.84 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 13.47 (1H, s, OH);  $\delta_C$  (CDCl<sub>3</sub>) 17.77, 21.68, 25.76, 55.70, 56.13, 94.14, 102.01, 114.61, 116.47, 117.49, 118.59, 122.02, 128.60, 129.07, 130.12, 131.79, 143.73, 159.20, 162.96, 163.16, 192.17; HRMS: M<sup>+</sup>, found 382.1819. C<sub>23</sub>H<sub>26</sub>O<sub>5</sub> requires 382.1780.

**4.7.2. 3',5'-Diprenyl-2'-hydroxyl-4'-methoxy-4-methoxymethoxychalcone (18a).** Compound (18a) as yellow needle crystal;  $R_f$  (20% EtOAc/hexane) 0.42;  $\delta_H$  (CDCl<sub>3</sub>) 1.70 (3H, d,  $J=1.0$  Hz, CH<sub>3</sub>), 1.76 (3H, s, CH<sub>3</sub>), 1.79 (3H, d,  $J=1.0$  Hz, CH<sub>3</sub>), 1.80 (3H, s, CH<sub>3</sub>), 3.34 (2H, d,  $J=7.0$  Hz, Ph-CH<sub>2</sub>CH), 3.41 (2H, d,  $J=6.7$  Hz, Ph-CH<sub>2</sub>CH), 3.50 (3H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 3.78 (3H, s, OCH<sub>3</sub>), 5.23 (2H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 5.25–5.32 (2H, m, C=CHCH<sub>2</sub> × 2), 7.09 (2H, d,  $J=8.8$  Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.47 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 7.58 (1H, s, C<sub>6</sub>H), 7.60 (2H, d,  $J=8.8$  Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.86 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 13.27 (1H, s, OH).

**4.7.3. 2'-Hydroxyl-4'-methoxy-4-methoxymethoxychalcone (19a).** Compound (19a) as yellow needle crystal, mp (EtOAc/hexane) 74.2–75.2 °C;  $R_f$  (20% EtOAc/hexane) 0.26;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3005, 2956, 2937, 2920, 2901, 2849, 2833, 2788, 2750, 2688, 2665, 2560, 2373, 1631, 1604, 1577, 1509, 1468, 1444, 1421, 1367, 1327, 1311, 1296, 1282, 1220, 1173, 1152, 1135, 1113, 1080, 1018;  $\delta_H$  (CDCl<sub>3</sub>) 3.49 (3H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 3.85 (3H, s, OCH<sub>3</sub>), 5.22 (2H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 6.47 (1H, s, C<sub>3</sub>H), 6.48 (1H, d,  $J=9.2$  Hz, C<sub>5</sub>H), 7.08 (2H, d,  $J=8.7$  Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.46 (1H, d,  $J=15.5$  Hz, C<sub>6</sub>H), 7.60 (2H, d,  $J=8.7$  Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.82 (1H, d,  $J=9.2$  Hz, C<sub>6</sub>H), 7.85 (1H, d,  $J=15.5$  Hz, C<sub>6</sub>H), 13.52 (1H, s, OH);  $\delta_C$  (CDCl<sub>3</sub>) 55.58, 56.21, 94.21, 101.09, 107.65, 114.15, 116.57, 118.35, 128.57, 130.25, 131.15, 144.11, 159.36, 166.10, 166.66, 191.87; HRMS: M<sup>+</sup>, 314.1181. C<sub>18</sub>H<sub>18</sub>O<sub>5</sub> requires 314.1154.

#### 4.8. 4-Hydroxyderricin (1a)

To a stirred solution of 15a (192 mg, 0.5 mmol) in MeOH (50 cm<sup>3</sup>) was added *p*-toluenesulfonic acid monohydrate (95 mg, 0.5 mmol) and stirred at 30 °C for 24 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was evaporated under vacuum. After addition of 30 cm<sup>3</sup> of water, the mixture was extracted with ethyl acetate (3 × 50 cm<sup>3</sup>). The organic layers were combined, washed with brine, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound 1a (167 mg, 99%) as yellow needle crystal, mp (EtOAc/hexane) 136.0–137.0 °C;  $R_f$  (33% EtOAc/hexane) 0.18;  $\nu_{\max}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3640, 3050, 3000, 2950, 2890, 1650, 1620, 1590, 1520, 1507, 1450, 1430, 1390, 1322, 1250, 1230, 1180, 1122, 1082;  $\delta_H$  (CDCl<sub>3</sub>) 1.68 (3H, d,  $J=0.6$  Hz, CH<sub>3</sub>), 1.80 (3H, d,  $J=0.2$  Hz, CH<sub>3</sub>), 3.39 (2H, d,  $J=7.0$  Hz, Ph-CH<sub>2</sub>CH), 3.91 (3H, s, OCH<sub>3</sub>), 5.21–5.25 (1H, m, C=CHCH<sub>2</sub>), 5.50 (1H, br s, OH), 6.48 (1H, d,  $J=9.0$  Hz, C<sub>5</sub>H), 6.89 (2H, d,  $J=8.6$  Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.45 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 7.53 (2H, d,  $J=8.6$  Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.79 (1H, d,  $J=9.0$  Hz, C<sub>6</sub>H), 7.83 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 13.48 (1H, s, OH);  $\delta_C$  (CDCl<sub>3</sub>) 17.82, 21.73, 25.81, 55.78, 102.10, 114.66, 116.00, 117.59, 118.18, 122.03, 128.00, 129.14, 130.52, 131.94, 143.97, 157.97, 162.99, 163.25, 192.36; HRMS: M<sup>+</sup>, found 338.150. C<sub>21</sub>H<sub>22</sub>O<sub>4</sub> requires 338.1518.

#### 4.9. 8-Acetyl-2,2-dimethyl-3-hydroxy-5-methoxychroman (9)

To a stirred solution of 6 (696 mg, 3.0 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>) was added 77% 3-chloroperbenzoic acid (*m*-CPBA) (807 mg, 3.6 mmol) at 0 °C, after which the reaction mixture was stirred for 0.5 h at room temperature. After consumption of compound 6 (TLC), montmorillonite K10 (696 mg) was added and stirred 1 h at room temperature. The reaction mixture was filtrated. After addition of 10 cm<sup>3</sup> of ethyl acetate, the organic layer was washed with saturated Na<sub>2</sub>CO<sub>3</sub>, water, brine, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound 9 (603 mg, 81%) as colorless crystal; mp (EtOAc/hexane) 100.8–101.8 °C;  $R_f$  (33% EtOAc/hexane) 0.12;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3367, 2980, 2931, 2899, 2866, 2841, 1643, 1590, 1487, 1467, 1433, 1362, 1326, 1271, 1223, 1192, 1174, 1160, 1142, 1122, 1096, 1053, 1024, 1013;  $\delta_H$  (CDCl<sub>3</sub>) 1.38 (3H, s, CH<sub>3</sub>), 1.41 (3H, s, CH<sub>3</sub>), 1.78 (1H, br d,  $J=5.8$  Hz, OH), 2.60 (3H, s, COCH<sub>3</sub>), 2.69 (1H, dd,  $J=5.6$  and 17.6 Hz, C<sub>4</sub>H), 2.93 (1H, dd,  $J=5.2$  and 17.6 Hz, C<sub>4</sub>H), 3.84–3.86 (1H, m, C<sub>3</sub>H), 3.87 (3H, s, OCH<sub>3</sub>), 6.50 (1H, d,  $J=8.8$  Hz, C<sub>6</sub>H), 7.75 (1H, d,  $J=8.8$  Hz, C<sub>7</sub>H);  $\delta_C$  (CDCl<sub>3</sub>) 21.86, 24.86, 26.51, 32.18, 55.66, 68.71, 77.57, 102.29, 108.13, 121.26, 130.20, 153.95, 161.65, 198.24; HRMS: M<sup>+</sup>, found 250.2988. C<sub>23</sub>H<sub>26</sub>O<sub>5</sub> requires 250.2903.

#### 4.10. 4-Methoxymethylxanthoangelol H (20)

To a stirred solution of 9 (151 mg, 0.6 mmol) and 7a (120 mg, 0.72 mmol) in ethanol (10 cm<sup>3</sup>) was slowly added 3 M NaOH (10 cm<sup>3</sup>) at 0 °C, after which the reaction mixture was stirred at room temperature for 20 h. After completion of reaction (TLC), the solution was extracted with ethyl acetate (3 × 25 cm<sup>3</sup>). The organic layers were combined, washed with saturated sodium chloride solution, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound 20 (182 mg, 76%) as yellow needle crystal; mp (EtOAc/hexane) 134.8–135.8 °C;  $R_f$  (33% EtOAc/hexane) 0.10;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3453, 3100, 3078, 3035, 3020, 2979, 2938, 2912, 2846, 2830, 1639, 1591, 1508, 1490, 1468, 1449, 1435, 1422, 1404, 1370, 1346, 1330, 1308, 1281, 1226, 1207, 1190, 1167, 1153, 1100, 1080, 1008;  $\delta_H$  (CDCl<sub>3</sub>) 1.39 (3H, s, CH<sub>3</sub>), 1.41 (3H, s, CH<sub>3</sub>), 2.72 (1H, dd,  $J=5.5$  and 17.6 Hz, C<sub>4</sub>H), 2.94 (1H, dd,  $J=5.2$  and 17.6 Hz, C<sub>4</sub>H), 3.49 (3H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 3.83–3.87 (1H, m, C<sub>3</sub>H), 3.87 (3H, s, OCH<sub>3</sub>), 5.21 (2H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 6.52 (1H, d,  $J=8.7$  Hz, C<sub>5</sub>H), 7.05 (2H, d,  $J=8.8$  Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.53 (2H, d,  $J=8.8$  Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.54 (1H, d,  $J=15.8$  Hz, C<sub>6</sub>H), 7.63 (1H, d,  $J=15.8$  Hz, C<sub>6</sub>H), 7.71 (1H, d,  $J=8.7$  Hz, C<sub>6</sub>H);  $\delta_C$  (CDCl<sub>3</sub>) 22.02, 26.58, 55.67, 56.14, 68.83, 77.48, 94.24, 108.12, 116.48, 122.23, 125.83, 129.44, 129.67, 130.02, 141.01, 153.24, 158.67, 161.35, 190.63; HRMS: M<sup>+</sup>, found 398.1729. C<sub>23</sub>H<sub>26</sub>O<sub>6</sub> requires 398.1765.

#### 4.11. Xanthoangelol H (2)

A mixture of 20 (198 mg, 0.5 mmol) and *p*-toluenesulfonic acid monohydrate (96 mg, 0.5 mmol) in MeOH (12 cm<sup>3</sup>) was stirred under reflux for 2 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was evaporated under vacuum. After addition of 10 cm<sup>3</sup> of water, the mixture was extracted with ethyl acetate (3 × 10 cm<sup>3</sup>). The organic layers were combined, washed with brine, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound 2 (166 mg, 94%) as yellow needle crystal, mp (EtOH) 219–220 °C;  $R_f$  (50% EtOAc/hexane) 0.10;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3270, 3118, 3005, 2977, 2938, 2872, 2841, 1641, 1592, 1556, 1439, 1401, 1385, 1367, 1335, 1310, 1283, 1234, 1209, 1186, 1166, 1141, 1101, 1073, 1055, 1022;  $\delta_H$  (DMSO-*d*<sub>6</sub>) 1.23 (3H, s, CH<sub>3</sub>), 1.30 (3H, s, CH<sub>3</sub>),

2.45 (1H, dd,  $J=7.0$  and  $17.3$  Hz,  $C_4'H$ ), 2.82 (1H, dd,  $J=5.4$  and  $17.3$  Hz,  $C_4''H$ ), 3.66–3.70 (1H, m,  $C_3H$ ), 3.83 (3H, s,  $OCH_3$ ), 5.23 (1H, br s,  $OH$ ), 6.62 (1H, d,  $J=8.8$  Hz,  $C_5'H$ ), 6.82 (2H, d,  $J=8.8$  Hz,  $C_3H$  and  $C_5H$ ), 7.42 (1H, s,  $C_2H$ ), 7.42 (1H, s,  $C_6'H$ ), 7.48 (1H, d,  $J=8.7$  Hz,  $C_6''H$ ), 7.51 (2H, d,  $J=8.8$  Hz,  $C_2H$  and  $C_6H$ );  $\delta_C$  (DMSO- $d_6$ ) 20.71, 25.35, 26.20, 55.69, 66.89, 77.56, 102.47, 109.07, 115.92, 121.49, 124.07, 125.97, 129.38, 129.94, 141.05, 152.89, 159.57, 160.56, 189.60; HRMS:  $M^+$ , found 354.1446.  $C_{21}H_{22}O_5$  requires 354.1467.

#### 4.12. 8-Acetyl-2,2-dimethyl-5-methoxychroman (10)

A mixture of **6** (59 mg, 0.25 mmol) and montmorillonite K10 (60 mg) was heated at  $50^\circ\text{C}$  under  $N_2$  for 40 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **10** (56 mg, 96%) as colorless oil;  $R_f$  (10% EtOAc/hexane) 0.16;  $\nu_{\max}$  ( $CHCl_3$ )/ $cm^{-1}$  3050, 3000, 2950, 1680, 1590, 1495, 1470, 1450, 1435, 1395, 1380, 1365, 1280, 1220, 1160, 1120, 1100;  $\delta_H$  ( $CDCl_3$ ) 1.38 (6H, s,  $CH_3 \times 2$ ), 1.84 (2H, t,  $J=6.9$  Hz,  $C_3H$ ), 2.59 (3H, s,  $COCH_3$ ), 2.66 (2H, t,  $J=6.9$  Hz,  $C_4H$ ), 3.86 (3H, s,  $OCH_3$ ), 6.45 (1H, d,  $J=8.8$  Hz,  $C_6H$ ), 7.72 (1H, d,  $J=8.8$  Hz,  $C_7H$ );  $\delta_C$  ( $CDCl_3$ ) 17.07, 26.78, 31.60, 62.20, 55.55, 74.95, 101.50, 109.80, 121.31, 129.64, 155.19, 161.23, 198.58; HRMS:  $M^+$ , found 234.1268.  $C_{14}H_{18}O_3$  requires 234.1256.

#### 4.13. 4-Methoxymethyldeoxyxanthoangelol H (21)

To a stirred solution of **10** (77 mg, 0.25 mmol) and **7a** (50 mg, 0.3 mmol) in ethanol ( $3\text{ cm}^3$ ) was slowly added 3 M NaOH ( $3\text{ cm}^3$ ) at  $0^\circ\text{C}$ , after which the reaction mixture was stirred at room temperature for 20 h. After completion of reaction (TLC), the solution was extracted with ethyl acetate ( $3 \times 15\text{ cm}^3$ ). The organic layers were combined, washed with saturated sodium chloride solution, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **21** (90 mg, 95%) as yellow needle crystal; mp (EtOAc/hexane)  $72.8$ – $73.8^\circ\text{C}$ ;  $R_f$  (10% hexane/EtOAc) 0.10;  $\nu_{\max}$  ( $CHCl_3$ )/ $cm^{-1}$  3004, 3000, 2952, 2930, 1658, 1600, 1520, 1495, 1485, 1445, 1423, 1338, 1320, 1282, 1243, 1240, 1180, 1160, 1122, 1100, 1080, 1000;  $\delta_H$  ( $CDCl_3$ ) 1.38 (6H, s,  $CH_3 \times 2$ ), 1.83 (2H, t,  $J=6.9$  Hz,  $C_3'H$ ), 2.68 (2H, t,  $J=6.9$  Hz,  $C_4'H$ ), 3.49 (3H, s,  $OCH_2OCH_3$ ), 3.90 (3H, s,  $OCH_3$ ), 5.20 (2H, s,  $OCH_2OCH_3$ ), 6.49 (1H, d,  $J=8.7$  Hz,  $C_5'H$ ), 7.05 (2H, d,  $J=8.8$  Hz,  $C_3'H$  and  $C_5'H$ ), 7.49 (1H, d,  $J=15.4$  Hz,  $C_2'H$ ), 7.60 (2H, d,  $J=8.8$  Hz,  $C_2'H$  and  $C_6'H$ ), 7.79 (1H, d,  $J=8.7$  Hz,  $C_6''H$ ), 7.85 (1H, d,  $J=15.4$  Hz,  $C_6'H$ );  $\delta_C$  ( $CDCl_3$ ) 17.15, 26.86, 31.72, 55.57, 56.09, 74.87, 94.21, 101.74, 109.90, 116.42, 122.28, 126.11, 129.57, 138.08, 140.44, 154.50, 158.53, 160.96, 190.91; HRMS:  $M^+$ , found 382.1768.  $C_{23}H_{26}O_5$  requires 382.1780.

#### 4.14. Deoxyxanthoangelol H (3)

A mixture of **21** (77 mg, 0.2 mmol) and *p*-toluenesulfonic acid monohydrate (38 mg, 0.2 mmol) in MeOH ( $5\text{ cm}^3$ ) was stirred under reflux for 1 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was evaporated under vacuum. After addition of  $7\text{ cm}^3$  of water, the mixture was extracted with ethyl acetate ( $3 \times 10\text{ cm}^3$ ). The organic layers were combined, washed with brine, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **3** (60 mg, 89%) as yellow needle crystal; mp (EtOH)  $214.0$ – $215.0^\circ\text{C}$ ;  $R_f$  (33% hexane/EtOAc) 0.10;  $\nu_{\max}$  (KBr)/ $cm^{-1}$  3104, 3014, 2981, 2945, 2843, 2805, 1630, 1592, 1529, 1510, 1487, 1439, 1421, 1382, 1368, 1338, 1284, 1244, 1227, 1202, 1188, 1164, 1119, 1098, 1075, 1018;  $\delta_H$  (DMSO- $d_6$ ) 1.37 (6H, s,  $CH_3 \times 2$ ), 1.85

(2H, t,  $J=6.8$  Hz,  $C_3''H$ ), 2.66 (2H, t,  $J=6.8$  Hz,  $C_4''H$ ), 3.89 (3H, s,  $OCH_3$ ), 6.67 (1H, d,  $J=8.8$  Hz,  $C_5'H$ ), 6.88 (2H, d,  $J=8.6$  Hz,  $C_3H$  and  $C_5H$ ), 7.47 (1H, s,  $C_2H$ ), 7.47 (1H, s,  $C_6'H$ ), 7.56 (1H, d,  $J=8.6$  Hz,  $C_6''H$ ), 7.57 (2H, d,  $J=8.8$  Hz,  $C_2H$  and  $C_6H$ ), 10.10 (1H, br s,  $OH$ );  $\delta_C$  (DMSO- $d_6$ ) 16.77, 26.39, 30.81, 55.65, 74.76, 102.15, 119.57, 115.92, 121.72, 124.13, 125.95, 129.30, 129.94, 140.97, 153.69, 159.55, 160.40, 189.78; HRMS:  $M^+$ , found 3382.1510.  $C_{21}H_{22}O_4$  requires 338.1518.

#### 4.15. 4-Methoxymethyl deoxydihydroxanthoangelol H (22)

A mixture of **21** (495 mg, 1.3 mmol) and 10% palladium on carbon (50 mg) in EtOH ( $5\text{ cm}^3$ ) was stirred at room temperature under  $H_2$  for 0.5 h. After completion of the reaction (TLC), the reaction mixture was vacuum-filtered through a pad of Celite. The mixture was evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **22** (467 mg, 94%) as colorless oil;  $R_f$  (20% EtOAc/hexane) 0.20;  $\nu_{\max}$  ( $CHCl_3$ )/ $cm^{-1}$  3050, 3000, 2990, 2940, 2860, 1675, 1600, 1520, 1500, 1478, 1450, 1438, 1380, 1358, 1285, 1220, 1160, 1100, 1090, 1050;  $\delta_H$  ( $CDCl_3$ ) 1.35 (6H, s,  $CH_3 \times 2$ ), 1.79 (2H, t,  $J=6.9$  Hz,  $C_3''H$ ), 2.65 (2H, t,  $J=6.9$  Hz,  $C_4''H$ ), 2.96 (2H, t,  $J=7.8$  Hz,  $C_6'H$ ), 3.29 (2H, t,  $J=7.8$  Hz,  $C_2'H$ ), 3.47 (3H, s,  $OCH_2OCH_3$ ), 3.86 (3H, s,  $OCH_3$ ), 5.15 (2H, s,  $OCH_2OCH_3$ ), 6.45 (1H, d,  $J=8.8$  Hz,  $C_5'H$ ), 6.95 (2H, d,  $J=8.7$  Hz,  $C_3'H$  and  $C_5'H$ ), 7.14 (2H, d,  $J=8.7$  Hz,  $C_2'H$  and  $C_6'H$ ), 7.67 (1H, d,  $J=8.8$  Hz,  $C_6''H$ );  $\delta_C$  ( $CDCl_3$ ) 17.14, 26.81, 29.79, 31.67, 45.22, 55.59, 55.90, 75.03, 94.64, 101.65, 109.84, 116.22, 121.36, 129.36, 129.80, 135.49, 154.77, 155.36, 161.09, 200.58; HRMS:  $M^+$ , found 384.198.  $C_{23}H_{28}O_6$  requires 384.1937.

#### 4.16. Deoxydihydroxanthoangelol H (4)

A mixture of **22** (385 mg, 1.0 mmol) and *p*-toluenesulfonic acid monohydrate (190 mg, 1.0 mmol) in MeOH ( $10\text{ cm}^3$ ) was stirred under reflux for 1 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was evaporated under vacuum. After addition of  $10\text{ cm}^3$  of water, the mixture was extracted with ethyl acetate ( $3 \times 30\text{ cm}^3$ ). The organic layers were combined, washed with brine, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **4** (315 mg, 93%) as colorless crystal; mp (EtOH)  $120.0$ – $121.0^\circ\text{C}$ ;  $R_f$  (20% EtOAc/hexane) 0.10;  $\nu_{\max}$  (KBr)/ $cm^{-1}$  3390, 3002, 2905, 1650, 1628, 1595, 1525, 1460, 1455, 1435, 1390, 1375, 1300, 1280, 1235, 1220, 1165, 1100;  $\delta_H$  (MeOD- $d_4$ ) 1.34 (6H, s,  $CH_3 \times 2$ ), 1.82 (2H, t,  $J=6.8$  Hz,  $C_3''H$ ), 2.66 (2H, t,  $J=6.8$  Hz,  $C_4''H$ ), 2.66 (2H, t,  $J=8.0$  Hz,  $C_6'H$ ), 3.24 (2H, t,  $J=8.0$  Hz,  $C_2'H$ ), 3.86 (3H, s,  $OCH_3$ ), 6.55 (1H, d,  $J=9.2$  Hz,  $C_5'H$ ), 6.67 (2H, d,  $J=8.4$  Hz,  $C_3'H$  and  $C_5'H$ ), 7.00 (2H, d,  $J=8.4$  Hz,  $C_2'H$  and  $C_6'H$ ), 7.54 (1H, d,  $J=8.8$  Hz,  $C_6''H$ );  $\delta_C$  (MeOD- $d_4$ ) 18.11, 26.95, 31.10, 32.62, 46.68, 56.21, 76.42, 102.97, 111.27, 116.10, 122.29, 130.16, 130.08, 130.80, 133.72, 156.09, 156.50, 162.97, 203.56; HRMS:  $M^+$ , found 340.1665.  $C_{21}H_{24}O_4$  requires 340.1675.

#### 4.17. 2'-Hydroxyl-4'-methoxymethoxyacetophenone (8b)

To a stirred solution of 2',4'-dihydroxyacetophenone (**23**) (1.55 g, 10.2 mmol) and anhydrous  $K_2CO_3$  (4.16 g, 30 mmol) in dry acetone ( $60\text{ cm}^3$ ) was slowly added 80% chloromethyl methyl ether (1.21 g, 12 mmol) at  $0^\circ\text{C}$  and stirred for 3 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **8b** (1.86 g, 93%) as colorless oil;  $R_f$  (20% EtOAc/hexane) 0.4;  $\nu_{\max}$  (neat)/ $cm^{-1}$  3095, 3076, 3049, 3003, 2964, 2942, 2918, 2856, 2832, 1623, 1587, 1503, 1466, 1445, 1428, 1408, 1364, 1335, 1303, 1265, 1233, 1210, 1169, 1160,



1142, 1080, 1066, and 1002;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.56 (3H, s, CH<sub>3</sub>), 3.48 (3H, s, OCH<sub>3</sub>), 5.21 (2H, s, OCH<sub>2</sub>O), 6.55 (1H, dd,  $J=2.4$  and 8.8 Hz, C<sub>5</sub>H), 6.59 (1H, d,  $J=2.4$  Hz, C<sub>3</sub>H), 7.65 (1H, d,  $J=8.8$  Hz, C<sub>6</sub>H), 12.61 (1H, s, OH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 26.21, 56.31, 93.93, 103.69, 108.12, 114.60, 132.34, 163.52, 164.78, 202.72; HRMS: M<sup>+</sup>, found 196.0745. C<sub>10</sub>H<sub>12</sub>O<sub>4</sub> requires 196.1999.

#### 4.18. 2'-Prenyloxy-4'-methoxymethoxyacetophenone (11b)

A mixture of 2'-hydroxy-4'-methoxymethoxyacetophenone (**8b**) (196 mg, 1 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (415 mg, 3 mmol), and 80% 1-chloro-3-methyl-2-butene (261 mg, 2 mmol) was stirred in dry acetone (5 cm<sup>3</sup>) under reflux for 24 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **11b** (219 mg, 83%) as colorless oil;  $R_{\text{f}}$  (5% EtOAc/hexane) 0.10;  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup> 2978, 2931, 2911, 2827, 1666, 1598, 1573, 1496, 1431, 1384, 1358, 1314, 1255, 1213, 1170, 1155, 1135, 1083, 1062, 1016;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.76 (3H, s, CH<sub>3</sub>), 1.80 (3H, d,  $J=0.7$  Hz, CH<sub>3</sub>), 2.58 (3H, s, COCH<sub>3</sub>), 3.49 (3H, s, OCH<sub>3</sub>), 4.59 (2H, d,  $J=6.6$  Hz, OCH<sub>2</sub>CH), 5.48–5.52 (1H, m, CH<sub>2</sub>CH=C), 6.60 (1H, d,  $J=2.2$  Hz, C<sub>3</sub>H), 6.64 (1H, dd,  $J=2.2$  and 8.7 Hz, C<sub>5</sub>H), 7.80 (1H, d,  $J=8.7$  Hz, C<sub>6</sub>H);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 18.27, 25.75, 32.05, 56.25, 65.44, 94.19, 100.81, 107.61, 119.01, 122.29, 132.38, 138.44, 160.31, 161.94, 198.08; HRMS: M<sup>+</sup>, found 264.1383. C<sub>15</sub>H<sub>20</sub>O<sub>4</sub> requires 264.1362.

#### 4.19. 2'-Geranyloxy-4'-methoxymethoxyacetophenone (11c)

A mixture of 2'-hydroxy-4'-methoxymethoxyacetophenone (**8b**) (196 mg, 1 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (415 mg, 3 mmol), and geranyl bromide (326 mg, 1.5 mmol) was stirred in dry acetone (5 cm<sup>3</sup>) under reflux for 24 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **11c** (321 mg, 97%) as colorless oil;  $R_{\text{f}}$  (5% EtOAc/hexane) 0.15;  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup> 2964, 2925, 2854, 2827, 1653, 1606, 1577, 1495, 1448, 1431, 1379, 1331, 1315, 1379, 1331, 1315, 1275, 1248, 1207, 1171, 1154, 1122, 1080, 1013;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.61 (3H, s, CH<sub>3</sub>), 1.67 (3H, d,  $J=0.9$  Hz, CH<sub>3</sub>), 1.75 (3H, d,  $J=0.4$  Hz, CH<sub>3</sub>), 2.08–2.15 (4H, m, C<sub>4</sub>'H and C<sub>5</sub>'H), 2.59 (3H, s, COCH<sub>3</sub>), 3.48 (3H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 4.62 (2H, d,  $J=6.6$  Hz, C<sub>1</sub>'H), 5.06–5.10 (1H, m, C<sub>6</sub>'H), 5.20 (2H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 5.49–5.52 (1H, m, C<sub>2</sub>'H), 6.60 (1H, d,  $J=2.2$  Hz, C<sub>3</sub>H), 6.64 (1H, dd,  $J=2.2$  and 8.7 Hz, C<sub>5</sub>H), 7.80 (1H, d,  $J=8.7$  Hz, C<sub>6</sub>H);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 16.64, 17.70, 25.66, 26.22, 32.05, 39.46, 56.25, 65.42, 94.19, 100.78, 107.63, 118.85, 122.27, 123.61, 131.91, 132.39, 141.78, 161.96, 198.09; HRMS: M<sup>+</sup>, found 332.1996. C<sub>15</sub>H<sub>20</sub>O<sub>4</sub> requires 332.1988.

#### 4.20. 2'-Geranyloxy-4'-methoxyacetophenone (11d)

A mixture of 2'-hydroxy-4'-methoxyacetophenone (**8a**) (1.63 g, 5 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (2.07 g, 15 mmol), and geranyl bromide (1.63 g, 7.5 mmol) was stirred in dry acetone (50 cm<sup>3</sup>) under reflux for 24 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **11d** (1.38 g, 87%) as colorless oil;  $R_{\text{f}}$  (5% EtOAc/hexane) 0.15;  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup> 2968, 2925, 2856, 1664, 1598, 1574, 1498, 1443, 1378, 1358, 1308, 1293, 1265, 1201, 1170, 1137, 1120, 1071, 1036;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.60 (3H, s, CH<sub>3</sub>), 1.67 (3H, s, CH<sub>3</sub>), 1.75 (3H, d,  $J=0.3$  Hz, CH<sub>3</sub>), 2.08–2.14 (4H, m, C<sub>4</sub>'H and C<sub>5</sub>'H), 2.58 (3H, s, COCH<sub>3</sub>), 3.84 (3H, s, OCH<sub>3</sub>), 4.61 (2H, d,  $J=6.5$  Hz, C<sub>1</sub>'H), 5.07–5.10

(1H, m, C<sub>6</sub>'H), 5.49–5.53 (1H, m, C<sub>2</sub>'H), 6.45 (1H, d,  $J=2.2$  Hz, C<sub>3</sub>H), 6.51 (1H, dd,  $J=2.2$  and 8.7 Hz, C<sub>5</sub>H), 7.83 (1H, d,  $J=8.7$  Hz, C<sub>6</sub>H);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 16.60, 17.66, 25.61, 26.16, 32.02, 39.39, 55.43, 65.34, 99.22, 105.04, 118.88, 121.42, 123.55, 141.62, 160.43, 164.34, 197.89.

#### 4.21. 4,4'-Bis(methoxymethoxy)-2'-prenyloxychalcone (16b)

To a stirred solution of **11b** (3.97 g, 15 mmol) and **7a** (2.70 g, 18 mmol) in ethanol (70 cm<sup>3</sup>) was slowly added 3 M NaOH (80 cm<sup>3</sup>) at 0 °C, after which the reaction mixture was stirred at room temperature for 20 h. After completion of reaction (TLC), the solution was extracted with ethyl acetate (3×250 cm<sup>3</sup>). The organic layers were combined, washed with saturated sodium chloride solution, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **16b** (5.81 g, 94%) as yellow oil;  $R_{\text{f}}$  (20% EtOAc/hexane) 0.20;  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup> 2955, 2933, 2905, 2827, 1735, 1652, 1600, 1573, 1509, 1428, 1382, 1329, 1314, 1173, 1153, 1121, 1080;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.75 (3H, d,  $J=0.6$  Hz, CH<sub>3</sub>), 1.79 (3H, d,  $J=0.6$  Hz, CH<sub>3</sub>), 3.49 (3H, s, OCH<sub>3</sub>), 3.50 (3H, s, OCH<sub>3</sub>), 4.60 (2H, d,  $J=6.8$  Hz, Ph–CH<sub>2</sub>CH), 5.21 (2H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 5.22 (2H, s, OCH<sub>2</sub>OCH<sub>3</sub>), 5.51–5.55 (1H, m, C=CHCH<sub>2</sub>), 6.64 (1H, d,  $J=2.0$  Hz, C<sub>3</sub>H), 6.70 (1H, dd,  $J=2.2$  and 8.6 Hz, C<sub>5</sub>H), 7.03 (2H, d,  $J=6.8$  Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.52 (2H, d,  $J=6.8$  Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.56 (1H, d,  $J=15.8$  Hz, C<sub>7</sub>H), 7.64 (1H, d,  $J=15.8$  Hz, C<sub>6</sub>H), 7.79 (1H, d,  $J=8.6$  Hz, C<sub>6</sub>H);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 18.29, 25.77, 56.13, 56.26, 65.61, 94.25, 101.23, 108.00, 116.38, 119.14, 123.23, 125.87, 129.50, 129.80, 132.81, 138.80, 141.36, 158.66, 159.80, 161.65, 190.24; HRMS: M<sup>+</sup>, found 412.1916. C<sub>24</sub>H<sub>28</sub>O<sub>6</sub> requires 412.1886.

#### 4.22. 4,4'-Dimethoxy-2'-prenyloxychalcone (16c)

To a stirred solution of **11a** (1170 mg, 5 mmol) and 4-methoxybenzaldehyde (**7b**) (820 mg, 6 mmol) in ethanol (50 cm<sup>3</sup>) was slowly added 3 M NaOH (50 cm<sup>3</sup>) at 0 °C, after which the reaction mixture was stirred at room temperature for 72 h. After completion of reaction (TLC), the solution was extracted with ethyl acetate (3×200 cm<sup>3</sup>). The organic layers were combined, washed with saturated sodium chloride solution, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **16c** (1430 mg, 81%) as yellow needle crystal; mp (EtOAc/hexane) 93.4–94.4 °C;  $R_{\text{f}}$  (20% EtOAc/hexane) 0.26;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3111, 3029, 3018, 2994, 2982, 2969, 22,949, 2936, 2911, 2836, 1647, 1602, 1572, 1509, 1499, 1460, 1440, 1420, 1387, 1328, 1309, 1283, 1246, 1213, 1194, 1174, 1119, 1024, 1003;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.74 (3H, d,  $J=0.4$  Hz, CH<sub>3</sub>), 1.79 (3H, d,  $J=0.6$  Hz, CH<sub>3</sub>), 3.84 (3H, s, OCH<sub>3</sub>), 3.86 (3H, s, OCH<sub>3</sub>), 4.59 (2H, d,  $J=6.8$  Hz, Ph–CH<sub>2</sub>CH), 5.53–5.57 (1H, m, C=CHCH<sub>2</sub>), 6.49 (1H, d,  $J=2.3$  Hz, C<sub>3</sub>H), 6.56 (1H, dd,  $J=2.3$  and 8.7 Hz, C<sub>5</sub>H), 6.90 (2H, d,  $J=8.8$  Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.53 (2H, d,  $J=8.8$  Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.58 (1H, d,  $J=15.7$  Hz, C<sub>7</sub>H), 7.65 (1H, d,  $J=15.7$  Hz, C<sub>6</sub>H), 7.83 (1H, d,  $J=8.7$  Hz, C<sub>6</sub>H);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 18.29, 25.78, 55.37, 55.52, 65.59, 99.73, 105.44, 114.23, 119.19, 122.46, 125.48, 128.50, 129.88, 133.07, 138.75, 141.39, 159.95, 161.08, 164.08, 190.06; HRMS: M<sup>+</sup>, found 352.1647. C<sub>23</sub>H<sub>26</sub>O<sub>5</sub> requires 352.1675.

#### 4.23. 4'-Methoxy-2'-prenyloxychalcone (16d)

To a stirred solution of **11a** (4.69 g, 20 mmol) and benzaldehyde (**7c**) (2.55 g, 24 mmol) in ethanol (120 cm<sup>3</sup>) was slowly added 3 M NaOH (110 cm<sup>3</sup>) at 0 °C, after which the reaction mixture was stirred at room temperature for 72 h. After completion of reaction (TLC), the solution was extracted with ethyl acetate (3×300 cm<sup>3</sup>). The organic layers were combined, washed with saturated sodium chloride solution, dried over sodium sulfate, filtrated, and

evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **16d** (5.68 g, 88%) as yellow needle crystal; mp (EtOAc/hexane) 65.7–66.7 °C;  $R_f$  (20% EtOAc/hexane) 0.32;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3102, 3086, 3058, 3049, 3031, 3010, 2979, 2962, 2935, 2913, 2962, 2935, 2913, 2889, 2840, 2913, 2889, 2839, 1676, 1648, 1612, 1587, 1496, 1477, 1461, 1445, 1385, 1330, 1296, 1279, 1248, 1213, 1120, 1173, 1119, 1073, 1056, 1031, 1024;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.74 (3H, d,  $J=0.5$  Hz,  $\text{CH}_3$ ), 1.78 (3H, d,  $J=0.7$  Hz,  $\text{CH}_3$ ), 3.87 (3H, s,  $\text{OCH}_3$ ), 4.60 (2H, d,  $J=6.8$  Hz,  $\text{Ph}-\text{CH}_2\text{CH}$ ), 5.53–5.57 (1H, m,  $\text{C}=\text{CHCH}_2$ ), 6.50 (1H, d,  $J=2.3$  Hz,  $\text{C}_3\text{H}$ ), 6.60 (1H, dd,  $J=2.3$  and 8.7 Hz,  $\text{C}_5\text{H}$ ), 7.36–7.38 (3H, m,  $\text{C}_3\text{H}$ ,  $\text{C}_4\text{H}$ , and  $\text{C}_5\text{H}$ ), 7.57–7.59 (2H, m,  $\text{C}_2\text{H}$  and  $\text{C}_6\text{H}$ ), 7.66 (1H, d,  $J=15.8$  Hz,  $\text{C}_\alpha\text{H}$ ), 7.72 (1H, d,  $J=15.8$  Hz,  $\text{C}_\beta\text{H}$ ), 7.86 (1H, d,  $J=8.7$  Hz,  $\text{C}_6\text{H}$ );  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 17.84, 21.75, 25.83, 55.79, 102.18, 114.65, 117.62, 120.63, 122.05, 128.50, 128.98, 129.27, 130.56, 131.90, 134.92, 144.11, 163.08, 163.39, 192.23; HRMS:  $\text{M}^+$ , 322.1561.  $\text{C}_{21}\text{H}_{22}\text{O}_3$  requires 322.1569.

#### 4.24. 4,4'-Bis(methoxymethoxy)-2'-gerenyloxychalcone (16e)

To a stirred solution of **11c** (1.33 g, 4.0 mmol) and **7a** (0.79 g, 4.8 mmol) in ethanol (30  $\text{cm}^3$ ) was slowly added 3 M NaOH (30  $\text{cm}^3$ ) at 0 °C, after which the reaction mixture was stirred at room temperature for 72 h. After completion of reaction (TLC), the solution was extracted with ethyl acetate (3  $\times$  150  $\text{cm}^3$ ). The organic layers were combined, washed with saturated sodium chloride solution, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **16e** (1.76 g, 92%) as yellow oil; mp (EtOAc/hexane) 65.7–66.7 °C;  $R_f$  (20% EtOAc/hexane) 0.32;  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  2959, 2927, 2852, 2827, 1652, 1601, 1575, 1509, 1428, 1378, 1328, 1314, 1276, 1241, 1207, 1172, 1153, 1122, 1080;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.56 (3H, s,  $\text{CH}_3$ ), 1.65 (3H, s,  $\text{CH}_3$ ), 1.74 (3H, d,  $J=0.8$  Hz,  $\text{CH}_3$ ), 2.07 (4H, br s,  $\text{C}_4\text{H}$  and  $\text{C}_5\text{H}$ ), 3.48 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 3.50 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 4.63 (2H, d,  $J=6.6$  Hz,  $\text{C}_1\text{H}$ ), 5.05–5.09 (1H, m,  $\text{C}_6\text{H}$ ), 5.20 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.22 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.50–5.54 (1H, m,  $\text{C}_2\text{H}$ ), 6.65 (1H, d,  $J=2.2$  Hz,  $\text{C}_3\text{H}$ ), 6.70 (1H, dd,  $J=2.2$  and 8.6 Hz,  $\text{C}_5\text{H}$ ), 7.02 (2H, d,  $J=8.7$  Hz,  $\text{C}_3\text{H}$  and  $\text{C}_5\text{H}$ ), 7.54 (2H, d,  $J=8.7$  Hz,  $\text{C}_2\text{H}$  and  $\text{C}_6\text{H}$ ), 7.55 (1H, d,  $J=15.8$  Hz,  $\text{C}_\alpha\text{H}$ ), 7.64 (1H, d,  $J=15.8$  Hz,  $\text{C}_\beta\text{H}$ ), 7.78 (1H, d,  $J=8.6$  Hz,  $\text{C}_6\text{H}$ );  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 16.69, 16.79, 17.65, 22.29, 25.43, 25.62, 26.25, 37.26, 38.98, 39.46, 56.07, 56.22, 65.67, 94.20, 94.22, 101.21, 107.99, 110.08, 116.37, 118.80, 118.89, 123.24, 123.65, 125.77, 129.40, 129.78, 131.83, 132.76, 141.38, 141.90, 158.70, 159.76, 161.64, 190.28; HRMS:  $\text{M}^+$ , 480.2502.  $\text{C}_{29}\text{H}_{36}\text{O}_6$  requires 480.2512.

#### 4.25. 2'-Geranyloxy-4'-methoxy-4-methoxymethoxychalcone (16f)

To a stirred solution of **11d** (150 mg, 0.5 mmol) and **7a** (90 mg, 0.6 mmol) in ethanol (6  $\text{cm}^3$ ) was slowly added 3 M NaOH (5  $\text{cm}^3$ ) at 0 °C, after which the reaction mixture was stirred at room temperature for 72 h. After completion of reaction (TLC), the solution was extracted with ethyl acetate (3  $\times$  50  $\text{cm}^3$ ). The organic layers were combined, washed with saturated sodium chloride solution, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **16f** (177 mg, 79%) as yellow oil;  $R_f$  (10% EtOAc/hexane) 0.15;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3102, 3086, 3058, 3049, 3031, 3010, 2979, 2962, 2935, 2913, 2962, 2935, 2913, 2889, 2840, 2913, 2889, 2839, 1676, 1648, 1612, 1587, 1496, 1477, 1461, 1445, 1385, 1330, 1296, 1279, 1248, 1213, 1120, 1173, 1119, 1073, 1056, 1031, 1024;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.56 (3H, s,  $\text{CH}_3$ ), 1.65 (3H, s,  $\text{CH}_3$ ), 1.74 (3H, d,  $J=0.8$  Hz,  $\text{CH}_3$ ), 2.06–2.08 (4H, m,  $\text{C}_4\text{H}$  and  $\text{C}_5\text{H}$ ), 3.47 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 3.84 (3H, s,  $\text{OCH}_3$ ), 4.62 (2H, d,  $J=6.5$  Hz,  $\text{C}_1\text{H}$ ), 5.05–5.08 (1H, m,

$\text{C}_6\text{H}$ ) 5.18 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.51–5.55 (1H, m,  $\text{C}_2\text{H}$ ), 6.49 (1H, d,  $J=2.1$  Hz,  $\text{C}_3\text{H}$ ), 6.55 (1H, dd,  $J=2.2$  and 8.7 Hz,  $\text{C}_5\text{H}$ ), 7.02 (2H, d,  $J=8.7$  Hz,  $\text{C}_3\text{H}$  and  $\text{C}_5\text{H}$ ), 7.52 (2H, d,  $J=8.7$  Hz,  $\text{C}_2\text{H}$  and  $\text{C}_6\text{H}$ ), 7.58 (1H, d,  $J=15.8$  Hz,  $\text{C}_\alpha\text{H}$ ), 7.65 (1H, d,  $J=15.8$  Hz,  $\text{C}_\beta\text{H}$ ), 7.83 (1H, d,  $J=8.7$  Hz,  $\text{C}_6\text{H}$ );  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 16.68, 17.54, 25.50, 26.113, 39.33, 55.36, 55.95, 65.52, 94.08, 99.55, 105.36, 116.25, 118.72, 122.28, 123.52, 125.73, 129.34, 129.64, 131.73, 132.92, 141.04, 141.73, 158.55, 159.81, 163.99, 189.91.

#### 4.26. Rearrangement of compound 16b

To a stirred solution of **16b** (2053 mg, 5 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (100  $\text{cm}^3$ ) was added montmorillonite K10 (2053 mg) at 0 °C and stirred for 0.5 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **15b** (668 mg, 33%), **17b** (557 mg, 28%), **18b** (23 mg, 1%), **19b** (473 mg, 28%).

4.26.1. 4,4'-Bis(methoxymethoxy)-2'-hydroxyl-3'-prenylchalcone (**15b**). Compound (**15b**) as yellow needle crystal; mp (EtOAc/hexane) 81.0–82.0 °C;  $R_f$  (20% EtOAc/hexane) 0.36;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  2989, 2975, 2954, 2921, 2912, 2853, 2824, 1633, 1611, 1585, 1561, 1507, 1491, 1419, 1372, 1306, 1293, 1274, 1239, 1199, 1169, 1152, 1115, 1083, 1049, 1011;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.68 (3H, d,  $J=0.8$  Hz,  $\text{CH}_3$ ), 1.81 (3H, s,  $\text{CH}_3$ ), 3.42 (2H, d,  $J=7.1$  Hz,  $\text{Ph}-\text{CH}_2\text{CH}$ ), 3.48 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 3.49 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.22 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.22–5.28 (1H, m,  $\text{C}=\text{CHCH}_2$ ), 5.28 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 6.68 (1H, d,  $J=9.0$  Hz,  $\text{C}_5\text{H}$ ), 7.08 (2H, d,  $J=8.7$  Hz,  $\text{C}_3\text{H}$  and  $\text{C}_5\text{H}$ ), 7.48 (1H, d,  $J=15.4$  Hz,  $\text{C}_\alpha\text{H}$ ), 7.60 (2H, d,  $J=8.7$  Hz,  $\text{C}_2\text{H}$  and  $\text{C}_6\text{H}$ ), 7.75 (1H, d,  $J=9.0$  Hz,  $\text{C}_6\text{H}$ ), 7.85 (1H, d,  $J=15.4$  Hz,  $\text{C}_\beta\text{H}$ ), 13.48 (1H, s, OH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 17.85, 21.97, 25.80, 56.20, 56.25, 93.84, 94.21, 104.80, 115.11, 116.56, 118.49, 118.58, 122.06, 128.62, 128.77, 130.23, 131.79, 144.02, 159.31, 160.71, 163.28, 192.40; HRMS:  $\text{M}^+$ , 412.1861.  $\text{C}_{24}\text{H}_{28}\text{O}_6$  requires 412.1886.

4.26.2. 4,4'-Bis(methoxymethoxy)-2'-hydroxyl-5'-prenylchalcone (**17b**). Compound (**17b**) as yellow needle crystal; mp (EtOAc/hexane) 62.0–63.0 °C;  $R_f$  (20% EtOAc/hexane) 0.38;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3087, 2993, 2957, 2917, 2853, 2825, 2797, 2686, 1634, 1604, 1572, 1512, 1496, 1460, 1443, 1421, 1412, 1366, 1322, 1302, 1278, 1241, 1221, 1180, 1162, 1122, 1103, 1074;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.75 (3H, s,  $\text{CH}_3$ ), 1.77 (3H, d,  $J=0.9$  Hz,  $\text{CH}_3$ ), 3.29 (2H, d,  $J=7.2$  Hz,  $\text{Ph}-\text{CH}_2\text{CH}$ ), 3.48 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 3.50 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.23 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.25 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.27–5.31 (1H, m,  $\text{C}=\text{CHCH}_2$ ), 6.65 (1H, s,  $\text{C}_3\text{H}$ ), 7.09 (2H, d,  $J=8.8$  Hz,  $\text{C}_3\text{H}$  and  $\text{C}_5\text{H}$ ), 7.46 (1H, d,  $J=15.4$  Hz,  $\text{C}_\alpha\text{H}$ ), 7.60 (2H, d,  $J=8.8$  Hz,  $\text{C}_2\text{H}$  and  $\text{C}_6\text{H}$ ), 7.62 (1H, s,  $\text{C}_6\text{H}$ ), 7.84 (1H, d,  $J=15.4$  Hz,  $\text{C}_\beta\text{H}$ ), 13.30 (1H, s, OH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 17.89, 25.79, 28.37, 56.21, 56.34, 93.99, 94.22, 102.18, 114.28, 116.58, 118.54, 121.92, 122.41, 128.66, 130.05, 130.21, 132.82, 143.92, 159.31, 161.37, 164.81, 191.96; HRMS:  $\text{M}^+$ , found 412.1890.  $\text{C}_{24}\text{H}_{28}\text{O}_6$  requires 412.1886.

4.26.3. 4,4'-Bis(methoxymethoxy)-3',5'-diprenyl-2'-hydroxylchalcone (**18b**). Compound (**18b**) as yellow needle crystal;  $R_f$  (20% EtOAc/hexane) 0.44;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.70 (3H, s,  $\text{CH}_3$ ), 1.75 (3H, s,  $\text{CH}_3$ ), 1.79 (3H, s,  $\text{CH}_3$ ), 1.80 (3H, s,  $\text{CH}_3$ ), 3.38 (2H, d,  $J=6.9$  Hz,  $\text{Ph}-\text{CH}_2\text{CH}$ ), 3.42 (2H, d,  $J=6.4$  Hz,  $\text{Ph}-\text{CH}_2\text{CH}$ ), 3.50 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 3.61 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.02 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.23 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.20–5.23 (1H, m,  $\text{C}=\text{CHCH}_2$ ), 5.30–5.33 (1H, m,  $\text{C}=\text{CHCH}_2$ ), 7.09 (2H, d,  $J=8.7$  Hz,  $\text{C}_3\text{H}$  and  $\text{C}_5\text{H}$ ), 7.46 (1H, d,  $J=15.4$  Hz,  $\text{C}_\alpha\text{H}$ ), 7.58 (1H, s,  $\text{C}_6\text{H}$ ), 7.60 (2H, d,  $J=8.7$  Hz,  $\text{C}_2\text{H}$  and  $\text{C}_6\text{H}$ ), 7.85 (1H, d,  $J=15.4$  Hz,  $\text{C}_\beta\text{H}$ ), 13.30 (1H, s, OH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 56.21, 56.40, 94.04, 94.21, 103.98, 108.14, 115.01, 116.57,

118.27, 128.52, 130.29, 131.24, 144.33, 159.41, 163.53, 166.18, 192.06.

4.26.4. *4,4'*-Bis(methoxymethoxy)-2'-hydroxylchalcone (**19b**). Compound (**19b**) as yellow needle crystal; mp (EtOAc/hexane) 75.2–76.2 °C;  $R_f$  (20% EtOAc/hexane) 0.32;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3079, 3049, 2956, 2939, 2907, 2830, 2791, 2681, 2592, 1633, 1603, 1568, 1508, 1420, 1360, 1312, 1299, 1277, 1216, 1198, 1160, 1126, 1084;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 3.49 (6H, s, OCH<sub>2</sub>OCH<sub>3</sub> × 2), 5.22 (4H, s, OCH<sub>2</sub>OCH<sub>3</sub> × 2), 6.59 (1H, dd,  $J=2.4$  and 8.9 Hz, C<sub>5</sub>H), 6.64 (1H, d,  $J=2.4$  Hz, C<sub>3</sub>H), 7.08 (2H, d,  $J=8.8$  Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.47 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 7.60 (2H, d,  $J=8.8$  Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.84 (1H, d,  $J=8.9$  Hz, C<sub>6</sub>H), 7.86 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 13.36 (1H, s, OH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 56.16, 56.35, 94.00, 94.17, 103.93, 108.10, 114.97, 116.52, 118.24, 128.48, 130.24, 131.20, 144.28, 159.37, 163.48, 166.13, 192.01; HRMS: M<sup>+</sup>, found 344.1310. C<sub>19</sub>H<sub>20</sub>O<sub>6</sub> requires 334.1260.

#### 4.27. Rearrangement of compound 16c

To a stirred solution of **16c** (1019 mg, 2.9 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 cm<sup>3</sup>) was added montmorillonite K10 (1020 mg) at 0 °C and stirred for 1.0 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **1c** (378 mg, 37%), **5c** (276 mg, 27%), **18c** (8 mg, 0.7%), **19c** (197 mg, 24%).

4.27.1. *4,4'*-Dimethoxy-2'-hydroxyl-3'-prenylchalcone (**1c**). Compound (**1c**) as yellow needle crystal, mp (EtOAc/hexane) 97.6–98.2 °C;  $R_f$  (20% EtOAc/hexane) 0.40;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3006, 2985, 2979, 2917, 2847, 1633, 1607, 1576, 1515, 1496, 1466, 1444, 1415, 1371, 1323, 1310, 1295, 1283, 1261, 1239, 1283, 1261, 1239, 1194, 1175, 1153, 1117, 1098, 1070, 1024;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.68 (3H, d,  $J=1.0$  Hz, CH<sub>3</sub>), 1.80 (3H, s, CH<sub>3</sub>), 3.39 (2H, d,  $J=7.1$  Hz, Ph–CH<sub>2</sub>CH), 3.85 (3H, s, OCH<sub>3</sub>), 3.90 (3H, s, OCH<sub>3</sub>), 5.22–5.26 (1H, m, C=CHCH<sub>2</sub>), 6.48 (1H, d,  $J=9.0$  Hz, C<sub>5</sub>H), 6.93 (2H, d,  $J=8.8$  Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.47 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 7.59 (2H, d,  $J=8.8$  Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.63 (1H, d,  $J=9.0$  Hz, C<sub>6</sub>H), 7.84 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 13.47 (1H, s, OH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 17.83, 21.74, 25.83, 55.43, 55.77, 102.04, 114.45, 114.70, 117.55, 118.14, 122.08, 127.65, 129.09, 130.60, 131.88, 143.88, 143.97, 161.72, 163.02, 163.19, 192.28; HRMS: M<sup>+</sup>, found 352.1685. C<sub>22</sub>H<sub>24</sub>O<sub>4</sub> requires 352.1675.

4.27.2. *4,4'*-Dimethoxy-2'-hydroxyl-5'-prenylchalcone (**5c**). Compound (**5c**) as yellow needle crystal; mp (EtOAc/hexane) 95.5–96.1 °C;  $R_f$  (20% EtOAc/hexane) 0.48;  $\nu_{\max}$  (CHCl<sub>3</sub>)/ $\text{cm}^{-1}$  3021, 3006, 2983, 2964, 2945, 2923, 2852, 2836, 1635, 1607, 1565, 1513, 1494, 1460, 1443, 1423, 1387, 1364, 1301, 1281, 1254, 1234, 1219, 1174, 1127, 1103, 1027;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.74 (3H, s, CH<sub>3</sub>), 1.78 (3H, d,  $J=0.8$  Hz, CH<sub>3</sub>), 3.26 (2H, d,  $J=7.2$  Hz, Ph–CH<sub>2</sub>CH), 3.86 (3H, s, OCH<sub>3</sub>), 3.87 (3H, s, OCH<sub>3</sub>), 5.26–5.30 (1H, m, C=CHCH<sub>2</sub>), 6.43 (1H, s, C<sub>3</sub>H), 6.95 (2H, d,  $J=8.8$  Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.44 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 7.60 (1H, s, C<sub>6</sub>H), 7.60 (2H, d,  $J=8.8$  Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.84 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 13.50 (1H, s, OH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 17.87, 25.80, 28.03, 55.43, 55.70, 99.36, 113.40, 114.47, 118.10, 121.56, 122.31, 127.67, 129.67, 130.29, 132.93, 143.86, 161.73, 164.08, 165.33, 191.81; HRMS: M<sup>+</sup>, found 352.1697. C<sub>22</sub>H<sub>24</sub>O<sub>4</sub> requires 352.1675.

4.27.3. *4,4'*-Dimethoxy-3',5'-diprenyl-2'-hydroxylchalcone (**18c**). Compound (**18c**) as yellow needle crystal;  $R_f$  (20% EtOAc/hexane) 0.56;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.70 (3H, d,  $J=1.0$  Hz, CH<sub>3</sub>), 1.77 (3H, s, CH<sub>3</sub>), 1.79 (3H, d,  $J=1.0$  Hz, CH<sub>3</sub>), 1.80 (3H, s, CH<sub>3</sub>), 3.34 (2H, d,  $J=7.0$  Hz, Ph–CH<sub>2</sub>CH), 3.42 (2H, d,  $J=6.9$  Hz, Ph–CH<sub>2</sub>CH), 3.78 (3H, s, OCH<sub>3</sub>), 3.87 (3H, s, OCH<sub>3</sub>), 5.24–5.32 (2H, m, C=CHCH<sub>2</sub> × 2), 6.96 (2H, d,  $J=8.8$  Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.46 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 7.58 (1H, s,

C<sub>6</sub>H), 7.61 (2H, d,  $J=8.8$  Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.86 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 13.30 (1H, s, OH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 17.96, 17.99, 22.98, 25.73, 25.76, 28.24, 55.45, 61.26, 114.50, 116.64, 118.20, 122.55, 123.07, 123.66, 125.43, 127.59, 128.31, 130.37, 131.86, 132.86, 144.42, 161.84, 162.26, 162.88, 192.85.

4.27.4. *4,4'*-Dimethoxy-2'-hydroxylchalcone (**19c**). Compound (**19c**) as yellow needle crystal; mp (EtOAc/hexane) 114.4–115.3 °C;  $R_f$  (20% EtOAc/hexane) 0.36;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3080, 3009, 2973, 2940, 2916, 2844, 2750, 2721, 2687, 2667, 2596, 1627, 1604, 1582, 1512, 1462, 1442, 1365, 1312, 1282, 1259, 1217, 1178, 1128, 1019;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 3.85 (3H, s, OCH<sub>3</sub>), 3.85 (3H, s, OCH<sub>3</sub>), 6.46 (1H, d,  $J=1.3$  Hz, C<sub>3</sub>H), 6.48 (1H, dd,  $J=1.3$  and 9.2 Hz, C<sub>5</sub>H), 6.94 (2H, d,  $J=8.8$  Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.44 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 7.60 (2H, d,  $J=8.8$  Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.82 (1H, d,  $J=9.2$  Hz, C<sub>6</sub>H), 7.85 (1H, d,  $J=15.4$  Hz, C<sub>6</sub>H), 13.56 (1H, s, OH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 55.44, 55.58, 101.09, 107.61, 114.17, 114.48, 117.84, 127.55, 130.37, 131.13, 144.28, 161.82, 166.05, 166.64, 191.90; HRMS: M<sup>+</sup>, found 284.1045. C<sub>17</sub>H<sub>16</sub>O<sub>4</sub> requires 284.1049.

#### 4.28. Rearrangement of compound 16d

To a stirred solution of **16d** (644 mg, 2 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was added montmorillonite K10 (644 mg) at 0 °C and stirred for 0.5 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **1d** (276 mg, 43%), **5d** (166 mg, 26%), **18d** (6 mg, 0.8%), **19d** (134 mg, 26%).

4.28.1. *Derricin (1d)*. Compound (**1d**) as yellow needle crystal; mp (EtOAc/hexane) 85.5–86.5 °C;  $R_f$  (20% EtOAc/hexane) 0.44;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3059, 3033, 3013, 2992, 2957, 2912, 2849, 2745, 2719, 2641, 1635, 1605, 1573, 1496, 1446, 1418, 1361, 1325, 1311, 1280, 1232, 1205, 1188, 1167, 1120, 1098, 1078;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.68 (3H, d,  $J=1.0$  Hz, CH<sub>3</sub>), 1.78 (3H, s, CH<sub>3</sub>), 3.38 (2H, d,  $J=7.1$  Hz, Ph–CH<sub>2</sub>CH), 3.89 (3H, s, OCH<sub>3</sub>), 5.21–5.26 (1H, m, C=CHCH<sub>2</sub>), 6.48 (1H, d,  $J=9.0$  Hz, C<sub>5</sub>H), 7.39–7.42 (3H, m, C<sub>3</sub>H, C<sub>4</sub>H, and C<sub>5</sub>H), 7.58 (1H, d,  $J=15.5$  Hz, C<sub>6</sub>H), 7.63 (2H, m, C<sub>2</sub>H and C<sub>6</sub>H), 7.78 (1H, d,  $J=9.0$  Hz, C<sub>6</sub>H), 7.85 (1H, d,  $J=15.5$  Hz, C<sub>6</sub>H), 13.37 (1H, s, OH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 17.84, 21.75, 25.83, 55.79, 102.18, 114.65, 117.62, 120.63, 122.05, 128.50, 128.98, 129.27, 130.56, 131.90, 134.92, 144.11, 163.08, 163.39, 192.23; HRMS: M<sup>+</sup>, found 322.1561. C<sub>21</sub>H<sub>22</sub>O<sub>3</sub> requires 322.1569.

4.28.2. *2'-Hydroxyl-4'-methoxy-5'-prenylchalcone (5d)*. Compound (**5d**) as yellow needle crystal; mp (EtOAc/hexane) 100.7–101.2 °C;  $R_f$  (20% EtOAc/hexane) 0.56;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3081, 3008, 2978, 2963, 2942, 2917, 2895, 2854, 2697, 1640, 1577, 1497, 1459, 1443, 1390, 1365, 1322, 1305, 1278, 1238, 1212, 1176, 1131, 1028;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.73 (3H, s, CH<sub>3</sub>), 1.78 (3H, d,  $J=1.0$  Hz, CH<sub>3</sub>), 3.26 (2H, d,  $J=7.2$  Hz, Ph–CH<sub>2</sub>CH), 3.86 (3H, s, OCH<sub>3</sub>), 5.26–5.31 (1H, m, C=CHCH<sub>2</sub>), 6.43 (1H, s, C<sub>3</sub>H), 7.41–7.43 (3H, m, C<sub>3</sub>H, C<sub>4</sub>H and C<sub>5</sub>H), 7.55 (1H, d,  $J=15.5$  Hz, C<sub>6</sub>H), 7.59 (1H, s, C<sub>6</sub>H), 7.64 (2H, m, C<sub>2</sub>H and C<sub>6</sub>H), 7.86 (1H, d,  $J=15.5$  Hz, C<sub>6</sub>H), 13.40 (1H, s, OH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 17.81, 25.79, 28.02, 55.73, 99.38, 113.38, 120.62, 121.72, 122.24, 128.48, 129.00, 130.55, 133.02, 134.96, 143.98, 164.30, 165.46, 191.76; HRMS: M<sup>+</sup>, found 322.1577. C<sub>21</sub>H<sub>22</sub>O<sub>3</sub> requires 322.1569.

4.28.3. *3',5'-Diprenyl-2'-hydroxyl-4'-methoxychalcone (18d)*. Compound (**18d**) as yellow needle crystal;  $R_f$  (20% EtOAc/hexane, 4:1) 0.64;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.70 (3H, s, CH<sub>3</sub>), 1.76 (3H, s, CH<sub>3</sub>), 1.78 (3H, s, CH<sub>3</sub>), 1.81 (3H, s, CH<sub>3</sub>), 3.34 (2H, d,  $J=7.0$  Hz, Ph–CH<sub>2</sub>CH), 3.42 (2H, d,  $J=6.6$  Hz, Ph–CH<sub>2</sub>CH), 3.77 (3H, s, OCH<sub>3</sub>), 5.24–5.32 (2H, m, C=CHCH<sub>2</sub> × 2), 7.43–7.44 (3H, m, C<sub>3</sub>H, C<sub>4</sub>H, and C<sub>5</sub>H), 7.58 (1H, d,

$J=15.5$  Hz,  $C_2H$ ), 7.59 (1H, s,  $C_6H$ ), 7.63–7.66 (2H, m,  $C_2H$  and  $C_6H$ ), 7.88 (1H, d,  $J=15.5$  Hz,  $C_6H$ ), 13.19 (1H, s, OH).

4.28.4. 2'-Hydroxyl-4'-methoxychalcone (**19d**). Compound (**19d**) as yellow needle crystal; mp (EtOAc/hexane) 106.7–107.7 °C  $R_f$  (20% EtOAc/hexane) 0.44;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3087, 3064, 3034, 3008, 2975, 2937, 2915, 2845, 2747, 2692, 2666, 2594, 2537, 1634, 1573, 1510, 1496, 1466, 1445, 1412, 1382, 1363, 1323, 1303, 1277, 1223, 1132, 1073, 1018;  $\delta_H$  ( $\text{CDCl}_3$ ) 3.84 (6H, s,  $\text{OCH}_2\text{OCH}_3 \times 2$ ), 6.46 (1H, d,  $J=2.6$  Hz,  $C_3H$ ), 6.48 (1H, dd,  $J=2.6$  and 8.7 Hz,  $C_5H$ ), 7.40–7.42 (3H, m,  $C_3H$ ,  $C_4H$ , and  $C_5H$ ), 7.56 (1H, d,  $J=15.5$  Hz,  $C_2H$ ), 7.62–7.65 (2H, m,  $C_2H$  and  $C_6H$ ), 7.81 (1H, d,  $J=8.7$  Hz,  $C_6H$ ), 7.87 (1H, d,  $J=15.5$  Hz,  $C_6H$ ), 13.44 (1H, s, OH);  $\delta_C$  ( $\text{CDCl}_3$ ) 55.59, 101.12, 107.74, 114.12, 120.32, 128.55, 129.00, 130.67, 131.27, 134.81, 144.39, 166.25, 166.73, 191.84; HRMS:  $M^+$ , found 254.0891.  $\text{C}_{16}\text{H}_{14}\text{O}_3$  requires 254.0943.

#### 4.29. Rearrangement of compound 16e

To a stirred solution of **16e** (240 mg, 0.5 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (5  $\text{cm}^3$ ) was added montmorillonite K10 (240 mg) at 0 °C and stirred for 2 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **15e** (105 mg, 44%), **5d** (30 mg, 12%), **19b** (73 mg, 42%).

4.29.1. 4,4'-Bis(methoxymethoxy)-3'-geranyl-2'-hydroxychalcone (**15e**). Compound (**15e**) as yellow oil;  $R_f$  (20% EtOAc/hexane) 0.20  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  2991, 2963, 2925, 2855, 2824, 1634, 1613, 1587, 1562, 1507, 1489, 1421, 1372, 1307, 1296, 1273, 1240, 1197, 1172, 1153, 1113, 1083, 1049, 1020;  $\delta_H$  ( $\text{CDCl}_3$ ) 1.56 (3H, s,  $\text{CH}_3$ ), 1.64 (3H, d,  $J=1.4$  Hz,  $\text{CH}_3$ ), 1.81 (3H, d,  $J=0.6$  Hz,  $\text{CH}_3$ ), 1.95–1.99 (2H, m,  $C_4H$ ), 2.03–2.09 (2H, m,  $C_5H$ ), 3.43 (2H, d,  $J=7.1$  Hz,  $C_1H$ ), 3.48 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 3.49 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.04–5.09 (1H, m,  $C_6H$ ), 5.22 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.22–5.28 (1H, m,  $C_2H$ ), 5.28 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 6.68 (1H, d,  $J=9.0$  Hz,  $C_5H$ ), 7.07 (2H, d,  $J=8.7$  Hz,  $C_3H$  and  $C_5H$ ), 7.48 (1H, d,  $J=15.4$  Hz,  $C_2H$ ), 7.60 (2H, d,  $J=8.7$  Hz,  $C_2H$  and  $C_6H$ ), 7.75 (1H, d,  $J=9.0$  Hz,  $C_6H$ ), 7.85 (1H, d,  $J=15.4$  Hz,  $C_6H$ ), 13.48 (1H, s, OH);  $\delta_C$  ( $\text{CDCl}_3$ ) 16.15, 17.62, 21.87, 25.63, 26.72, 39.79, 56.18, 56.22, 93.83, 94.22, 104.79, 115.11, 116.56, 118.59, 118.63, 121.87, 124.40, 128.64, 128.73, 130.20, 131.21, 135.30, 143.99, 159.30, 160.75, 163.30, 192.41; HRMS:  $M^+$ , found 480.2502.  $\text{C}_{29}\text{H}_{36}\text{O}_6$  requires 480.2512.

4.29.2. 4,4'-Bis(methoxymethoxy)-5'-geranyl-2'-hydroxychalcone (**17e**). Compound (**17e**) as yellow oil;  $R_f$  (20% EtOAc/hexane) 0.33;  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  2965, 2917, 2849, 2827, 1634, 1604, 1567, 1509, 1490, 1443, 1423, 1362, 1304, 1274, 1239, 1304, 1274, 1239, 1215, 1171, 1153, 1126, 1076;  $\delta_H$  ( $\text{CDCl}_3$ ) 1.59 (3H, s,  $\text{CH}_3$ ), 1.67 (3H, s,  $\text{CH}_3$ ), 1.75 (3H, s,  $\text{CH}_3$ ), 2.05–2.08 (2H, m,  $C_4H$ ), 2.13–2.17 (2H, m,  $C_5H$ ), 3.31 (2H, d,  $J=7.3$  Hz,  $C_1H$ ), 3.48 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 3.50 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.13–5.17 (1H, m,  $C_6H$ ), 5.25 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.33 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.32–5.35 (1H, m,  $C_2H$ ), 6.66 (1H, s,  $C_3H$ ), 7.07 (2H, d,  $J=8.7$  Hz,  $C_3H$  and  $C_5H$ ), 7.46 (1H, d,  $J=15.4$  Hz,  $C_2H$ ), 7.59 (2H, d,  $J=8.7$  Hz,  $C_2H$  and  $C_6H$ ), 7.64 (1H, s,  $C_6H$ ), 7.85 (1H, d,  $J=15.4$  Hz,  $C_6H$ ), 13.31 (1H, s, OH);  $\delta_C$  ( $\text{CDCl}_3$ ) 16.22, 17.66, 26.66, 27.17, 27.97, 39.83, 56.17, 56.33, 94.02, 94.22, 102.16, 114.26, 116.56, 118.48, 121.81, 122.05, 124.06, 129.87, 130.20, 143.95, 159.31, 164.81, 191.96; HRMS:  $M^+$ , found 480.2511.  $\text{C}_{29}\text{H}_{36}\text{O}_6$  requires 480.2512.

#### 4.30. Rearrangement of compound 16f

To a stirred solution of **16f** (226 mg, 0.5 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) was added montmorillonite K10 (225 mg) at 0 °C and stirred for 1 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was filtrated and

evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **15f** (81 mg, 36%), **17f** (20 mg, 9%), **18f** (2 mg, 0.1%), **19a** (85 mg, 54%).

4.30.1. 3'-Geranyl-2'-hydroxy-4'-methoxy-4-methoxymethoxychalcone (**15f**). Compound (**15f**) as yellow oil;  $R_f$  (10% EtOAc/hexane) 0.18;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  2963, 2916, 2846, 1633, 1611, 1577, 1568, 1509, 1496, 1442, 1421, 1373, 1312, 1281, 1230, 1201, 1173, 1152, 1114, 1080;  $\delta_H$  ( $\text{CDCl}_3$ ) 1.57 (3H, s,  $\text{CH}_3$ ), 1.64 (3H, d,  $J=0.9$  Hz,  $\text{CH}_3$ ), 1.79 (3H, d,  $J=0.8$  Hz,  $\text{CH}_3$ ), 1.95–1.99 (2H, m,  $C_4H$ ), 2.03–2.09 (2H, m,  $C_5H$ ), 3.39 (2H, d,  $J=7.0$  Hz,  $C_1H$ ), 3.49 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 3.90 (3H, s,  $\text{OCH}_3$ ), 5.05–5.09 (1H, m,  $C_6H$ ), 5.21 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.22–5.25 (1H, m,  $C_2H$ ), 6.49 (1H, d,  $J=9.2$  Hz,  $C_5H$ ), 7.08 (2H, d,  $J=8.8$  Hz,  $C_3H$  and  $C_5H$ ), 7.49 (1H, d,  $J=15.4$  Hz,  $C_2H$ ), 7.60 (2H, d,  $J=8.8$  Hz,  $C_2H$  and  $C_6H$ ), 7.79 (1H, d,  $J=9.2$  Hz,  $C_6H$ ), 7.84 (1H, d,  $J=15.4$  Hz,  $C_6H$ ), 13.43 (1H, s, OH);  $\delta_C$  ( $\text{CDCl}_3$ ) 16.14, 17.66, 21.67, 25.66, 26.74, 39.81, 55.75, 56.19, 94.22, 102.06, 114.68, 116.55, 117.08, 118.69, 121.91, 124.48, 128.70, 129.08, 130.18, 131.15, 135.32, 143.78, 159.26, 163.07, 163.29, 192.25; HRMS:  $M^+$ , found 450.2414.  $\text{C}_{28}\text{H}_{34}\text{O}_5$  requires 450.2406.

4.30.2. 5'-Geranyl-2'-hydroxy-4'-methoxy-4-methoxymethoxychalcone (**17f**). Compound (**17f**) as yellow oil;  $R_f$  (10% EtOAc/hexane) 0.22;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3006, 2972, 2926, 2851, 1632, 1583, 1566, 1504, 1444, 1383, 1320, 1304, 1279, 1227, 1207, 1155, 1124, 1079;  $\delta_H$  ( $\text{CDCl}_3$ ) 1.59 (3H, s,  $\text{CH}_3$ ), 1.67 (3H, d,  $J=0.9$  Hz,  $\text{CH}_3$ ), 1.72 (3H, s,  $\text{CH}_3$ ), 2.06–2.10 (2H, m,  $C_4H$ ), 2.14–2.20 (2H, m,  $C_5H$ ), 3.27 (2H, d,  $J=7.2$  Hz,  $C_1H$ ), 3.49 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 3.86 (3H, s,  $\text{OCH}_3$ ), 5.13–5.17 (1H, m,  $C_6H$ ), 5.22 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.30–5.34 (1H, m,  $C_2H$ ), 6.44 (1H, s,  $C_3H$ ), 7.07 (2H, d,  $J=8.8$  Hz,  $C_3H$  and  $C_5H$ ), 7.45 (1H, d,  $J=15.4$  Hz,  $C_2H$ ), 7.58 (2H, d,  $J=8.8$  Hz,  $C_2H$  and  $C_6H$ ), 7.60 (1H, s,  $C_6H$ ), 7.84 (1H, d,  $J=15.4$  Hz,  $C_6H$ ), 13.49 (1H, s, OH);  $\delta_C$  ( $\text{CDCl}_3$ ) 16.20, 17.70, 25.69, 27.26, 27.62, 39.86, 55.69, 56.18, 94.22, 99.32, 113.37, 116.56, 118.55, 121.47, 121.94, 124.11, 128.69, 129.49, 130.18, 131.60, 137.09, 143.74, 159.27, 164.17, 165.37, 191.79; HRMS:  $M^+$ , found 450.2411.  $\text{C}_{28}\text{H}_{34}\text{O}_5$  requires 450.2406.

4.30.3. 3',5'-Digeranyl-2'-hydroxyl-4'-methoxy-4-methoxymethoxychalcone (**18f**). Compound (**18f**) as yellow oil;  $R_f$  (10% EtOAc/hexane) 0.33;  $\delta_H$  ( $\text{CDCl}_3$ ) 1.57 (3H, s,  $\text{CH}_3$ ), 1.58 (3H, s,  $\text{CH}_3$ ), 1.63 (3H, s,  $\text{CH}_3$ ), 1.66 (3H, s,  $\text{CH}_3$ ), 1.76 (3H, s,  $\text{CH}_3$ ), 1.80 (3H, s,  $\text{CH}_3$ ), 1.99–2.18 (8H, m,  $C_4H$ ,  $C_4H$ ,  $C_5H$ , and  $C_5H$ ), 3.35 (2H, d,  $J=7.0$  Hz,  $C_1H$ ), 3.42 (2H, d,  $J=6.6$  Hz,  $C_1H$ ), 3.50 (3H, s,  $\text{OCH}_2\text{OCH}_3$ ), 3.78 (3H, s,  $\text{OCH}_3$ ), 5.04–5.06 (1H, m,  $C_6H$ ), 5.13–5.16 (1H, m,  $C_6H$ ), 5.23 (2H, s,  $\text{OCH}_2\text{OCH}_3$ ), 5.25–5.28 (1H, m,  $C_2H$ ), 5.31–5.35 (1H, m,  $C_2H$ ), 7.07 (2H, d,  $J=8.7$  Hz,  $C_3H$  and  $C_5H$ ), 7.48 (1H, d,  $J=15.4$  Hz,  $C_2H$ ), 7.59 (2H, d,  $J=8.7$  Hz,  $C_2H$  and  $C_6H$ ), 7.60 (1H, s,  $C_6H$ ), 7.86 (1H, d,  $J=15.4$  Hz,  $C_6H$ ), 13.29 (1H, s, OH).

#### 4.31. Isobavachalcone (1b)

To a stirred solution of **15b** (81 mg, 0.19 mmol) in MeOH (10  $\text{cm}^3$ ) was added 3 M aqueous HCl (2  $\text{cm}^3$ ) at room temperature, after which the reaction mixture was stirred under reflux for 0.5 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was evaporated under vacuum. After addition of 10  $\text{cm}^3$  of water, the mixture was extracted with ethyl acetate (3  $\times$  30  $\text{cm}^3$ ). The organic layers were combined, washed with brine, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **1b** (46 mg, 72%) as yellow needle crystal; mp (EtOAc/hexane) 156.8–157.8 °C;  $R_f$  (20% EtOAc/hexane) 0.04;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3240, 3033, 2995, 2968, 2916, 2856, 2724, 1605, 1554, 1514, 1486, 1446, 1373, 1322, 1294, 1241, 1169, 1111, 1098, 1042, 1003;  $\delta_H$  ( $\text{DMSO}-d_6$ ) 1.61 (3H, s,  $\text{CH}_3$ ), 1.71 (3H, s,  $\text{CH}_3$ ), 3.22 (2H, d,  $J=7.1$  Hz,

Ph–CH<sub>2</sub>CH), 5.14–5.18 (1H, m, C=CHCH<sub>2</sub>), 6.46 (1H, d, *J*=8.9 Hz, C<sub>3</sub>H), 6.83 (2H, d, *J*=8.7 Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.74 (2H, s, C<sub>2</sub>H and C<sub>6</sub>H), 7.74 (2H, d, *J*=8.7 Hz, C<sub>2</sub>H and C<sub>6</sub>H), 8.02 (1H, d, *J*=8.7 Hz, C<sub>6</sub>H), 10.11 (1H, br s, OH), 10.54 (1H, br s, OH), 13.98 (1H, s, OH);  $\delta_C$  (DMSO-*d*<sub>6</sub>) 17.67, 21.23, 25.44, 107.28, 112.68, 114.43, 115.81, 117.36, 122.34, 125.76, 129.76, 130.42, 131.14, 144.08, 160.19, 162.23, 163.50, 191.74; HRMS: M<sup>+</sup>, found 324.1330. C<sub>20</sub>H<sub>20</sub>O<sub>4</sub> requires 324.1362.

#### 4.32. Burousochalcone B (5b)

To a stirred solution of **17a** (50 mg, 0.12 mmol) in MeOH (5 cm<sup>3</sup>) was added CBr<sub>4</sub> (8 mg, 0.024 mmol) at room temperature, after which the reaction mixture was stirred under reflux for 8 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was evaporated under vacuum. The residue was purified by PLC with hexane/ethyl acetate to afford compound **5b** (24 mg, 61%) and bavachin (10 mg, 25%).

**Bousochalcone B (5b)** as yellow needle crystal; mp (EtOAc/hexane) 161.7–162.2 °C; *R*<sub>f</sub> (33% EtOAc/hexane) 0.22;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3309, 3031, 2966, 2917, 2854, 2729, 1636, 1606, 1582, 1571, 1543, 1512, 1438, 1420, 1368, 1318, 1292, 1254, 1217, 1167, 1126, 1106, 1021;  $\delta_H$  (DMSO-*d*<sub>6</sub>) 1.68 (3H, d, *J*=0.8 Hz, CH<sub>3</sub>), 1.72 (3H, s, CH<sub>3</sub>), 3.22 (2H, d, *J*=7.0 Hz, Ph–CH<sub>2</sub>CH), 5.26–5.30 (1H, m, C=CHCH<sub>2</sub>), 6.33 (1H, s, C<sub>3</sub>H), 6.86 (2H, d, *J*=8.5 Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.73 (2H, s, C<sub>2</sub>H and C<sub>6</sub>H), 7.75 (2H, d, *J*=8.5 Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.97 (1H, s, C<sub>6</sub>H), 10.12 (1H, s, OH), 10.66 (1H, s, OH), 13.46 (1H, s, OH);  $\delta_C$  (DMSO-*d*<sub>6</sub>) 17.74, 25.43, 27.91, 102.26, 112.69, 115.81, 117.54, 120.42, 123.36, 125.77, 130.75, 131.12, 131.62, 143.97, 160.19, 162.90, 164.00, 191.32; HRMS: M<sup>+</sup>, found 324.1376. C<sub>20</sub>H<sub>20</sub>O<sub>4</sub> requires 324.1362.

**Bavachin** as yellow needle crystal; mp (EtOAc/hexane) 186.8–187.8 °C; *R*<sub>f</sub> (50% EtOAc/hexane) 0.32;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3328, 3207, 3134, 3089, 2981, 2964, 2909, 2857, 2798, 2740, 2643, 1655, 1585, 1520, 1504, 1468, 1453, 1372, 1349, 1335, 1306, 1279, 1259, 1167;  $\delta_H$  (acetone-*d*<sub>6</sub>) 1.61 (3H, s, CH<sub>3</sub>), 1.63 (3H, d, *J*=0.8 Hz, CH<sub>3</sub>), 2.54 (1H, dd, *J*=2.9 and 16.7 Hz, C<sub>3</sub>H), 2.92 (1H, dd, *J*=13.0 and 16.7 Hz, C<sub>3</sub>H), 3.17 (2H, d, *J*=7.3 Hz, Ph–CH<sub>2</sub>CH), 5.21–5.26 (1H, m, C=CHCH<sub>2</sub>), 6.35 (1H, s, C<sub>8</sub>H), 6.79 (2H, d, *J*=8.6 Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.28 (2H, d, *J*=8.6 Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.49 (1H, s, C<sub>5</sub>H), 8.43 (1H, br s, OH), 9.46 (1H, br s, OH);  $\delta_C$  (CDCl<sub>3</sub>) 17.83, 25.94, 28.23, 44.75, 80.53, 103.24, 114.89, 116.12, 123.22, 123.82, 128.25, 128.96, 131.41, 132.97, 158.55, 162.79, 162.96, 190.76; HRMS: M<sup>+</sup>, found 324.1383. C<sub>20</sub>H<sub>20</sub>O<sub>4</sub> requires 324.1362.

#### 4.33. Bavachalcone (5a)

To a stirred solution of **17a** (51 mg, 0.13 mmol) in MeOH (5 cm<sup>3</sup>) was added CBr<sub>4</sub> (4.5 mg, 0.013 mmol) at room temperature, after which the reaction mixture was stirred under reflux for 2.5 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was evaporated under vacuum. The residue was purified by PLC with hexane/ethyl acetate to afford compound **5a** (35 mg, 84%) as yellow needle crystal; mp (EtOAc/hexane) 169.9–170.1 °C; *R*<sub>f</sub> (33% EtOAc/hexane) 0.34;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3436, 3319, 3069, 2973, 2943, 2911, 2854, 2821, 2751, 2697, 2604, 1628, 1604, 1544, 1508, 1443, 1363, 1306, 1284, 1205, 1170, 1130, 1105;  $\delta_H$  (acetone-*d*<sub>6</sub>) 1.58 (3H, d, *J*=1.0 Hz, CH<sub>3</sub>), 1.59 (3H, s, CH<sub>3</sub>), 3.13 (2H, d, *J*=7.2 Hz, Ph–CH<sub>2</sub>CH), 3.78 (3H, s, OCH<sub>3</sub>), 5.12–5.17 (1H, m, C=CHCH<sub>2</sub>), 6.34 (1H, s, C<sub>2</sub>H), 6.80 (2H, d, *J*=8.6 Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.56 (2H, d, *J*=8.6 Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.59 (1H, d, *J*=15.4 Hz, C<sub>2</sub>H), 7.70 (1H, d, *J*=15.4 Hz, C<sub>6</sub>H), 7.80 (1H, s, C<sub>6</sub>H), 8.93 (1H, s, OH), 13.51 (1H, s, OH);  $\delta_C$  (acetone-*d*<sub>6</sub>) 17.89, 25.88, 29.28, 56.28, 100.00, 114.16, 118.35, 122.38, 123.78, 127.56, 131.21, 131.74, 132.50, 145.15, 161.08, 165.09, 166.44, 192.89; HRMS: M<sup>+</sup>, found 338.1530. C<sub>21</sub>H<sub>22</sub>O<sub>4</sub> requires 338.1518.

#### 4.34. Xanthoangelol (1e)

To a stirred solution of **15e** (50 mg, 0.10 mmol) in 2-PrOH (10 cm<sup>3</sup>) was added CBr<sub>4</sub> (6.9 mg, 0.02 mmol) at room temperature, after which the reaction mixture was stirred under reflux for 5 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was evaporated under vacuum. The residue was purified by PLC with hexane/ethyl acetate to afford compound **5a** (31 mg, 77%) as yellow needle crystal; mp (EtOAc/hexane) 122.7–123.7 °C; *R*<sub>f</sub> (33% EtOAc/hexane) 0.12;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3376, 3183, 3164, 2972, 2923, 2878, 2855, 1628, 1604, 1544, 1513, 1485, 1442, 1372, 1320, 1284, 1244, 1210, 1166, 1110, 1030;  $\delta_H$  (CDCl<sub>3</sub>) 1.59 (3H, s, CH<sub>3</sub>), 1.68 (3H, s, CH<sub>3</sub>), 1.83 (3H, s, CH<sub>3</sub>), 2.08–2.13 (4H, m, C<sub>4</sub>H and C<sub>5</sub>H), 3.49 (2H, d, *J*=7.1 Hz, C<sub>1</sub>H), 5.04–5.07 (1H, m, C<sub>6</sub>H), 5.29–5.32 (1H, m, C<sub>2</sub>H), 5.69 (1H, br s, OH), 6.25 (1H, br s, OH), 6.43 (1H, d, *J*=8.9 Hz, C<sub>5</sub>H), 6.88 (2H, d, *J*=8.6 Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.46 (1H, d, *J*=15.4 Hz, C<sub>2</sub>H), 7.55 (2H, d, *J*=8.6 Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.73 (1H, d, *J*=8.9 Hz, C<sub>6</sub>H), 7.84 (1H, d, *J*=15.4 Hz, C<sub>6</sub>H), 13.88 (1H, s, OH);  $\delta_C$  (CDCl<sub>3</sub>) 16.29, 17.72, 21.72, 25.68, 26.33, 39.72, 107.90, 113.95, 114.02, 115.60, 118.19, 121.00, 123.68, 127.92, 129.23, 130.54, 132.15, 139.92, 143.93, 157.83, 161.84, 163.85, 192.14. HRMS: M<sup>+</sup>, found 392.1966. C<sub>25</sub>H<sub>28</sub>O<sub>4</sub> requires 392.1988.

#### 4.35. Xanthoangelol F (1f)

To a stirred solution of **15f** (52 mg, 0.12 mmol) in MeOH (2 cm<sup>3</sup>) and CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>) was added *p*-toluenesulfonic acid monohydrate (66 mg, 0.36 mmol) and stirred at room temperature for 48 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was evaporated under vacuum. After addition of 10 cm<sup>3</sup> of water, the mixture was extracted with ethyl acetate (3 × 15 cm<sup>3</sup>). The organic layers were combined, washed with brine, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **1f** (43 mg, 92%) as yellow needle crystal, mp (EtOAc/hexane) 124.0–125.0 °C; *R*<sub>f</sub> (33% EtOAc/hexane) 0.15;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3278, 2968, 2925, 2844, 1626, 1605, 1579, 1543, 1511, 1490, 1455, 1442, 1411, 1373, 1322, 1279, 1248, 1223, 1201, 1169, 1120, 1072;  $\delta_H$  (CDCl<sub>3</sub>) 1.56 (3H, s, CH<sub>3</sub>), 1.63 (3H, d, *J*=0.9 Hz, CH<sub>3</sub>), 1.79 (3H, d, *J*=0.9 Hz, CH<sub>3</sub>), 1.95–1.99 (2H, m, C<sub>4</sub>H), 2.03–2.09 (2H, m, C<sub>5</sub>H), 3.39 (2H, d, *J*=7.0 Hz, C<sub>1</sub>H), 3.90 (3H, s, OCH<sub>3</sub>), 5.07–5.09 (1H, m, C<sub>6</sub>H), 5.21–5.25 (1H, m, C<sub>2</sub>H), 5.82 (1H, br s, OH), 6.49 (1H, d, *J*=9.2 Hz, C<sub>5</sub>H), 6.87 (2H, d, *J*=8.6 Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.46 (1H, d, *J*=15.4 Hz, C<sub>2</sub>H), 7.54 (2H, d, *J*=8.6 Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.78 (1H, d, *J*=9.2 Hz, C<sub>6</sub>H), 7.82 (1H, d, *J*=15.4 Hz, C<sub>6</sub>H), 13.44 (1H, s, OH);  $\delta_C$  (CDCl<sub>3</sub>) 16.15, 17.66, 21.68, 25.66, 26.74, 39.80, 55.77, 102.16, 114.66, 116.04, 117.70, 118.14, 121.89, 124.47, 127.70, 129.17, 130.17, 131.19, 135.39, 144.09, 158.14, 163.03, 163.36, 192.47; HRMS: M<sup>+</sup>, found 406.2144. C<sub>26</sub>H<sub>30</sub>O<sub>4</sub> requires 406.2144.

#### 4.36. 4'-Methylisoliquiritinigenin (24a)

To a stirred solution of **19a** (628 mg, 2 mmol) in MeOH (30 cm<sup>3</sup>) was added *p*-toluenesulfonic acid monohydrate (380 mg, 2.0 mmol) and stirred under reflux for 3 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was evaporated under vacuum. After addition of 10 cm<sup>3</sup> of water, the mixture was extracted with ethyl acetate (3 × 20 cm<sup>3</sup>). The organic layers were combined, washed with brine, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **24a** (442 mg, 82%) as yellow powder crystal; mp (EtOAc/hexane) 163.3–164.3 °C; *R*<sub>f</sub> (20% EtOAc/hexane) 0.15;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3249, 3082, 3045, 3030, 3008, 2976, 2952, 1633, 1609, 1589, 1576, 1547, 1508, 1457, 1442, 1416, 1376, 1326, 1287, 1227, 1169, 1137, 1107, 1023;  $\delta_H$  (MeOD-*d*<sub>4</sub>) 3.84

(3H, s, OCH<sub>3</sub>), 6.43 (1H, d, *J*=2.5 Hz, C<sub>3</sub>H), 6.52 (1H, dd, *J*=2.5 and 9.0 Hz, C<sub>5</sub>H), 6.84 (2H, d, *J*=8.7 Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.59 (1H, d, *J*=15.4 Hz, C<sub>9</sub>H), 7.59 (2H, d, *J*=8.7 Hz, C<sub>2</sub>H and C<sub>6</sub>H), 7.79 (1H, d, *J*=15.4 Hz, C<sub>9</sub>H), 8.00 (1H, d, *J*=9.0 Hz, C<sub>6</sub>H); δ<sub>C</sub> (MeOD-*d*<sub>4</sub>) 56.11, 102.01, 108.33, 115.40, 116.95, 118.24, 127.81, 131.92, 132.91, 146.04, 161.67, 167.44, 167.64, 193.76; HRMS: M<sup>+</sup>, found 270.0884. C<sub>16</sub>H<sub>14</sub>O<sub>4</sub> requires 270.0892.

#### 4.37. Isoliquiritigenin (24b)

To a stirred solution of **19b** (106 mg, 0.3 mmol) in MeOH (10 cm<sup>3</sup>) was added 5 drops of concd HCl and stirred at room temperature for 5 h. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was evaporated under vacuum. After addition of 10 cm<sup>3</sup> of water, the mixture was extracted with ethyl acetate (3×30 cm<sup>3</sup>). The organic layers were combined, washed with brine, dried over sodium sulfate, filtrated, and evaporated under vacuum. The residue was purified by silica gel column chromatography with hexane/ethyl acetate to afford compound **24b** (46 mg, 60%) as yellow powder crystal; mp (MeOH) 197.3–198.3 °C; *R*<sub>f</sub> (50% EtOAc/hexane) 0.2; ν<sub>max</sub> (KBr)/cm<sup>-1</sup> 3518, 3435, 3291, 3034, 2916, 2831, 2713, 1633, 1589, 1555, 1513, 1449, 1373, 1322, 1298, 1278, 1221, 1198, 1173, 1164, 1127, 1028; δ<sub>H</sub> (DMSO-*d*<sub>6</sub>) 6.30 (1H, d, *J*=2.3 Hz, C<sub>3</sub>H), 6.42 (1H, dd, *J*=2.3 and 8.8 Hz, C<sub>5</sub>H), 6.85 (2H, d, *J*=8.7 Hz, C<sub>3</sub>H and C<sub>5</sub>H), 7.76 (2H, s, C<sub>9</sub>H and C<sub>6</sub>H), 7.60 (2H, d, *J*=8.7 Hz, C<sub>2</sub>H and C<sub>6</sub>H), 8.17 (1H, d, *J*=8.8 Hz, C<sub>6</sub>H), 10.14 (1H, br s, OH), 10.68 (1H, br s, OH), 13.62 (1H, s, OH); δ<sub>C</sub> (DMSO-*d*<sub>6</sub>) 102.56, 108.07, 112.98, 115.82, 117.39, 125.73, 131.19, 132.81, 144.24, 160.24, 164.91, 165.76, 191.51; HRMS: M<sup>+</sup>, found 256.0725. C<sub>15</sub>H<sub>12</sub>O<sub>4</sub> requires 256.0736.

#### 4.38. Antibacterial activity

*E. coli* NBRC 3301, *P. mirabilis* NBRC 13300, *P. fluorescens* NBRC 3757, *B. subtilis* NBRC 3757, *S. epidermidis* NBRC 12993, and *M. luteus* NBRC 3333 were provided by NITE Biological Resource Center, National Institute of Technology and Evaluation, Japan. Appropriate amounts of samples were dissolved in dimethyl sulfoxide, respectively, to afford sample solutions. Each sample solution was mixed with Mueller Hinton agar by twofold dilution at 70–80 °C, and the mixture was cooled at room temperature to give the test plate. Antibacterial assay was performed using the agar dilution method according to the standard MIC determination method of Japan Society of Chemotherapy.<sup>37</sup> The preincubated cultures of each bacterial species in Mueller Hinton broth at 30 °C for 48 h were adjusted, respectively, to approximately 10<sup>6</sup> CFU/ml (CFU: colony-forming units) with sterile and buffered saline (pH 7.0) according to McFarland turbidity standards and was streaked on the test plate containing the sample in concentration from 1 to 256 μg/ml. Streptomycin was used as a positive control.

#### References and notes

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