

Dimethyldioxirane Oxidation of Exocyclic (*E,E*)-Cinnamylideneketones*

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Exocyclic (*E,E*)-cinnamylideneketones were oxidized by an excess of isolated dimethyldioxirane (DMDO, in acetone solution) at room temperature, providing diastereomeric mixtures of the $\alpha,\beta,\gamma,\delta$ -diepoxides. In the case of derivatives bearing an *ortho*-nitrocinnamylidene moiety, α,β -monoepoxides were also isolated as minor products. The structures of all new compounds and the stereochemistry of the monoepoxides and diepoxide diastereomers were established by NMR studies.

Introduction

(*E,E*)-Cinnamylideneacetophenones (1,5-diphenyl-2,4-pentadien-1-ones) are well known $\alpha,\beta,\gamma,\delta$ -unsaturated ketones. Certain of their bromoderivatives have been seen as excellent candidates to design effective second-order non-linear optical materials,^[1] whereas other cinnamylideneketones exerted significant antiproliferative effects on multiresistant cancer cell lines.^[2] Despite the scarce number of potential biological or industrial applications of cinnamylideneacetophenones, these compounds have been widely used as starting materials for the synthesis of various heterocyclic compounds, such as 2-styryl-1,5-benzothiazepines,^[3] styryl-2-pyrazolines and styrylpyrazoles,^[4] 2-benzoyl-1,5-diphenylpyrroles,^[5] 2-styrylchromones,^[6] and 3-styrylchromones.^[7] Previously, we also investigated the epoxidation of (*E,E*)-cinnamylideneacetophenones with different oxidizing agents.^[8,9] When isolated dimethyldioxirane was used as oxidant, diastereomeric mixtures of $\alpha,\beta,\gamma,\delta$ -diepoxides were obtained, in some cases together with α,β -monoepoxides as minor by-products. When (*E,E*)-2'-hydroxycinnamylideneacetophenones were oxidized under the same reaction conditions, 2'-hydroxy- γ,δ -epoxycinnamylideneacetophenones could also be detected and isolated.^[8] Hydrogen peroxide or iodosylbenzene in combination with Jacobsen's salen Mn^{III} catalyst have also been used; in such cases, diastereomeric mixtures of $\alpha,\beta,\gamma,\delta$ -diepoxides and also γ,δ -monoepoxides were formed. It is worth mentioning that the Julia asymmetric epoxidation procedure has provided α,β -monoepoxide in one case.^[10]

The related exocyclic $\alpha,\beta,\gamma,\delta$ -unsaturated ketones have hitherto received less attention and the synthesis of their

few representatives has been described in the literature.^[11]

For this reason, as a continuation of our work on (*E,E*)-cinnamylideneacetophenones, we have undertaken studies on the synthesis and chemical transformations of such dienones. In our present paper, the synthesis and dimethyldioxirane epoxidation of exocyclic $\alpha,\beta,\gamma,\delta$ -unsaturated ketones are reported. We have decided to investigate the influence of various structural elements of the exocyclic $\alpha,\beta,\gamma,\delta$ -unsaturated ketones used, namely the ring size of the benzocyclanone ring and the influence of an *ortho*-substituent in the cinnamylidene moiety, because this substituent is in the vicinity of one of the two double bonds to be epoxidized.

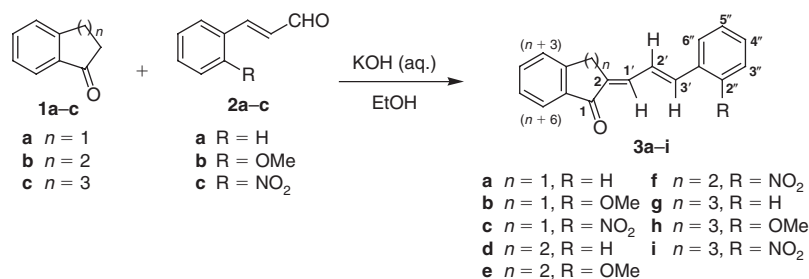
Results and Discussion

Synthesis

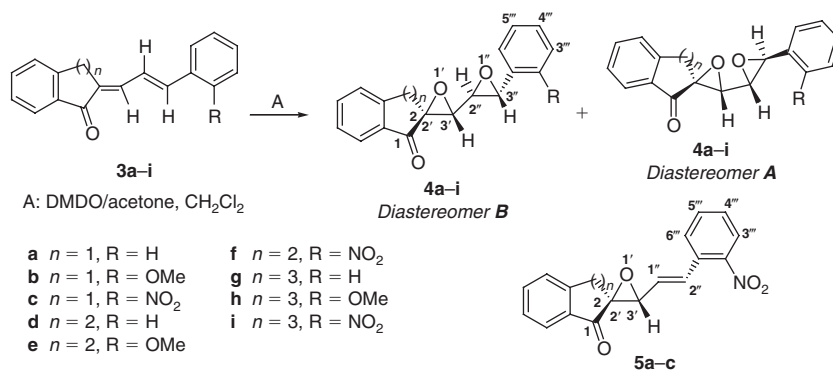
The benzocyclanones **3a–i** were synthesized by the base-catalyzed condensation of 1-indanone **1a**, 1-tetralone **1b**, and 1-benzosuberone **1c** with cinnamaldehydes **2a–c** to afford the appropriate dienones (Scheme 1). The (*E,E*)-benzocyclanones **3a,d,e,g** are known compounds,^[11] whereas (*E,E*)-cinnamylideneketones **3b,c,f,h,i** are new compounds and were obtained in very good yields (72–86%).

Isolated dimethyldioxirane proved to be a convenient oxidant for the stereoselective epoxidation of a wide variety of exocyclic α,β -unsaturated ketones.^[12] This versatile oxidant was beneficially used for the preparation of the $\alpha,\beta,\gamma,\delta$ -diepoxides of (*E,E*)-cinnamylideneacetophenones.^[8] On the basis of all these experiences, dimethyldioxirane was considered for the epoxidation of exocyclic $\alpha,\beta,\gamma,\delta$ -unsaturated ketones **3a–i** (Scheme 2).

*Dedicated to Professor Dr Branko Stanovnik on the occasion of his 70th birthday.



Scheme 1. Synthesis of cinnamylideneketones **3a-i**.



Scheme 2. Epoxidation of cinnamylideneketones **3a-i** with dimethyldioxirane (DMDO).

(*E,E*)-2-Cinnamylidene-1-indanones (**3a-c**), (*E,E*)-2-cinnamylidene-1-tetralones (**3d-f**) and (*E,E*)-2-cinnamylidene-1-benzosuberones (**3g-i**) were allowed to react with one molar equivalent of isolated dimethyldioxirane in acetone (0.07–0.10 M)^[13] at room temperature and the progress of the reaction was monitored by TLC. After a 24-h reaction time, the two main components in the reaction mixture were the starting material and the appropriate $\alpha,\beta,\gamma,\delta$ -diepoxide, accompanied by several by-products. Another molar equivalent of dimethyldioxirane was added to the reaction mixture each day until the complete conversion of the starting material (cf. Experimental). Except for the nitro-substituted dienones **3c,f,i**, only $\alpha,\beta,\gamma,\delta$ -diepoxides **4a,b,d,e,g,h** were isolated after the complete conversion of the starting dienones. The presence of an *ortho*-nitro group considerably slowed down the reaction and a complete conversion of the starting material required a higher amount of oxidant and much longer reaction times (cf. Experimental). In these cases, α,β -monoepoxides **5a-c** were first detected by NMR spectroscopy and then isolated by preparative TLC.

Based on our experimental results, it can be concluded that the ring size of the benzocyclanone ring and the *ortho*-methoxy substituent in the cinnamylidene moiety of the starting material have no influence on this epoxidation reaction. In the case of the unsubstituted and methoxysubstituted compounds, no difference was observed in the reactivity of the two double bonds under the reaction conditions used. However, the *ortho*-nitro group considerably reduced the reactivity of the γ,δ -double bond to the electrophilic oxidant dimethyldioxirane (DMDO), giving rise to the formation of α,β -monoepoxides. These results agreed with those obtained in the epoxidation of linear cinnamylideneacetophenones,^[8] where the γ,δ -monoepoxides isolated in the case of compounds bearing a 2'-hydroxyl group involved intramolecular hydrogen

bonding with the carbonyl group, reducing the reactivity of the α,β -double bond and enhancing the reactivity of the γ,δ -double bond towards the electrophilic DMDO. In the present case, the electron-withdrawing effects of the nitro and carbonyl groups are slightly compensated for by the α -alkyl chain effect, making the $C_\alpha=C_\beta$ double bond more reactive towards the electrophilic DMDO. This effect results in the formation of the α,β -monoepoxides **5a-c** from the oxidation of *ortho*-nitro-2-cinnamylidenebenzacyclanones **3c,f,i**, as in the case of the epoxidation of 4-nitrocinnamylideneacetophenone with iodosylbenzene and a catalytic amount of salen Mn^{III}.^[9]

NMR Spectroscopy

The main features of the ¹H NMR spectra of 2-cinnamylidenebenzocyclanones **3a-i** are the resonances of their vinylic protons. H-3' appears as a doublet, as a result of the coupling with H-2' at δ_H 7.0–7.2 ppm and the coupling constant ³ $J_{H3'-H2'}$ 15–16 Hz indicates the *trans* configuration of the C2'=C3' double bond. However, the complete stereochemistry of the $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl system was established with the aid of the nuclear Overhauser effect (NOE) cross peaks observed in the corresponding nuclear Overhauser effect correlation spectra (NOESY) (Fig. 1a), which support the close proximity of H-2' and the aliphatic protons of the cyclanone ring and also of H-1' and H-3' and are only consistent with the structure presented in Schemes 1 and 2. The deshielding mesomeric effect of the carbonyl group is responsible for the high resonance frequency of H-1' and H-3' (δ_H 7.4–7.6 ppm) relative to that obtained for H-2'.

The comparison of the ¹H NMR spectra of compounds **3c,f,i** with those of **5a-c** allowed the detection of a signal, as a doublet ($J \sim 7$ Hz), at δ_H 3.92–4.12 ppm and the presence of only two vinylic protons at δ_H 6.07–6.18 (double doublet, $J \sim 7$ and 16 Hz) and 7.32–7.39 (doublet, $J \sim 16$ Hz) ppm. These data are

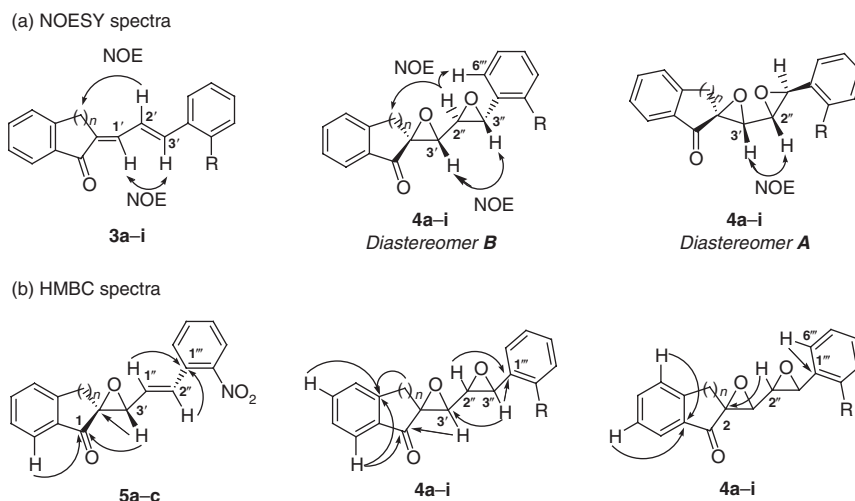


Fig. 1. (a) Main nuclear Overhauser effect (NOE) correlation spectroscopy cross peaks found in the nuclear Overhauser effect correlation spectra (NOESY) of compounds **3a-i** and **4a-i** (diastereomers **A** and **B**). (b) Important connectivities found in the heteronuclear multiple bond correlation (HMBC) spectra of compounds **5a-c** and **4a-i**.

only compatible with the formation of α,β -epoxides **5a-c**, which was also confirmed by the connectivities found in their heteronuclear multiple bond correlation (HMBC) spectra, namely the connectivities of H-3' with those of the carbonyl carbons (δ_C 193.1–201.1 ppm) and also of H-1'' and H-2'' with those of C-1'' (δ_C 131.7–131.9 ppm) (Fig. 1b). In the NOESY spectra of α,β -epoxides **5a-c**, there are NOE crosspeaks between the signals H-1'' and H-2'' with those of H-3' and of the cyclanone rings. These data and the absence of NOE crosspeaks between the signal of H-3' and the signals of the remaining aliphatic protons confirms the stereochemistry of the oxirane ring depicted in Scheme 2 and Fig. 1b, as expected for an epoxide obtained from a *trans*-alkene with a concerted mechanism.

The ^{13}C NMR spectra of the α,β -epoxides **5a-c** present the signals of the epoxide carbon resonances at δ_C 61.6–66.6 ppm and those of the vinylic system at δ_C 127.1–128.2 (C-1'') and 131.8–132.2 (C-2'') ppm.

The ^1H NMR spectra of $\alpha,\beta,\gamma,\delta$ -diepoxides **4a-i** are quite complex, presenting two distinct regions (aliphatic and aromatic regions). In the aliphatic region, the presence of two groups of signals indicates that we have a diastereomeric mixture of compounds, and the assignment of the signals of both diastereomers for **4a-i** was based on the correlations found in the correlation spectra (COSY) of these compounds. The NOE effects found in the NOESY spectra of these compounds led us to establish the stereochemistry of both diastereomers **A** and diastereomers **B**, and the proportion of the mixture as (38%–50%)**A**:(50%–62%)**B**, (40%–70%)**A**:(30%–60%)**B** and (71%–97%)**A**:(3%–29%)**B** for compounds bearing five-, six- and seven-membered cyclanone rings, respectively, was calculated from the area of proton signals. This stereochemistry was based on the close proximities between H-3'' and H-3' and of H-2'' with H-6'' and some of the aliphatic signals of the cyclanone ring for diastereomers **B** and between H-3' and H-2'' for diastereomers **A** (Fig. 1a). In the HMBC spectra of $\alpha,\beta,\gamma,\delta$ -diepoxides **4a-i**, the correlations between the carbonyl carbon resonances (δ_C 192.4–200.9) and the signals of an epoxide ring appearing as a doublet at δ_H 3.24–3.70 allowed assignment of these proton resonances to H-3'. From the 2D-COSY experiments, all the proton resonances of the $\alpha,\beta,\gamma,\delta$ -diepoxide system were assigned, H-3'

(doublet at δ_H 3.24–3.70), H-2'' (double doublet at δ_H 2.97–3.18), and H-3'' (doublet at δ_H 3.90–4.69). The coupling constant values $J_{H2''-H3''} \sim 1.7$ –2.1 Hz are consistent with a *trans* configuration of the γ,δ -epoxide,^[9,14] whereas those of $J_{H3'-H2''}$ are dependent on the size of the cyclanone ring and on the stereochemistry of the diastereomers (**4a-c**, J 3.8–4.9 Hz for **A** and J 5.6–6.0 Hz for **B**; **4d-f**, J 4.4–6.0 Hz for **A** and J 6.1–6.6 Hz for **B**; **4g-i**, J 5.0–6.3 Hz for **A** and J 6.8–7.2 Hz for **B**). The aromatic region of the ^1H NMR spectra of $\alpha,\beta,\gamma,\delta$ -diepoxides **4a-i** presents several multiplets, which were assigned with the aid of all 2D NMR spectra.

The ^{13}C NMR spectra of the diastereomeric mixture of $\alpha,\beta,\gamma,\delta$ -diepoxides **4a-i** present a duplication of signals with four distinct zones: those at lower-frequency values (δ_C 22.7–32.2) assigned to the carbon resonances of the aliphatic protons of the cyclanone rings; those at δ_C 51.6–63.7 belonged to the carbon resonances of the epoxide rings; those at δ_C 110.1–158.1 due to the carbon resonances of aromatic rings, and those at higher values of frequency (δ_C 192.4–200.9) attributed to the resonance of the carbonyl carbons. The carbon resonances of the C-3'', C-2'', C-3', and C-2 of both diastereomers were assigned with the aid of the heteronuclear single-quantum correlation (HSQC) spectra, appearing at δ_C 51.6–58.1, 57.9–59.7, 59.6–62.2, and 62.0–63.7, respectively. The assignment of the carbon resonances of all compounds was confirmed by the connectivities found in the HMBC spectra (Fig. 1b).

Conclusions

Epoxidation of (*E,E*)-2-cinnamylidene-1-indanones, (*E,E*)-2-cinnamylidene-1-tetralones, and (*E,E*)-2-cinnamylidene-1-benzosuberones has been achieved. Dimethyldioxirane in acetone proved to be a convenient oxidant for this purpose, and under these reaction conditions, the major products were a diastereomeric mixture of $\alpha,\beta,\gamma,\delta$ -diepoxides in each case. The oxidation reaction was more efficient on compounds bearing neutral or electron-rich substituents on the cinnamylidene aromatic ring. The presence of an *ortho*-nitro substituent slowed down the reaction rate and as a consequence the α,β -monoepoxides were also isolated.

Experimental

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 300 spectrometer (at 300.13 and 75.47 MHz, respectively); chemical shifts are reported in ppm (δ) using TMS as internal reference and coupling constants (J) are given in Hz. The ^1H assignments were made using two-dimensional gradient selected correlation spectroscopy (gCOSY) and NOESY (800 ms mixing time) experiments, whereas in the case of ^{13}C assignments, we used two-dimensional gradient selected heteronuclear single quantum coherence (gHSQC) and two-dimensional gradient selected heteronuclear multiple bond coherence (gHMBC) (delays for one-bond and long-range $J\text{C/H}$ couplings were optimized for 145 and 7 Hz, respectively) experiments. The IR spectra were obtained with a Perkin–Elmer 16 PC instrument. Mass spectra were recorded on a VG trio-2 apparatus. Elemental analyses (C, H) were measured in-house with a Carlo Erba 1106 instrument. Dimethyldioxirane (as an acetone solution) was prepared as described^[13] and its peroxide content was determined iodometrically.

General Method for the Preparation of Exocyclic $\alpha,\beta,\gamma,\delta$ -Unsaturated Ketones **3a–i**

A mixture of the cyclic ketone (**1a–c**, 10.0 mmol), the appropriate *trans*-cinnamaldehyde (**2a–c**, 12.0 mmol), 10% aqueous solution of KOH (10 mL), and ethanol (50 mL) was stirred at room temperature for 4 h, then poured into H_2O (100 mL). The precipitate was separated by filtration, washed with water, and recrystallized from methanol to give exocyclic $\alpha,\beta,\gamma,\delta$ -unsaturated ketones **3a–i**. Compounds **3a,d,e,g** are known substances,^[11] whereas the physical and spectroscopic data of the new compounds **3b,c,f,h,i** are given below.

(*E,E*)-2-[3-(2-Methoxyphenyl)allylidene]-1-indanone **3b**

(2.38 g, 86%), mp 160–161°C. δ_{H} (CDCl_3) 3.85 (2H, br s, H-3), 3.91 (3H, s, 2''-OCH₃), 6.92 (1H, d, J 8.1, H-3''), 6.98 (1H, dd, J 7.7 and 7.5, H-5''), 7.10 (1H, dd, J 15.5 and 11.9, H-2'), 7.31 (1H, ddd, J 8.1, 7.7, and 1.6, H-4''), 7.41 (1H, dd, J 7.6 and 7.4, H-6), 7.42 (1H, d, J 15.5, H-3'), 7.47 (1H, dt, J 11.9 and 2.0, H-1'), 7.53 (1H, d, J 7.4, H-4), 7.59 (1H, d, J 7.5, H-6''), 7.60 (1H, dt, J 7.4 and 1.1, H-5), 7.88 (1H, d, J 7.6, H-7). δ_{C} (CDCl_3) 30.4 (C-3), 55.5 (2'-OCH₃), 111.1 (C-3''), 120.7 (C-5''), 124.1 (C-7), 124.9 (C-2'), 125.3 (C-1''), 126.2 (C-4), 127.40 (C-6), 127.44 (C-6''), 130.4 (C-4''), 134.2 (C-5), 134.4 (C-1'), 135.4 (C-2), 137.3 (C-3'), 139.4 (C-7a), 148.9 (C-3a), 157.5 (C-2''), 193.7 (C-1). m/z 276 (M^{+} , 100), 261 (27), 169 (38), 115 (39). $\nu_{\text{max}}/\text{cm}^{-1}$ 1685, 1611, 1484, 1465, 1326, 1292, 1244, 1176, 1152, 1099, 1028, 981, 934, 748. (Found: C 82.70, H 5.91. $\text{C}_{19}\text{H}_{16}\text{O}_2$ requires C 82.58, H 5.84%).

(*E,E*)-2-[3-(2-Nitrophenyl)allylidene]-1-indanone **3c**

(2.21 g, 76%), mp 220–221°C. δ_{H} (CDCl_3) 3.88 (2H, s, H-3), 7.01 (1H, dd, J 14.8 and 11.0, H-2'), 7.43 (1H, dd, J 7.9 and 7.7, H-6), 7.44 (1H, d, J 11.0, H-1'), 7.48 (1H, dd, J 7.7 and 7.4, H-4''), 7.53 (1H, d, J 14.8, H-3'), 7.54 (1H, d, J 8.2, H-4), 7.62 (1H, dd, J 8.2 and 7.9, H-5), 7.65 (1H, dd, J 7.4 and 7.3, H-5''), 7.76 (1H, d, J 7.3, H-6''), 7.88 (1H, d, J 7.7, H-7), 8.00 (1H, dd, J 7.7 and 1.0, H-3''). δ_{C} (CDCl_3) 30.3 (C-3), 124.3 (C-7), 125.0 (C-3''), 126.3 (C-4), 127.6 (C-6), 128.4 (C-6''), 129.0 (C-2'), 129.2 (C-4''), 131.9 (C-1''), 132.1 (C-1'), 133.2 (C-5''), 134.7 (C-5), 135.9 (C-3'), 138.2 (C-2), 138.9 (C-7a),

147.9 (C-2''), 148.8 (C-3a), 193.5 (C-1). m/z 291 (M^{+} , 2), 274 (100), 244 (44), 115 (89). $\nu_{\text{max}}/\text{cm}^{-1}$ 1695, 1623, 1518, 1468, 1341, 1250, 1162, 1106, 973, 938, 790, 733. (Found: C 74.31, H 4.42. $\text{C}_{18}\text{H}_{13}\text{NO}_3$ requires C 74.22, H 4.49%).

(*E,E*)-2-[3-(2-Nitrophenyl)allylidene]-1-tetralone **3f**

(2.20 g, 72%), mp 192–193°C. δ_{H} (CDCl_3) 3.03 (4H, s, H-3 and H-4), 7.13 (1H, dd, J 15.0 and 11.7, H-2'), 7.28 (1H, d, J 7.4, H-5), 7.36 (1H, t, J 7.4, H-7), 7.46 (1H, ddd, J 7.7, 7.4, and 1.0, H-4''), 7.50 (1H, t, J 7.4, H-6), 7.51 (1H, d, J 15.0, H-3'), 7.56 (1H, d, J 11.7, H-1'), 7.63 (1H, ddd, J 7.6, 7.4, and 0.8, H-5''), 7.76 (1H, dd, J 7.6 and 1.0, H-6''), 7.98 (1H, dd, J 7.7 and 0.8, H-3''), 8.12 (1H, dd, J 7.4 and 1.2, H-8). δ_{C} (CDCl_3) 26.2 (C-3), 28.7 (C-4), 124.9 (C-3''), 127.1 (C-7), 128.1 (C-2'), 128.19 and 128.22 (C-5 and C-8), 128.4 (C-6''), 128.9 (C-4''), 132.2 (C-1''), 133.1 (C-5''), 133.3 (C-6), 133.5 (C-8a), 134.6 (C-1'), 134.8 (C-3'), 136.7 (C-2), 143.3 (C-4a), 147.9 (C-2''), 187.1 (C-1). m/z 305 (M^{+} , 2), 288 (100), 170 (48), 115 (86). $\nu_{\text{max}}/\text{cm}^{-1}$ 1662, 1606, 1581, 1517, 1340, 1240, 1161, 1131, 1026, 973, 925, 865, 790, 736, 708, 640. (Found: C 74.66, H 4.87. $\text{C}_{19}\text{H}_{15}\text{NO}_3$ requires C 74.74, H 4.95%).

(*E,E*)-2-[3-(2-Methoxyphenyl)allylidene]-1-benzosuberone **3h**

(2.25 g, 74%), mp 108–109°C. δ_{H} (CDCl_3) 1.98 (2H, quint, J 6.8, H-4), 2.56 (2H, t, J 6.8, H-3), 2.81 (2H, t, J 6.8, H-5), 3.90 (3H, s, 2''-OCH₃), 6.92 (1H, d, J 8.1, H-3''), 6.98 (1H, ddd, J 7.7, 7.6, and 0.6, H-5''), 7.16 (1H, dd, J 15.5 and 11.6, H-2'), 7.18 (1H, dd, J 7.4 and 1.0, H-6), 7.30 (1H, ddd, J 8.1, 7.7, and 1.7, H-4''), 7.35 (1H, dt, J 7.3 and 1.0, H-8), 7.43 (1H, d, J 15.5, H-3'), 7.45 (1H, ddd, J 7.4, 7.3, and 1.5, H-7), 7.53 (1H, d, J 11.6, H-1'), 7.58 (1H, dd, J 7.7 and 1.7, H-6''), 7.74 (1H, dd, J 7.3 and 1.5, H-9). δ_{C} (CDCl_3) 24.5 (C-3), 26.6 (C-4), 31.2 (C-5), 55.5 (2''-OCH₃), 111.0 (C-3''), 120.7 (C-5''), 124.0 (C-2'), 125.6 (C-1''), 126.9 (C-8), 127.2 (C-6''), 128.8 (C-6), 128.9 (C-9), 130.0 (C-4''), 132.1 (C-7), 136.3 (C-3'), 137.0 (C-2), 137.8 (C-1'), 139.2 (C-9a), 139.5 (C-5a), 157.3 (C-2''), 198.0 (C-1). m/z 304 (M^{+} , 100), 273 (11), 197 (19), 115 (31). $\nu_{\text{max}}/\text{cm}^{-1}$ 1649, 1604, 1583, 1483, 1452, 1301, 1246, 1162, 1101, 1024, 969, 746, 712. (Found: C 82.77, H 6.69. $\text{C}_{21}\text{H}_{20}\text{O}_2$ requires C 82.86, H 6.62%).

(*E,E*)-2-[3-(2-Nitrophenyl)allylidene]-1-benzosuberone **3i**

(2.58 g, 81%), mp 179–180°C. δ_{H} (CDCl_3) 1.99 (2H, quint, J 6.8, H-4), 2.57 (2H, t, J 6.8, H-3), 2.82 (2H, t, J 6.8, H-5), 7.08 (1H, dd, J 15.3 and 11.4, H-2'), 7.19 (1H, d, J 7.6, H-6), 7.35 (1H, ddd, J 7.6, 7.5, and 1.1, H-8), 7.466 (1H, t, J 7.6, H-7), 7.468 (1H, ddd, J 8.2, 7.8, and 1.3, H-4''), 7.48 (1H, d, J 11.4, H-1'), 7.52 (1H, d, J 15.3, H-3'), 7.63 (1H, ddd, J 7.8, 7.7, and 1.0, H-5''), 7.74 (1H, dd, J 7.7 and 1.3, H-6''), 7.75 (1H, dd, J 7.5 and 1.5, H-9), 7.99 (1H, dd, J 8.2 and 1.0, H-3''). δ_{C} (CDCl_3) 24.6 (C-3), 26.5 (C-4), 31.1 (C-5), 124.9 (C-3''), 127.0 (C-8), 128.1 (C-2'), 128.4 (C-6''), 128.9, 129.0, and 129.1 (C-6, C-7, and C-9), 132.2 (C-1''), 132.4 (C-4''), 133.1 (C-5''), 135.0 (C-3'), 135.1 (C-1'), 138.6 (C-9a), 139.4 (C-5a), 140.0 (C-2), 147.9 (C-2''), 197.6 (C-1). m/z 319 (M^{+} , 1), 302 (94), 184 (80), 115 (100). $\nu_{\text{max}}/\text{cm}^{-1}$ 1652, 1605, 1581, 1521, 1451, 1346, 1303, 1247, 1167, 1106, 1040, 969, 869, 779, 742, 675. (Found: C 72.31, H 5.42. $\text{C}_{20}\text{H}_{17}\text{NO}_3$ requires C 72.22, H 5.36%).

General Procedure for the Dimethyldioxirane Oxidation of Exocyclic $\alpha,\beta,\gamma,\delta$ -Unsaturated Ketones 3a–i

The required amount of isolated DMDO in acetone (0.07–0.10 M) was added to the anhydrous CH_2Cl_2 solution (20 mL) of the appropriate exocyclic $\alpha,\beta,\gamma,\delta$ -unsaturated ketone (**3a–i**, 5.0 mmol) at room temperature. The mixture was left to stand at room temperature and the progress of the reaction was monitored by TLC. Another equivalent of DMDO was added every day until the complete conversion of the starting material. The complete conversion of compounds **3a,b,d,e,g,h** into the corresponding $\alpha,\beta,\gamma,\delta$ -diepoxides **4a,b,d,e,g,h** was performed by using 5 equivalents of dimethyldioxirane within 120 h, whereas the nitrosubstituted compounds **3c,f,i** could be converted to their $\alpha,\beta,\gamma,\delta$ -diepoxides **4c,f,i** with 18 equivalents of DMDO in 432 h. After the complete consumption of the starting material, the solvent was evaporated under reduced pressure and the residue was crystallized from methanol to afford the diastereomeric mixture of $\alpha,\beta,\gamma,\delta$ -diepoxides **4a,b,d,e,g,h** (**4a**, 1.10 g, 79%; **4b**, 1.12 g, 73%; **4d**, 1.04 g, 71%; **4e**, 1.18 g, 73%; **4g**, 1.09 g, 71%; **4h**, 1.24 g, 74%). In the case of nitro-derivatives, the resulting residue was purified by preparative TLC, using a 9:1 mixture of CH_2Cl_2 :light petroleum as eluent. After several elutions, the fraction with the higher R_f value was identified as the α,β -monoepoxides **5a–c** (**5a**, 230 mg, 15%; **5b**, 225 mg, 14%; **5c**, 201 mg, 12%) and that with the lower R_f value identified as the $\alpha,\beta,\gamma,\delta$ -diepoxides **4c,f,i** (**4c**, 1.13 g, 70%; **4f**, 1.16 g, 69%; **4i**, 1.23 g, 70%).

Diastereomeric Mixture (38A:62B) of Spiro[indan-1-one-2,2'-(2-phenyl-1,2-epoxypropyl)oxirane] 4a

Diastereomer A: rel-(2R,3'S,2''S,3''R)-Spiro[indan-1-one-2,2'-(2-phenyl-1,2-epoxypropyl)oxirane] δ_{H} (CDCl_3) 3.20 (1H, dd, J 3.8 and 1.9, H-2''), 3.36 and 3.59 (2 \times 1H, 2d, J 18.6, H-3), 3.66 (1H, d, J 3.8, H-3'), 3.92 (1H, d, J 1.9, H-3''), 7.27–7.42 (5H, m, H-2'', 3'', 4'', 5'', 6''), 7.47 (1H, t, J 7.6, H-6), 7.53 (1H, dd, J 7.6 and 0.6, H-4), 7.70 (1H, t, J 7.6, H-5), 7.85 (1H, d, J 7.6, H-7). δ_{C} (CDCl_3) 29.7 (C-3), 55.6 (C-3''), 58.8 (C-2''), 59.6 (C-3'), 63.55 (C-2), 124.1 (C-7), 125.6 (C-2''', 6'''), 126.74 (C-4), 128.1 (C-6), 128.66 (C-3''', 5'''), 128.70 (C-4'''), 135.5 (C-1'''), 135.5 (C-7a), 135.9 (C-5), 151.4 (C-3a), 199.5 (C-1).

Diastereomer B: rel-(2R,3'S,2''R,3''S)-Spiro[indan-1-one-2,2'-(2-phenyl-1,2-epoxypropyl)oxirane] δ_{H} (CDCl_3) 3.06 (1H, dd, J 6.0 and 1.9, H-2''), 3.34 and 3.62 (2 \times 1H, 2d, J 18.0, H-3), 3.52 (1H, d, J 6.0, H-3'), 4.03 (1H, d, J 1.9, H-3''), 7.27–7.42 (5H, m, H-2'', 3'', 4'', 5'', 6''), 7.47 (1H, t, J 7.6, H-6), 7.55 (1H, dd, J 7.1 and 1.0, H-4), 7.70 (1H, dd, J 7.6 and 7.1, H-5), 7.85 (1H, d, J 7.6, H-7). δ_{C} (CDCl_3) 29.1 (C-3), 57.0 (C-3''), 59.7 (C-2''), 59.8 (C-3'), 63.60 (C-2), 124.2 (C-7), 125.6 (C-2''', 6'''), 126.71 (C-4), 128.2 (C-6), 128.66 (C-3''', 5'''), 128.70 (C-4'''), 135.5 (C-1'''), 135.8 (C-7a), 135.9 (C-5), 150.8 (C-3a), 199.1 (C-1).

mp 119–120°C. m/z 278 (M^+ , 1), 219 (35), 115 (78), 91 (100). $\nu_{\text{max}}/\text{cm}^{-1}$ 1724, 1610, 1470, 1299, 1256, 1203, 986, 930, 737, 696, 597. (Found: C 77.76, H 5.01. $\text{C}_{18}\text{H}_{14}\text{O}_3$ requires C 77.68, H 5.07%).

Diastereomeric Mixture (47A:53B) of Spiro[indan-1-one-2,2'-(2-methoxyphenyl)-1,2-epoxypropyl]oxirane] 4b

Diastereomer A: rel-(2R,3'S,2''S,3''R)-Spiro[indan-1-one-2,2'-(2-methoxyphenyl)-1,2-epoxypropyl]oxirane] δ_{H} (CDCl_3) 3.06 (1H, dd, J 4.2 and 2.1, H-2''), 3.34 and 3.63 (2 \times 1H, 2d, J 18.5, H-3), 3.64 (1H, d, J 4.2, H-3'), 4.21 (1H, d, J 2.1, H-3''),

6.90 (1H, d, J 8.0, H-3'''), 6.96 (1H, t, J 7.9, H-5'''), 7.18 (1H, d, J 7.9, H-6'''), 7.27–7.30 (1H, m, H-4'''), 7.46 (1H, t, J 7.5, H-6), 7.53 (1H, d, J 7.5, H-4), 7.70 (1H, t, J 7.5, H-5), 7.85* (1H, d, J 7.5, H-7). δ_{C} (CDCl_3) 29.5 (C-3), 51.7 (C-3''), 55.3 (2'''-OCH₃), 59.2 (C-2''), 60.1 (C-3'), 63.7 (C-2), 110.2 (C-3'''), 120.7 (C-5'''), 124.12 (C-7), 124.4 (C-1'''), 125.2 (C-6'''), 126.7 (C-4), 128.0 (C-6), 129.2 (C-4'''), 135.57 (C-7a), 135.8 (C-5), 151.4 (C-3a), 157.8 (C-2'''), 199.7 (C-1).

Diastereomer B: rel-(2R,3'S,2''R,3''S)-Spiro[indan-1-one-2,2'-(2-methoxyphenyl)-1,2-epoxypropyl]oxirane] δ_{H} (CDCl_3) 3.00 (1H, dd, J 5.6 and 1.8, H-2''), 3.33 and 3.66 (2 \times 1H, 2d, J 18.2, H-3), 3.58 (1H, d, J 5.6, H-3'), 4.37 (1H, d, J 1.8, H-3''), 6.90 (1H, d, J 8.0, H-3'''), 6.96 (1H, t, J 7.9, H-5'''), 7.18 (1H, d, J 7.9, H-6'''), 7.27–7.30 (1H, m, H-4'''), 7.46 (1H, dd, J 7.7 and 7.5, H-6), 7.53 (1H, d, J 7.5, H-4), 7.70 (1H, t, J 7.5, H-5), 7.86* (1H, d, J 7.7, H-7). δ_{C} (CDCl_3) 29.2 (C-3), 53.0 (C-3''), 55.4 (2'''-OCH₃), 58.3 (C-2''), 59.9 (C-3'), 63.4 (C-2), 110.1 (C-3'''), 120.6 (C-5'''), 124.15 (C-7), 124.2 (C-1'''), 125.0 (C-6'''), 126.7 (C-4), 128.1 (C-6), 129.3 (C-4'''), 135.63 (C-7a), 135.8 (C-5), 151.0 (C-3a), 158.0 (C-2'''), 199.4 (C-1). *Can be interchanged.

mp 162–163°C. m/z 308 (M^+ , 3), 219 (45), 121 (62), 91 (100). $\nu_{\text{max}}/\text{cm}^{-1}$ 1720, 1605, 1497, 1467, 1248, 1107, 1027, 986, 930, 887, 846, 744, 596. (Found: C 73.92, H 5.18. $\text{C}_{19}\text{H}_{16}\text{O}_4$ requires C 74.01, H 5.23%).

Diastereomeric Mixture (50A:50B) of Spiro[indan-1-one-2,2'-(2-nitrophenyl)-1,2-epoxypropyl]oxirane] 4c

Diastereomer A: rel-(2R,3'S,2''S,3''R)-Spiro[indan-1-one-2,2'-(2-nitrophenyl)-1,2-epoxypropyl]oxirane] δ_{H} (CDCl_3) 3.03 (1H, dd, J 4.9 and 2.1, H-2''), 3.40 and 3.61 (2 \times 1H, 2d, J 18.2, H-3), 3.70 (1H, d, J 4.9, H-3'), 4.69 (1H, d, J 1.9, H-3''), 7.47 (1H, t, J 7.4, H-6), 7.51–7.56 (2H, m, H-4 and H-4'''), 7.66 (1H, dd, J 7.5 and 1.4, H-6''), 7.67–7.73 (2H, m, H-5 and H-5'''), 7.85–7.88 (1H, m, H-7), 8.22 (1H, dd, J 8.1 and 1.3, H-3'''). δ_{C} (CDCl_3) 29.5 (C-3), 54.1 (C-3''), 58.8 (C-2''), 60.0 (C-3'), 63.4 (C-2), 124.2 (C-7), 124.9 (C-3'''), 126.7 (C-4), 126.9 (C-6'''), 128.2 (C-6), 129.13* (C-4'''), 132.6 (C-1'''), 134.4* (C-5'''), 135.4 (C-7a), 136.0 (C-5), 147.6 (C-2'''), 150.9 (C-3a), 199.4 (C-1).

Diastereomer B: rel-(2R,3'S,2''R,3''S)-Spiro[indan-1-one-2,2'-(2-nitrophenyl)-1,2-epoxypropyl]oxirane] δ_{H} (CDCl_3) 2.97 (1H, dd, J 6.1 and 2.0, H-2''), 3.30 and 3.56 (2 \times 1H, 2d, J 18.2, H-3), 3.63 (1H, d, J 6.1, H-3'), 4.45 (1H, d, J 2.0, H-3''), 7.47 (1H, t, J 7.4, H-6), 7.51–7.56 (2H, m, H-4 and H-4'''), 7.60 (1H, dd, J 7.9 and 1.5, H-6''), 7.67–7.73 (2H, m, H-5 and H-5'''), 7.85–7.88 (1H, m, H-7), 8.19 (1H, dd, J 8.3 and 1.2, H-3'''). δ_{C} (CDCl_3) 29.2 (C-3), 55.4 (C-3''), 59.4 (C-2''), 59.6 (C-3'), 63.2 (C-2), 124.2 (C-7), 124.8 (C-3'''), 126.7 (C-4), 127.3 (C-6'''), 128.1 (C-6), 129.05* (C-4'''), 132.9 (C-1'''), 134.6* (C-5'''), 135.6 (C-7a), 135.9 (C-5), 147.2 (C-2'''), 151.3 (C-3a), 199.1 (C-1). *Can be interchanged.

mp 142–143°C. m/z 323 (M^+ , 1), 160 (69), 115 (42), 91 (100). $\nu_{\text{max}}/\text{cm}^{-1}$ 1720, 1607, 1520, 1468, 1342, 1303, 1252, 1201, 950, 855, 789, 733, 670. (Found: C 66.98, H 4.11. $\text{C}_{18}\text{H}_{13}\text{O}_5$ requires C 66.87, H 4.05%).

Diastereomeric Mixture (40A:60B) of Spiro[(3,4-dihydro-2H-naphthalen-1-one)-2,2'-(2-phenyl-1,2-epoxypropyl)oxirane] 4d

Diastereomer A: rel-(2R,3'S,2''S,3''R)-Spiro[(3,4-dihydro-2H-naphthalen-1-one)-2,2'-(2-phenyl-1,2-epoxypropyl)oxirane] δ_{H} (CDCl_3) 2.38 (1H, dt, J 13.8 and 5.0, H-3), 2.49–2.58 (1H, m,

H-3), 3.18 (1H, dd, *J* 4.4 and 1.8, H-2''), 3.25–3.37 (2H, m, H-4), 3.28 (1H, d, *J* 4.4, H-3'), 3.90 (1H, d, *J* 1.8, H-3''), 7.26–7.40 (7H, m, H-5, H-7, H-2''', 3'', 4'', 5'', 6'''), 7.55 (1H, t, *J* 7.5, H-6), 8.06 (1H, d, *J* 7.8, H-8). δ_{C} (CDCl₃) 26.47 (C-3), 28.0 (C-4), 55.2 (C-3''), 58.5 (C-2''), 61.2 (C-3'), 62.2 (C-2), 125.5 (C-2''', 6'''), 127.1 (C-7), 127.8 (C-8), 128.59 (C-3''', 5'''), 128.7 (C-4'''), 128.8 (C-5), 132.42 (C-8a), 134.3 (C-6), 135.7 (C-1'''), 143.51 (C-4a), 192.6 (C-1).

Diastereomer B: rel-(2R,3'S,2''R,3''S)-Spiro[(3,4-dihydro-2H-naphthalen-1-one)-2,2'-[2-(2-phenyl-1,2-epoxypropyl)oxirane]] δ_{H} (CDCl₃) 2.31 (1H, dt, *J* 13.7 and 4.6, H-3), 2.60 (1H, ddd, *J* 13.7, 11.6, and 4.8, H-3), 3.09 (1H, dd, *J* 6.3 and 1.6, H-2''), 3.20 (1H, dt, *J* 11.6 and 4.6, H-4), 3.28 (1H, d, *J* 6.3, H-3'), 3.31–3.38 (1H, m, H-4), 4.01 (1H, d, *J* 1.6, H-3''), 7.29–7.40 (7H, m, H-5, H-7, H-2''', 3'', 4'', 5'', 6'''), 7.56 (1H, t, *J* 7.2, H-6), 8.09 (1H, d, *J* 7.8, H-8). δ_{C} (CDCl₃) 26.53 (C-3), 28.0 (C-4), 57.7 (C-3''), 58.4 (C-2''), 61.6 (C-3'), 62.1 (C-2), 125.6 (C-2''', 6'''), 127.0 (C-7), 127.7 (C-8), 128.58 (C-3''', 5'''), 128.7 (C-4'''), 128.8 (C-5), 132.44 (C-8a), 134.3 (C-6), 135.6 (C-1'''), 143.47 (C-4a), 192.6 (C-1).

mp 153–154°C. *m/z* 292 (M⁺, 1), 233 (62), 115 (78), 91 (100). ν_{max} /cm⁻¹ 1691, 1604, 1461, 1309, 1220, 1162, 946, 881, 845, 761, 699, 612, 547. (Found: C 78.16, H 5.47. C₁₉H₁₆O₃ requires C 78.06, H 5.52%).

Diastereomeric Mixture (57A:43B) of Spiro[(3,4-dihydro-2H-naphthalen-1-one)-2,2'-[2-(2-methoxyphenyl)-1,2-epoxypropyl]oxirane] 4e

Diastereomer A: rel-(2R,3'S,2''S,3''R)-Spiro[(3,4-dihydro-2H-naphthalen-1-one)-2,2'-[2-(2-methoxyphenyl)-1,2-epoxypropyl]oxirane] δ_{H} (CDCl₃) 2.36 (1H, dt, *J* 16.0 and 4.9, H-3), 2.59 (1H, ddd, *J* 16.0, 11.8, and 4.7, H-3), 3.04 (1H, dd, *J* 5.0 and 2.0, H-2''), 3.12–3.29 (2H, m, H-4), 3.37 (1H, d, *J* 5.0, H-3'), 3.86 (3H, s, OCH₃), 4.21 (1H, d, *J* 2.0, H-3''), 6.90 (1H, d, *J* 8.3, H-3'''), 6.97 (1H, t, *J* 7.4, H-5'''), 7.20 (1H, dd, *J* 7.4 and 1.6, H-6'''), 7.26–7.33 (1H, m, H-4'''), 7.34 (1H, d, *J* 7.8, H-5), 7.39 (1H, t, *J* 7.4, H-7), 7.57 (1H, ddd, *J* 7.8, 7.4, and 1.4, H-6), 8.10 (1H, dd, *J* 7.4 and 0.9, H-8). δ_{C} (CDCl₃) 26.8 (C-3), 27.8 (C-4), 51.6 (C-3''), 55.3 (2''-OCH₃), 58.2 (C-2''), 62.1 (C-3'), 62.3 (C-2), 110.1 (C-3'''), 120.8 (C-5'''), 124.4 (C-1'''), 125.2 (C-6'''), 127.0 (C-7), 127.9 (C-8), 128.7 (C-5), 129.2 (C-4'''), 132.6 (C-8a), 134.3 (C-6), 143.7 (C-4a), 157.8 (C-2'''), 192.7 (C-1).

Diastereomer B: rel-(2R,3'S,2''R,3''S)-Spiro[(3,4-dihydro-2H-naphthalen-1-one)-2,2'-[2-(2-methoxyphenyl)-1,2-epoxypropyl]oxirane] δ_{H} (CDCl₃) 2.37 (1H, dt, *J* 16.0 and 4.9, H-3), 2.59 (1H, ddd, *J* 16.0, 11.8, and 4.7, H-3), 3.02 (1H, dd, *J* 6.1 and 1.8, H-2''), 3.17–3.33 (2H, m, H-4), 3.31 (1H, d, *J* 6.1, H-3'), 3.88 (3H, s, OCH₃), 4.35 (1H, d, *J* 1.8, H-3''), 6.90 (1H, d, *J* 8.3, H-3'''), 6.95 (1H, t, *J* 7.6, H-5'''), 7.17 (1H, dd, *J* 7.6 and 1.6, H-6'''), 7.26–7.33 (1H, m, H-4'''), 7.33 (1H, d, *J* 7.8, H-5), 7.37 (1H, t, *J* 7.6, H-7), 7.56 (1H, ddd, *J* 7.8, 7.6, and 1.4, H-6), 8.09 (1H, dd, *J* 7.6 and 1.0, H-8). δ_{C} (CDCl₃) 26.5 (C-3), 28.1 (C-4), 53.9 (C-3''), 55.4 (2''-OCH₃), 57.9 (C-2''), 61.7 (C-3'), 62.3 (C-2), 110.2 (C-3'''), 120.6 (C-5'''), 124.3 (C-1'''), 125.1 (C-6'''), 127.1 (C-7), 127.8 (C-8), 128.8 (C-5), 129.3 (C-4'''), 132.6 (C-8a), 134.3 (C-6), 143.6 (C-4a), 158.1 (C-2'''), 192.8 (C-1).

mp 107–108°C. *m/z* 322 (M⁺, 3), 233 (73), 121 (55), 91 (100). ν_{max} /cm⁻¹ 1686, 1602, 1497, 1466, 1303, 1250, 1222, 1107, 1027, 943, 889, 744, 708. (Found: C 74.61, H 5.57. C₂₀H₁₈O₄ requires C 74.52, H 5.63%).

Diastereomeric Mixture (70A:30B) of Spiro[(3,4-dihydro-2H-naphthalen-1-one)-2,2'-[2-(2-nitrophenyl)-1,2-epoxypropyl]oxirane] 4f

Diastereomer A: rel-(2R,3'S,2''S,3''R)-Spiro[(3,4-dihydro-2H-naphthalen-1-one)-2,2'-[2-(2-nitrophenyl)-1,2-epoxypropyl]oxirane] δ_{H} (CDCl₃) 2.35 (1H, dt, *J* 14.7 and 4.7, H-3), 2.51 (1H, dt, *J* 14.7 and 4.5, H-3), 3.02 (1H, dd, *J* 6.0 and 1.8, H-2''), 3.12 (1H, dt, *J* 16.4 and 4.7, H-4), 3.24–3.30 (1H, m, H-4), 3.48 (1H, d, *J* 6.0, H-3'), 4.49 (1H, d, *J* 1.8, H-3''), 7.32 (1H, d, *J* 7.5, H-5), 7.38 (1H, t, *J* 7.5, H-7), 7.52–7.55 (1H, m, H-4'''), 7.59 (1H, t, *J* 7.5, H-6), 7.67 (1H, d, *J* 7.3, H-6'''), 7.72 (1H, t, *J* 7.3, H-5'''), 8.09 (1H, d, *J* 7.5, H-8), 8.20 (1H, d, *J* 8.2, H-3'''). δ_{C} (CDCl₃) 26.6 (C-3), 27.4 (C-4), 54.0 (C-3''), 58.5 (C-2''), 61.7 (C-2), 62.0 (C-3'), 124.8 (C-3'''), 127.0 (C-6), 127.3 (C-6'''), 127.9 (C-8), 128.8 (C-5), 129.06 (C-4'''), 132.4 (C-8a), 133.0 (C-1'''), 134.4 (C-7), 134.7 (C-5'''), 143.7 (C-4a), 147.3 (C-2'''), 192.4 (C-1).

Diastereomer B: rel-(2R,3'S,2''R,3''S)-Spiro[(3,4-dihydro-2H-naphthalen-1-one)-2,2'-[2-(2-nitrophenyl)-1,2-epoxypropyl]oxirane] δ_{H} (CDCl₃) 2.32 (1H, dt, *J* 15.2 and 4.6, H-3), 2.63 (1H, dt, *J* 15.2 and 4.7, H-3), 3.00 (1H, dd, *J* 6.6 and 1.8, H-2''), 3.20 (1H, dt, *J* 12.0 and 4.6, H-4), 3.27–3.37 (1H, m, H-4), 3.42 (1H, d, *J* 6.6, H-3'), 4.64 (1H, d, *J* 1.8, H-3''), 7.33 (1H, d, *J* 7.5, H-5), 7.38 (1H, t, *J* 7.7, H-7), 7.55–7.60 (2H, m, H-6, H-4'''), 7.69 (1H, d, *J* 7.3, H-6'''), 7.72 (1H, t, *J* 7.3, H-5'''), 8.09 (1H, dd, *J* 7.7, H-8), 8.21 (1H, d, *J* 8.3, H-3'''). δ_{H} (CDCl₃) 26.7 (C-3), 28.0 (C-4), 56.1 (C-3''), 58.3 (C-2''), 61.2 (C-3'), 62.0 (C-2), 124.8 (C-3'''), 127.0 (C-6), 127.3 (C-6'''), 127.8 (C-8), 128.8 (C-5), 129.12 (C-4'''), 132.0 (C-8a), 132.7 (C-1'''), 134.4 (C-7), 134.7 (C-5'''), 143.6 (C-4a), 146.8 (C-2'''), 192.4 (C-1).

mp 113–114°C. *m/z* 337 (M⁺, 1), 173 (90), 131 (32), 115 (100). ν_{max} /cm⁻¹ 1688, 1599, 1522, 1456, 1346, 1312, 1227, 940, 860, 791, 738, 698, 665. (Found: C 67.53, H 4.54. C₁₉H₁₅NO₅ requires C 67.65, H 4.48%).

Diastereomeric Mixture (71A:29B) of Spiro[(6,7,8,9-tetrahydrobenzocyclohepten-5-one)-2,2'-[2-(2-phenyl-1,2-epoxypropyl)oxirane] 4g

Diastereomer A: rel-(2R,3'S,2''S,3''R)-Spiro[(6,7,8,9-tetrahydrobenzocyclohepten-5-one)-2,2'-[2-(2-phenyl-1,2-epoxypropyl)oxirane] δ_{H} (CDCl₃) 1.91–1.99 (m, 2H, H-4), 1.99–2.09 (1H, m, H-3), 2.11–2.32 (1H, m, H-3), 2.98–3.04 (2H, m, H-5), 3.16 (1H, dd, *J* 5.0 and 2.0, H-2''), 3.38 (1H, d, *J* 5.0, H-3'), 3.95 (1H, d, *J* 2.0, H-3''), 7.25 (1H, d, *J* 7.3, H-6), 7.29–7.32 (2H, m, H-2''', 6'''), 7.35–7.40 (4H, m, H-8 and H-3''', 4'', 5'''), 7.53 (1H, dt, *J* 7.3 and 1.4, H-7), 7.79 (1H, dd, *J* 7.7 and 1.4, H-9). δ_{C} (CDCl₃) 22.9 (C-4), 24.7 (C-3), 32.2 (C-5), 55.3 (C-3''), 59.1 (C-2''), 61.3 (C-3'), 63.3 (C-2), 125.4 (C-2''', 6'''), 127.2 (C-8), 128.63 (C-4'''), 128.7 (C-3''', 5'''), 129.1 (C-9), 129.6 (C-6), 133.5 (C-7), 135.7 (C-1'''), 136.7 (C-9a), 140.0 (C-5a), 200.6 (C-1).

Diastereomer B: rel-(2R,3'S,2''R,3''S)-Spiro[(6,7,8,9-tetrahydrobenzocyclohepten-5-one)-2,2'-[2-(2-phenyl-1,2-epoxypropyl)oxirane] δ_{H} (CDCl₃) 1.91–1.99 (2H, m, H-4), 1.99–2.09 (1H, m, H-3), 2.11–2.32 (1H, m, H-3), 2.98–3.04 (2H, m, H-5), 3.02 (1H, dd, *J* 7.2 and 1.7, H-2''), 3.24 (1H, d, *J* 7.2, H-3'), 4.03 (1H, d, *J* 1.7, H-3''), 7.27 (1H, d, *J* 7.0, H-6), 7.31–7.33 (2H, m, H-2''', 6'''), 7.35–7.40 (4H, m, H-8 and H-3''', 4'', 5'''), 7.53 (1H, dt, *J* 7.0 and 1.5, H-7), 7.78 (1H, dd, *J* 7.7 and 1.4, H-9). δ_{C} (CDCl₃) 22.7 (C-4), 24.6 (C-3), 32.2 (C-5), 58.1 (C-3''), 58.9 (C-2''), 61.6 (C-3'), 63.2 (C-2), 125.5 (C-2''', 6'''), 127.1 (C-8), 128.63 (C-4'''), 128.66 (C-3''', 5'''), 129.0 (C-9), 129.7 (C-6), 133.5 (C-7), 135.6 (C-1'''), 136.8 (C-9a), 140.3 (C-5a), 200.6 (C-1).

mp 156–157°C. m/z 306 (M^{+} , 1), 247 (13), 118 (54), 91 (100). $\nu_{\max}/\text{cm}^{-1}$ 1693, 1597, 1457, 1297, 1269, 1207, 1100, 967, 943, 898, 826, 758, 615, 550. (Found: C 78.51, H 5.86. $\text{C}_{20}\text{H}_{18}\text{O}_3$ requires C 78.41, H 5.92%).

Diastereomeric Mixture (80A:20B) of Spiro[(6,7,8,9-tetrahydrobenzocyclohepten-5-one)-2,2'-[2-(2-methoxyphenyl)-1,2-epoxypropyl]oxirane] 4h

Diastereomer A: rel-(2R,3'S,2''S,3''R)-Spiro[(6,7,8,9-tetrahydrobenzocyclohepten-5-one)-2,2'-[2-(2-methoxyphenyl)-1,2-epoxypropyl]oxirane] δ_{H} (CDCl_3) 1.85–2.00 (2H, m, H-4), 1.95–2.04 (1H, m, H-3), 2.24–2.34 (1H, m, H-3), 2.99 (1H, dd, J 6.0 and 2.1, H-2''), 2.95–2.98 (1H, m, H-5), 3.08 (1H, dd, J 12.2 and 5.8, H-5), 3.32 (1H, d, J 6.0, H-3'), 3.90 (3H, s, 2'''-OCH₃), 4.29 (1H, d, J 2.1, H-3''), 6.92 (1H, d, J 8.1, H-3'''), 6.99 (1H, d, J 7.4, H-5'''), 7.21 (1H, dd, J 7.4 and 1.7, H-6'''), 7.25 (1H, d, J 7.5, H-6), 7.31 (1H, ddd, J 8.1, 7.4, and 1.7, H-4'''), 7.37 (1H, dt, J 7.5 and 1.1, H-8), 7.53 (1H, dt, J 7.5 and 1.4, H-7), 7.80 (1H, dd, J 7.5 and 1.4, H-9). δ_{C} (CDCl_3) 22.9 (C-4), 25.0 (C-3), 32.2 (C-5), 51.5 (C-3''), 55.29 (2'''-OCH₃), 58.9 (C-2''), 62.2 (C-3'), 63.0 (C-2), 110.0 (C-3'''), 120.8 (C-5'''), 124.3 (C-1'''), 124.9 (C-6'''), 127.2 (C-8), 129.1 (C-9), 129.2 (C-4'''), 129.5 (C-6), 133.5 (C-7), 136.78 (C-9a), 140.1 (C-5a), 157.8 (C-2''), 200.9 (C-1).

Diastereomer B: rel-(2R,3'S,2''R,3''S)-Spiro[(6,7,8,9-tetrahydrobenzocyclohepten-5-one)-2,2'-[2-(2-methoxyphenyl)-1,2-epoxypropyl]oxirane] δ_{H} (CDCl_3) 1.85–2.00 (2H, m, H-4), 1.95–2.04 (1H, m, H-3), 2.24–2.34 (1H, m, H-3), 2.90–2.93 (1H, m, H-5), 2.95–2.98 (1H, m, H-2''), 3.13 (1H, dd, J 14.0 and 5.7, H-5), 3.31 (1H, d, J 6.8, H-3'), 3.88 (3H, s, 2'''-OCH₃), 4.37 (1H, d, J 1.8, H-3''), 6.90 (1H, d, J 8.1, H-3'''), 6.99 (1H, t, J 7.4, H-5'''), 7.18 (1H, dd, J 7.4 and 1.7, H-6'''), 7.27 (1H, d, J 7.5, H-6), 7.29 (1H, ddd, J 8.1, 7.4, and 1.7, H-4'''), 7.36 (1H, dt, J 7.5 and 1.1, H-8), 7.53 (1H, dt, J 7.5 and 1.4, H-7), 7.79 (1H, dd, J 7.5 and 1.4, H-9). δ_{C} (CDCl_3) 22.7 (C-4), 24.5 (C-3), 32.2 (C-5), 54.2 (C-3''), 55.32 (2'''-OCH₃), 58.4 (C-2''), 61.6 (C-3'), 63.3 (C-2), 110.1 (C-3'''), 120.5 (C-5'''), 124.3 (C-1'''), 124.9 (C-6'''), 127.1 (C-8), 129.0 (C-9), 129.3 (C-4'''), 129.6 (C-6), 133.5 (C-7), 136.82 (C-9a), 140.3 (C-5a), 158.0 (C-2''), 200.9 (C-1).

mp 145–146°C. m/z 336 (M^{+} , 2), 247 (27), 121 (76), 91 (100). $\nu_{\max}/\text{cm}^{-1}$ 1694, 1599, 1496, 1457, 1289, 1253, 1165, 1027, 944, 895, 764, 647. (Found: C 74.89, H 5.91. $\text{C}_{21}\text{H}_{20}\text{O}_4$ requires C 74.98, H 5.99%).

Diastereomeric Mixture (97A:3B) of Spiro[(6,7,8,9-tetrahydrobenzocyclohepten-5-one)-2,2'-[2-(2-nitrophenyl)-1,2-epoxypropyl]oxirane] 4i

Diastereomer A: rel-(2R,3'S,2''S,3''R)-Spiro[(6,7,8,9-tetrahydrobenzocyclohepten-5-one)-2,2'-[2-(2-nitrophenyl)-1,2-epoxypropyl]oxirane] δ_{H} (CDCl_3) 1.84–1.93 (2H, m, H-4), 2.00 (1H, ddd, J 14.6, 6.7, and 3.3, H-3), 2.25 (1H, ddd, J 14.6, 9.5, and 7.8, H-3), 3.00 (1H, dd, J 6.3 and 2.1, H-2''), 2.96–3.02 (1H, m, H-5), 3.14 (1H, ddd, J 14.3, 10.1, and 7.3, H-5), 3.46 (1H, d, J 6.3, H-3'), 4.60 (1H, d, J 2.1, H-3''), 7.23 (1H, d, J 7.6, H-6), 7.36 (1H, dt, J 7.6 and 1.2, H-8), 7.52 (1H, dt, J 7.6 and 1.4, H-7), 7.54 (1H, ddd, J 8.0, 7.5, and 1.7, H-4'''), 7.66 (1H, dd, J 7.9 and 1.7, H-6'''), 7.72 (1H, ddd, J 7.9, 7.5, and 1.1, H-5'''), 7.75 (1H, dd, J 7.6 and 1.4, H-9), 8.21 (1H, dd, J 8.0 and 1.1, H-3'''). δ_{C} (CDCl_3) 23.0 (C-4), 24.9 (C-3), 31.9 (C-5), 53.9 (C-3''), 59.0 (C-2''), 61.7 (C-3'), 63.0 (C-2), 124.89 (C-3'''), 127.1 (C-8 and C-6'''), 129.0 (C-9), 129.1 (C-4'''), 129.5 (C-6), 132.9 (C-1'''),

133.5 (C-7), 134.6 (C-5'''), 137.0 (C-9a), 140.1 (C-5a), 147.4 (C-2''), 200.9 (C-1).

Diastereomer B: rel-(2R,3'S,2''R,3''S)-Spiro[(6,7,8,9-tetrahydrobenzocyclohepten-5-one)-2,2'-[2-(2-nitrophenyl)-1,2-epoxypropyl]oxirane] δ_{H} (CDCl_3) 1.84–1.93 (2H, m, H-4), 2.00 (1H, ddd, J 14.6, 6.7, and 3.3, H-3), 2.25 (1H, ddd, J 14.6, 9.5, and 7.8, H-3), 3.00 (1H, dd, J 7.0 and 1.8, H-2''), 2.98–3.04 (1H, m, H-5), 3.14 (1H, ddd, J 14.3, 10.1, and 7.3, H-5), 3.38 (1H, d, J 7.0, H-3'), 4.69 (1H, d, J 1.8, H-3''), 7.23 (1H, d, J 7.6, H-6), 7.36 (1H, dt, J 7.7 and 1.2, H-8), 7.49–7.57 (2H, m, H-7 and H-4'''), 7.62 (1H, dd, J 7.6 and 1.6, H-6'''), 7.72 (1H, ddd, J 7.9, 7.6, and 1.1, H-5'''), 7.78 (1H, dd, J 7.7 and 1.4, H-9), 8.22 (1H, dd, J 8.0 and 1.1, H-3'''). δ_{C} (CDCl_3) 22.7 (C-4), 24.6 (C-3), 32.2 (C-5), 56.5 (C-3''), 58.7 (C-2''), 61.2 (C-3'), 63.0 (C-2), 124.94 (C-3'''), 126.9 and 127.1 (C-8 and C-6'''), 129.0 (C-9), 129.1 (C-4'''), 129.6 (C-6), 132.6 (C-1'''), 133.5 (C-7), 134.3 (C-5'''), 136.9 (C-9a), 140.2 (C-5a), 147.4 (C-2''), 200.9 (C-1).

mp 197–198°C. m/z 351 (M^{+} , 1), 187 (63), 118 (64), 91 (100). $\nu_{\max}/\text{cm}^{-1}$ 1693, 1598, 1531, 1458, 1348, 1296, 1206, 906, 799, 765, 704. (Found: C 68.46, H 4.82. $\text{C}_{20}\text{H}_{17}\text{NO}_5$ requires C 68.36, H 4.88%).

rel-(2R,3'S)-Spiro[indan-1-one-2,2'-[2-(2-nitrophenyl)ethenyl]oxirane] 5a

δ_{H} (CDCl_3) 3.34 and 3.44 (2H, AB, J 18.2, H-3), 4.12 (1H, dd, J 6.9 and 0.5, H-3'), 6.07 (1H, dd, J 15.9 and 6.9, H-1''), 7.35 (1H, d, J 15.9, H-2''), 7.43–7.51 (2H, m, H-4'' and H-6), 7.52 (1H, d, J 7.4, H-4), 7.62–7.63 (2H, m, H-5''' and H-6'''), 7.68 (1H, dd, J 7.4 and 1.2, H-5), 7.85 (1H, d, J 7.8, H-7), 8.01 (1H, d, J 8.1, H-3'''). δ_{C} (CDCl_3) 29.0 (C-3), 61.6 (C-3'), 66.6 (C-2), 124.1 (C-7), 124.8 (C-3'''), 126.7 (C-4), 128.1 (C-6), 128.2 (C-1''), 128.9 (C-4'''), 129.0 (C-6'''), 131.7 (C-1'''), 131.8 (C-2''), 135.4 (C-5'''), 135.7 (C-7a), 135.8 (C-8), 147.5 (C-2''), 150.9 (C-3a), 199.5 (C-1). m/z (Electrospray ionization (ESI)-MS): 308.0919. $\text{C}_{18}\text{H}_{14}\text{NO}_4$ requires $[M + H]^+$ 308.0923.

rel-(2R,3'S)-Spiro[(3,4-dihydro-2H-naphthalen-1-one)-2,2'-[2-(2-nitrophenyl)ethenyl]oxirane] 5b

δ_{H} (CDCl_3) 2.27 (1H, dt, J 13.7 and 4.4, H-3), 2.60 (1H, ddd, J 13.7, 9.4, and 7.3, H-3), 3.09–3.13 (2H, m, H-4), 3.92 (1H, d, J 6.5, H-3'), 6.18 (1H, dd, J 15.8 and 6.5, H-1''), 7.30 (1H, d, J 7.5, H-5), 7.32 (1H, d, J 15.8, H-2''), 7.37 (1H, dd, J 7.9 and 7.5, H-7), 7.47 (1H, ddd, J 8.4, 5.7, and 2.9, H-4'''), 7.55 (1H, dt, J 7.5 and 1.4, H-6), 7.60–7.64 (2H, m, H-5''' and H-6'''), 8.00 (1H, dd, J 8.4 and 1.1, H-3'''), 8.09 (1H, dd, J 7.9 and 1.4, H-8). δ_{C} (CDCl_3) 26.2 (C-3), 27.8 (C-4), 62.8 (C-3'), 64.7 (C-2), 124.7 (C-3'''), 127.03 and 127.05 (C-7 and C-1''), 127.7 (C-8), 128.8 (C-5), 128.90 and 128.94 (C-4''' and C-6'''), 131.8 (C-1'''), 132.2 (C-2''), 132.6 (C-8a), 132.6 (C-5'''), 134.3 (C-6), 143.4 (C-4a), 147.5 (C-2''), 193.1 (C-1). m/z (ESI-MS): 322.1074. $\text{C}_{19}\text{H}_{16}\text{NO}_4$ requires $[M + H]^+$ 322.1079.

rel-(2R,3'S)-Spiro[(6,7,8,9-tetrahydrobenzocyclohepten-5-one)-2,2'-[2-(2-nitrophenyl)ethenyl]oxirane] 5c

δ_{H} (CDCl_3) 1.86–1.94 (1H, m, H-4), 1.96–2.06 (2H, m, H-3 and H-4), 2.23–2.36 (1H, m, H-3), 2.88–3.05 (2H, m, H-5), 4.00 (1H, d, J 7.1, H-3'), 6.16 (1H, dd, J 15.5 and 7.1, H-1''), 7.21 (1H, d, J 7.6, H-6), 7.37 (1H, dt, J 7.6 and 0.9, H-8), 7.39 (1H, d, J 15.5, H-2''), 7.45–7.51 (1H, m, H-4'''), 7.51 (1H, dt, J 7.6 and 1.4, H-7), 7.60–7.64 (2H, m, H-5''' and H-6'''), 7.79 (1H, dd, J 7.6 and 1.4, H-9), 8.02 (1H, d, J 7.8, H-3'''). δ_{C} (CDCl_3) 22.7 (C-4), 24.5 (C-3), 32.1 (C-5), 62.8 (C-3'), 65.7 (C-2), 124.8 (C-3'''),

127.1 (C-8), 127.2 (C-1''), 128.90 and 128.94 (C-4''' and C-6'''), 129.1 (C-9), 129.6 (C-6), 131.8 (C-2''), 131.9 (C-1'''), 133.42 and 133.44 (C-8 and C-5'''), 136.9 (C-9a), 140.2 (C-5a), 147.6 (C-2'''), 201.1 (C-1). *m/z* (ESI-MS): 352.1185. C₂₀H₁₈NO₄ requires [M + H]⁺ 335.1158.

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