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Regioselectivity in the ene reaction of singlet oxygen with *ortho*-prenylphenol derivatives

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Abstract—The ene reaction of singlet oxygen with prenylated dihydroxyacetophenones led to the 2-hydroperoxy-3-methylbut-3-enyl derivatives as the major product. This original regioselectivity outlined a new effect, in competition with the previously established large group non-bonding effect. The oxidation products distribution could be explained by a stabilising interaction between the phenolic hydrogen, *ortho* to the prenyl side chain, and the perepoxide intermediate. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

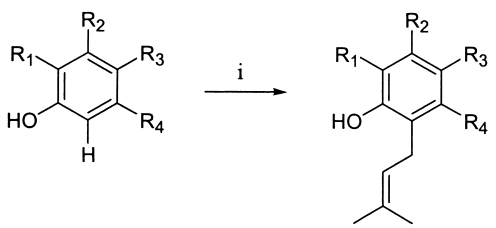
As part of our continuous research on bioactive natural product synthesis, we recently reported the first results of a study dealing with a new and selective access to *ortho*-(2-hydroxy-3-methylbut-3-enyl)phenols derivatives by direct photoxygenation of *ortho*-prenylphenol precursors.[1] Since the total synthesis of natural prenylated coumarins was particularly difficult, acetophenonic derivatives were chosen as simplified models in this preliminary study.

Furthermore an original oxidation products distribution was observed in the ene reaction of singlet oxygen with the prenyl side chain. The main issues of this paper is to report the full data of our preceding work and to elucidate the regioselective character of the Schenck reaction with the prenyl appendage.

2. Results and discussion

As previously described,[2] prenylation of 2,4-dihydroxyacetophenone was achieved in Lewis acidic medium with 2-methylbut-3-en-2-ol as the alkylating agent (Scheme 1). In these conditions, the two monoprenylated derivatives **1** and **2** and the bis-prenylated compound **3** were obtained in 9, 21, and 6% yield respectively (Table 1). The same method applied to the 2,6-dihydroxyacetophenone furnished **4** and **5** in 42 and 11% yield, respectively. We also prepared a series of prenylated monophenolic derivatives in order to enlarge the scope of our work on the Schenck ene reaction of singlet oxygen with *ortho*-prenylphenols. Yields, reported in Table 1, were not optimised. In each experiment, an important part of starting material was recovered after purification of the crude product over column chromatography.

For the photooxidation step, we chose the smoothest experimental conditions which have been previously reported. Thus, singlet oxygen was generated at −30°C in CH_2Cl_2 in the presence of tetraphenylporphin (TPP) as the photosensitizer. The photooxygenation–reduction sequence, applied to **1**, furnished a mixture of secondary and tertiary allylic alcohols in an 93% overall yield, determined by ^1H NMR spectroscopy (Scheme 2). This result proved the high chimioselectivity of the ene reaction towards the prenyl group, although phenolic functions were free.[3] Purification of the crude product by silica gel chromatography afforded **13** along with a mixture of **14** and **15**. The latter product resulted from an intramolecular



Scheme 1. Lewis acid mediated prenylation of phenolic derivatives. (i) 2-methylbut-3-en-2-ol, BF_3–Et_2O, dioxane, rt.

Keywords: Schenck ene reaction; prenyl chain; regioselectivity; large group effect; phenolic assistance.

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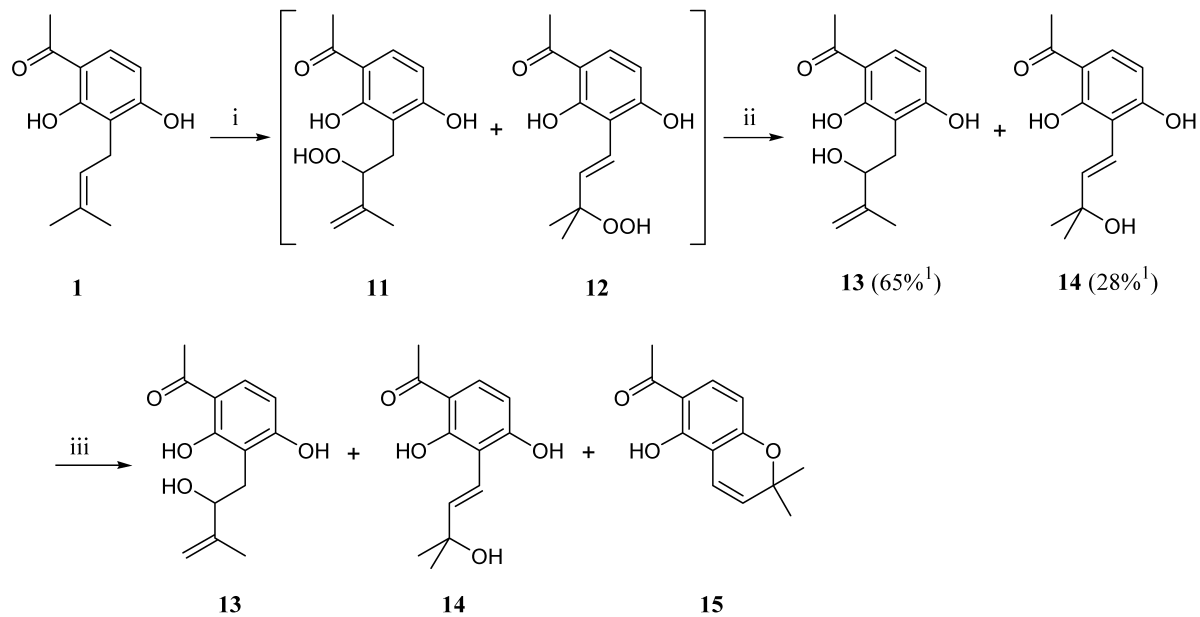
Table 1. C-Prenylated derivatives produced via Scheme 1

Compound	R_1	R_2	R_3	R_4	Yield % (%[a])
1	H	H	$COCH_3$	OH	9 (18)
2	H	OH	$COCH_3$	H	21 (41)
3	CH_2–CH=$C(CH_3)_2$	H	$COCH_3$	OH	5 (9)
4	$COCH_3$	OH	H	H	42 (69)
5	$COCH_3$	OH	CH_2–CH=$C(CH_3)_2$	H	11 (18)
6	H	H	CH_3	H	31 (44)
7	H	H	Ph	H	22 (64)
8	H	H	$COCH_3$	H	8 (33)
9	H	H	Br	H	15 (26)
10	H	H	Cl	H	12 (32)

[a] Yield based on recovered starting material.

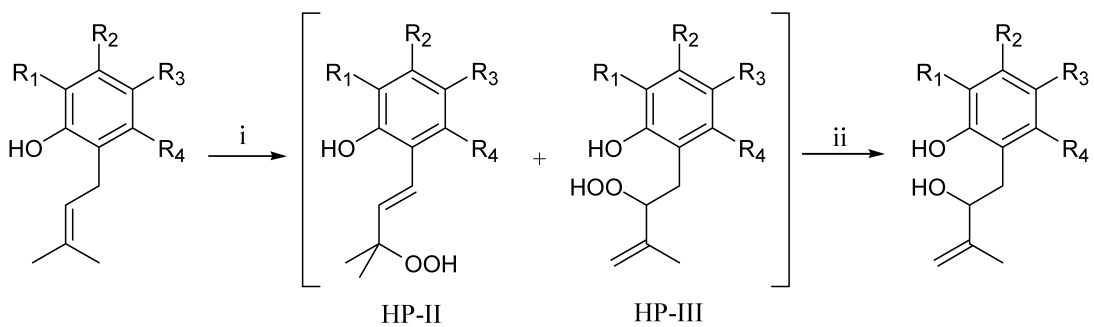


Scheme 2. Photooxygenation–reduction sequence achieved at −30°C. (i) *hν*, O_2, TPP, CH_2Cl_2, −30°C; (ii) PPh_3, CH_2Cl_2, −30°C, 15 h; (iii) SiO_2 (30% AcOEt/cyclohexane).

cyclisation of the 3-hydroxy-3-methylbut-1-enyl side chain with the unchelated phenolic group.

Photooxygenation–reduction sequence, achieved at 15°C, allowed us to isolate the secondary allylic alcohol as the sole product in 66% yield (Scheme 3 and Table 2, entry 1). It is known that tertiary allylic hydroperoxides could rearrange into secondary corresponding hydroperoxides.[4] In our case, the selectivity was explained by the instability of the tertiary allylic hydroperoxide intermediate (HP-III, Scheme 3) and was proved through ^{1}H NMR analysis of the mixture of allylic hydroperoxides **11** and **12**, prepared at −30°C which provided, after reduction, similar yields for the corresponding alcohols **13** and **14** (Scheme 4a).[1] The characteristic ^{1}H NMR signals for **12** rapidly disappeared when the temperature was allowed to rise at 15°C (Scheme 4b).

Thus, by running the two-step sequence at 15°C, several



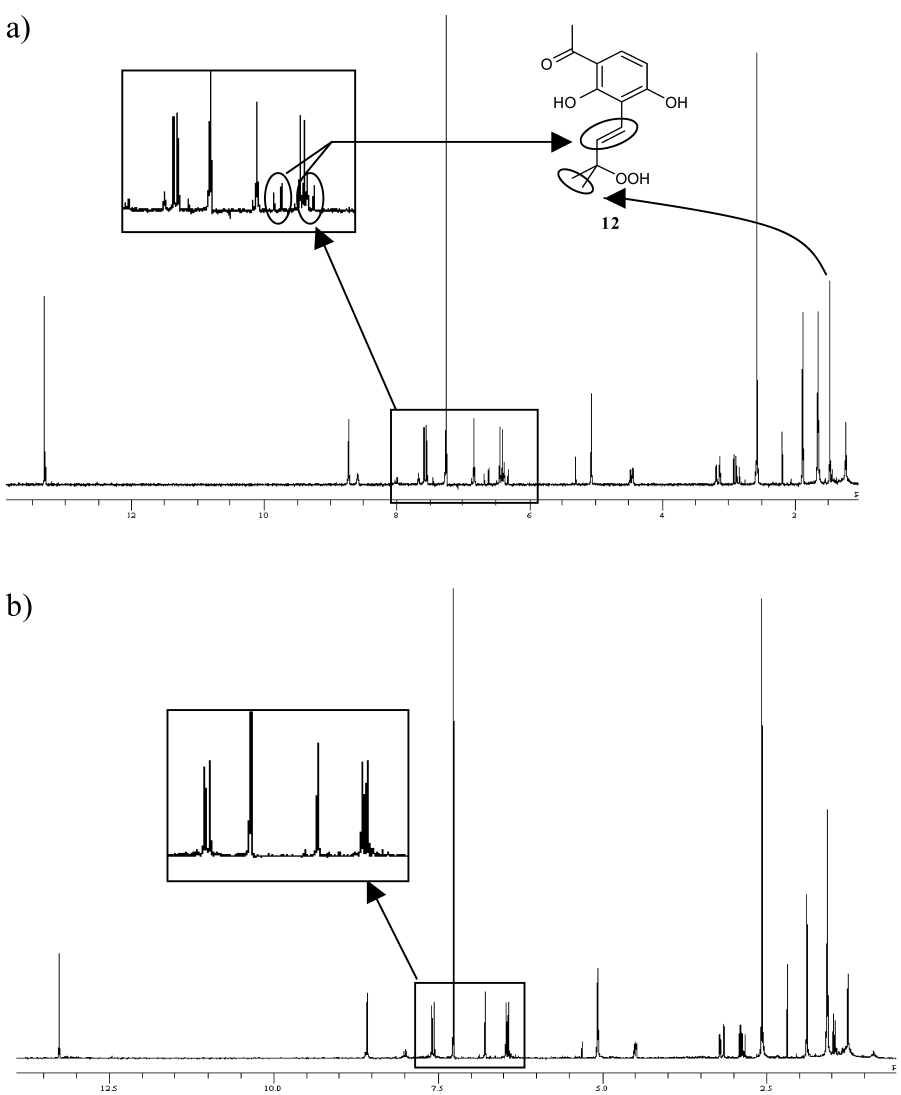
Scheme 3. Photooxygenation–reduction sequence achieved at 15°C. (i) *hν*, O_2, TPP, CH_2Cl_2, 15°C; (ii) PPh_3, CH_2Cl_2, 15°C, 15 h.

Table 2. Synthesis of secondary allylic alcohol via Scheme 3

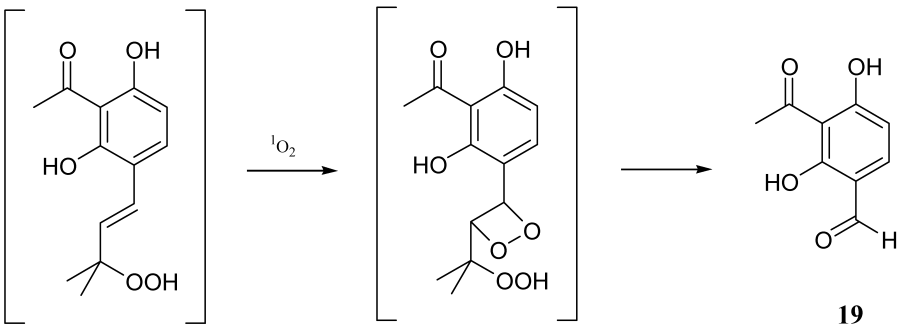
Entry	Starting material	R_1	R_2	R_3	R_4	Secondary allylic alcohol	Yield %
1	**1**	H	H	$COCH_3$	OH	**13**	66
2	**2**	H	OH	$COCH_3$	H	**16**	84
3	**3**	$CH_2-CH(OH)-C(CH_3)=CH_2$	H	$COCH_3$	OH	**17**	56
4	**4**	$COCH_3$	OH	H	H	**18**	65[a]
5	**6**	H	H	CH_3	H	**20**	43
6	**7**	H	H	Ph	H	**21**	56[b]
7	**8**	H	H	$COCH_3$	H	**23**	58
8	**9**	H	H	Br	H	**24**	44
9	**10**	H	H	Cl	H	**25**	51

[a] Accompanied by 3-acetyl-2,4-dihydroxybenzaldehyde **19** in 16% yield.
[b] Accompanied by 2-(3-hydroxy-3-methylbut-1-enyl)-4-phenylphenol **22** in 32% yield.

secondary allylic alcohols were obtained with yields ranging from 43 to 84% (Table 2). In most cases, intermediate tertiary allylic hydroperoxide (HP-III, Scheme 3) afforded spontaneously many degradation products in such low quantity that they could not be characterized. Nevertheless, isolation of by-products was possible in two different experiments. Indeed, 3-acetyl-2,4-dihydroxybenzaldehyde **19** was isolated, along with **18**, from **4** in 16% yield. **19**, which was detectable by ^{1}H NMR analysis after the photooxidation step, could result from the decomposition of an intermediate dioxetane, obtained from a [2+2] addition of singlet oxygen on the tertiary allylic hydroperoxide double bond (Scheme 5).[5] 2-(3-hydroxy-3-methylbut-1-enyl)-4-phenylphenol **22** was obtained from **7** at 15°C in 32% yield, along with **21** (Scheme 6). This unexpected result could be explained by a greater stability of the corresponding hydroperoxide at this temperature.



Scheme 4. 270 MHz ^{1}H NMR spectra ($CDCl_3$) of the photoxygenation reaction conducted at 0°C (a) and at room temperature (b) from **1**.

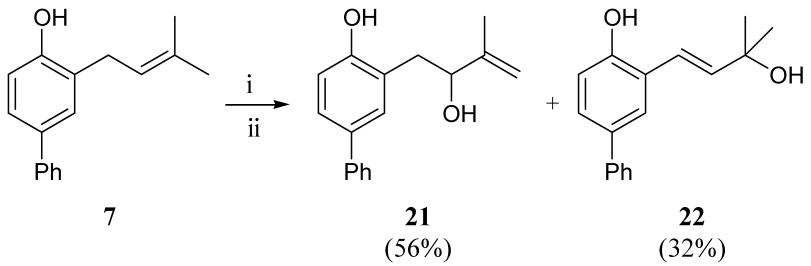


Scheme 5. Formation of **19** during the photooxygenation step.

In the past, a great deal of work has been focused on the regiochemical character of the singlet oxygen ene reaction. These studies led to the definition of various effects that could dictate the oxidation products distribution. Among them and regarding *ortho*-prenylphenol structure, only the cis effect and the large group non-bonded effect could be involved in the distribution of our allylic hydroperoxides.[6] As previously described for the photooxidation of 3-methyl-but-2-enylbenzene,[7] tertiary allylic hydroperoxides were expected as major products. In our case, the main products in the photooxygenation–reduction sequence were the *ortho*-(2-hydroxy-3-methylbut-3-enyl)phenol derivatives. Therefore, these results outlined a significant difference with the empirical rule of the large group non-bonded effect, phenyl substituents being probably responsible of such regioselectivity. A similar modification of the oxidation products distribution was already observed in the reaction of $^1O_2$ with geminal dimethyl trisubstituted homoallylic alcohols.[6] Then, an assistance of the hydroxyl group was postulated to explain such unusual regioselectivity. Therefore, in our case, we suspected that the *ortho*-phenolic group could be involved in the same type of stabilizing interaction with the perepoxide intermediate. To confirm this hypothesis, different derivatives related to **4** were prepared and submitted to the photooxidation–reduction sequence (Schemes 7 and 8). Then, we analysed and discussed the ratio of secondary and tertiary allylic alcohols (ratio II/III, Table 3).

Since the reduction step was considered as a quantitative reaction, the ratio II/III of allylic alcohols was exactly identical to the ratio of the corresponding hydroperoxides.

Compared to the previous results reported in Table 2, formation of the alcohol **27a** in a 30% yield at 15°C (entry 1, Table 3) pointed out the greater stability of the tertiary allylic hydroperoxide when the phenolic group, *para* to the prenyl side chain, was protected. Moreover, the first three experiments (entry 1–3, Table 3) revealed that neither the temperature of reaction nor the nature of the protective group significantly affected the value of the ratio II/III. As the dihydroxyacetophenone **4** furnished the alcohol **18** in 65% yield (entry 4, Table 2), the value of the ratio II/III obtained from **4a** and **4b** (entry 2,3, Table 3) demonstrated that protection of the phenolic group, *para* to the prenyl appendage, disfavoured the formation of the secondary allylic hydroperoxide. On an other hand, with the protection of the phenolic group, *ortho* to the prenyl chain

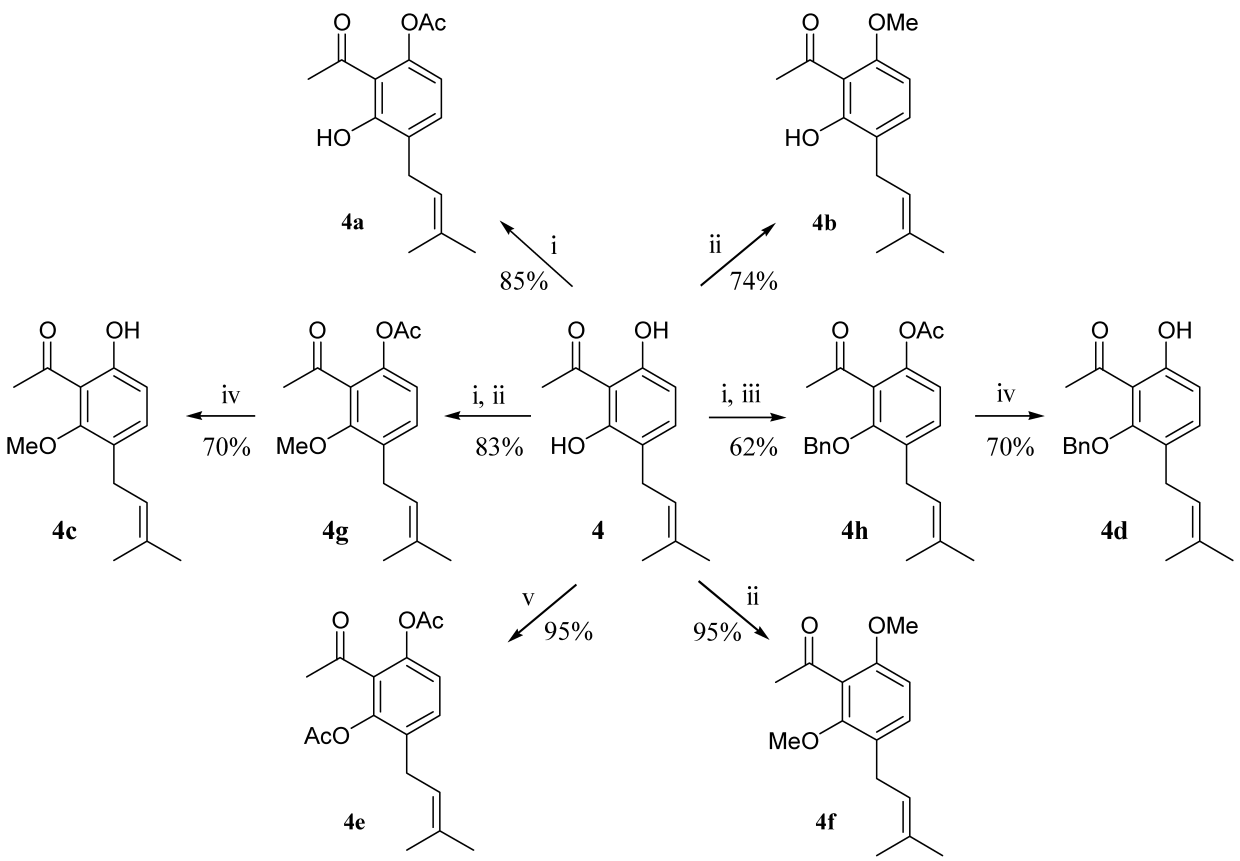


Scheme 6. *Reagents and conditions*: (i) $h\nu$, O_2, TPP, CH_2Cl_2, 15°C; (ii) PPh_3, CH_2Cl_2, 15°C, 15 h.

Table 3. Ratio of secondary and tertiary allylic alcohols in the photooxygenation–reduction sequence of **4a–f**

Entry	Starting material	R_1	R_2	Yields (%) Secondary allylic alcohol **26a–f** (II)	Tertiary allylic alcohol **27a–f** (III)	Ratio II/III
1	**4a**	$COCH_3$	H	43	30	59/41[a]
2	**4a**	$COCH_3$	H	45	36	55/45[b]
3	**4b**	CH_3	H	40	34	54/46[b]
4	**4c**	H	CH_3	29	41	41/59[b]
5	**4d**	H	CH_2Ph	35	51	41/59[b]
6	**4e**	$COCH_3$	$COCH_3$	26	45	34/66[a]
7	**4f**	CH_3	CH_3	33	55	37/63[a]

[a] Photooxygenation–reduction sequence achieved at 15°C.
[b] Photooxygenation–reduction sequence achieved at −30°C.

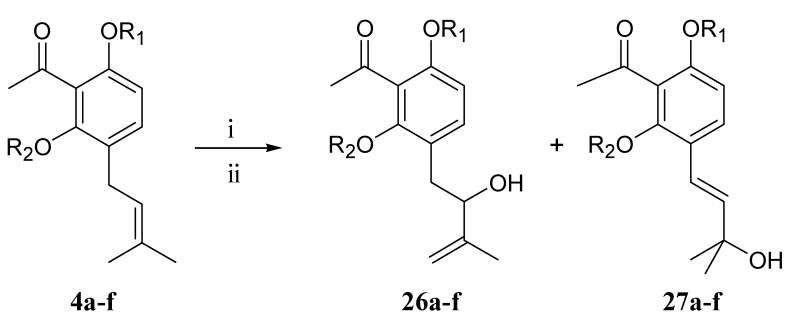


Scheme 7. *Reagents and conditions*: (i) CH_3COCl (1 equiv.), NEt_3 (1 equiv.), CH_2Cl_2, rt; (ii) Me_2SO_4 (1 equiv.), K_2CO_3, acetone, reflux; (iii) $C_6H_5CH_2Br$ (1.5 equiv.), $(C_4H_9)_4N^+I^-$, K_2CO_3, acetone, reflux; (iv) $NaHCO_3$, MeOH, H_2O, rt; (v) CH_3COCl (4 equiv.), NEt_3 (4 equiv.), CH_2Cl_2, rt.

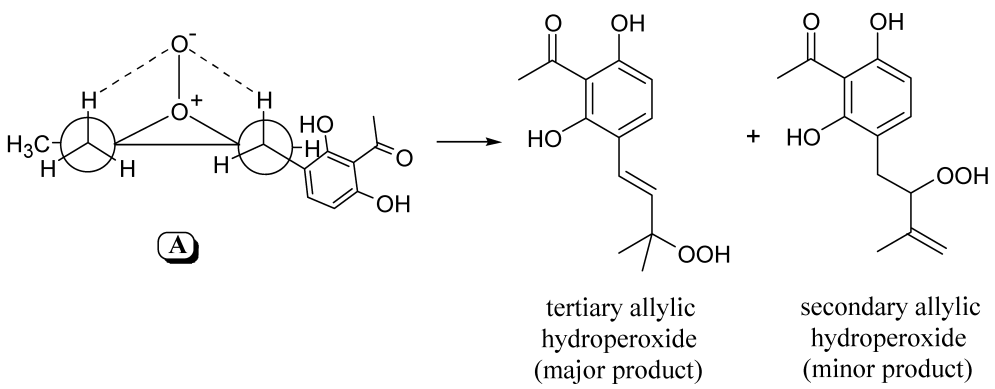
(entry 4,5, Table 3), formation of tertiary allylic hydroperoxides was more favoured. The same regioselectivity trend was observed when both phenolic groups were protected (entry 6,7, Table 3).

Following these experimental results, it was obvious that evolution of the ratio II/III in favour of tertiary allylic alcohols could be associated with the chemical modification of the phenolic group, *ortho* to the prenyl side chain. Photooxidation of a prenylated dihydroxyacetophenone led predominantly to the secondary allylic hydroperoxide derivative. Furthermore, with the protection of the *ortho*-phenolic function ($R_2 \neq H$, Scheme 8), hydrogen abstraction from the methylene group, leading to tertiary allylic hydroperoxides, was more favoured than abstraction from the methyl groups. To explain such observations, we envisaged a competition between two coexistent possibilities for the stabilization of the perepoxide, which was likely the most acceptable intermediate.[8] In accordance with the previously defined '*cis* effect',[6] the conformation A (Scheme 9) implied the interaction of the negatively charged oxygen of the perepoxide with two allylic hydrogens, in a perpendicular alignment to the double bond plane. Thereby regarding this conformation, a mixture of tertiary and secondary hydroperoxides was obtained. Due to the well known large group non-bonded effect,[6] allylic hydrogens next to the phenyl group were more reactive. As a consequence, transition state A led to the tertiary allylic hydroperoxide as the major photooxidation product.

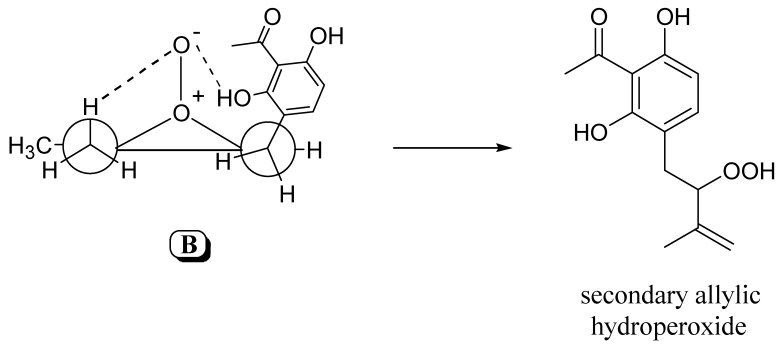
In the conformation B (Scheme 10), stabilization of the perepoxide intermediate no longer involved two allylic hydrogens. Thus, hydrogen bonding between the negatively charged oxygen and the phenolic function, *ortho* to the



Scheme 8. *Reagents and conditions*: (i) *hν*, O_2, TPP, CH_2Cl_2; (ii) PPh_3, CH_2Cl_2, 15 h.



Scheme 9. Classical stabilization of the perepoxide intermediate.



Scheme 10. Stabilizing interaction hypothesis involving the perepoxide intermediate and the nearby phenolic hydrogen.

prenyl side chain, is proposed instead of an interaction with the methylene hydrogens. Hence, transition state B could only afford the secondary allylic hydroperoxide.

Both phenols of the dihydroxyacetophenone **4** interacted with the nearby ketone through hydrogen bonding. Therefore, because of the protection of the phenolic group, *para* to the prenyl side chain, the remaining phenol of **4a** and **4b** was involved in a stronger chelation. As a consequence, the phenolic hydrogen was less available to interact with the negatively charged oxygen of the perepoxide intermediate. In that case, transition state A was more favoured than transition state B, leading to a noticeable decreased percentage of secondary allylic alcohols in the ratio II/III (entry 2,3, Table 3), compared to the 65% yield for **18** obtained from dihydroxyacetophenone **4** (entry 4, Table 2).

3. Conclusion

In conclusion, in the present study, we reported a straightforward access to *ortho*-(2-hydroxy-3-methylbut-3-enyl)phenol derivatives from *ortho*-prenylphenol precursors based on the Schenck reaction. We demonstrated that achieving the photooxydation–reduction sequence at 15°C afforded solely the secondary allylic alcohol. As the tertiary allylic hydroperoxide was the minor oxidation product, our work also pointed out an original regioselectivity in the ene reaction of singlet oxygen with *ortho*-prenylphenol compounds. Hence, contrary to a reaction exclusively controled by the large group non-bonded effect, allylic hydrogens of methyl groups were more reactive than allylic hydrogens next to the phenyl ring. For the mechanistic interpretation of these experimental results, we could envisage a stabilizing interaction of the negatively charged oxygen of the perepoxide intermediate with the phenolic hydrogen, *ortho* to the prenyl side chain. Such effect was previously demonstrated with hydroxyl groups in the photooxygenation of homoallylic and allylic alcohols.[6,9] Therefore, we believe that in the series of substrates examined here, both the classical large group effect and the phenolic hydrogen assistance dictated the ene products distribution. As many natural products isolated in our laboratory were substituted by a 2-hydroxy-3-methylbut-3-enyl appendage, *ortho* to a phenolic function, application of the photooxygenation–reduction sequence to their synthesis will be reported in a forthcoming paper.

4. Experimental

4.1. General

Dioxane was distilled from sodium, using benzophenone as indicator, dichloromethane was distilled from calcium hydride. Si gel 60 (Macherey–Nagel, 230–400 mesh) was used for column chromatography and precoated Si gel plates (Macherey–Nagel, SIL G/UV254, 0.25 mm) were used for preparative TLC. NMR spectra were recorded in $CDCl_3$ or CD_3OD solutions on Bruker Avance DRX 500 and Jeol GSX 270 WB instruments. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. HREIMS (70 eV) and

HRFABMS were recorded on a Jeol JMS-700 spectrometer. Melting points were determined on an Electrothermal 8100 melting point apparatus and are uncorrected.

4.2. General procedure for the preparation of prenylated phenolic compounds

To a dioxane solution (8 ml/g) of phenolic derivative, purchased commercially, was added 0.3 equiv. of boron trifluoride etherate. Then, a dioxane solution of 2-methyl-but-3-en-2-ol (1.2 equiv.) was poured dropwise over a period of 50 min. The mixture was stirred at room temperature for several days. Then an aqueous solution (15%, 20 ml) of sodium acetate was added and the reaction mixture was concentrated for elimination of dioxane. 50 ml of ethyl acetate was added and the organic phase was washed four times with a sodium acetate solution in water (15%) (50 ml), dried over sodium sulfate and filtered. A viscous crude oil was obtained after solvent elimination. The mixture was then separated using liquid chromatography.

4.2.1. 1-[2,4-Dihydroxy-3-(3-methylbut-2-enyl)phenyl]-ethanone 1. The typical conditions described in Section 4.2 were employed with 2,4-dihydroxyacetophenone (5 g, 32.9 mmol). After 2 days, purification of the crude product by column chromatography (15% AcOEt/cyclohexane) yielded **1** as a white powder (651 mg, 9%), mp: 128–130°C; IR (cm^{-1}): 3170, 1623, 1589, 1273; ^1H NMR ($CDCl_3$, 270 MHz): δ 13.10 (s, 1H, OH), 7.55 (d, 1H arom., J=8.5 Hz), 6.39 (d, 1H arom., J=8.5 Hz), 6.12 (s, 1H, OH), 5.27 (t, 1H, CH_2CH, J=7 Hz), 3.45 (d, 2H, CH_2CH, J=7 Hz), 2.57 (s, 3H, $COCH_3$), 1.84 (s, 3H, CH_3), 1.77 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 202.8 (C=O), 162.5, 161.5 (2×quat. arom. C), 135.9 ($CH=C(CH_3)_2$), 130.3 (arom. CH), 121.0 (CH_2CH), 113.8 (2×quat. arom. C), 107.8 (arom. CH), 26.2 ($COCH_3$), 25.8 (CH_3), 21.6 (CH_2CH), 17.9 (CH_3); EI-HRMS Calcd for $C_{13}H_{16}O_3$ (M^+) 220.1099, Found 220.1102.

4.2.2. 1-[2,4-Dihydroxy-5-(3-methylbut-2-enyl)phenyl]-ethanone 2. The typical conditions described in Section 4.2 were employed with 2,4-dihydroxyacetophenone (5 g, 32.9 mmol). After 2 days, purification of the crude product by column chromatography (15% AcOEt/cyclohexane) yielded **2** as a white powder (1.52 g, 21%), mp: 124–125°C; IR (cm^{-1}): 3285, 1637, 1235; ^1H NMR ($CDCl_3$, 270 MHz): δ 12.53 (s, 1H, OH), 9.41 (s, 1H, OH), 7.45 (s, 1H arom.), 6.37 (s, 1H arom.), 5.30 (t, 1H, CH_2CH, J=7 Hz), 3.31 (d, 2H, CH_2CH, J=7 Hz), 2.57 (s, 3H, $COCH_3$), 1.80 (s, 6H, 2×CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 202.8 (C=O), 163.7, 161.7 (2×quat. arom. C), 135.6 ($CH=C(CH_3)_2$), 132.3 (arom. CH), 121.4 (CH_2CH), 118.8, 114.2 (2×quat. arom. C), 103.8 (arom. CH), 29.1 (CH_2CH), 26.1 ($COCH_3$), 25.7 (CH_3), 17.8 (CH_3); EI-HRMS Calcd for $C_{13}H_{16}O_3$ (M^+) 220.1099, Found 220.1101.

4.2.3. 1-[2,4-Dihydroxy-3,5-bis-(3-methylbut-2-enyl)-phenyl]ethanone 3. The typical conditions described in Section 4.2 were employed with 2,4-dihydroxyacetophenone (5 g, 32.9 mmol). After 2 days, purification of the crude product by column chromatography (15% AcOEt/cyclohexane) yielded **3** as a white powder (434 mg, 5%), mp: 99–100°C; IR (cm^{-1}): 3299, 1630, 1583, 1207; ^1H NMR ($CDCl_3$, 270 MHz): δ 12.94 (s, 1H, OH), 7.36 (s, 1H arom.), 6.23 (s, 1H, OH), 5.29 (t, 1H, CH_2CH, J=7 Hz), 5.25 (t, 1H, CH_2CH, J=7 Hz), 3.41 (d, 2H, CH_2CH, J=7 Hz), 3.29 (d, 2H, CH_2CH, J=7 Hz), 2.55 (s, $COCH_3$), 1.83 (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.76 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 202.7 (C=O), 161.0, 160.0 (2×quat. arom. C), 135.1, 134.5 (2×$CH=C(CH_3)_2$), 129.5 (arom. CH), 121.7, 121.3 (2×CH_2CH), 118.8, 114.1, 113.4 (3×quat. arom. C), 29.0 (CH_2CH), 26.2 ($COCH_3$), 25.8 (2×CH_3), 21.8 (CH_2CH), 17.9 (2×CH_3); EI-HRMS Calcd for $C_{18}H_{24}O_3$ (M^+) 288.1725, Found 288.1716.

4.2.4. 1-[2,6-Dihydroxy-3-(3-methylbut-2-enyl)phenyl]-ethanone 4. The typical conditions described in Section 4.2 were employed with 2,6-dihydroxyacetophenone (3 g, 19.7 mmol). After 2 days, purification of the crude product by column chromatography (15% AcOEt/cyclohexane) yielded **4** as a yellow powder (1.82 g, 42%), mp: 80–81°C; IR (cm^{-1}): 3347, 1616, 1597, 1257; ^1H NMR ($CDCl_3$, 270 MHz): δ 9.87 (br s, 1H, OH), 9.24 (br s, 1H, OH), 7.13 (d, 1H arom., J=8 Hz), 6.33 (d, 1H arom., J=8 Hz), 5.29 (t, 1H, CH_2CH, J=7.5 Hz), 3.29 (d, 2H, CH_2CH, J=7.5 Hz), 2.73 (s, 3H, $COCH_3$), 1.78 (s, 6H, 2×CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 205.3 (C=O), 159.6, 159.4 (2×quat. arom. C), 136.2 (arom. CH), 135.1 ($CH=C(CH_3)_2$), 121.6 (CH_2CH), 119.2, 110.2 (2×quat. arom. C), 107.4 (arom. CH), 33.6 ($COCH_3$), 28.8 (CH_2CH), 25.8 (CH_3), 17.8 (CH_3); EI-HRMS Calcd for $C_{13}H_{16}O_3$ (M^+) 220.1099, Found 220.1102.

4.2.5. 1-[2,6-Dihydroxy-3,5-bis(3-methylbut-2-enyl)-phenyl]ethanone 5. The typical conditions described in Section 4.2 were employed with 2,6-dihydroxyacetophenone (3 g, 19.7 mmol). After 2 days, purification of the crude product by column chromatography (15% AcOEt/cyclohexane) yielded **5** as a yellow oil (625 mg, 11%), IR (cm^{-1}): 3418, 1618, 1228, 1090; ^1H NMR ($CDCl_3$, 270 MHz): δ 9.64 (br s, 2H, OH), 7.01 (s, 2H arom.), 5.29 (t, 2H, 2×CH_2CH, J=7 Hz), 3.28 (d, 4H, 2×CH_2CH, J=7 Hz), 2.72 (s, 3H, $COCH_3$), 1.78 (s, 12H, 4×CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 205.5 (C=O), 157.7 (2×quat. arom. C), 136.7 (arom. CH), 134.8 (2×$CH=C(CH_3)_2$), 121.9 (2×CH_2CH), 118.2, 110.4 (3×quat. arom. C), 33.7 ($COCH_3$), 28.8 (2×CH_2CH), 25.8 (2×CH_3), 17.8 (2×CH_3); EI-HRMS Calcd for $C_{18}H_{24}O_3$ (M^+) 288.1725, Found 288.1730.

4.2.6. 4-Methyl-2-(3-methylbut-2-enyl)phenol 6. The typical conditions described in Section 4.2 were employed with *para*-methylphenol (0.5 g, 4.6 mmol). After 4 days, purification of the crude product by column chromatography (CH_2Cl_2) yielded **6** as a orange oil (253 mg, 31%), IR (cm^{-1}): 3375, 1494, 1248; ^1H NMR ($CDCl_3$, 270 MHz): δ 6.89–6.95 (m, 2H arom.), 6.72 (d, 1H arom., J=9 Hz), 5.33 (t, 1H, CH_2CH, J=7 Hz), 5.03 (s, 1H, OH), 3.34 (d, 2H, CH_2CH, J=7 Hz), 2.28 (s, p-CH_3), 1.80 (s, 3H, CH_3), 1.79 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 151.9 (quat. arom. C), 134.3 ($CH=C(CH_3)_2$), 130.5 (arom. CH), 129.8 (quat. arom. C), 127.8 (arom. CH), 126.6 (quat. arom. C), 121.9 (CH_2CH), 115.4 (arom. CH), 29.7 (CH_2CH), 25.8

(CH$_3$), 20.5 (p-CH$_3$), 17.8 (CH$_3$); EI-HRMS Calcd for $C_{12}H_{16}O$ (M^+) 176.1201, Found 176.1210.

4.2.7. 2-(3-Methylbut-2-enyl)-4-phenylphenol 7. The typical conditions described in Section 4.2 were employed with *para*-phenylphenol (1 g, 5.9 mmol). After 3 days, purification of the crude product by column chromatography (10% AcOEt/cyclohexane) yielded **7** as a colorless oil (308 mg, 22%), IR (cm^{-1}): 3443, 1486; ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.56 (d, 2H arom., J=9 Hz), 7.30–7.45 (m, 5H arom.), 6.88 (d, 1H arom., J=9 Hz), 5.38 (t, 1H, CH$_2$CH, J=7 Hz), 5.19 (s, 1H, OH), 3.43 (d, 2H, CH_2CH, J=7 Hz), 1.82 (s, 3H, CH_3), 1.80 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 155.3, 141.0 (2×quat. arom. C), 135.0 (CH=C(CH$_3$)$_2$), 133.9 (quat. arom. C), 128.8, 128.6, 126.7, 126.6, 126.2 (7×arom. CH), 125.8 (quat. arom. C), 121.6 (CH$_2$$C$H), 116.0 (arom. CH), 30.0 (CH$_2$CH), 25.8 (CH$_3$), 17.9 (CH$_3$); EI-HRMS Calcd for $C_{17}H_{18}O$ (M^+) 238.1358, Found 238.1358.

4.2.8. 4-[(3-Methylbut-2-enyl)oxy]-1,1′-biphenyl 7a. The typical conditions described in Section 4.2 were employed with *para*-phenylphenol (1 g, 5.9 mmol). After 3 days, purification of the crude product by column chromatography (10% AcOEt/cyclohexane) yielded **7a** as a white solid (120 mg, 9%), mp: 59–61°C; IR (cm^{-1}): 1607, 1488, 1270; ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.59–7.51 (m, 4H arom.), 7.45–7.40 (m, 5H arom.), 7.34–7.28 (m, 1H arom.), 7.01 (d, 2H arom., J=9 Hz), 5.55 (t, 1H, CH$_2$CH, J=7 Hz), 4.57 (d, 2H, CH_2CH, J=7 Hz), 1.84 (s, 3H, CH_3), 1.79 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 158.3, 140.7 (quat. arom. C), 138.2 (CH=C(CH$_3$)$_2$), 133.6 (quat. arom. C), 128.6, 128.0, 126.6, 126.5 (7×arom. CH), 119.6 (CH$_2$$C$H), 114.8 (arom. CH), 64.8 (CH$_2$CH), 25.9 (CH$_3$), 18.3 (CH$_3$); EI-HRMS Calcd for $C_{17}H_{18}O$ (M^+) 238.1358, Found 238.1360.

4.2.9. 3,5-Bis(3-methylbut-2-enyl)-4-phenylphenol 7b. The typical conditions described in Section 4.2 were employed with *para*-phenylphenol (1 g, 5.9 mmol). After 3 days, purification of the crude product by column chromatography (10% AcOEt/cyclohexane) yielded **7b** as a colorless oil (54 mg, 3%), IR (cm^{-1}): 3459, 1469, 1183; ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.57–7.52 (m, 2H arom.), 7.45–7.38 (m, 2H arom.), 7.33–7.28 (m, 1H arom.), 7.23 (s, 2H arom.), 5.44 (s, 1H, OH), 5.38 (t, 1H, CH$_2$CH, J=7.5 Hz), 3.43 (d, 2H, CH_2CH, J=7.5 Hz), 1.82 (s, 3H, CH_3), 1.80 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 152.2, 141.2 (quat. arom. C), 134.3 (2×CH=C(CH$_3$)$_2$), 133.4 (quat. arom. C), 128.5, 127.4, 126.8, 126.6 (7×arom. CH), 122.0 (2×CH$_2$$C$H), 29.9 (2×$CH_2$CH), 25.9 (2×$CH_3$), 18.0 (2×$CH_3$); EI-HRMS Calcd for $C_{22}H_{26}O$ (M^+) 306.1984, Found 305.1543.

4.2.10. 1-[4-Hydroxy-3-(3-methylbut-2-enyl)phenyl]-ethanone 8. The typical conditions described in Section 4.2 were employed with 4-hydroxyacetophenone (0.5 g, 3.7 mmol). After 2 days, purification of the crude product by column chromatography (30% AcOEt/cyclohexane) yielded **8** as a white powder (60 mg, 8%), mp: 66–68°C; IR (cm^{-1}): 3239, 1653, 1587, 1276; ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.78 (dd, 1H arom., J=8 Hz, 2.5 Hz), 7.75 (d, 1H arom., J=2.5 Hz), 6.88 (d, 1H arom., J=8 Hz), 6.70 (s, 1H, OH), 5.33 (t, 1H, CH$_2$CH, J=7.5 Hz), 3.41 (d, 2H, CH_2CH, J=7.5 Hz), 2.57 (s, 3H, COCH_3), 1.79 (s, 3H, CH_3), 1.78 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 198.1 (C=O), 159.4 (quat. arom. C), 134.9 (CH=C(CH$_3$)$_2$), 130.8 (arom. CH), 129.8 (quat. arom. C), 128.9 (arom. CH), 127.4 (quat. arom. C), 121.2 (CH$_2$$C$H), 115.4 (arom. CH), 29.3 (CH$_2$CH), 26.3 (COCH$_3$), 25.8 (CH$_3$), 17.9 (CH$_3$); EI-HRMS Calcd for $C_{13}H_{16}O_2$ (M^+) 204.1150, Found 204.1150.

4.2.11. 1-[4-(3-Methylbut-2-enyloxy)phenyl]ethanone 8a. The typical conditions described in Section 4.2 were employed with 4-hydroxyacetophenone (0.5 g, 3.7 mmol). After 2 days, purification of the crude product by column chromatography (30% AcOEt/cyclohexane) yielded **8a** as a colorless oil (44 mg, 6%), IR (cm^{-1}): 1675, 1598, 1244; ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.93 (d, 2H arom., J=9 Hz), 6.93 (d, 2H arom., J=9 Hz), 5.49 (t, 1H, CH$_2$CH, J=7 Hz), 4.57 (d, 2H, CH_2CH, J=7 Hz), 2.56 (s, 3H, COCH_3), 1.80 (s, 3H, CH_3), 1.76 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 196.8 (C=O), 162.8 (quat. arom. C), 138.6 (CH=C(CH$_3$)$_2$), 130.5 (arom. CH), 130.1 (quat. arom. C), 118.9 (CH$_2$$C$H), 114.3 (arom. CH), 64.9 (CH$_2$CH), 26.3 (COCH$_3$), 25.8 (CH$_3$), 18.2 (CH$_3$); EI-HRMS Calcd for $C_{13}H_{16}O_2$ (M^+) 204.1150, Found 204.115.

4.2.12. 4-Bromo-2-(3-methylbut-2-enyl)phenol 9. The typical conditions described in Section 4.2 were employed with *para*-bromophenol (5 g, 17.3 mmol). After 3 days, purification of the crude product by column chromatography (35% AcOEt/cyclohexane) yielded **9** as a orange oil (626 mg, 15%), IR (cm^{-1}): 3416, 1481, 1266; ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.22 (s, 1H arom.), 7.20 (d, 1H arom., J=7 Hz), 6.69 (d, 1H arom., J=7 Hz), 5.33 (t, 1H, CH$_2$CH, J=7 Hz), 5.25 (s, 1H, OH), 3.37 (d, 2H, CH_2CH, J=7 Hz), 1.84 (s, 3H, CH_3), 1.82 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 153.4 (quat. arom. C), 135.6 (CH=C(CH$_3$)$_2$), 132.4, 130.1 (arom. CH), 129.2 (quat. arom. C), 120.8 (CH$_2$$C$H), 117.3 (arom. CH), 112.6 (quat. arom. C), 29.4 (CH$_2$CH), 25.8 (CH$_3$4), 17.9 (CH$_3$); EI-HRMS Calcd for $C_{11}H_{13}BrO$ (M^+) 240.0150, Found 240.0145.

4.2.13. 1-Bromo-4-[(3-methylbut-2-enyl)oxy]benzene 9a. The typical conditions described in Section 4.2 were employed with *para*-bromophenol (5 g, 17.3 mmol). After 3 days, purification of the crude product by column chromatography (35% AcOEt/cyclohexane) yielded **9a** as an orange oil (334 mg, 8%), IR (cm^{-1}): 1486, 1234; ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.37 (d, 2H arom., J=9 Hz), 6.80 (d, 2H arom., J=9 Hz), 5.47 (t, 1H, CH$_2$CH, J=7 Hz), 4.48 (d, 2H, CH_2CH, J=7 Hz), 1.80 (s, 3H, CH_3), 1.75 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 157.9 (quat. arom. C), 138.6 (CH=C(CH$_3$)$_2$), 132.2 (arom. CH), 119.2 (CH$_2$$C$H), 116.5 (arom. CH), 112.7 (quat. arom. C), 65.0 (CH$_2$CH), 25.8 (CH$_3$4), 18.2 (CH$_3$).

4.2.14. 4-Chloro-2-(3-methylbut-2-enyl)phenol 10. The typical conditions described in Section 4.2 were employed with *para*-chlorophenol (5 g, 38.9 mmol). After 3 days, purification of the crude product by column chromatography (35% AcOEt/cyclohexane) yielded **10** as a orange oil (930 mg, 12%), IR (cm^{-1}): 3401, 1482, 1264; ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.20 (d, 1H arom., J=2.5 Hz), 7.14

(dd, 1H arom., J=8.5 Hz, 2.5 Hz), 6.64 (dd, 1H arom., J=8.5 Hz, 2.5 Hz), 5.27 (t, 1H, CH_2CH, J=7 Hz), 5.13 (s, 1H, OH), 3.29 (d, 2H, CH_2CH, J=7 Hz), 1.76 (s, 3H, CH_3), 1.72 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 152.9 (quat. arom. C), 135.6 ($CH{=}C(CH_3)_2$), 129.6 (arom. CH), 128.6 (quat. arom. C), 127.2 (arom. CH), 125.3 (quat. arom. C), 120.8 (CH_2CH), 116.8 (arom. CH), 29.5 (CH_2CH), 25.8 (CH_3), 17.9 (CH_3); EI-HRMS Calcd for $C_{11}H^{13}ClO$ (M^+) 196.0655, Found 196.0647.

4.2.15. 1-Chloro-4-[(3-methylbut-2-enyl)oxy]benzene 10a. The typical conditions described in Section 4.2 were employed with *para*-chlorophenol (5 g, 38.9 mmol). After 3 days, purification of the crude product by column chromatography (35% AcOEt/cyclohexane) yielded **10a** as a colorless oil (860 mg, 11%), IR (cm^{-1}): 1490, 1237; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.28 (d, 2H arom., J=9 Hz), 6.90 (d, 2H arom., J=9 Hz), 5.53 (t, 1H, CH_2CH, J=7 Hz), 4.54 (d, 2H, CH_2CH, J=7 Hz), 1.85 (s, 3H, CH_3), 1.80 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 157.4 (quat. arom. C), 137.9 ($CH{=}C(CH_3)_2$), 129.2 (arom. CH), 119.3 (CH_2CH), 118.2 (quat. arom. C), 115.9 (arom. CH), 65.0 (CH_2CH), 25.8 (CH_3), 18.2 (CH_3); EI-HRMS Calcd for $C_{11}H^{13}ClO$ (M^+) 196.0655, Found 196.066.

4.3. General procedure for the photooxygenation–reduction sequence at 15°C

Dried air was bubbled through a CH_2Cl_2 solution (30 ml) of phenolic prenylated compound (30 mg) and tetraphenylporphine (3 mg, 0.005 mmol) as the photosensitizer. The reaction mixture was water-cooled at 15°C and irradiated with a halogen lamp (500 W) for 1.5 h. Then 1.1 equiv. of triphenylphosphine was added and the solution was stirred overnight at room temperature.

4.4. Purification

Procedure A. The reaction mixture was washed four times with 30 ml of an aqueous solution of potassium carbonate (10%). The combined aqueous layers were acidified down to pH=3 by addition of water-diluted chlorhydric acid (10%). Then this solution was extracted four times with 30 ml of dichloromethane. The combined organic layers were concentrated under reduced pressure and were subjected to a second cycle of basic extraction. The final organic layers were evaporated under reduced pressure and yielded the purified secondary allylic alcohol derivative.

Procedure B. This procedure only differed from the preceding procedure by the nature of the basic solution. Here, we used an aqueous solution of potassium hydroxide (5%).

4.4.1. 1-[2,4-Dihydroxy-3-(2-hydroxy-3-methylbut-3-enyl)phenyl]ethanone 13. The typical conditions described in Section 4.3 were employed with **1** (30 mg, 0.14 mmol). The purification of the crude product according to procedure A followed by a recristallization in AcOEt/hexane afforded **13** as white cristals (21 mg, 66%), mp: 79–80°C; IR (cm^{-1}): 3442, 1617, 1270; ^1H NMR ($CDCl_3$, 270 MHz): δ 13.11 (s, 1H, OH), 7.55 (d, 1H arom., J=9 Hz), 6.47 (d, 1H arom., J=9 Hz), 4.99 (br s, 1H, C=CH_2), 4.86 (br s, 1H, C=CH_2), 4.38 (dd, 1H, CH_2CHOH, J=8 Hz, 2 Hz), 3.15 (dd, 1H, CH_2CHOH, J=15 Hz, 2 Hz), 2.85 (dd, 1H, CH_2CHOH, J=15 Hz, 8 Hz), 2.55 (s, 3H, $COCH_3$), 1.85 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 202.8 (C=O), 163.3, 163.0 (2×quat. arom. C), 146.7 ($CH_2{=}C(CH_3)$), 130.9 (arom. CH), 113.4, 112.8 (2×quat. arom. C), 110.4 ($CH_2{=}C(CH_3)$), 109.0 (arom. CH), 77.5 (CH_2CHOH), 28.3 (CH_2CHOH), 26.2 ($COCH_3$), 18.5 (CH_3); FAB-HRMS Calcd for $C_{13}H_{17}O_4$ ($[M+H]^+$) 237.1127, Found 237.1129.

4.4.2. 1-[2,4-Dihydroxy-5-(2-hydroxy-3-methylbut-3-enyl)phenyl]ethanone 16. The typical conditions described in Section 4.3 were employed with **2** (30 mg, 0.14 mmol). The purification of the crude product according to procedure A yielded **16** as a green oil (27 mg, 84%), IR (cm^{-1}): 3442, 1638, 1598, 1280; ^1H NMR ($CDCl_3$, 270 MHz): δ 12.48 (s, 1H, OH), 9.41 (s, 1H, OH), 7.37 (s, 1H arom.), 6.41 (s, 1H arom.), 5.01 (br s, 1H, C=CH_2), 4.89 (br s, 1H, C=CH_2), 4.38 (dd, 1H, CH_2CHOH, J=8.5 Hz, 2.5 Hz), 2.90 (dd, 1H, CH_2CHOH, J=15 Hz, 2.5 Hz), 2.77 (dd, 1H, CH_2CHOH, J=15 Hz, 8.5 Hz), 2.52 (s, 3H, $COCH_3$), 1.80 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 202.8 (C=O), 164.3, 163.6 (2×quat. arom. C), 146.0 ($CH_2{=}C(CH_3)$), 134.1 (arom. CH), 117.6, 113.5 (2×quat. arom. C), 111.7 ($CH_2{=}C(CH_3)$), 105.1 (arom. CH), 77.8 (CH_2CHOH), 37.6 (CH_2CHOH), 26.1 ($COCH_3$), 18.0 (CH_3); FAB-HRMS Calcd for $C_{13}H_{17}O_4$ ($[M+H]^+$) 237.1127, Found 237.1121.

4.4.3. 1-[2,4-Dihydroxy-3,5-bis-(2-hydroxy-3-methylbut-3-enyl)phenyl]ethanone 17. The typical conditions described in Section 4.3 were employed with **3** (30 mg, 0.10 mmol). The purification of the crude product according to procedure A yielded **17** as an orange oil (19 mg, 56%), IR (cm^{-1}): 3442, 1626, 1372; ^1H NMR ($CDCl_3$, 270 MHz): δ 13.00 (s, 1H, OH), 9.80 (s, 1H, OH), 7.38 (s, 1H arom.), 5.00 (br s, 2H, C=CH_2), 4.88 (br s, 1H, C=CH_2), 4.85 (br s, 1H, C=CH_2), 4.30–4.35 (m, 2H, 2×CH_2CHOH), 3.09–3.17 (m, 2H, CH_2CHOH), 2.81–2.94 (m, 2H, CH_2CHOH), 2.56 (s, 3H, $COCH_3$), 1.85 (s, 3H, CH_3), 1.82 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 202.7 (C=O), 161.9, 161.5 (2×quat. arom. C), 147.1, 146.7 (2×$CH_2{=}C(CH_3)$), 131.9 (arom. CH), 117.7, 113.7 (2×quat. arom. C), 111.1, 110.2 (2×$CH_2{=}C(CH_3)$), 76.6, 76.8 (2×CH_2CHOH), 37.6 (2×CH_2CHOH), 29.0 ($COCH_3$), 18.3, 18.1 (2×CH_3); EI-HRMS Calcd for $C_{18}H_{24}O_5$ (M^+) 320.1624, Found 320.1620.

4.4.4. 1-[2,6-Dihydroxy-3-(2-hydroxy-3-methylbut-3-enyl)phenyl]ethanone 18. The typical conditions described in Section 4.3 were employed with **4** (30 mg, 0.14 mmol). After purification of the crude product according to procedure A, a preparative TLC of the oily residue followed by a recristallization in AcOEt/hexane afforded **18** as yellow cristals (21 mg, 65%), mp: 100–101°C; IR (cm^{-1}): 3223, 1626, 1269; ^1H NMR ($CDCl_3$, 270 MHz): δ 12.38 (s, 1H, OH), 9.88 (s, 1H, OH), 7.07 (d, 1H arom., J=8.5 Hz), 6.40 (d, 1H arom., J=8.5 Hz), 5.00 (br s, 1H, C=CH_2), 4.90 (br s, 1H, C=CH_2), 4.39 (dd, 1H, CH_2CHOH, J=8.5 Hz, 3 Hz), 2.89 (dd, 1H, CH_2CHOH, J=15 Hz, 8.5 Hz), 2.76 (dd, 1H, CH_2CHOH, J=15 Hz, 3 Hz), 2.75 (s, 3H, $COCH_3$), 1.81 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 206.0 (C=O), 162.5, 159.1 (2×quat. arom. C), 146.1 ($CH_2{=}C(CH_3)$), 138.1 (arom. CH), 116.4, 111.5 (2×quat. arom. C), 111.4 ($CH_2{=}C(CH_3)$), 108.6 (arom. CH), 78.2

(CH_2CHOH), 37.6 (CH_2CHOH), 33.8 ($COCH_3$), 18.2 (CH_3); EI-HRMS Calcd for $C_{13}H_{16}O_4$ (M^+) 236.1048, Found 236.1051.

4.4.5. 3-Acetyl-2,4-dihydroxybenzaldehyde 19. The typical conditions described in Section 4.3 were employed with **4** (30 mg, 0.14 mmol). After purification of the crude product according to procedure A, a preparative TLC of the oily residue afforded **19** as a colorless oil (4 mg, 16%), IR (cm^{-1}): 1625, 1590, 1242; ^1H NMR ($CDCl_3$, 270 MHz): δ 14.37 (s, 1H, OH), 13.42 (s, 1H, OH), 9.68 (s, 1H, CHO), 7.58 (d, 1H arom., J=8.5 Hz), 6.58 (d, 1H arom., J=8.5 Hz), 2.80 (s, 3H, $COCH_3$); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 205.1 ($COCH_3$), 194.5 (CHO), 171.4, 167.2 (2×quat. arom. C), 140.4 (arom. CH), 113.3 (quat. arom. C), 110.9 (arom. CH), 109.3 (quat. arom. C), 33.4 ($COCH_3$); EI-HRMS Calcd for $C_9H_8O_4$ (M^+) 180.0423, Found 180.0420.

4.4.6. 2-(2-Hydroxy-3-methylbut-3-enyl)-4-methylphenol 20. The typical conditions described in Section 4.3 were employed with **6** (30 mg, 0.17 mmol). The purification of the crude product according to procedure B yielded **20** as a beige solid (14 mg, 43%), mp: 55–57°C, IR (cm^{-1}): 3301, 1501, 1243; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.97 (s, 1H, OH), 6.96 (dd, 1H arom., J=8.5 Hz, 2 Hz), 6.86 (d, 1H arom., J=2 Hz), 6.82 (d, 1H arom., J=8.5 Hz), 5.01 (br s, 1H, C=CH_2), 4.89 (br s, 1H, C=CH_2), 4.36 (dd, 1H, CH_2CHOH, J=9 Hz, 2 Hz), 2.95 (dd, 1H, CH_2CHOH, J=14.5 Hz, 9 Hz), 2.73 (dd, 1H, CH_2CHOH, J=14.5 Hz, 2 Hz), 2.26 (s, 3H, p-CH_3), 1.83 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 153.2 (quat. arom. C), 146.1 (CH_2=$C(CH_3)$), 131.8 (arom. CH), 129.5 (quat. arom. C), 128.8 (arom. CH), 125.4 (quat. arom. C), 117.0 (arom. CH), 111.1 (CH_2=C(CH_3)), 78.4 (CH_2CHOH), 38.0 (CH_2-CHOH), 20.4 (p-CH_3), 18.1 (CH_3); FAB-HRMS Calcd for $C_{12}H_{16}O_2$ (M^+) 192.1150, Found 192.1155.

4.4.7. 2-(2-Hydroxy-3-methylbut-3-enyl)-4-phenylphenol 21. The typical conditions described in Section 4.3 were employed with **7** (30 mg, 0.13 mmol). Purification of the crude product by preparative TLC (30% AcOEt/cyclohexane) yielded **21** as a white solid (18 mg, 56%), mp: 115–116°C, IR (cm^{-1}): 3229, 1281; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.55 (dd, 2H arom., J=8 Hz, 1.5 Hz), 7.45–7.39 (m, 3H arom.), 7.34–7.31 (m, 1H arom.), 7.29 (d, 1H arom., J=2.5 Hz), 7.01 (d, 1H arom., J=8.5 Hz), 4.98 (br s, 1H, C=CH_2), 4.85 (br s, 1H, C=CH_2), 4.45 (dd, 1H, CH_2CHOH, J=9 Hz, 2 Hz), 3.06 (dd, 1H, CH_2CHOH, J=14.5 Hz, 9 Hz), 2.87 (dd, 1H, CH_2CHOH, J=14.5 Hz, 2 Hz), 1.86 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 155.3 (quat. arom. C), 146.5 (CH_2=$C(CH_3)$), 140.9, 133.5 (2×quat. arom. C), 130.0, 128.6, 127.1, 126.7, 126.5 (7×arom. CH), 125.8 (quat. arom. C), 117.6 (arom. CH), 111.3 (CH_2=C(CH_3)), 78.4 (CH_2CHOH), 38.2 (CH_2-CHOH), 18.2 (CH_3); EI-HRMS Calcd for $C_{17}H_{18}O_2$ (M^+) 254.1307, Found 254.1294.

4.4.8. 2-(3-Hydroxy-3-methylbut-1-enyl)-4-phenylphenol 22. The typical conditions described in Section 4.3 were employed with **7** (30 mg, 0.13 mmol). Purification of the crude product by preparative TLC (30% AcOEt/cyclohexane) yielded **22** as a yellow solid (10 mg, 32%), mp: 156–157°C, IR (cm^{-1}): 3297, 1272; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.59 (d, 1H arom., J=2 Hz), 7.53 (d, 2H arom., J=8 Hz), 7.37 (dd, 2H arom., J=8 Hz, 7.5 Hz), 7.29 (dd, 1H arom., J=8.5 Hz, 2 Hz), 7.24 (t, 1H arom., J=7.5 Hz), 6.90 (d, 1H, CH=CH, J=16.5 Hz), 6.84 (d, 1H arom., J=8.5 Hz), 6.44 (d, 1H, CH=CH, J=16.5 Hz), 1.40 (s, 6H, 2×CH_3); EI-HRMS Calcd for $C_{17}H_{18}O_2$ (M^+) 254.1307, Found 254.1297.

4.4.9. 1-[4-Hydroxy-3-(2-hydroxy-3-methylbut-3-enyl)-phenyl]ethanone 23. The typical conditions described in Section 4.3 were employed with **8** (30 mg, 0.15 mmol). The purification of the crude product according to procedure B yielded **23** as a white solid (19 mg, 58%), mp: 96–97°C, IR (cm^{-1}): 3368, 1662, 1587, 1281; ^1H NMR ($CDCl_3$, 270 MHz): δ 9.21 (s, 1H, OH), 7.77 (dd, 1H arom., J=8.5 Hz, 2.5 Hz), 7.71 (d, 1H arom., J=2.5 Hz), 6.94 (d, 1H arom., J=8.5 Hz), 5.01 (br s, 1H, C=CH_2), 4.88 (br s, 1H, C=CH_2), 4.43 (dd, 1H, CH_2CHOH, J=8.5 Hz, 2.5 Hz), 2.95 (dd, 1H, CH_2CHOH, J=14.5 Hz, 8.5 Hz), 2.73 (dd, 1H, CH_2CHOH, J=14.5 Hz, 2.5 Hz), 2.54 (s, 3H, $COCH_3$), 1.81 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 197.5 (C=O), 160.8 (quat. arom. C), 146.1 (CH_2=$C(CH_3)$), 130.2, 129.9 (2×arom. CH), 129.7, 125.6 (2×quat. arom. C), 117.0 (arom. CH), 111.4 (CH_2=C(CH_3)), 77.7 (CH_2-$CHOH$), 38.2 (CH_2CHOH), 26.3 ($COCH_3$), 18.2 (CH_3); EI-HRMS Calcd for $C_{13}H_{16}O_3$ (M^+) 220.1099, Found 220.1103.

4.4.10. 2-(2-Hydroxy-3-methylbut-3-enyl)-4-bromo-phenol 24. The typical conditions described in Section 4.3 were employed with **9** (30 mg, 0.12 mmol). The purification of the crude product according to procedure B yielded **24** as a colorless oil (14 mg, 44%), IR (cm^{-1}): 3287, 1481, 1239; ^1H NMR ($CDCl_3$, 270 MHz): δ 8.26 (s, 1H, OH), 7.24 (dd, 1H arom., J=8.5 Hz, 2.5 Hz), 7.15 (d, 1H arom., J=2.5 Hz), 6.81 (d, 1H arom., J=8.5 Hz), 5.01 (br s, 1H, C=CH_2), 4.91 (br s, 1H, C=CH_2), 4.40 (dd, 1H, CH_2CHOH, J=8.5 Hz, 2 Hz), 2.94 (dd, 1H, CH_2CHOH, J=15 Hz, 8.5 Hz), 2.74 (dd, 1H, CH_2CHOH, J=15 Hz, 2 Hz), 2.54 (s, 1H, CH_2CHOH), 1.82 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 154.9 (quat. arom. C), 146.1 (CH_2=$C(CH_3)$), 133.6, 131.1 (2×arom. CH), 127.8 (quat. arom. C), 119.1 (arom. CH), 111.5 (CH_2=C(CH_3)), 112.0 (quat. arom. C), 78.1 (CH_2CHOH), 37.7 (CH_2CHOH), 18.1 (CH_3); EI-HRMS Calcd for $C_{11}H_{13}BrO_2$ (M^+) 256.0099, Found 256.0087.

4.4.11. 2-(2-Hydroxy-3-methylbut-3-enyl)-4-chloro-phenol 25. The typical conditions described in Section 4.3 were employed with 10 (30 mg, 0.15 mmol). The purification of the crude product according to procedure B yielded **25** as a colorless oil (17 mg, 51%), IR (cm^{-1}): 3384, 1485, 1245; ^1H NMR ($CDCl_3$, 270 MHz): δ 8.19 (s, 1H, OH), 7.11 (dd, 1H arom., J=8.5 Hz, 2.5 Hz), 7.01 (d, 1H arom., J=2.5 Hz), 6.85 (d, 1H arom., J=8.5 Hz), 5.01 (br s, 1H, C=CH_2), 4.91 (br s, 1H, C=CH_2), 4.41 (dd, 1H, CH_2CHOH, J=9 Hz, 2.5 Hz), 2.95 (dd, 1H, CH_2CHOH, J=15 Hz, 9 Hz), 2.75 (dd, 1H, CH_2CHOH, J=15 Hz, 2.5 Hz), 2.49 (s, 1H, CH_2CHOH), 1.82 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 154.4 (quat. arom. C), 146.1 (CH_2=$C(CH_3)$), 130.7, 128.1 (2×arom. CH), 127.2, 124.7 (2×quat. arom. C), 118.6 (arom. CH), 111.4 (CH_2=C(CH_3)), 78.1

(CH_2CHOH), 37.7 (CH_2CHOH), 18.1 (CH_3); EI-HRMS Calcd for $C_{11}H^{13}ClO_2$ (M^+) 212.0604, Found 212.0604.

4.4.12. 2-Acetyl-3-hydroxy-4-(3-methylbut-2-enyl)phenyl acetate 4a. To a CH_2Cl_2 solution (30 ml) of dihydroxyacetophenone **4** (300 mg, 1.36 mmol) were added triethylamine (0.19 ml, 1.36 mmol) and acetyl chloride (97 μl, 1.36 mmol). The resulting solution was strirred overnight at room temperature. Then the reaction mixture was successively washed with 2×25 ml of water, 2×25 ml of diluted HCl and 2×25 ml of water. The organic layer was dried over sodium sulfate, filtered and the solvent was evaporated under reduced pressure. Purification of the crude product by column chromatography (10% AcOEt/cyclohexane) yielded **4a** as an orange oil (304 mg, 85%), IR (cm^{-1}): 3443, 1771, 1628, 1192; ^1H NMR ($CDCl_3$, 270 MHz): δ 13.08 (s, 1H, OH), 7.31 (d, 1H arom., *J*=7.5 Hz), 6.54 (d, 1H arom., *J*=7.5 Hz), 5.30 (t, 1H, CH_2CH, *J*=7.5 Hz), 3.33 (d, 2H, CH_2CH, *J*=7.5 Hz), 2.62 (s, 3H, $COCH_3$), 2.37 (s, 3H, $OCOCH_3$), 1.79 (s, 3H, CH_3), 1.70 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 203.3 ($COCH_3$), 169.1 ($OCOCH_3$), 161.7, 149.1 (2×quat. arom. C), 134.9 (arom. CH), 133.7 ($CH{=}C(CH_3)_2$), 128.7 (quat. arom. C), 121.2 (CH_2CH), 113.6 (quat. arom. C), 113.1 (arom. CH), 32.2 ($COCH_3$), 27.7 (CH_2CH), 25.8 (CH_3), 21.6 ($OCOCH_3$), 17.8 (CH_3); EI-HRMS Calcd for $C_{15}H_{18}O_4$ (M^+) 262.1205, Found 262.1202.

4.4.13. 1-[2-Hydroxy-6-methoxy-3-(3-methylbut-2-enyl)-phenyl]ethanone 4b. To an acetone solution (20 ml) of dihydroxyacetophenone **4** (100 mg, 0.45 mmol) were successively added potassium carbonate (63 mg, 0.45 mmol) and dimethyl sulfate (43 μl, 0.45 mmol). Then the solution was heated under reflux for 5 h. After being cooled at room temperature, the reaction mixture was filtered and evaporated under reduced pressure. The residue was redissolved in 20 ml of CH_2Cl_2. The organic layer was washed three times with 15 ml of water and dried over Na_2SO_4. After removal of the solvent, the product was purified by column chromatography (7% AcOEt/cyclohexane) to yield 4b (79 mg, 74%), IR (cm^{-1}): 3448, 1616, 1426 (C=C), 1244; ^1H NMR ($CDCl_3$, 270 MHz): δ 13.63 (s, 1H, OH), 7.22 (d, 1H arom., *J*=8.5 Hz), 6.33 (d, 1H arom., *J*=8.5 Hz), 5.30 (t, 1H, CH_2CH, *J*=7.5 Hz), 3.87 (s, 3H, OCH_3), 3.28 (d, 2H, CH_2CH, *J*=7.5 Hz), 2.67 (s, 3H, $COCH_3$), 1.75 (s, 3H, CH_3), 1.71 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 205.3, 162.3, 159.7 (2×quat. arom. C), 135.4 (arom. CH), 132.9 ($CH{=}C(CH_3)_2$), 122.5 (quat. arom. C), 122.1 (CH_2CH), 110.8 (quat. arom. C), 100.3 (arom. CH), 55.4 (OCH_3), 33.6 ($COCH_3$), 27.3 (CH_2CH), 25.8 (CH_3), 17.7 (CH_3); EI-HRMS Calcd for $C_{14}H_{18}O_3$ (M^+) 234.1256, Found 234.1246.

4.4.14. 2-Acetyl-3-methoxy-4-(3-methylbut-2-enyl)phenyl acetate 4g. To an acetone solution (25 ml) of dihydroxyacetophenone **4a** (125 mg, 0.48 mmol) were successively added potassium carbonate (100 mg, 0.72 mmol) and dimethyl sulfate (68 μl, 0.72 mmol). Then the solution was heated under reflux for 2 h. After being cooled at room temperature, the reaction mixture was filtered and evaporated under reduced pressure. The residue was redissolved in 20 ml of CH_2Cl_2. The organic layer was washed three times with 15 ml of water and dried over Na_2SO_4. Removal of the solvent under reduced pressure yielded **4g** as a colorless oil (128 mg, 97%), IR (cm^{-1}): 1772, 1700, 1199; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.22 (d, 1H arom., *J*=7.5 Hz), 6.82 (d, 1H arom., *J*=7.5 Hz), 5.25 (t, 1H, CH_2CH, *J*=7.5 Hz), 3.72 (s, 3H, OCH_3), 3.34 (d, 2H, CH_2CH, *J*=7.5 Hz), 2.53 (s, 3H, $COCH_3$), 2.23 (s, 3H, $OCOCH_3$), 1.75 (s, 3H, CH_3), 1.72 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 201.1 ($COCH_3$), 169.3 ($OCOCH_3$), 155.5, 145.2 (2×quat. arom. C), 133.3 ($CH{=}C(CH_3)_2$), 132.9 (quat. arom. C), 131.4 (arom. CH), 128.8 (quat. arom. C), 121.8 (CH_2CH), 118.4 (arom. CH), 62.7 (OCH_3), 31.5 ($COCH_3$), 27.6 (CH_2CH), 25.7 (CH_3), 20.8 ($OCOCH_3$), 17.8 (CH_3); EI-MS *m/z* 276 (M^+, 20), 234 (74), 220 (14), 219 (100), 177 (12), 43 (51).

4.4.15. 1-[6-Hydroxy-2-methoxy-3-(3-methylbut-2-enyl)-phenyl]ethanone 4c. Monoacetate derivative **4g** (72 mg, 0.26 mmol) was dissolved in a 2:1:1 ratio mixture (12 ml) of methanol/aqueous saturated $NaHCO_3$ solution/water. This reaction mixture was stirred at room temperature for 40 min. Then diluted HCl (10%) was added down to pH=2. The resulting mixture was extracted four times with 15 ml of AcOEt. The combined organic layers were washed with 2×25 ml of water and dried over Na_2SO_4. Removal of the solvent under reduced pressure yielded, without further purification, **4c** as a colorless oil (59 mg, 70%), IR (cm^{-1}): 3448, 1632, 1468, 1219; ^1H NMR ($CDCl_3$, 270 MHz): δ 12.44 (s, 1H, OH), 7.28 (d, 1H arom., *J*=9 Hz), 6.73 (d, 1H arom., *J*=9 Hz), 5.24 (t, 1H, CH_2CH, *J*=7.5 Hz), 3.76 (s, 3H, OCH_3), 3.30 (d, 2H, CH_2CH, *J*=7.5 Hz), 2.75 (s, 3H, $COCH_3$), 1.76 (s, 3H, CH_3), 1.741 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 205.2 (C=O), 161.7, 159.4 (2×quat. arom. C), 137.4 (arom. CH), 133.1 ($CH{=}C(CH_3)_2$), 125.3 (quat. arom. C), 122.6 (CH_2CH), 115.1 (quat. arom. C), 114.2 (arom. CH), 62.5 (OCH_3), 31.7 ($COCH_3$), 27.3 (CH_2CH), 25.7 (CH_3), 17.9 (CH_3); EI-HRMS Calcd for $C_{14}H_{18}O_3$ (M^+) 234.1256, Found 234.1261.

4.4.16. 2-Acetyl-3-benzyloxy-4-(3-methylbut-2-enyl)phenyl acetate 4h. To an acetone solution (20 ml) of dihydroxyacetophenone **4a** (100 mg, 0.38 mmol) were successively added benzyl bromide (68 μl, 0.57 mmol) potassium carbonate (190 mg) and tetrabutylammonium iodide (211 mg, 0.57 mmol). Then the solution was heated under reflux for 3 h. After being cooled at room temperature, the reaction mixture was filtered and evaporated under reduced pressure. The residue was redissolved in 20 ml of AcOEt. The organic layer was washed three times with 15 ml of water and dried over Na_2SO_4. After removal of the solvent, the product was purified by column chromatography (10% AcOEt/cyclohexane) to yield 4 h (98 mg, 73%), IR (cm^{-1}): 1766, 1700, 1200; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.43–7.36 (m, 5H arom.), 7.25 (d, 1H arom., *J*=8.5 Hz), 6.87 (d, 1H arom., *J*=8.5 Hz), 5.24 (t, 1H, CH_2CH, *J*=7 Hz), 4.83 (s, 2H, OCH_2Ph), 3.35 (d, 2H, CH_2CH, *J*=7 Hz), 2.52 (s, 3H, $COCH_3$), 2.26 (s, 3H, $OCOCH_3$), 1.75 (s, 3H, CH_3), 1.67 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 201.4 ($COCH_3$), 169.4 ($OCOCH_3$), 154.0, 145.2, 136.4, 133.6* (4×quat. arom. C), 133.3* ($CH{=}C(CH_3)_2$), 131.5, 128.6, 128.3, 128.1 (6×arom. CH), 127.3 (quat. arom. C), 121.8 (CH_2CH), 118.7 (arom. CH), 77.6 (OCH_2Ph), 31.8 ($COCH_3$), 27.7 (CH_2CH), 25.7 (CH_3),

20.9 ($OCOCH_3$), 17.9 (CH_3); EI-HRMS Calcd for $C_{22}H_{24}O_4$ (M^+) 352.1675, Found 352.1662.

4.4.17. 1-[2-(Benzyloxy)-6-hydroxy-3-(3-methylbut-2-enyl)phenyl]ethanone 4d. Monoacetate derivative **4h** (98 mg, 0.28 mmol) was dissolved in a 2:1:1 ratio mixture (12 ml) of methanol/aqueous saturated $NaHCO_3$ solution/water. This reaction mixture was stirred at room temperature for 40 min. Then diluted HCl (10%) was added down to pH=2. The resulting mixture was extracted four times with 15 ml of AcOEt. The combined organic layers were washed with 2×25 ml of water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, purification of the crude product by column chromatography (50% CH_2Cl_2/cyclohexane) yielded **4d** as a colorless oil (60 mg, 70%), IR (cm^{-1}): 3443, 1632, 1468, 1217; ^1H NMR ($CDCl_3$, 270 MHz): δ 12.31 (s, 1H, OH), 7.43–7.35 (m, 5H arom.), 7.32 (d, 1H arom., J=8.5 Hz), 6.78 (d, 1H arom., J=8.5 Hz), 5.23 (t, 1H, CH_2CH, J=7.5 Hz), 4.85 (s, 2H, OCH_2Ph), 3.32 (d, 2H, CH_2CH, J=7.5 Hz), 2.69 (s, 3H, $COCH_3$), 1.75 (s, 3H, CH_3), 1.67 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 205.3 ($COCH_3$), 161.4, 157.7 (2×quat. arom. C), 137.3 (arom. CH), 136.3 (quat. arom. C), 133.3 ($CH{=}C(CH_3)_2$), 128.6, 128.3, 127.4 (5×arom. CH), 125.6 (quat. arom. C), 122.4 (CH_2CH), 115.8 (quat. arom. C), 114.3 (arom. CH), 77.6 (OCH_2Ph), 31.9 ($COCH_3$), 27.4 (CH_2CH), 25.7 (CH_3), 17.8 (CH_3); EI-HRMS Calcd for $C_{20}H_{22}O_3$ (M^+) 310.1568, Found 310.1562.

4.4.18. 2-Acetyl-3-acetyloxy-4-(3-methylbut-2-enyl)-phenyl acetate 4e. To a CH_2Cl_2 solution (120 ml) of dihydroxyacetophenone **4** (1 g, 4.54 mmol) were added triethylamine (2.54 ml, 18.1 mmol) and dropwise a CH_2Cl_2 solution (3 ml) of acetyl chloride (1.30 ml, 18.1 mmol). The resulting solution was strirred 4 h at room temperature. Then the reaction mixture was successively washed with 2×25 ml of water, 2×25 ml of diluted HCl and 2×25 ml of water. The organic layer was dried over sodium sulfate, filtered and the solvent was evaporated under reduced pressure to yield the diacetate derivative 4e as an orange oil (1.31 g, 95%), IR (cm^{-1}): 1767, 1702, 1185; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.29 (d, 1H arom., J=7.5 Hz), 7.01 (d, 1H arom., J=7.5 Hz), 5.20 (t, 1H, CH_2CH, J=7 Hz), 3.21 (d, 2H, CH_2CH, J=7 Hz), 2.45 (s, 3H, $COCH_3$), 2.28 (s, 3H, $OCOCH_3$), 2.27 (s, 3H, $OCOCH_3$), 1.75 (s, 3H, CH_3), 1.69 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 198.9 ($COCH_3$), 168.7 (2×$OCOCH_3$), 145.7, 145.4, 132.3 (3×quat. arom. C), 134.1 ($CH{=}C(CH_3)_2$), 131.4 (arom. CH), 128.0 (quat. arom. C), 120.7 (CH_2CH), 120.3 (arom. CH), 30.8 ($COCH_3$), 28.4 (CH_2CH), 25.7 (CH_3), 21.0, 20.6 (2×$OCOCH_3$), 17.8 (CH_3); CI-HRMS Calcd for $C_{17}H_{21}O_5$ ($[M+H]^+$) 305.1389, Found 305.1365.

4.4.19. 1-[2,6-Dimethoxy-3-(3-methylbut-2-enyl)phenyl]-ethanone 4f. To an acetone solution (20 ml) of dihydroxyacetophenone **4** (100 mg, 0.45 mmol) were successively added potassium carbonate (226 mg, 1.63 mmol) and dimethyl sulfate (1.2 ml, 1.81 mmol). Then the solution was heated under reflux for 5 h. After being cooled at room temperature, the reaction mixture was filtered and evaporated under reduced pressure. The residue was redissolved in 20 ml of CH_2Cl_2. The organic layer was washed three times with 15 ml of water and dried over Na_2SO_4. Removal of the solvent under reduced pressure yielded **4f** (107 mg, 95%), IR (cm^{-1}): 1706, 1271, 1244; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.13 (d, 1H arom., J=8.5 Hz), 6.63 (d, 1H arom., J=8.5 Hz), 5.25 (t, 1H, CH_2CH, J=7 Hz), 3.79 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.21 (d, 2H, CH_2CH, J=7 Hz), 2.52 (s, 3H, $COCH_3$), 1.75 (s, 3H, CH_3), 1.72 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 203.2 (C=O), 154.9, 154.8 (2×quat. arom. C), 132.7 ($CH{=}C(CH_3)_2$), 130.9 (arom. CH), 127.4, 125.9 (2×quat. arom. C), 122.7 (CH_2CH), 106.9 (arom. CH), 62.8, 55.8 (2×OCH_3), 32.4 ($COCH_3$), 27.4 (CH_2CH), 25.7 (CH_3), 17.8 (CH_3); EI-HRMS Calcd for $C_{15}H_{20}O_3$ (M^+) 248.1413, Found 248.1412.

4.5. General procedure for the photooxygenation–reduction sequence at −30°C

A CH_2Cl_2 solution (30 ml) of prenylated compound (**19a**–**19e**) (30 mg) and tetraphenylporphine (3 mg, 0.005 mmol), as the photosensitizer, was cooled at −30°C and then was irradiated at −30°C with a halogen lamp (500 W). After total consumption of the starting material, a slight excess of triphenylphosphine (1.1 equiv.) was added and the resulting mixture was stirred overnight at −30°C.

4.5.1. 2-Acetyl-3-hydroxy-4-(2-hydroxy-3-methylbut-3-enyl)phenyl acetate 26a. The typical conditions given in Section 4.5 were employed, starting with **4a** (30 mg, 0.11 mmol). Purification of the crude product by preparative TLC (20% AcOEt/cyclohexane) yielded **26a** as a beige solid (14 mg, 45%), mp: 90–91°C, IR (cm^{-1}): 3378, 1756, 1631, 1195; ^1H NMR ($CDCl_3$, 270 MHz): δ 13.13 (s, 1H, OH), 7.37 (d, 1H arom., J=8 Hz), 6.58 (d, 1H arom., J=8 Hz), 4.99 (br s, 1H, C=CH_2), 4.86 (br s, 1H, C=CH_2), 4.35 (dd, 1H, CH_2CHOH, J=8.5 Hz, 3.5 Hz), 3.00 (dd, 1H, CH_2-CHOH, J=14 Hz, 3.5 Hz), 2.78 (dd, 1H, CH_2CHOH, J=14 Hz, 8.5 Hz), 2.63 (s, 3H, $COCH_3$), 2.38 (s, 3H, $OCOCH_3$), 1.83 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 203.4 ($COCH_3$), 168.8 ($OCOCH_3$), 161.7, 149.8 (2×quat. arom. C), 147.2 ($CH_2{=}C(CH_3)$), 136.9 (arom. CH), 125.8, 114.0 (2×quat. arom. C), 113.4 (arom. CH), 110.8 ($CH_2{=}C(CH_3)$), 75.2 (CH_2CHOH), 36.4 (CH_2-CHOH), 32.2 ($COCH_3$), 21.6 ($OCOCH_3$), 18.1 (CH_3); EI-HRMS Calcd for $C_{15}H_{18}O_5$ (M^+) 278.1154, Found 278.1148.

4.5.2. 2-Acetyl-3-hydroxy-4-(3-hydroxy-3-methylbut-1-enyl)phenyl acetate 27a. The typical conditions given in Section 4.5 were employed, starting with **4a** (30 mg, 0.11 mmol). Purification of the crude product by preparative TLC (20% AcOEt/cyclohexane) followed by a recristallization (AcOEt/hexane) yielded **27a** as green cristals (11 mg, 36%), mp: 86–88°C, IR (cm^{-1}): 3442, 1771, 1627, 1189; ^1H NMR (CD_3OD, 270 MHz): δ 7.60 (d, 1H arom., J=8.5 Hz), 6.90 (s, 1H, ArCH=CH, J=16 Hz), 6.60 (d, 1H arom., J=8.5 Hz), 6.41 (d, 1H, ArCH=CH, J=16 Hz), 2.62 (s, 3H, $COCH_3$), 2.36 (s, 3H, $OCOCH_3$), 1.38 (s, 6H, 2×CH_3); ^{13}C NMR (CD_3OD, 67.5 MHz): δ 205.2 ($COCH_3$), 170.6 ($OCOCH_3$), 161.1, 151.7 (2×quat. arom. C), 140.1 (ArCH=CH), 132.8 (arom. CH), 125.8 (quat. arom. C), 120.5 (ArCH=CH), 115.8 (quat. arom. C), 115.2 (arom. CH), 71.6 ($C(CH_3)_2$), 32.5 ($COCH_3$), 29.9 (2×CH_3), 21.4

($OCOCH_3$); EI-HRMS Calcd for $C_{15}H_{18}O_5$ (M^+) 278.1154, Found 278.1124.

4.5.3. 1-[2-Hydroxy-3-(2-hydroxy-3-methylbut-3-enyl)-6-methoxyphenyl]ethanone 26b. The typical conditions given in Section 4.5 were employed, starting with **4b** (30 mg, 0.13 mmol). Purification of the crude product by preparative TLC (20% AcOEt/cyclohexane) yielded **26b** as a colorless oil (13 mg, 40%), IR (cm^{-1}): 3443, 1610, 1247; ^1H NMR ($CDCl_3$, 270 MHz): δ 13.81 (s, 1H, OH), 7.28 (d, 1H arom., J=8.5 Hz), 6.37 (d, 1H arom., J=8.5 Hz), 4.98 (br s, 1H, C=CH_2), 4.84 (br s, 1H, C=CH_2), 4.32 (dd, 1H, CH_2CHOH, J=8.5 Hz, 4 Hz), 3.90 (s, 3H, OCH_3), 2.94 (dd, 1H, CH_2CHOH, J=14 Hz, 4 Hz), 2.74 (dd, 1H, CH_2CHOH, J=14 Hz, 8.5 Hz), 2.69 (s, 3H, $COCH_3$), 1.83 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 205.5 ($COCH_3$), 162.5, 160.3 (2×quat. arom. C), 147.4 (CH_2=$C(CH_3)$), 137.6 (arom. CH), 119.5, 110.9 (2×quat. arom. C), 110.5 (CH_2=$C(CH_3)$), 100.7 (arom. CH), 75.5 (CH_2CHOH), 55.5 (OCH_3), 36.2 (CH_2CHOH), 33.6 ($COCH_3$), 18.2 (CH_3); EI-HRMS Calcd for $C_{14}H_{18}O_4$ (M^+) 250.1205, Found 250.1209.

4.5.4. 1-[2-Hydroxy-3-(3-hydroxy-3-methylbut-1-enyl)-6-methoxyphenyl]ethanone 27b. The typical conditions given in Section 4.5 were employed, starting with **4b** (30 mg, 0.13 mmol). Purification of the crude product by preparative TLC (20% AcOEt/cyclohexane) yielded **27b** as a colorless oil (11 mg, 34%), IR (cm^{-1}): 3357, 1610, 1251; ^1H NMR (CD_3OD, 270 MHz): δ 7.61 (d, 1H arom., J=8.5 Hz), 6.83 (s, 1H, ArCH=CH, J=16 Hz), 6.55 (d, 1H arom., J=8.5 Hz), 6.29 (d, 1H, ArCH=CH, J=16 Hz), 3.92 (s, 3H, OCH_3), 2.65 (s, 3H, $COCH_3$), 1.37 (s, 6H, 2×CH_3); ^{13}C NMR (CD_3OD, 67.5 MHz): δ 206.9 ($COCH_3$), 162.5, 162.4 (2×quat. arom. C), 137.6 (ArCH=CH), 134.4 (arom. CH), 120.9 (ArCH=CH), 120.2, 111.9 (2×quat. arom. C), 102.7 (arom. CH), 71.7 ($C(CH_3)_2$), 56.2 (OCH_3), 33.9 ($COCH_3$), 30.0 (2×CH_3); EI-HRMS Calcd for $C_{14}H_{18}O_4$ (M^+) 250.1205, Found 250.1205.

4.5.5. 1-[6-Hydroxy-3-(2-hydroxy-3-methylbut-3-enyl)-2-methoxyphenyl]ethanone 26c. The typical conditions given in Section 4.5 were employed, starting with **4c** (30 mg, 0.13 mmol). Purification of the crude product by preparative TLC (40% AcOEt/cyclohexane) yielded **26c** as a colorless oil (9 mg, 29%), IR (cm^{-1}): 3444, 1628, 1585, 1220; ^1H NMR ($CDCl_3$, 270 MHz): δ 12.38 (s, 1H, OH), 7.07 (d, 1H arom., J=8.5 Hz), 6.40 (d, 1H arom., J=8.5 Hz), 4.98 (br s, 1H, C=CH_2), 4.87 (br s, 1H, C=CH_2), 4.31 (dd, 1H, CH_2CHOH, J=8.5 Hz, 4.5 Hz), 3.79 (s, 3H, OCH_3), 2.87 (dd, 1H, CH_2CHOH, J=14 Hz, 4.5 Hz), 2.78 (dd, 1H, CH_2CHOH, J=14 Hz, 8.5 Hz), 2.76 (s, 3H, $COCH_3$), 1.83 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 205.0 ($COCH_3$), 162.2, 160.0 (2×quat. arom. C), 147.0 (CH_2=$C(CH_3)$), 138.3 (arom. CH), 122.3, 115.3 (2×quat. arom. C), 114.4 (arom. CH), 111.2 (CH_2=$C(CH_3)$), 76.0 (CH_2CHOH), 62.9 (OCH_3), 35.6 (CH_2CHOH), 31.4 ($COCH_3$), 18.0 (CH_3); EI-MS m/z 250 (M^+,6) 179 (100), 165 (16), 121 (16), 77 (19), 43 (30).

4.5.6. 1-[6-Hydroxy-3-(3-hydroxy-3-methylbut-1-enyl)-2-methoxyphenyl]ethanone 27c. The typical conditions given in Section 4.5 were employed, starting with **4c** (30 mg, 0.13 mmol). Purification of the crude product by preparative TLC (40% AcOEt/cyclohexane) yielded **27c** as a colorless oil (13 mg, 41%), IR (cm^{-1}): 3423, 1627, 1219; ^1H NMR (CD_3OD, 270 MHz): δ 7.58 (d, 1H arom., J=8.5 Hz), 6.76 (s, 1H, ArCH=CH, J=16 Hz), 6.69 (d, 1H arom., J=8.5 Hz), 6.28 (d, 1H, ArCH=CH, J=16 Hz), 3.77 (s, 3H, OCH_3), 2.68 (s, 3H, $COCH_3$), 1.38 (s, 6H, 2×CH_3); ^{13}C NMR (CD_3OD, 67.5 MHz): δ 206.3 ($COCH_3$), 162.0, 159.7 (2×quat. arom. C), 138.7 (ArCH=CH), 133.7 (arom. CH), 129.9, 123.5 (2×quat. arom. C), 121.2 (ArCH=CH), 114.8 (arom. CH), 71.6 ($C(CH_3)_2$), 63.2 (OCH_3), 32.3 ($COCH_3$), 30.0 (2×CH_3); EI-HRMS Calcd for $C_{14}H_{18}O_4$ (M^+) 250.1205, Found 250.1202.

4.5.7. 1-[2-(Benzyloxy)-6-hydroxy-3-(2-hydroxy-3-methylbut-3-enyl)phenyl]ethanone 26d. The typical conditions given in Section 4.5 were employed, starting with **4d** (30 mg, 0.10 mmol). Purification of the crude product by preparative TLC (30% AcOEt/cyclohexane) followed by a recristallization (AcOEt/hexane) yielded **26d** as green cristals (11 mg, 35%), mp: 56–57°C, IR (cm^{-1}): 3312, 1627, 1472, 1364, 1226; ^1H NMR ($CDCl_3$, 270 MHz): δ 12.20 (s, 1H, OH), 7.41–7.37 (m, 6H arom.), 6.80 (d, 1H arom., J=8.5 Hz), 4.94 (br s, 1H, C=CH_2), 4.89 (s, 1H, OCH_2Ph), 4.87 (s, 1H, OCH_2Ph), 4.84 (br s, 1H, C=CH_2), 4.32 (dd, 1H, CH_2CHOH, J=8.5 Hz, 5 Hz), 2.83 (dd, 1H, CH_2CHOH, J=14 Hz, 5 Hz), 2.75 (dd, 1H, CH_2CHOH, J=14 Hz, 8.5 Hz), 2.71 (s, 3H, $COCH_3$), 1.75 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 205.1 ($COCH_3$), 161.8, 158.4 (2×quat. arom. C), 147.0 (CH_2=$C(CH_3)$), 138.2 (arom. CH), 136.0 (quat. arom. C), 128.7, 128.5, 127.6 (5×arom. CH), 122.7, 116.1 (2×quat. arom. C), 114.5 (arom. CH), 111.2 (CH_2=$C(CH_3)$), 78.2 (OCH_2Ph), 76.0 (CH_2CHOH), 35.8 (CH_2CHOH), 31.6 ($COCH_3$), 17.9 (CH_3); EI-HRMS Calcd for $C_{20}H_{22}O_4$ (M^+) 326.1518, Found 326.1529.

4.5.8. 1-[2-(Benzyloxy)-6-hydroxy-3-(3-hydroxy-3-methylbut-1-enyl)phenyl]ethanone 27d. The typical conditions given in Section 4.5 were employed, starting with **4d** (30 mg, 0.13 mmol). Purification of the crude product by preparative TLC (30% AcOEt/cyclohexane) followed by a recristallization (AcOEt/hexane) yielded **27d** as yellow needles (16 mg, 51%), IR (cm^{-1}): 3415, 1631, 1366, 1218; ^1H NMR (CD_3OD, 270 MHz): δ 7.59 (d, 1H arom., J=9 Hz), 7.43–7.36 (5H arom.), 6.81 (s, 1H, ArCH=CH, J=16 Hz), 6.72 (d, 1H arom., J=9 Hz), 6.29 (d, 1H, ArCH=CH, J=16 Hz), 4.89 (s, 2H, OCH_2Ph), 2.58 (s, 3H, $COCH_3$), 1.33 (s, 6H, 2×CH_3); ^{13}C NMR (CD_3OD, 67.5 MHz): δ 206.2 ($COCH_3$), 161.2, 157.7 (2×quat. arom. C), 138.8 (ArCH=CH), 133.2 (quat. arom. C), 133.1 (arom. CH), 129.6, 129.4, 129.3 (5×arom. CH), 123.8 (quat. arom. C), 121.4 (ArCH=CH), 119.8 (quat. arom. C), 114.8 (arom. CH), 78.5 (OCH_2Ph), 71.5 ($C(CH_3)_2$), 32.6 ($COCH_3$), 29.2 (2×CH_3); EI-HRMS Calcd for $C_{20}H_{22}O_4$ (M^+) 326.1518, Found 326.1503.

4.5.9. 2-Acetyl-3-acetyloxy-4-(2-hydroxy-3-methylbut-3-enyl)phenyl acetate 26e. The typical conditions given in Section 4.5 were employed, starting with **4e** (30 mg, 0.11 mmol). Purification of the crude product by preparative TLC (35% AcOEt/cyclohexane) yielded **26e** as a colorless oil (8 mg, 26%), IR (cm^{-1}): 1767, 1700, 1369, 1186; ^1H

NMR ($CDCl_3$, 270 MHz): δ 7.41 (d, 1H arom., J=8.5 Hz), 7.06 (d, 1H arom., J=8.5 Hz), 4.99 (br s, 1H, C=CH_2), 4.88 (br s, 1H, C=CH_2), 4.24 (dd, 1H, CH_2CHOH, J=9 Hz, 4 Hz), 2.80 (dd, 1H, CH_2CHOH, J=14 Hz, 4 Hz), 2.69 (dd, 1H, CH_2CHOH, J=14 Hz, 9 Hz), 2.46 (s, 3H, $COCH_3$), 2.30 (s, 3H, $OCOCH_3$), 2.29 (s, 3H, $OCOCH_3$), 1.80 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 198.9 ($COCH_3$), 169.1, 168.6 (2×$OCOCH_3$), 146.8* (CH_2=$C(CH_3)$), 146.3*, 145.9 (2×quat. arom. C), 132.9 (arom. CH), 129.6, 128.2 (2×quat. arom. C), 120.4 (arom. CH), 111.3 (CH_2=$C(CH_3)$), 75.2 (CH_2CHOH), 36.3 (CH_2CHOH), 31.0 ($COCH_3$), 21.0, 20.7 (2×$OCOCH_3$), 17.9 (CH_3); EI-HRMS Calcd for $C_{17}H_{20}O_6$ (M^+) 320.1260, Found 320.1255.

4.5.10. 2-Acetyl-3-acetyloxy-4-(3-hydroxy-3-methylbut-1-enyl)phenyl acetate 27e. The typical conditions given in Section 4.5 were employed, starting with **4e** (30 mg, 0.11 mmol). Purification of the crude product by preparative TLC (35% AcOEt/cyclohexane) yielded **27e** as a colorless oil (14 mg, 45%), IR (cm^{-1}): 1767, 1702, 1369, 1187; ^{1}H NMR (CD_3OD, 270 MHz): δ 7.69 (d, 1H arom., J=8.5 Hz), 7.10 (d, 1H arom., J=8.5 Hz), 6.58 (s, 1H, ArCH=CH, J=16 Hz), 6.41 (d, 1H, ArCH=CH, J=16 Hz), 2.42 (s, 3H, $COCH_3$), 2.29 (s, 3H, $OCOCH_3$), 2.26 (s, 3H, $OCOCH_3$), 1.36 (s, 6H, 2×CH_3); ^{13}C NMR (CD_3OD, 67.5 MHz): δ 200.8 ($COCH_3$), 170.6 (2×$OCOCH_3$), 148.1, 146.1 (2×quat. arom. C), 143.2 (ArCH=CH), 130.6, 129.9 (2×quat. arom. C), 129.5 (arom. CH), 122.2 (ArCH=CH), 119.7 (arom. CH), 71.6 ($C(CH_3)_2$), 31.3 ($COCH_3$), 29.9 (2×CH_3), 20.7, 20.5 (2×$OCOCH_3$); EI-HRMS Calcd for $C_{17}H_{20}O_6$ (M^+) 320.1260, Found 320.1258.

4.5.11. 1-[3-(2-Hydroxy-3-methylbut-3-enyl)-2,6-dimethoxyphenyl]ethanone 26f. The typical conditions given in Section 4.5 were employed, starting with **4f** (30 mg, 0.12 mmol). Purification of the crude product by preparative TLC (30% AcOEt/cyclohexane) yielded **26f** as a colorless oil (11 mg, 33%), IR (cm^{-1}): 3463, 1701, 1485, 1244; ^{1}H NMR ($CDCl_3$, 270 MHz): 7.20 (d, 1H arom., J=8.5 Hz), 6.66 (d, 1H arom., J=8.5 Hz), 4.98 (br s, 1H, C=CH_2), 4.85 (br s, 1H, C=CH_2), 4.26 (dd, 1H, CH_2-CHOH, J=8.5 Hz, 4 Hz), 3.80 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 2.88 (dd, 1H, CH_2CHOH, J=14 Hz, 4 Hz), 2.71 (dd, 1H, CH_2CHOH, J=14 Hz, 8.5 Hz), 2.51 (s, 3H, $COCH_3$), 1.81 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 203.0 ($COCH_3$), 155.4, 155.3 (2×quat. arom. C), 147.1 (CH_2=$C(CH_3)$), 132.3 (arom. CH), 125.8, 124.2 (2×quat. arom. C), 110.8 (CH_2=$C(CH_3)$), 106.9 (arom. CH), 75.9 (CH_2CHOH), 62.9 (OCH_3), 55.8 (OCH_3), 36.0 (CH_2CHOH), 32.4 ($COCH_3$), 18.0 (CH_3); EI-HRMS Calcd for $C_{15}H_{20}O_4$ (M^+) 264.1362, Found 264.1359.

4.5.12. 1-[3-(3-Hydroxy-3-methylbut-1-enyl)-2,6-dimethoxyphenyl]ethanone 27f. The typical conditions given in Section 4.5 were employed, starting with **4f** (30 mg, 0.12 mmol). Purification of the crude product by preparative TLC (30% AcOEt/cyclohexane) yielded **27f** as a colorless oil (18 mg, 55%), IR (cm^{-1}): 3445, 1704, 1244; ^{1}H NMR (CD_3OD, 270 MHz): δ 7.41 (d, 1H arom., J=9 Hz), 6.71 (d, 1H arom., J=8.5 Hz), 6.67 (s, 1H, ArCH=CH, J=16 Hz), 6.29 (d, 1H, ArCH=CH, J=16 Hz), 3.81 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 2.50 (s, 3H, $COCH_3$), 1.43 (s, 6H, 2×CH_3); ^{13}C NMR (CD_3OD, 67.5 MHz): δ 202.8 ($COCH_3$), 155.8, 154.5 (2×quat. arom. C), 137.7 (ArCH=CH), 128.1 (arom. CH), 128.1, 123.5 (2×quat. arom. C), 120.0 (ArCH=CH), 107.2 (arom. CH), 71.1 ($C(CH_3)_2$), 63.0 (OCH_3), 55.8 (OCH_3), 32.4 ($COCH_3$), 29.6 (2×CH_3); EI-HRMS Calcd for $C_{15}H_{20}O_4$ (M^+) 264.1362, Found 264.1350.

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