# Epoxidation of (*E*,*E*)-Cinnamylideneacetophenones with Hydrogen Peroxide and Iodosylbenzene with Salen-Mn$^{III}$ as the Catalyst

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*Dedicated to Prof. Miguel Yus on the occasion of his 60th birthday*

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(*E*,*E*)-Cinnamylideneacetophenones **3a–j** were epoxidized under mild conditions with Jacobsen's catalyst **4** and hydrogen peroxide or iodosylbenzene as oxidants. γ,δ-Monoepoxides and a diastereomeric mixture of α,β:γ,δ-diepoxides were obtained in each case, and only the α,β-monoepoxide of 4-nitrocinnamylideneacetophenone (**3d**) was isolated. The presence of a methyl group in the vinylic moiety of substrates **3i**,**j** allowed the formation of two γ,δ-monoepoxide diastereomers. The epoxidation of (*E*,*E*)-2′-hydroxycinnamylideneacetophenones **3h**,**j** led to the formation of the corresponding γ,δ-monoepoxides as well as (*E*)-2,3-*trans*-3-hydroxy-2-styryl-4-chromanones, which originated from the in situ cyclisation of 2,3-epoxy-1-(2-hydroxyphenyl)-5-phenyl-4-penten-1-ones. The structures of all new compounds and the stereochemistry of the mono- and diepoxide diastereomers were established by NMR studies.


## Introduction

Salen Mn$^{III}$ complexes are efficient catalysts for the epoxidation of various olefinic compounds.[1–3] Since the pioneering work of Kochi et al.,[4] many contributors have reviewed a wide range of applications of these powerful and selective catalysts.[5–7] Several oxidants have been used as effective oxygen donors in these epoxidations, with iodosylbenzene[8–11] and sodium hypochlorite[12–14] being the most frequently reported. Among other common olefin oxidants hydrogen peroxide,[15–17] oxone®,[18] dimethyldioxirane (DMD),[19–23] *m*-chloroperbenzoic acid (MCPBA),[24] molecular oxygen[25] and more recently also tetrabutylammonium monosulfate[24,26,27] and tetrabutylammonium periodate[28] have been used. Alkene epoxidation can also be achieved with simple co-catalysts such as imidazoles, pyridines and tertiary amine *N*-oxides, which act as axial ligands and, in some cases, as phase-transfer catalysts.[29–31]

(*E*,*E*)-Cinnamylideneacetophenones constitute an important group of unsaturated ketones that are prepared from the aldol condensations of appropriate acetophenones and cinnamaldehydes. Over the last few decades, considerable attention has been payed to the synthesis of these compounds, and many chemical transformations were accomplished with a great number of derivatives.[32–34]

Studies on the asymmetric epoxidation reaction developed by Juliá and Colonna[35] showed that a wide variety of substrates, such as enones, enediones and unsaturated keto esters, could be oxidized into optically active epoxides with basic hydrogen peroxide and poly(amino acids).[36–38] Later on, the same group[39,40] reported the use of a non-aqueous variant of the Juliá–Colonna reaction for the epoxidation of dienones and trienones, which includes the synthesis of α,β-monoepoxides of ketones related to cinnamylideneacetophenones. In 2001, our group reported the oxidation of cinnamylideneacetophenones with dimethyldioxirane,[41] which also led to the formation of α,β-monoepoxides as well as diastereomeric mixtures of α,β:γ,δ-diepoxides. Since then, as far as we know, no epoxidation studies have been reported for these kinds of unsaturated derivatives as substrates. On this basis, we launched a new study of the epoxidation of (*E*,*E*)-cinnamylideneacetophenones **3a–j**, catalysed by the commercially available Jacobsen's catalyst **4** [salen Mn$^{III}$, *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride] and with hydrogen peroxide and iodosylbenzene as oxidants. These

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investigations were the continuation of our previous work on the epoxidation of 2-styrylchromones, a related but cyclic dienone system.[42]

## Results and Discussion

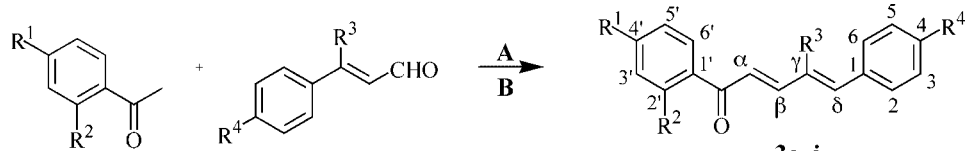
### Syntheses

(*E*,*E*)-Cinnamylideneacetophenones **3a**–**c**,**e**,**f**,**h**–**j** were prepared by aqueous base-catalysed aldol reaction of cinnamaldehydes and acetophenones in methanolic solutions, except for the nitro derivatives, which were prepared under milder conditions (NaH/THF) to afford the (*E*,*E*)-nitrocinnamylideneacetophenones **3d**,**g** in better yields (Scheme 1). Since cinnamaldehydes **2b**–**d** are not commercially available, we have synthesized them by the method developed by Cachi and co-workers,[43] involving a two-step approach, namely a Heck reaction followed by hydrolysis.

The first attempt to epoxidise (*E*,*E*)-cinnamylideneacetophenone (**3a**) with hydrogen peroxide in a 1:1 mixture of dichloromethane/methanol without catalyst according to the method reported by Lévai et al.[44] failed to give any epoxide, and only the unreacted starting material was recovered. A similar reaction with 0.05 equiv. of Jacobsen's catalyst **4** for 4 h at room temperature revealed a new product (11%) with a lower $R_f$ value in addition to the starting material **1a**. The analysis of the $^1H$, $^{13}C$, HSQC and HMBC NMR spectra of this new compound confirmed the formation of the 4,5-epoxy-1,5-diphenyl-2-penten-1-one (γ,δ-epoxide, **5a**)[45]. The formation of this compound can be explained in terms of the less electrophilic character of the $C_\gamma$=$C_\delta$ bond compared with that of the $C_\alpha$=$C_\beta$ bond, since the epoxidation of alkenes catalysed by salen $Mn^{III}$ complexes has been demonstrated to take place preferentially on double bonds with higher electron density.[46,47] It is noteworthy that in the epoxidation of these types of compounds with DMD[41] α,β-monoepoxides have been obtained. When performing the same reaction at higher temperature (40 °C), TLC showed not only the starting material **3a** and the γ,δ-monoepoxide **5a** but also a new compound with an even lower $R_f$ value. The $^1H$ NMR spectrum of the isolated new product identified it as a diastereomeric mixture (nearly 1:1) of 2,3:4,5-diepoxy-1,5-diphenylpentan-1-ones (α,β:γ,δ-diepoxides, **6a**),[45] the stereochemistry of the diastereomers being established by NOE (Scheme 2, see NMR spectroscopy discussion).

Several attempts were made to improve the yield of the epoxidation of (*E*,*E*)-cinnamylideneacetophenone (**3a**) by varying the amount of oxidant, temperature and reaction time and adding various nitrogen co-catalysts. The best results were achieved with hydrogen peroxide as the oxidant (3 equiv.), salen $Mn^{III}$ complex **4** as the catalyst (0.05 equiv.) and 1-methylimidazole (1-MeIm) as the co-catalyst at 40 °C for 4 h. These conditions gave a 21% yield of γ,δ-monoepoxide **5a**, a 10% yield of α,β:γ,δ-diepoxide **6a** and 38% of starting material **3a** was recovered (Table 1, Entry 1).

These optimized conditions were applied to the epoxidation of cinnamylideneacetophenones **3b**–**j**, and the results are presented in Table 1. The epoxidation of cinnamylideneacetophenones **3c**–**g** afforded similar results, yielding γ,δ-monoepoxides **5c**–**f**, α,β:γ,δ-diepoxides **6c**–**g** and some recovered starting material (Table 1). However, in the case of 4-nitrocinnamylideneacetophenone (**3d**) it was also possible to isolate the α,β-monoepoxide **7d** (Table 1, Entry 4). This can be explained by the electron-withdrawing effect of the nitro group, which overrules the effect of the carbonyl group, making the $C_\alpha$=$C_\beta$ bond more nucleophilic. TLC analysis of the epoxidation reaction of 4-methoxycinnamylideneacetophenone (**3b**) showed the formation of several products, and all attempts to isolate them failed (Table 1, Entry 2). It is very likely that a facile ring opening of the desired epoxide **5b**, due to the stabilization of the benzylic cation, and subsequent secondary reactions are responsible for this failure.




**1a–e**

**a**: $R^1 = R^2 = H$
**b**: $R^1 = OMe$, $R^2 = H$
**c**: $R^1 = Me$, $R^2 = H$
**d**: $R^1 = NO_2$, $R^2 = H$
**e**: $R^1 = H$, $R^2 = OH$

**2a–e**

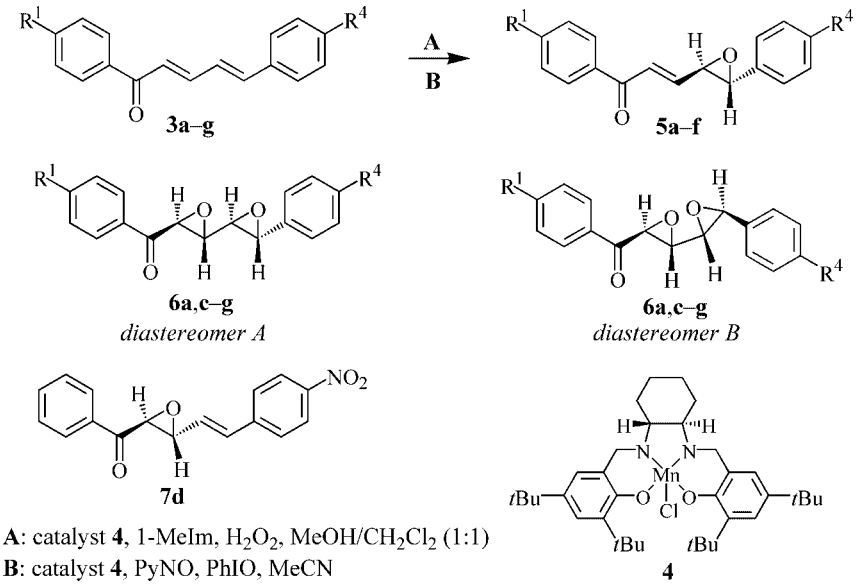
**a**: $R^3 = R^4 = H$
**b**: $R^3 = H$, $R^4 = OMe$
**c**: $R^3 = H$, $R^4 = Me$
**d**: $R^3 = H$, $R^4 = NO_2$
**e**: $R^3 = Me$, $R^4 = H$

**A**: MeOH, $NaOH/H_2O$, room temp., 20 h
**B**: dry THF, NaH, room temp., 12 h (only for **3d**,**g**)

**3a–j**

**a**: $R^1 = R^2 = R^3 = R^4 = H$
**b**: $R^1 = R^2 = R^3 = H$, $R^4 = OMe$
**c**: $R^1 = R^2 = R^3 = H$, $R^4 = Me$
**d**: $R^1 = R^2 = R^3 = H$, $R^4 = NO_2$
**e**: $R^1 = OMe$, $R^2 = R^3 = R^4 = H$
**f**: $R^1 = Me$, $R^2 = R^3 = R^4 = H$
**g**: $R^1 = NO_2$, $R^2 = R^3 = H$, $R^4 = H$
**h**: $R^1 = R^3 = R^4 = H$, $R^2 = OH$
**i**: $R^1 = R^2 = R^4 = H$, $R^3 = Me$
**j**: $R^1 = R^4 = H$, $R^2 = OH$, $R^3 = Me$

Scheme 1.




Scheme 2.

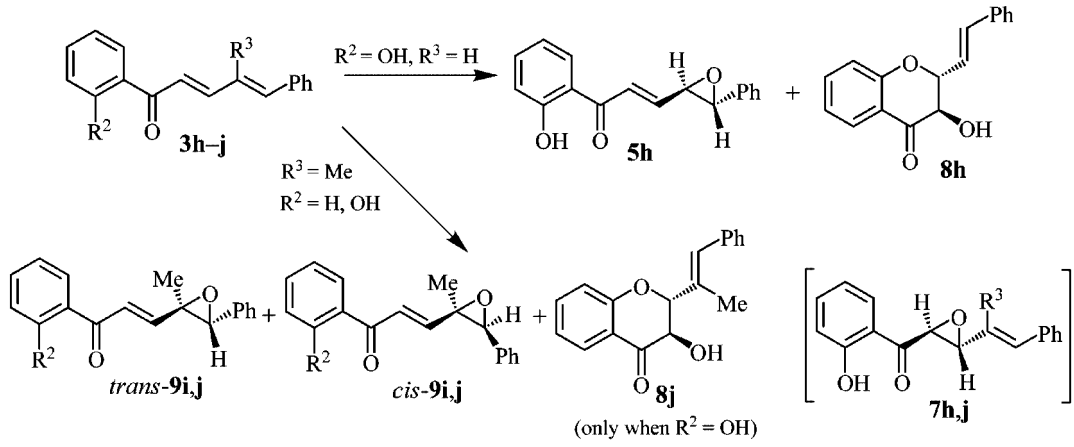
Table 1. Yields in the epoxidation reactions of (*E*,*E*)-cinnamylideneacetophenones **3a**–**j**.

| Entry | Reactant | Product | $H_2O_2$[a] | | PhIO[b] |
|---|---|---|---|---|---|
| | | | % Yield | % Effective yield[c] | % Yield |
| 1 | **3a** | **5a** | 21 | 34 | 18 |
| | | **6a** | 10 | 17 | 43 |
| 2 | **3b** | **5b** | | see text | |
| | | **6b** | | | |
| 3 | **3c** | **5c** | 13 | 15 | 11 |
| | | **6c**[d] | 9 | 9 | 23 |
| 4 | **3d** | **5d** | 9 | 17 | 22 |
| | | **6d**[d] | 18 | 38 | 33 |
| | | **7d** | 7 | 15 | 39 |
| 5 | **3e** | **5e** | 25 | 40 | 18 |
| | | **6e**[d] | 11 | 18 | 41 |
| 6 | **3f** | **5f** | 14 | 19 | 15 |
| | | **6f**[d] | 7 | 10 | 55 |
| 7 | **3g** | **5g** | –[e] | –[e] | –[e] |
| | | **6g**[d] | 10 | 23 | 62 |
| 8 | **3h** | **5h** | 11 | 14 | 4 |
| | | **8h** | 14 | 19 | 2 |
| 9 | **3i** | *trans*-**9i** | 16 | 26 | 60 |
| | | *cis*-**9i** | 26 | 43 | 7 |
| 10 | **3j** | **8j** | 19 | 29 | 13 |
| | | *trans*-**9j** | 13 | 19 | 9 |
| | | *cis*-**9j** | 10 | 15 | 3 |

[a] $H_2O_2$ (3 equiv.), catalyst **4** (0.05 equiv.), 1-MeIm (0.7 equiv.), 40 °C, 4 h, 1:1 MeOH/$CH_2Cl_2$. [b] PhIO (2 equiv.), catalyst **4** (0.05 equiv.), PyNO (0.5 equiv.), room temp., 4 h, MeCN. [c] Yield calculated on the basis of the amount of the reacted cinnamylideneacetophenone. [d] Obtained as a diastereomeric mixture (for ratios, see the Experimental Section). [e] None detected.

TLC analysis of the epoxidation of 2′-hydroxy-cinnamylideneacetophenone (**3h**) with hydrogen peroxide revealed the presence of three spots; the one with the largest $R_f$ value proved to be unreacted starting material **3h**, the one with the next-largest $R_f$ value was identified as 4,5-epoxy-1-(2-hydroxyphenyl)-5-phenyl-2-penten-1-one (**5h**) and the one with the smallest $R_f$ value was assigned as (*E*)-2,3-*trans*-3-hydroxy-2-styryl-4-chromanone (**8h**), the product of the in situ cyclisation of α,β-epoxide **7h** (Scheme 3 and Table 1, Entry 8). This cyclisation product **8h** is different from the one obtained in the epoxidation of **3h** with DMD,[41] where the cyclisation of a α,β:γ,δ-diepoxide gave a coumaranone derivative. In the present study, the cyclisation of the α,β-monoepoxide **7h** gave chromanone **8h**, as was reported for 2′-hydroxychalcone epoxides.[48–50] The observed preference of the attack of the phenolic hydroxy group at $C_\beta$ can be rationalized in terms of the high stability of the allylic $C_\beta$ carbocation and its better solvation by methanol in comparison with solvation by the acetone used in the DMD experiments.

In the epoxidation of γ-methylcinnamylideneacetophenone (**3i**) with hydrogen peroxide, two isomeric γ,δ-monoepoxides have been isolated and characterized by NMR spectroscopy, and no α,β:γ,δ-diepoxide was detected (Scheme 3 and Table 1, Entry 9). This surprising regioselectivity can be explained in terms of the enhanced nucleophilicity of the $C_\gamma$=$C_\delta$ bond due to the electron-donating effect of the methyl group, making the double bond more sensitive for the attack of the electrophilic oxidizing species. The NOESY spectra of these two diastereomers allowed us to assign their stereochemistry and to identify them as *trans*-**9i** and *cis*-**9i** (see the NMR discussion below). The formation of these two diastereomers can be envisaged by the mechanistic proposal for the epoxidation reactions of alkenes with the salen $Mn^{III}$ catalyst, where the alkenes can react in a stepwise radical process followed by ring closure from both sides of the molecule, affording the two possible diastereomers.[51,52] This means that the incorporation of the methyl group initiates a shift in the mechanism, since no diastereomeric γ,δ-monoepoxides **5a**,**c**–**g** were observed in the reaction of substrates lacking this unit.




Scheme 3.

Finally, the epoxidation of 2′-hydroxy-γ-methylcinnamylideneacetophenone (**3j**) afforded the expected products. In accordance with the reactivity patterns outlined above and due to the presence of the methyl group at $C_\gamma$, both γ,δ-monoepoxides ***trans*-9j** and ***cis*-9j** have been obtained. The formation of 4-chromanone **8j** due to the presence of the 2′-hydroxy group (Scheme 3 and Table 1, Entry 10) resembles the formation of **8h**.

Since the combination of iodosylbenzene and Jacobsen's catalyst constitutes an efficient oxidizing system in the case of (*E*)-2-styrylchromones,[42] we examined the epoxidation of (*E*,*E*)-cinnamylideneacetophenones **3a**–**j** under the same conditions. Several reactions were performed to optimize the conditions. First, an acetonitrile solution of **3a** was treated with 2 equiv. of iodosylbenzene and a catalytic amount of salen $Mn^{III}$. After 24 h at room temperature, preparative TLC analysis revealed the presence of 3 products. The first spot, corresponding to starting material **3a**, in marginal quantity, a second spot with a smaller $R_f$ value, corresponding to γ,δ-monoepoxide **5a** (5%) and the third spot, corresponding to α,β:γ,δ-diepoxide **6a** (4%) (Scheme 2). This result led us to use co-catalysts, which were found to be beneficial in the reaction with hydrogen peroxide, as well. The yields from the epoxidation of cinnamylideneacetophenone (**3a**) were tripled with pyridine *N*-oxide (PyNO) and 4-phenylpyridine *N*-oxide (PPNO). A study of the influence of reaction time on the epoxidation of **3a** with these two co-catalysts was then carried out (Table 2). With PyNO, only 4 h were necessary to achieve the best epoxidation yields (i.e. 18% of γ,δ-monoepoxide **5a** and 43% of α,β:γ,δ-diepoxide **6a**). After 12 h, the yields decreased, particularly in the case of **6a**. With PPNO, a gradual increase in the formation of **5a** and **6a** within the reaction time was observed, and 72 h was needed to achieve similar yields to those obtained with PyNO. After 72 h, a decrease in the yields of γ,δ-monoepoxide **5a** and α,β:γ,δ-diepoxide **6a** was observed. The optimized conditions (2 equiv. of iodosylbenzene, 0.05 equiv. of catalyst **4**, 0.5 equiv. of PyNO, acetonitrile, 4 h at room temperature) were applied to the other (*E*,*E*)-cinnamylideneacetophenones **3b**–**j**, and the corresponding epoxidation products were obtained with the yields presented in Table 1 (Scheme 2).

Table 2. Isolated yields in the epoxidation reactions of (*E*,*E*)-cinnamylideneacetophenone (**3a**) with pyridine *N*-oxide (PyNO) and 4-phenylpyridine *N*-oxide (PPNO) as co-catalysts and iodosylbenzene as the oxidant.

| Entry | Co-catalyst | *t* [h] | % Yield | |
|---|---|---|---|---|
| | | | **5a** | **6a** |
| 1 | PyNO | 4 | 18 | 43 |
| 2 | PPNO | | 13 | 21 |
| 3 | PyNO | 12 | 19 | 43 |
| 4 | PPNO | | 15 | 35 |
| 5 | PyNO | 24 | 17 | 35 |
| 6 | PPNO | | 19 | 31 |
| 7 | PyNO | 48 | 13 | 32 |
| 8 | PPNO | | 21 | 36 |
| 9 | PyNO | 72 | – | – |
| 10 | PPNO | | 17 | 41 |
| 11 | PyNO | 96 | – | – |
| 12 | PPNO | | 14 | 31 |

The epoxidation of alkenes catalysed by salen $Mn^{III}$ complexes is usually favoured by the presence of electron-donating substituents, and the corresponding epoxides are obtained in better yields.[46,47] Our results presented in Table 1 (Entries 1–4) seem to indicate the contrary. However, these results cannot be explained by the reactivity of the unsaturated ketones **3a**–**d**, but by the stability of the obtained epoxides **5a**–**d** and **6a**–**d**. In the presence of electron-withdrawing substituents, the epoxides **5d**, **6d** and **7d** were obtained in good combined yields (34% with $H_2O_2$ and 94% with PhIO, Table 1, Entry 4), whereas in the case of electron-donating substituents, the yields decreased (combined yields of **5c** + **6c** were 22% with $H_2O_2$ and 34% with PhIO, in comparison with 31% and 61%, respectively, found in the reactions of the parent compound **3a**). In the presence of a strong electron-donating group we could not isolate any epoxide (Table 1, Entry 2). This conclusion was confirmed when the epoxidation of **3b** was carried out in deuterated acetonitrile and monitored by $^1H$ NMR spec-

troscopy. After several minutes of reaction under the conditions presented in Table 1, we observed the signals of γ,δ-monoepoxide **5b** (doublet of doublets at $\delta$ = 6.54 ppm, $J$ = 15.4 and 7.4 Hz, corresponding to the resonance of β-H) and other small signals in the aliphatic region ($\delta$ = 4.12–5.01 ppm), which increased with the reaction time, probably due to the decomposition of monoepoxide **5b**. The characteristic signal of monoepoxide **5b** did not increase, and no signals typical of α,β:γ,δ-diepoxide **6b** were observed.

The presence of electron-donating or electron-withdrawing substituents on the A ring of cinnamylideneacetophenones did not affect the yields of the obtained epoxides (Table 1, Entries 1 and 5–7), while the presence of a weak electron-donating substituent on the vinylic moiety slightly increased the yield of the epoxidation reaction (Table 1, Entries 1 and 9). However, the *cis*-γ,δ-monoepoxide *cis*-**9i** was obtained in a better yield than the *trans*-γ,δ-monoepoxide *trans*-**9i** with hydrogen peroxide, while the use of iodosylbenzene resulted in the *trans*-γ,δ-monoepoxide *trans*-**9i** as the major product with a high *trans*/*cis* (8.6:1, Table 1, Entry 9). This difference can be rationalized in terms of shifting the mechanism of the epoxidation from the stepwise radical process (vide supra) towards a concerted one in the less solvating acetonitrile; this solvent can stabilize the radicaloid species to a lesser extent. The presence of a 2′-hydroxy group drastically decreased the total yield of the obtained epoxides, especially with iodosylbenzene as the oxidant (Table 1, Entries 1, 8 and 10).

After the analysis of all the results collected in Table 1 we can conclude that the epoxidation of cinnamylideneacetophenones **3a**,**c**–**f**,**i** with iodosylbenzene gives the epoxides **5a**,**c**–**f**,**i** + **6a**,**c**–**f**,**i** in better total yields than did the reaction with hydrogen peroxide, and this might be due to the instability of the obtained epoxides, as described above. From Table 1 one can also notice that the yields of γ,δ-monoepoxides **5a**,**c**–**f** are double those of the α,β:γ,δ-diepoxides **6a**,**c**–**f** when the epoxidation was performed with hydrogen peroxide as the oxidant, but when iodosylbenzene was the oxidant we observed the inverse, (i.e., the α,β:γ,δ-diepoxides **6a**,**c**–**h** were obtained in better yields than were the γ,δ-monoepoxides **5a**,**c**–**h**.) This difference can be interpreted in terms of the higher sensitivity of the α,β:γ,δ-diepoxides toward attack of the nucleophilic solvent, decreasing the isolated yields of the diepoxides in the hydrogen peroxide systems.

Since we used Jacobsen's catalyst **4** in the described epoxidations, and therefore, the reactions were effected by a chiral non-racemic $Mn^{V}$oxo species in both methods, it was important to determine the enantiomeric ratio of the obtained monoepoxides. Unfortunately, HPLC analysis measurements of γ,δ-monoepoxide **5a** with a chiral column (Chiralcel OD) showed that no stereodifferentiation took place, and the product was a racemic mixture of the two enantiomers.

### Nuclear Magnetic Resonance Spectroscopy

The $^{1}$H NMR spectra of the 1,5-diaryl-4,5-epoxy-2-penten-1-ones **5a**,**c**–**f** revealed the presence of two signals in the aliphatic region ($\delta$ = 3.59–3.61 ppm and $\delta$ = 3.86–4.01 ppm), which were attributed to the resonances of δ-H and γ-H, respectively. Another main feature of these spectra was the doublet of doublets at $\delta$ = 6.92–6.95 ppm, corresponding to the resonance of β-H, which appears at lower frequency values than that of α-H ($\delta$ = 7.28–7.33 ppm). The $^{3}J_{\alpha H-\beta H}$ value of about 15 Hz indicates a *trans* configuration of the $C_{\alpha}$=$C_{\beta}$ bond of γ,δ-monoepoxides **5a**,**c**–**f**, as expected on the basis of the *trans*,*trans* configuration of the starting (*E*,*E*)-cinnamylideneacetophenones **3a**,**c**–**f**. The structure of monoepoxides **5a**,**c**–**f** was supported by the connectivities found in their HMBC spectra, mainly those of α-H and β-H with the carbonyl C atom (δ = 187.7–189.5 ppm) and also of the δ-H with C-1 (δ = 133.0–143.4 ppm) and C-2,6 (δ = 125.5–126.3 ppm) (Figure 1), allowing us to confirm the presence of the epoxy ring in the γ,δ-position and the assignments of α-H, β-H, γ-H and δ-H.

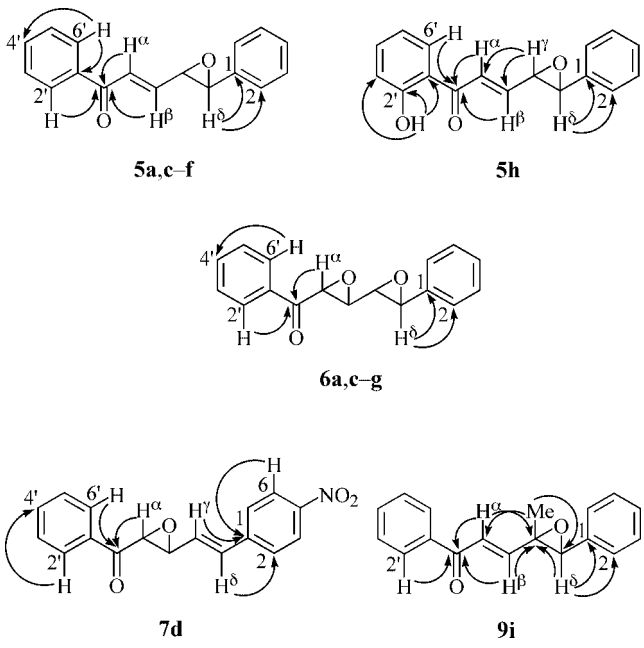



Figure 1. Important connectivities found in the HMBC spectra of compounds **5a**,**c**–**f**,**h**, **6a**,**c**–**g**, **7d** and **9i**.

The unequivocal assignment of 2,3-epoxy-1-phenyl-5-(4-nitrophenyl)-4-penten-1-one (**7d**) was also based on the connectivities found in its HMBC spectrum. The signal appearing as a doublet in the aliphatic region ($\delta$ = 4.36 ppm) correlates with the carbonyl C atom ($\delta$ = 193.0 ppm), and thus, was assigned to the resonance of α-H. The correlations of the vinylic protons γ-H and δ-H with C-1 ($\delta$ = 141.7 ppm) and C-2,6 ($\delta$ = 127.2 ppm), respectively, confirm the structure of α,β-monoepoxide **7d** (Figure 1).

The main feature of the $^{13}$C NMR spectra of the γ,δ-monoepoxides **5a**,**c**–**f** was the resonance of the carbonyl carbon, which appeared at high frequency values ($\delta$ = 187.7–189.5 ppm). The unequivocal assignments of the other C resonances were made with the aid of HSQC and

HMBC spectra. At lower frequency values it was possible to identify the C resonances of C-γ and C-δ at $\delta$ = 60.2–61.3 ppm and 61.4–61.6 ppm, respectively. The C resonances of C-α and C-β appeared at $\delta$ = 127.0–128.0 ppm and 142.1–143.7 ppm, respectively, and the latter was assigned to the higher frequency values on the basis of the mesomeric deshielding effect of the carbonyl group.

The $^1$H NMR spectra of the γ-methyl-γ,δ-monoepoxides *trans*-**9i**,**j** and *cis*-**9i**,**j** showed two singlets at $\delta$ = 1.31–1.74 ppm and 4.05–4.24 ppm, assigned to the proton resonances of the γ-methyl group and δ-H, respectively. The presence of the γ-methyl group also promoted important changes in the resonances of α-H and β-H, with the resonance of β-H being the most affected, in contrast to that of the γ,δ-monoepoxides, which are unsubstituted at the γ-position (**5a**,**c**–**f**). Thus, the resonances assigned to α-H ($\delta$ = 6.96–7.34 ppm) appeared at higher frequency than those assigned to β-H ($\delta$ = 6.59–7.19 ppm). The configuration of the two diastereomers *trans*-**9i**,**j** and *cis*-**9i**,**j** were established by the NOE signals found in their NOESY spectra. For the *cis*-**9i**,**j** diastereomers, a strong NOE cross peak between the signals of the γ-methyl protons and that of δ-H was observed; whereas for the *trans*-**9i**,**j** diastereomers, a strong NOE cross peak between the signals of the γ-methyl protons and that of 2,6-H of the phenyl ring was found (see Figure 2).

The $^1$H NMR spectra of 2′-hydroxy-cinnamylideneacetophenone γ,δ-monoepoxides **5j**, *trans*-**9j** and *cis*-**9j** showed a singlet corresponding to the resonance of the hydroxy proton (2′-O*H*) at $\delta$ = 12.38–12.60 ppm. This signal appears at high frequency values due to an intramolecular hydrogen bond with the carbonyl group.

The $^1$H NMR spectra of α,β:γ,δ-diepoxides **6a**,**c**–**g** are quite complex, presenting two distinct regions (aliphatic and aromatic). In the aliphatic region, the presence of two groups of four signals indicates a diastereomeric mixture of these diepoxides. The stereochemistry of both diastereomers **A** and **B** was established by the NOE signals found in their NOESY spectra, and the composition of the mixture as 51–58% of isomer **A** and 42–49% of isomer **B** was calculated from the integrated area of the corresponding proton signals. This stereochemistry was based on the proximities between α-H and γ-H and between β-H and δ-H for diastereomers **A** and between α-H and δ-H and between β-H and γ-H for diastereomers **B** (Figure 2). In the HMBC spectra of α,β:γ,δ-diepoxides **6a**,**c**–**g**, the correlations between the carbonyl C atom resonances ($\delta$ = 191.2–193.3 ppm) and the signals appearing as a doublet at $\delta$ = 3.90–4.08 ppm allowed us to assign these proton resonances to α-H (since there are no correlation between C=O and δ-H). From the 2D-COSY experiments, all the proton resonances of the α,β:γ,δ-diepoxide system have been assigned: γ-H (doublet of doublets at $\delta$ = 3.18–3.22 ppm), β-H (doublet of doublets at $\delta$ = 3.34–3.54 ppm), δ-H (doublet at $\delta$ = 3.90–4.08 ppm) and α-H (doublet at $\delta$ = 4.29–4.36 ppm). The aromatic region of the $^1$H NMR spectra of α,β:γ,δ-diepoxides **6a**,**c**–**g** presents several multiplets, which were assigned with the aid of 2D NMR spectra and by comparisons with similar compounds.[41]

The $^{13}$C NMR spectra of the diastereomeric mixture of α,β:γ,δ-diepoxides **6a**,**c**–**g** presents a duplication of signals in three distinct zones: those at lower frequency values ($\delta$ = 53.9–59.8 ppm), assigned to the C resonances of the α,β:γ,δ-diepoxy moiety, those at intermediate frequency values ($\delta$ = 114.0–164.3 ppm), assigned to the C resonances of the aromatic rings and those at higher frequency values ($\delta$ = 191.2–193.1 ppm and 191.4–193.3 ppm), attributed to the resonance of the carbonyl C atom of diastereomers **A** and **B**, respectively. The resonances of the carbonyl carbons of diastereomers **A** showed higher frequency values than those of the diastereomers **B**, except for the nitro derivatives **6d**,**g**, where the resonances of the carbonyl C atoms appeared in reverse order. The C resonances of C-α, C-β, C-γ and C-δ of diastereomers **A** and **B** were assigned with the aid of the HSQC spectra, appearing at $\delta$ = 54.4–54.7 ppm, 57.2–57.8 ppm, 59.4–59.8 ppm, 56.1–57.3 ppm and $\delta$ = 53.9–54.6 ppm, 55.8–56.6 ppm, 58.3–59.1 ppm and 55.3–56.4 ppm, respectively.

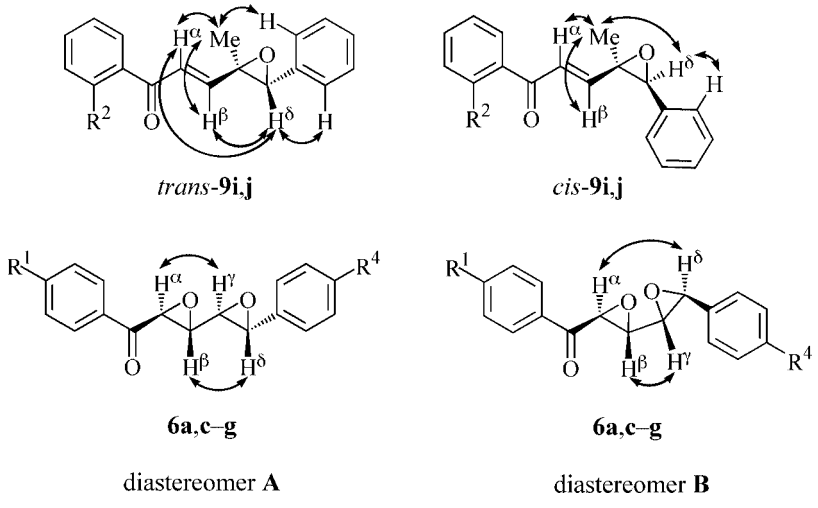



Figure 2. Main NOE cross peaks found in the NOESY spectra of α,β:γ,δ-diepoxides **6a**,**c**–**g** and γ-methyl-γ,δ-monoepoxides **9i**,**j**.

The assignment of the C resonances of all compounds was confirmed by the connectivities found in the HMBC spectra (Figure 1).

## Experimental Section

**General Remarks:** Melting points were measured with a Reichert Thermovar apparatus fitted with a microscope and are uncorrected. NMR spectra were recorded with a Bruker Avance 300 spectrometer (300.13 MHz for $^1$H and 75.47 MHz for $^{13}$C) in $CDCl_3$. Chemical shifts ($\delta$) are reported in ppm and coupling constants ($J$) in Hz with TMS as an internal standard. Unequivocal $^{13}$C assignments were made with 2D *g*HSQC and *g*HMBC (delays for one-bond and long-range C/H couplings were optimised for 145 and 7 Hz, respectively) experiments. Electron impact (EI, 70 eV) MS were recorded with VG Autospec Q and M spectrometers. Elemental analyses were obtained with a LECO 932 CHNS analyser. Preparative TLC was performed with Merck silica gel 60 $DGF_{254}$. Column chromatography was performed with Merck silica gel 60 (70–230 mesh). HPLC was performed with a Chiralcel OD column with hexane/2-propanol (90:10, v/v) as the eluent and a flow rate of 0.7 mL/min. Under these conditions, the enantiomers of epoxide **5a** were detected at 20 min and 21 min, respectively. All chemicals and solvents used were obtained from commercial sources and used as received or dried with standard procedures. Cinnamaldehydes **2b**–**d** have been prepared by a literature method.[43] Iodosylbenzene was prepared by hydrolysis of the commercially available iodobenzene diacetate under basic conditions.[4]

**General Procedure for the Synthesis of (*E*,*E*)-Cinnamylideneacetophenones 3a–c,e,f,h–j:** To a methanolic solution (200 mL) of the appropriate acetophenone (42.9 mmol) sodium hydroxide (60% aqueous solution, 200 mL) was slowly added. After cooling the solution to room temperature, the appropriate cinnamaldehyde (51.5 mmol) was added. The reaction mixture was stirred at room temperature for 20 h and then poured into a mixture of water (100 mL) and ice (100 g), and the pH was adjusted to 2 with dilute hydrochloric acid. The precipitate obtained was filtered, taken up in dichloromethane and purified by silica gel column chromatography with a 1:1 mixture of light petroleum/dichloromethane as the eluent. The solvent was removed in vacuo, and the residue was recrystallised from ethanol to obtain cinnamylideneacetophenones **3a**–**c**,**e**,**f**,**h**–**j** as yellow crystals. Products **3a**,**e**,**f**,**h**–**j** were shown to possess spectroscopic and analytical data identical to those previously reported.[32,33,53]

**(*E*,*E*)-4-Methoxycinnamylideneacetophenone (3b):** Yield of 6.57 g (58%). M.p. 113–115 °C (recrystallised from ethanol). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.84 (s, 3 H, 4-OC$H_3$), 6.86–7.01 (m, 2 H, γ-H and δ-H), 6.90 (d, $J$ = 8.8 Hz, 2 H, 2,6-H), 7.05 (d, $J$ = 14.8 Hz, 1 H, α-H), 7.45 (d, $J$ = 8.8 Hz, 2 H, 3,5-H), 7.48 (dd, $J$ = 7.8 and 7.2 Hz, 2 H, 3′,5′-H), 7.55 (tt, $J$ = 7.2 and 1.4 Hz, 1 H, 4′-H), 7.61 (dd, $J$ = 14.8 and 9.8 Hz, 1 H, β-H). 7.97 (dd, $J$ = 7.8 and 1.4 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 55.3 (4-O*C*H$_3$), 114.2 (C-2,6), 124.3 (C-α), 124.8 (C-γ), 128.3 (C-2′,6′), 128.5 (C-3′,5′), 128.8 (C-3,5), 128.9 (C-1), 132.5 (C-4′), 138.4 (C-1′), 141.8 (C-δ), 145.4 (C-β), 160.6 (C-4), 190.5 (C=O) ppm. MS: *m*/*z* (%) = 264 (100) $[M]^+$, 263 (18), 233 (19), 187 (10), 159 (27), 144 (22), 128 (17), 121 (13), 116 (17), 115 (34), 105 (30), 91 (9), 85 (11), 83 (16), 77 (37), 63 (10), 51 (22). $C_{18}H_{16}O_2$ (264.32): calcd. C 81.79, H 6.10; found C 81.59, H 6.16.

**(*E*,*E*)-4-Methylcinnamylideneacetophenone (3c):** Yield of 6.17 g (58%). M.p. 95–96 °C (recrystallised from ethanol). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.37 (s, 3 H, 4-C$H_3$), 6.95–7.06 (m, 2 H, γ-H and δ-H), 7.07 (d, $J$ = 14.8 Hz, 1 H, α-H), 7.18 (d, $J$ = 8.1 Hz, 2 H, 3,5-H), 7.40 (d, $J$ = 8.1 Hz, 2 H, 2,6-H), 7.49 (dd, $J$ = 8.0 and 7.3 Hz, 2 H, 3′,5′-H), 7.57 (tt, $J$ = 7.3 and 1.8 Hz, 1 H, 4′-H), 7.56–7.68 (m, 1 H, β-H), 7.98 (dd, $J$ = 8.0 and 1.8 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.4 (4-*C*H$_3$), 124.9 (C-α), 126.0 (C-γ), 127.3 (C-2,6), 128.4 (C-2′,6′), 128.5 (C-3′,5′), 129.6 (C-3,5), 132.6 (C-4′), 133.4 (C-1), 138.3 (C-1′), 139.5 (C-4), 142.1 (C-δ), 145.2 (C-β), 190.6 (C=O) ppm. MS: *m*/*z* (%) = 248 (100) $[M]^+$, 247 (33), 233 (28), 205 (15), 171 (8), 157 (15), 143 (24), 141 (13), 128 (36), 115 (14), 105 (29), 91 (8), 77 (27), 51 (7). $C_{18}H_{16}O$ (248.32): calcd. C 87.06, H 6.49; found C 86.78, H 6.53.

**Synthesis of (*E*,*E*)-Nitrocinnamylideneacetophenones 3d,g:** Sodium hydride (1.36 g, 56.5 mmol) was added to a solution of the appropriate acetophenone (25.7 mmol) in dry THF (80 mL), and the mixture was cooled to room temperature. The appropriate cinnamaldehyde (30.8 mmol) in dry THF (100 mL) was added, and the reaction mixture was stirred for 12 and then poured into a mixture of water (100 mL) and ice (100 g) and acidified with hydrochloric acid to pH ≈ 2. The solid obtained was filtered, taken up in dichloromethane and washed with water. The organic layer was dried and concentrated, and the residue was purified by silica gel column chromatography with a 1:1 mixture of light petroleum/dichloromethane as the eluent. The solvent was evaporated, and the residue was recrystallised from ethanol, giving the cinnamylideneacetophenones **3d**,**g** as yellow crystals.

**(*E*,*E*)-4-Nitrocinnamylideneacetophenone (3d):** Yield of 3.44 g (48%). M.p. 171–173 °C (recrystallised from ethanol). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.05 (d, $J$ = 15.5 Hz, 1 H, δ-H), 7.07–7.21 (m, 1 H, γ-H), 7.22 (d, $J$ = 14.9 Hz, 1 H, α-H), 7.51 (t, $J$ = 7.8 Hz, 2 H, 3′,5′-H), 7.60 (dd, $J$ = 14.9 and 10.7 Hz, 1 H, β-H), 7.61 (t, $J$ = 7.3 Hz, 1 H, 4′-H), 7.64 (d, $J$ = 8.8 Hz, 2 H, 2,6-H), 7.99 (dd, $J$ = 7.8 and 1.6 Hz, 2 H, 2′,6′-H), 8.24 (d, $J$ = 8.8 Hz, 2 H, 3,5-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 124.2 (C-3,5), 127.7 (C-2,6), 127.8 (C-α), 128.4 (C-2′,6′), 128.7 (C-3′,5′), 131.0 (C-γ), 133.0 (C-4′), 137.8 (C-1′), 138.5 (C-δ), 142.3 (C-1), 143.1 (C-β), 147.6 (C-4), 190.1 (C=O) ppm. MS: *m*/*z* (%) = 279 (100) $[M]^+$, 278 (21), 232 (17), 204 (17), 202 (16), 157 (36), 128 (39), 127 (21), 115 (21), 105 (48), 102 (13), 91 (6), 89 (7), 83 (8), 77 (63), 63 (7), 51 (22). $C_{17}H_{13}NO_3$ (279.29): calcd. C 73.11, H 4.69, N 5.02; found C 72.93, H 5.03, N 5.18.

**(*E*,*E*)-4′-Nitrocinnamylideneacetophenone (3g):** Yield of 3.73 g (52%). M.p. 91–93 °C (recrystallised from ethanol). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.00–7.12 (m, 3 H, α-H, γ-H and δ-H), 7.35–7.43 (m, 3 H, 3,4,5-H), 7.52 (dd, $J$ = 7.9 and 1.6 Hz, 2 H, 2,6-H), 7.65 (ddd, $J$ = 14.9, 8.5 and 1.9 Hz, 1 H, β-H), 8.10 (d, $J$ = 8.9 Hz, 2 H, 2′,6′-H), 8.34 (d, $J$ = 8.9 Hz, 2 H, 3′,5′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 123.8 (C-3′,5′), 124.4 (C-α), 126.4 (C-γ), 127.5 (C-2,6), 128.9 (C-3,5), 129.3 (C-2′,6′), 129.7 (C-4), 135.7 (C-1), 143.1 (C-1′), 143.6 (C-δ), 146.8 (C-β), 149.9 (C-4′), 188.9 (C=O) ppm. MS: *m*/*z* (%) = 279 (100) $[M]^+$, 278 (35), 233 (10), 232 (19), 215 (10), 203 (15), 202 (30), 178 (7), 157 (16), 156 (8), 150 (13), 129 (51), 128 (46), 127 (25), 115 (16), 104 (18), 102 (10), 91 (11), 83 (8), 77 (19), 76 (21), 63 (13), 51 (15). $C_{17}H_{13}NO_3$ (279.29): calcd. C 73.11, H 4.69, N 5.02; found C 72.94, H 4.68, N 5.10.

**General Procedure for the Epoxidation of (*E*,*E*)-Cinnamylideneacetophenones 3a–j with Hydrogen Peroxide as the Oxidant:** $H_2O_2$ (30% aqueous solution, 0.17 mL, 5 mmol) was added to a solution of the appropriate (*E*,*E*)-cinnamylideneacetophenone **3a**–**j** (0.5 mmol), 1-methylimidazole (0.03 mL, 0.35 mmol) and catalyst **4** (0.016 g, 0.025 mmol) in a 1:1 mixture of dichloromethane/meth-

anol (4 mL). The mixture was stirred at 40 °C for 4 h and then diluted with dichloromethane (50 mL) and washed with water, and the organic layer was separated and concentrated. The residue was purified by preparative silica gel TLC (eluent: a 1:2 mixture of light petroleum/dichloromethane), leading to the isolation of the unreacted starting materials **3a**–**j** and the epoxidation products **5a**,**c**–**f**, **6a**,**c**–**g**, **7d**, **8h**,**j**, *trans*-**9i**,**j** and ***cis***-**9i**,**j**. The yields in the epoxidation of (*E*,*E*)-cinnamylideneacetophenones **3a**–**j** were as follows: **5a** (21%), **6a** (10%), **5c** (13%), **5c** (9%), **5d** (9%), **6d** (18%), **7d** (7%), **5e** (25%), **6e** (11%), **5f** (14%), **6f** (7%), **6g** (10%), **5h** (11%), **8h** (14%), *trans*-**9i** (16%), ***cis***-**9i** (26%), **8j** (19%), *trans*-**9j** (13%) and *cis*-**9j** (10%).

**General Procedure for the Epoxidation of (*E*,*E*)-Cinnamylideneacetophenones 3a–j with Iodosylbenzene as the Oxidant:** Catalyst **4** (0.016 g, 0.025 mmol) was added to a solution of the appropriate (*E*,*E*)-cinnamylideneacetophenone **3a**–**j** (0.5 mmol) and pyridine *N*-oxide (0.02 g, 0.25 mmol) in acetonitrile (4 mL). Then iodosylbenzene (0.22 g, 1.0 mmol) was added, and the reaction mixture was stirred at room temperature for 4 h and then concentrated and submitted to the same purification and isolation as described above for the epoxidation with hydrogen peroxide. The yields in the epoxidation of (*E*,*E*)-cinnamylideneacetophenones **3a**–**j** were as follows: **5a** (18%), **6a** (43%), **5c** (11%), **6c** (23%), **5d** (22%), **6d** (33%), **7d** (39%), **5e** (18%), **6e** (41%), **5f** (15%), **6f** (55%), **6g** (62%), **5h** (4%), **8h** (2%), *trans*-**9i** (60%), *cis*-**9i** (7%), **8j** (13%), *trans*-**9j** (9%) and *cis*-**9j** (3%).

**(*4R**,*5R**)-4,5-Epoxy-1,5-diphenyl-2-penten-1-one (5a):** M.p. 68–70 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.61 (dd, $J$ = 6.6 and 1.8 Hz, 1 H, γ-H), 3.89 (d, $J$ = 1.8 Hz, 1 H, δ-H), 6.95 (dd, $J$ = 15.4 and 6.6 Hz, 1 H, β-H), 7.28 (d, $J$ = 15.4 Hz, 1 H, α-H), 7.28–7.42 (m, 5 H, 2,3,4,5,6-H), 7.50 (dd, $J$ = 7.6 and 7.4 Hz, 2 H, 3′,5′-H), 7.60 (tt, $J$ = 7.4 and 1.6 Hz, 1 H, 4′-H), 7.97 (dd, $J$ = 7.6 and 1.6 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 61.2 (C-γ), 61.5 (C-δ), 125.5 (C-2,6), 127.2 (C-α), 128.6 (C-2′,6′), 128.66 (C-3,4,5), 128.69 (C-3,5′), 133.2 (C-4′), 136.1 (C-1), 137.3 (C-1′), 143.5 (C-β), 189.5 (C=O) ppm. MS: *m*/*z* (%) = 250 (3) $[M]^+$, 234 (1), 221 (4), 159 (2), 145 (21), 144 (100), 115 (45), 105 (32), 89 (13), 77 (39), 63 (6), 51 (19). HRMS-EI: calcd. for $C_{17}H_{14}O_2$ $[M]^+$ 250.0994; found 250.0986.

**Diastereomeric Mixture (58:42) of 2,3:4,5-Diepoxy-1,5-diphenylpentan-1-one (6a):** Yellow oil.

**Diastereomer A. (2*R**,3*S**,4*R**,5*S**)-2,3:4,5-Diepoxy-1,5-diphenylpentan-1-one:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.18 (dd, $J$ = 4.6 and 1.9 Hz, 1 H, γ-H), 3.35 (dd, $J$ = 4.6 and 1.9 Hz, 1 H, β-H), 3.93 (d, $J$ = 1.9 Hz, 1 H, δ-H), 4.34 (d, $J$ = 1.9 Hz, 1 H, α-H), 7.26–7.39 (m, 5 H, 2,3,4,5,6-H), 7.52 (t, $J$ = 7.4 Hz, 2 H, 3′,5′-H), 7.65 (t, $J$ = 7.4 Hz, 1 H, 4′-H), 8.05 (dd, $J$ = 7.4 and 1.2 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 54.7 (C-α), 57.3 (C-δ), 57.7 (C-β), 59.8 (C-γ), 125.66 (C-2,6), 128.4 (C-2′,6′), 128.69 (C-3,5), 128.80 (C-4), 128.99 (C-3′,5′), 134.2 (C-4′), 135.3 (C-1′), 135.5 (C-1), 193.1 (C=O) ppm.

**Diastereomer B. (2*R**,3*S**,4*S**,5*R**)-2,3:4,5-Diepoxy-1,5-diphenylpentan-1-one:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.28 (dd, $J$ = 3.0 and 2.0 Hz, 1 H, γ-H), 3.46 (dd, $J$ = 3.0 and 2.0 Hz, 1 H, β-H), 3.96 (d, $J$ = 2.0 Hz, 1 H, δ-H), 4.36 (d, $J$ = 2.0 Hz, 1 H, α-H), 7.26–7.39 (m, 5 H, 2,3,4,5,6-H), 7.52 (t, $J$ = 7.4 Hz, 2 H, 3′,5′-H), 7.65 (t, $J$ = 7.4 Hz, 1 H, 4′-H), 8.05 (dd, $J$ = 7.4 and 1.2 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 54.2 (C-α), 56.3 (C-δ), 56.5 (C-β), 58.8 (C-γ), 125.70 (C-2,6), 128.5 (C-2′,6′), 128.69 (C-3,5), 128.74 (C-4), 128.96 (C-3′,5′), 134.2 (C-4′), 135.3 (C-1′), 135.8 (C-1), 193.3 (C=O) ppm.

MS: *m*/*z* (%) = 266 (<1) $[M]^+$, 250 (1), 237 (2), 207 (5), 174 (4), 161 (25), 147 (12), 131 (11), 115 (13), 105 (100), 91 (62), 89 (12), 79 (13), 77 (68), 65 (6), 63 (7), 51 (23). HRMR-EI: calcd. for $C_{17}H_{14}O_3$ $[M]^+$ 266.0943; found 266.0937.

**(4*R**,5*R**)-4,5-Epoxy-5-(4-methylphenyl)-1-phenyl-2-penten-1-one (5c):** M.p. 101–102 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.36 (s, 3 H, 4-C$H_3$), 3.59 (ddd, $J$ = 6.4, 1.8 and 0.6 Hz, 1 H, γ-H), 3.86 (d, $J$ = 1.8 Hz, 1 H, δ-H), 6.95 (dd, $J$ = 15.4 and 6.4 Hz, 1 H, β-H), 7.19 (d, $J$ = 8.6 Hz, 2 H, 3,5-H), 7.21 (d, $J$ = 8.6 Hz, 2 H, 2,6-H), 7.27 (dd, $J$ = 15.4 and 0.6 Hz, 1 H, α-H), 7.49 (dd, $J$ = 8.0 and 7.5 Hz, 2 H, 3′,5′-H), 7.59 (tt, $J$ = 7.5 and 1.4 Hz, 1 H, 4′-H), 7.97 (dd, $J$ = 8.0 and 1.4 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.2 (4-*C*$H_3$), 61.1 (C-γ), 61.6 (C-δ), 125.5 (C-2,6), 127.0 (C-α), 128.6 (C-2′,6′), 128.7 (C-3′,5′), 129.3 (C-3,5), 133.0 (C-1), 133.1 (C-4′), 137.3 (C-1′), 138.6 (C-4), 143.7 (C-β), 189.5 (C=O) ppm. MS: *m*/*z* (%) = 264 (1) $[M]^+$, 248 (1), 235 (4), 159 (3), 145 (15), 144 (100), 119 (8), 116 (15), 115 (37), 105 (21), 91 (11), 89 (3), 77 (26), 65 (4), 63 (2), 51 (7). HRMSEI: calcd. for $C_{18}H_{16}O_2$ $[M]^+$ 264.1150; found 264.1144.

**Diastereomeric Mixture (56:44) of 2,3:4,5-Diepoxy-5-(4-methylphenyl)-1-phenylpentan-1-one (6c):** M.p. 55–57 °C.

**Diastereomer A. (2*R**,3*S**,4*R**,5*S**)-2,3:4,5-Diepoxy-5-(4-methylphenyl)-1-phenylpentan-1-one:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.36 (s, 3 H, 4-C$H_3$), 3.19 (dd, $J$ = 4.6 and 2.0 Hz, 1 H, γ-H), 3.35 (dd, $J$ = 4.6 and 1.9 Hz, 1 H, β-H), 3.90 (d, $J$ = 2.0 Hz, 1 H, δ-H), 4.34 (d, $J$ = 1.9 Hz, 1 H, α-H), 7.18–7.19 (m, 4 H, 2,3,5,6-H), 7.50–7.55 (m, 2 H, 3′,5′-H), 7.63–7.69 (m, 1 H, 4′-H), 8.04–8.08 (m, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.2 (4-*C*$H_3$), 54.7 (C-α), 57.2 (C-δ), 57.8 (C-β), 59.6 (C-γ), 125.61 (C-2,6), 128.39 (C-2′,6′), 128.93 (C-3′,5′), 129.3 (C-3.5), 132.4 (C-1), 134.2 (C-4′), 135.2 (C-1′), 138.7 (C-4), 193.1 (C=O) ppm.

**Diastereomer B. (2*R**,3*S**,4*S**,5*R**)-2,3:4,5-Diepoxy-5-(4-methylphenyl)-1-phenylpentan-1-one:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.36 (s, 3 H, 4-C$H_3$), 3.28 (dd, $J$ = 3.0 and 2.0 Hz, 1 H, γ-H), 3.46 (dd, $J$ = 3.0 and 2.0 Hz, 1 H, β-H), 3.93 (d, $J$ = 2.0 Hz, 1 H, δ-H), 4.36 (d, $J$ = 2.0 Hz, 1 H, α-H), 7.18–7.19 (m, 4 H, 2,3,5,6-H), 7.50–7.55 (m, 2 H, 3′,5′-H), 7.63–7.69 (m, 1 H, 4′-H), 8.04–8.08 (m, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.2 (4-*C*$H_3$), 54.2 (C-α), 56.3 (C-δ), 56.5 (C-β), 58.6 (C-γ), 125.64 (C-2,6), 128.43 (C-2′,6′), 128.91 (C-3′,5′), 129.3 (C-3,5), 132.6 (C-1), 134.2 (C-4′), 135.2 (C-1′), 138.6 (C-4), 193.3 (C=O) ppm.

MS: *m*/*z* (%) = 280 (1) $[M]^+$, 265 (2), 251 (5), 221 (4), 207 (8), 175 (40), 160 (5), 145 (5), 131 (9), 121 (5), 115 (5), 119 (20), 106 (15), 105 (100), 91 (18), 77 (33), 65 (6), 51 (10). HRMS-EI: calcd. for $C_{18}H_{16}O_3$ $[M]^+$ 280.1099; found 280.1103.

**(4*R**,5*R**)-4,5-Epoxy-5-(4-nitrophenyl)-1-phenyl-2-penten-1-one (5d):** M.p. 99–101 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.61 (ddd, $J$ = 6.6, 1.7 and 0.6 Hz, 1 H, γ-H), 4.01 (d, $J$ = 1.7 Hz, 1 H, δ-H), 6.93 (dd, $J$ = 15.4 and 6.6 Hz, 1 H, β-H), 7.33 (d, $J$ = 15.4 Hz, 1 H, α-H), 7.50 (d, $J$ = 8.8 Hz, 2 H, 2,6-H), 7.51 (dd, $J$ = 7.8 and 7.2 Hz, 2 H, 3′,5′-H), 7.61 (tt, $J$ = 7.2 and 1.5 Hz, 1 H, 4′-H), 7.98 (dd, $J$ = 7.8 and 1.5 Hz, 2 H, 2′,6′-H), 8.26 (d, $J$ = 8.8 Hz, 2 H, 3,5-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 60.2 (C-δ), 61.5 (C-γ), 123.9 (C-3,5), 126.3 (C-2,6), 128.0 (C-α), 128.6 (C-2′,6′), 128.8 (C-3′,5′), 133.4 (C-4′), 137.0 (C-1′), 142.1 (C-β), 143.4 (C-1), 148.0 (C-4), 189.1 (C=O) ppm. MS: *m*/*z* (%) = 295 (<1) $[M]^+$, 266 (2), 190 (1), 145 (16), 144 (100), 116 (15), 115 (42), 105 (23), 89 (5), 77 (23), 63 (3), 51 (4). HRMS-EI: $C_{17}H_{13}NO_4$ $[M]^+$ 295.0845; found 295.0854.

**Diastereomeric Mixture (50:50) of 2,3:4,5-Diepoxy-5-(4-nitrophenyl)-1-phenylpentan-1-one (6d):** M.p. 122–124 °C.

**Diastereomer A. (2*R**,3*S**,4*R**,5*S**)-2,3:4,5-Diepoxy-5-(4-nitrophenyl)-1-phenylpentan-1-one:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.17 (dd, $J$ = 4.8 and 1.8 Hz, 1 H, γ-H), 3.38 (dd, $J$ = 4.8 and 2.0 Hz, 1 H, β-H), 4.06 (d, $J$ = 1.8 Hz, 1 H, δ-H), 4.36 (d, $J$ = 2.0 Hz, 1 H, α-H), 7.48 (d, $J$ = 8.8 Hz, 2 H, 2,6-H), 7.54 (t, $J$ = 7.7 Hz, 2 H, 3′,5′-H), 7.67 (tt, $J$ = 7.4 and 1.5 Hz, 1 H, 4′-H), 8.04–8.09 (m, 2 H, 2′,6′-H), 8.24 (d, $J$ = 8.8 Hz, 2 H, 3,5-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 54.7 (C-α), 56.1 (C-δ), 57.2 (C-β), 60.4 (C-γ), 123.9 (C-3,5), 126.4 (C-2,6), 128.44 (C-2′,6′), 128.98 (C-3′,5′), 134.4 (C-4′), 135.1 (C-1′), 143.2 (C-1), 148.1 (C-4), 192.9 (C=O) ppm.

**Diastereomer B. (2*R**,3*S**,4*S**,5*R**)-2,3:4,5-Diepoxy-5-(4-nitrophenyl)-1-phenylpentan-1-one:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.32 (dd, $J$ = 2.6 and 1.9 Hz, 1 H, γ-H), 3.54 (dd, $J$ = 2.6 and 2.0 Hz, 1 H, β-H), 4.08 (d, $J$ = 1.9 Hz, 1 H, δ-H), 4.39 (d, $J$ = 2.0 Hz, 1 H, α-H), 7.48 (d, $J$ = 8.8 Hz, 2 H, 2,6-H), 7.54 (t, $J$ = 7.7 Hz, 2 H, 3′,5′-H), 7.67 (tt, $J$ = 7.4 and 1.5 Hz, 1 H, 4′-H), 8.04–8.09 (m, 2 H, 2′,6′-H), 8.24 (d, $J$ = 8.8 Hz, 2 H, 3,5-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 54.1 (C-α), 55.3 (C-δ), 55.8 (C-β), 59.1 (C-γ), 123.9 (C-3,5), 126.4 (C-2,6), 128.40 (C-2′,6′), 128.96 (C-3′,5′), 134.3 (C-4′), 135.2 (C-1′), 142.9 (C-1), 148.0 (C-4), 192.7 (C=O) ppm.

MS: $m/z$ (%) = 311 (1) $[M]^+$, 282 (2), 266 (1), 254 (2), 206 (7), 160 (7), 136 (8), 131 (5), 115 (5), 106 (14), 105 (100), 91 (4), 89 (8), 78 (9), 77 (50), 65 (3), 63 (5), 51 (13). HRMS-EI: $C_{17}H_{13}NO_5$ $[M]^+$ 311.0794; found 311.0780.

**(2*R**,3*S**)-2,3-Epoxy-5-(4-nitrophenyl)-1-phenyl-4-penten-1-one (7d):** M.p. 111–113 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.79 (dd, $J$ = 7.7 and 1.8 Hz, 1 H, β-H), 4.36 (d, $J$ = 1.8 Hz, 1 H, α-H), 6.26 (dd, $J$ = 16.0 and 7.7 Hz, 1 H, γ-H), 6.96 (d, $J$ = 16.0 Hz, 1 H, δ-H), 7.53 (dd, $J$ = 8.2 and 7.6 Hz, 2 H, 3′,5′-H), 7.56 (d, $J$ = 8.8 Hz, 2 H, 2,6-H), 7.65 (tt, $J$ = 7.6 and 1.4 Hz, 1 H, 4′-H), 8.04 (dd, $J$ = 7.2 and 1.4 Hz, 2 H, 2′,6′-H), 8.21 (d, $J$ = 8.8 Hz, 2 H, 3,5-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 58.2 (C-β), 58.8 (C-α), 124.1 (C-3,5), 127.2 (C-2,6), 128.3 (C-2′,6′), 128.9 (C-3′,5′), 129.3 (C-γ), 133.7 (C-δ), 134.2 (C-4′), 135.3 (C-1′), 141.7 (C-1), 147.4 (C-4), 193.0 (C=O) ppm. MS: $m/z$ (%) = 295 (1) $[M]^+$, 267 (8), 266 (39), 238 (4), 220 (8), 192 (9), 160 (5), 151 (5), 144 (6), 116 (11), 115 (30), 106 (12), 105 (100), 90 (10), 89 (15), 85 (12), 83 (17), 78 (8), 77 (64), 65 (5), 63 (8), 51 (17). HRMS-EI: $C_{17}H_{13}NO_4$ $[M]^+$ 295.0845; found 295.0854.

**(4*R**,5*R**)-4,5-Epoxy-1-(4-methoxyphenyl)-5-phenyl-2-penten-1-one (5e):** M.p. 67–69 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.59 (ddd, $J$ = 6.5, 1.9 and 0.7 Hz, 1 H, γ-H), 3.88 (s, 3 H, 4′-OC$H_3$), 3.89 (d, $J$ = 1.9 Hz, 1 H, δ-H), 6.92 (dd, $J$ = 15.3 and 6.5 Hz, 1 H, β-H), 6.97 (d, $J$ = 9.0 Hz, 2 H, 3′,5′-H), 7.28 (d, $J$ = 15.3 Hz, 1 H, α-H), 7.30–7.33 (m, 2 H, 2,6-H), 7.34–7.39 (m, 3 H, 3,4,5-H), 7.98 (d, $J$ = 9.0 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 55.5 (C-δ), 61.3 (C-γ), 61.5 (4′-O$CH_3$), 113.9 (C-3′,5′), 125.5 (C-2,6), 127.0 (C-α), 128.6 (C-3,4,5), 130.2 (C-1′), 131.0 (C-2′,6′), 136.2 (C-1), 142.5 (C-β), 163.7 (C-4′), 187.7 (C=O) ppm. MS: $m/z$ (%) = 280 (4) $[M]^+$, 264 (2), 263 (2), 251 (8), 189 (3), 175 (19), 174 (100), 160 (6), 159 (43), 145 (8), 135 (58), 131 (17), 121 (3), 115 (9), 107 (6), 105 (16), 92 (17), 89 (10), 77 (34), 63 (8), 57 (3), 51 (1). HRMS-EI: $C_{18}H_{16}O_3$ $[M]^+$ 280.1099; found 280.1095.

**Diastereomeric Mixture (52:48) of 2,3:4,5-Diepoxy-1-(4-methoxyphenyl)-5-phenylpentan-1-one (6e):** Yellowish oil.

**Diastereomer A. (2*R**,3*S**,4*R**,5*S**)-2,3:4,5-Diepoxy-1-(4-methoxyphenyl)-5-phenylpentan-1-one:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.18 (dd, $J$ = 4.5 and 2.0 Hz, 1 H, γ-H), 3.34 (dd, $J$ = 4.5 and 1.9 Hz, 1 H, β-H), 3.88 (s, 3 H, 4′-OC$H_3$), 3.91 (d, $J$ = 1.9 Hz, 1 H, δ-H), 4.29 (d, $J$ = 2.0 Hz, 1 H, α-H), 6.97 (d, $J$ = 8.9 Hz, 2 H, 3′,5′-H), 7.26–7.30 (m, 2 H, 2,6-H), 7.33–7.36 (m, 3 H, 3,4,5-H), 8.04 (d, $J$ = 8.9 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 54.4 (C-α), 55.5 (4′-O$CH_3$), 57.1 (C-δ), 57.4 (C-β), 59.7 (C-γ), 114.1 (C-3′,5′), 125.57 (C-2,6), 128.32 (C-1′), 128.5 (C-3,5), 128.57 (C-4), 130.75 (C-2′,6′), 135.5 (C-1), 164.3 (C-4′), 191.2 (C=O) ppm.

**Diastereomer B. (2*R**,3*S**,4*S**,5*R**)-2,3:4,5-Diepoxy-1-(4-methoxyphenyl)-5-phenylpentan-1-one:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.26 (dd, $J$ = 3.2 and 2.0 Hz, 1 H, γ-H), 3.44 (dd, $J$ = 3.2 and 2.0 Hz, 1 H, β-H), 3.88 (s, 3 H, 4′-OC$H_3$), 3.94 (d, $J$ = 2.0 Hz, 1 H, δ-H), 4.30 (d, $J$ = 2.0 Hz, 1 H, α-H), 6.98 (d, $J$ = 8,9 Hz, 2 H, 3′,5′-H), 7.26–7.30 (m, 2 H, 2,6-H), 7.33–7.36 (m, 3 H, 3,4,5-H), 8.05 (d, $J$ = 8.9 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 53.9 (C-α), 55.5 (4′-O$CH_3$), 56.2 (C-δ), 56.3 (C-β), 58.8 (C-γ), 114.0 (C-3′,5′), 125.60 (C-2,6), 128.28 (C-1′), 128.5 (C-3,5), 128.62 (C-4), 130.79 (C-2′,6′), 135.7 (C-1), 164.3 (C-4′), 191.4 (C=O) ppm.

MS: $m/z$ (%) = 296 (1) $[M]^+$, 280 (2), 238 (3), 209 (2), 190 (3), 174 (3), 161 (11), 147 (2), 136 (16), 135 (100), 131 (3), 121 (4), 115 (4), 107 (11), 105 (13), 92 (10), 91 (28), 79 (9), 77 (31), 65 (5), 51 (9). HRMS-EI: $C_{18}H_{16}O_3$ $[M]^+$ 296.1049; found 296.1049.

**(4*R**,5*R**)-4,5-Epoxy-1-(4-methylphenyl)-5-phenyl-2-penten-1-one (5f):** Yellowish oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.43 (s, 3 H, 4′-C$H_3$), 3.60 (ddd, $J$ = 6.5, 1.6 and 0.5 Hz, 1 H, γ-H), 3.89 (d, $J$ = 1.6 Hz, 1 H, δ-H), 6.93 (dd, $J$ = 15.4 and 6.5 Hz, 1 H, β-H), 7.25–7.41 (m, 8 H, α-H, 2,3,4,5,6-H and 3′,5′-H), 7.89 (dd, $J$ = 6.5 and 1.7 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.7 (4′-$CH_3$), 61.2 (C-γ), 61.4 (C-δ), 125.5 (C-2,6), 127.2 (C-α), 128.6 (C-3,4,5), 128.7 (C-2′,6′), 129.4 (C-3′,5′), 134.7 (C-1′), 136.2 (C-1), 143.0 (C-β), 144.1 (C-4′), 188.9 (C=O) ppm. MS: $m/z$ (%) = 264 (1) $[M]^+$, 248 (2), 235 (6), 173 (2), 159 (19), 158 (100), 157 (9), 145 (3), 129 (28), 119 (26), 115 (21), 105 (9), 91 (25), 89 (10), 77 (11), 65 (11), 63 (6), 51 (6). HRMS-EI: $C_{18}H_{16}O_2$ $[M]^+$ 264.1150; found 264.1143.

**Diastereomeric Mixture (53:47) of 2,3:4,5-Diepoxy-1-(4-methylphenyl)-5-phenylpentan-1-one (6f):** Yellowish oil.

**Diastereomer A. (2*R**,3*S**,4*R**,5*S**)-2,3:4,5-Diepoxy-1-(4-methylphenyl)-5-phenylpentan-1-one:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.45 (s, 3 H, 4′-C$H_3$), 3.19 (dd, $J$ = 4.6 and 2.0 Hz 1 H, γ-H), 3.35 (dd, $J$ = 4.6 and 2.0 Hz, 1 H, β-H), 3.93 (d, $J$ = 2.0 Hz, 1 H, δ-H), 4.33 (d, $J$ = 2.0 Hz, 1 H, α-H), 7.28–7.38 (m, 7 H, 2,3,4,5,6-H and 3′,5′-H), 7.96 (d, $J$ = 8.3 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.7 (4′-C$H_3$), 54.6 (C-α), 57.2 (C-δ), 57.6 (C-β), 59.8 (C-γ), 125.6 (C-2,6), 128.41 (C-2′,6′), 129.63 (C-3′,5′), 128.52 (C-3,4,5), 132.8 (C-1′), 135.5 (C-1), 145.3 (C-4′), 192.6 (C=O) ppm.

**Diastereomer B. (2*R**,3*S**,4*S**,5*R**)-2,3:4,5-Diepoxy-1-(4-methylphenyl)-5-phenylpentan-1-one:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.45 (s, 3 H, 4′-C$H_3$), 3.28 (dd, $J$ = 3.1 and 2.0 Hz, 1 H, γ-H), 3.46 (dd, $J$ = 3.1 and 2.0 Hz, 1 H, β-H), 3.96 (d, $J$ = 2.0 Hz, 1 H, δ-H), 4.35 (d, $J$ = 2.0 Hz, 1 H, α-H), 7.28–7.38 (m, 7 H, 2,3,4,5,6-H and 3′,5′-H), 7.97 (d, $J$ = 8.3 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.7 (4′-C$H_3$), 54.0 (C-α), 56.3 (C-δ), 56.4 (C-β), 58.8 (C-γ), 125.7 (C-2,6), 128.45 (C-2′,6′), 128.62 (C-3′,5′), 128.54 (C-4), 128.61 (C-3,5), 132.8 (C-1′), 135.8 (C-1), 145.3 (C-4′), 192.8 (C=O) ppm.

MS: $m/z$ (%) = 280 (<1) $[M]^+$, 251 (2), 221 (3), 193 (1), 174 (3), 161 (18), 131 (6), 119 (100), 105 (12), 91 (63), 79 (6), 77 (10), 65 (11), 51 (3). HRMS-EI: $C_{18}H_{16}O_3$ $[M]^+$ 280.1099; found 280.1090.

**Diastereomeric Mixture (47:53) of 2,3:4,5-Diepoxy-1-(4-nitrophenyl)-5-phenylpentan-1-one (6g):** Yellowish oil.

**Diastereomer A. (2*R**,3*S**,4*R**,5*S**)-2,3:4,5-Diepoxy-1-(4-nitrophenyl)-5-phenylpentan-1-one:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.20 (dd, *J* = 4.6 and 1.9 Hz, 1 H, γ-H), 3.39 (dd, *J* = 4.6 and 1.9 Hz, 1 H, β-H), 3.94 (d, *J* = 1.9 Hz, 1 H, δ-H), 4.31 (d, *J* = 1.9 Hz, 1 H, α-H), 7.26–7.30 (m, 2 H, 2,6-H), 7.34–7.38 (d, 3 H, 3,4,5-H), 8.21 (d, *J* = 8.8 Hz, 2 H, 2′,6′-H), 8.34 (d, *J* = 8.8 Hz, 2 H, 3′,5′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 55.1 (C-α), 57.2 (C-δ), 57.8 (C-β), 59.4 (C-γ), 123.99 (C-3′,5′), 125.57 (C-2,6), 128.6 (C-3,5), 128.82 (C-4), 129.56 (C-2′,6′), 135.1 (C-1), 139.3 (C-1′), 150.7 (C-4′), 192.5 (C=O) ppm.

**Diastereomer B. (2*R**,3*S**,4*S**,5*R**)-2,3:4,5-Diepoxy-1-(4-nitrophenyl)-5-phenylpentan-1-one:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.31 (dd, *J* = 2.9 and 1.9 Hz, 1 H, γ-H), 3.51 (dd, *J* = 2.9 and 2.0 Hz, 1 H, β-H), 3.96 (d, *J* = 1.9 Hz, 1 H, δ-H), 4.34 (d, *J* = 2.0 Hz, 1 H, α-H), 7.26–7.30 (m, 2 H, 2,6-H), 7.34–7.38 (d, 3 H, 3,4,5-H), 8.22 (d, *J* = 8.9 Hz, 2 H, 2′,6′-H′), 8.34 (d, *J* = 8.9 Hz, 2 H, 3′,5′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 54.6 (C-α), 56.4 (C-δ), 56.6 (C-β), 58.3 (C-γ), 123.97 (C-3′,5′), 125.60 (C-2,6), 128.6 (C-3,5), 128.76 (C-4), 129.58 (C-2′,6′), 135.4 (C-1), 139.3 (C-1′), 150.7 (C-4′), 192.4 (C=O) ppm.

MS: *m*/*z* (%) = 311 (1) $[M]^+$, 282 (3), 252 (14), 205 (6), 174 (56), 161 (75), 159 (26), 150 (40), 135 (22), 131 (21), 121 (2), 115 (12), 105 (38), 104 (25), 92 (24), 91 (100), 79 (25), 77 (39), 76 (18), 65 (9), 55 (77), 51 (11). HRMS-EI: $C_{17}H_{13}NO_5$ $[M]^+$ 311.0794; found 311.0787.

**(4*R**,5*R**)-4,5-Epoxy-1-(2-hydroxyphenyl)-5-phenyl-2-penten-1-one (5h):** M.p. 75–77 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.63 (ddd, *J* = 6.2, 1.8 and 0.7 Hz, 1 H, γ-H), 3.90 (d, *J* = 1.8 Hz, 1 H, δ-H), 6.93 (ddd, *J* = 7.9, 7.8 and 1.0 Hz, 1 H, 5′-H), 7.02 (dd, *J* = 8.1 and 1.0 Hz, 1 H, 3′-H), 7.09 (dd, *J* = 15.1 and 6.2 Hz, 1 H, β-H), 7.31–7.34 (m, 2 H, 2,6-H), 7.35–7.40 (m, 3 H, 3,4,5-H), 7.40 (d, *J* = 15.1 Hz, 1 H, α-H), 7.51 (ddd, *J* = 8.1, 7.8 and 1.6 Hz, 1 H, 4′-H), 7.82 (dd, *J* = 7.9 and 1.6 Hz, 1 H, 6′-H), 12.55 (s, 1 H, 2′-O*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 61.0 (C-γ), 61.8 (C-δ), 118.6 (C-3′), 119.0 (C-5′), 119.4 (C-1′), 125.3 (C-α), 125.5 (C-2,6), 128.7 (C-3,5), 128.8 (C-4), 129.9 (C-6′), 135.9 (C-1), 136.8 (C-4′), 144.2 (C-β), 163.6 (C-2′), 193.0 (C=O) ppm. MS: *m*/*z* (%) = 266 (3) $[M]^+$, 250 (13), 237 (4), 161 (17), 160 (100), 145 (8), 131 (62), 121 (32), 115 (7), 105 (9), 91 (8), 89 (9), 78 (18), 77 (18), 65 (17), 63 (7), 53 (2), 51 (8). HRMS-EI: $C_{17}H_{14}O_3$ $[M]^+$ 266.0943; found 266.0940.

**(*E*,2*R**,3*S**)-3-Hydroxy-2-styryl-4-chromanone (8h):** M.p. 159–161 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.72 (d, *J* = 1.2 Hz, 1 H, 3-O*H*), 4.43 (d, *J* = 12.2 Hz, 1 H, 3-H), 4.80 (ddd, *J* = 12.2, 6.4 and 1.2 Hz, 1 H, 2-H), 6.52 (dd, *J* = 16.0 and 6.4 Hz, 1 H, α-H), 6.95 (d, *J* = 16.0 Hz, 1 H, β-H), 7.07 (d, *J* = 8.1 Hz, 1 H, 8-H), 7.09 (dt, *J* = 7.6 and 1.0 Hz, 1 H, 6-H), 7.26–7.38 (m, 3 H, 3′,4′,5′-H), 7.49 (dd, *J* = 8.2 and 1.3 Hz, 2 H, 2′,6′-H), 7.56 (dt, *J* = 8.1 and 1.7 Hz, 1 H, 7-H), 7.90 (dd, *J* = 7.6 and 1.7 Hz, 1 H, 5-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 73.1 (C-3), 82.3 (C-2), 118.1 (C-8), 118.5 (C-10), 122.0 (C-6), 124.0 (C-α), 126.9 (C-2′,6′), 127.3 (C-5), 128.4 (C-4′), 128.6 (C-3′,5′), 134.9 (C-β), 135.9 (C-1′), 136.9 (C-7), 161.5 (C-9), 194.1 (C-4) ppm. MS: *m*/*z* (%) = 266 (43) $[M]^+$, 237 (24), 209 (12), 146 (35), 145 (37), 131 (13), 121 (100), 117 (24), 115 (35), 105 (7), 92 (27), 91 (35), 77 (19), 71 (14), 65 (13), 57 (19), 51 (10). HRMS-EI: $C_{17}H_{16}O_3$ $[M]^+$ 280.0943; found 280.0941.

**(*E*,4*R**,5*R**)-4,5-Epoxy-4-methyl-1,5-diphenyl-2-penten-1-one (*trans*-9i):** Yellowish oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.31 (s, 3 H, γ-C*H*$_3$), 4.05 (s, 1 H, δ-H), 7.07 (d, *J* = 15.4 Hz, 1 H, β-H), 7.22 (d, *J* = 15.4 Hz, 1 H, α-H), 7.30–7.42 (m, 5 H, 2,3,4,5,6-H), 7.49 (dd, *J* = 7.9 and 7.4 Hz, 2 H, 3′,5′-H), 7.59 (tt, *J* = 7.4 and 1.6 Hz, 1 H, 4′-H), 7.99 (dd, *J* = 7.9 and 1.6 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 14.9 (γ-*C*H$_3$), 61.8 (C-γ), 66.7 (C-δ), 125.0 (C-α), 126.6 (C-2,6), 128.0 (C-4), 128.2 (C-3,5), 128.60 (C-3′,5′), 128.64 (C-2′,6′), 133.1 (C-4′), 134.7 (C-1), 137.5 (C-1′), 148.9 (C-β), 189.9 (C=O) ppm. MS: *m*/*z* (%) = 264 (1) $[M]^+$, 249 (2), 221 (4), 158 (100), 145 (2), 144 (2), 131 (4), 129 (7), 115 (16), 105 (47), 91 (5), 89 (6), 77 (4), 65 (2), 63 (3), 53 (23), 51 (26). HRMS-EI: $C_{18}H_{16}O_2$ $[M]^+$ 264.1150; found 264.1141.

**(*E*,4*R**,5*S**)-4,5-Epoxy-4-methyl-1,5-diphenyl-2-penten-1-one (*cis*-9i):** Yellowish oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.72 (s, 3 H, γ-C*H*$_3$), 4.22 (s, 1 H, δ-H), 6.59 (d, *J* = 15.8 Hz, 1 H, β-H), 6.96 (d, *J* = 15.8 Hz, 1 H, α-H), 7.25–7.35 (m, 5 H, 2,3,4,5,6-H), 7,38 (dd, *J* = 8.2 and 8.0 Hz, 2 H, 3′,5′-H), 7.51 (t, *J* = 8.0 and 1.3 Hz, 1 H, 4′-H), 7.68 (dd, *J* = 8.2 and 1.3 Hz, 2 H, 2′,6′-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.1 (γ-*C*H$_3$), 62.4 (C-γ), 66.6 (C-δ), 126.5 (C-2,6), 127.9 (C-3,5), 128.2 (C-α), 128.4 (C-4), 128.5 (C-3′,5′), 128.6 (C-2′,6′), 132.8 (C-4′), 134.6 (C-1), 137.3 (C-1′), 144.7 (C-β), 190.3 (C=O) ppm. MS: *m*/*z* (%) = 264 (1) $[M]^+$, 251 (2), 207 (10), 175 (31), 158 (18), 145 (5), 131 (12), 115 (7), 105 (100), 91 (57), 77 (66), 65 (3), 63 (5), 53 (3), 51 (22). HRMS-EI: $C_{18}H_{16}O_2$ $[M]^+$ 264.1150; found 264.1138.

**(*E*,2*R**,3*S**)-3-Hydroxy-α-methyl-2-styryl-4-chromanone (8j):** M.p. 122–123 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.14 (s, 3 H, α-C*H*$_3$), 3.70 (br. s, 1 H, 3-O*H*), 4.60–4.71 (m, 2 H, 2,3-H), 6.75 (d, *J* = 1.1 Hz, 1 H, β-H), 7.04 (d, *J* = 8.0 Hz, 1 H, 8-H), 7.08 (dt, *J* = 7.8 and 0.8 Hz, 1 H, 6-H), 7.25–7.40 (m, 5 H, 2′,3′,4′,5′,6′-H), 7.55 (dt, *J* = 8.0 and 1.6 Hz, 1 H, 7-H), 7.90 (dd, *J* = 7.8 and 1.6 Hz, 1 H, 5-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 13.3 (γ-*C*H$_3$), 71.1 (C-3), 88.0 (C-2), 118.1 (C-8), 118.4 (C-10), 121.9 (C-6), 127.2 (C-4′), 127.2 (C-5), 128.2 (C-3′,5′), 129.3 (C-2′,6′), 132.4 (C-β), 132.6 (C-α), 136.6 (C-1′), 136.8 (C-7), 161.9 (C-9), 194.8 (C-4) ppm. MS: *m*/*z* (%) = 280 (52) $[M]^+$, 278 (13), 263 (9), 251 (31), 223 (6), 207 (10), 201 (5), 174 (10), 160 (26), 159 (90), 145 (35), 131 (32), 121 (100), 115 (38), 105 (21), 92 (29), 91 (95), 82 (9), 77 (28), 65 (25), 63 (18), 57 (9), 51 (16). HRMS-EI: $C_{18}H_{16}O_3$ $[M]^+$ 280.1099; found 280.0986.

**(*E*,4*R**,5*R**)-4,5-Epoxy-1-(2-hydroxyphenyl)-4-methyl-5-phenyl-2-penten-1-one (*trans*-9j):** M.p. 54–55 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.33 (s, 3 H, γ-C*H*$_3$), 4.06 (s, 1 H, δ-H), 6.93 (ddd, *J* = 8.0, 7.9 and 1.0 Hz, 1 H, 5′-H), 7.02 (dd, *J* = 8.1 and 1.0 Hz, 1 H, 3′-H), 7.19 (d, *J* = 15.2 Hz, 1 H, β-H), 7.34 (d, *J* = 15.2 Hz, 1 H, α-H), 7.32–7.42 (m, 5 H, 2,3,4,5,6-H), 7.50 (ddd, *J* = 8.1, 7.9 and 1.6 Hz, 1 H, 4′-H), 7.85 (dd, *J* = 8.0 and 1.6 Hz, 2 H, 6′-H), 12.60 (s, 1 H, 2′-O*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 14.9 (γ-*C*H$_3$), 61.9 (C-γ), 67.0 (C-δ), 118.6 (C-3′), 118.9 (C-5′), 119.5 (C-1′), 123.3 (C-α), 126.6 (C-2,6), 128.1 (C-4), 128.3 (C-3,5), 130.0 (C-6′), 134.5 (C-1), 137.0 (C-4′), 149.6 (C-β), 163.6 (C-2′), 193.5 (C=O) ppm. MS: *m*/*z* (%) = 280 (1) $[M]^+$, 264 (2), 237 (3), 174 (100), 159 (37), 147 (7), 145 (6), 131 (53), 121 (38), 115 (8), 105 (11), 93 (12), 91 (10), 77 (20), 65 (24), 53 (19), 51 (11). HRMS-EI: $C_{18}H_{16}O_3$ $[M]^+$ 280.1099; found 280.1093.

**(*E*,4*R**,5*S**)-4,5-Epoxy-1-(2-hydroxyphenyl)-4-methyl-5-phenyl-2-penten-1-one (*cis*-9j):** M.p. 54–55 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.74 (s, 3 H, γ-C*H*$_3$), 4.24 (s, 1 H, δ-H), 6.75 (d, *J* = 15.4 Hz, 1 H, β-H), 6.86 (ddd, *J* = 7.9, 7.8 and 1.0 Hz, 1 H, 5′-H), 6.95 (dd, *J* = 8.1 and 1.0 Hz, 1 H, 3′-H), 7.13 (d, *J* = 15.4 Hz, 1 H, α-H), 7.27–7.35 (m, 5 H, 2,3,4,5,6-H), 7.46 (ddd, *J* = 8.1, 7.8 and 1.6 Hz, 1 H, 4′-H), 7.60 (dd, *J* = 7.9 and 1.6 Hz, 2 H, 6′-H), 12.38 (s, 1 H, 2′-O*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.2 (γ-*C*H$_3$), 62.4 (C-γ), 66.9 (C-δ), 118.5 (C-3′), 118.8 (C-5′), 119.4 (C-1′), 126.4 (C-

α), 126.5 (C-2,6), 128.1 (C-4), 128.3 (C-3,5), 129.9 (C-6′), 134.3 (C-1), 136.6 (C-4′), 144.9 (C-β), 163.4 (C-2′), 193.3 (C=O) ppm. MS: *m/z* (%) = 280 (7) $[M]^+$, 264 (16), 249 (5), 238 (12), 237 (35), 224 (11), 223 (14), 219 (17), 175 (19), 174 (100), 159 (37), 145 (8), 131 (55), 121 (34), 115 (9), 105 (9), 93 (11), 91 (8), 77 (16), 65 (18), 53 (13), 51 (7). HRMS-EI: $C_{18}H_{16}O_3$ $[M]^+$ 280.1099; found 280.1106.

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