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Microwave-Induced Synthesis and Regio- and Stereoselective Epoxidation of 3-Styrylchromones

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Dedicated to Professor Csaba Szántay on the occasion of his 80th birthday

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The microwave-assisted solvent-free synthesis of (*E*)-3-styrylchromones from 3-formylchromones and phenylmalonic acid on sodium acetate support has been developed; the method affords the styryl derivatives in moderate to good yields and with complete diastereoselectivity. Protocols for the highly regioselective epoxidation of (*E*)- and (*Z*)-3-styrylchromones have been elaborated. Treatment of the alkenes with dimethyldioxirane led to the exclusive formation of 3-(3-aryloxiran-2-yl)chromones with complete diastereoselectivity, whereas treatment with hydrogen peroxide under alkaline conditions afforded the corresponding 2,3-epoxy-3-styrylchromanones as the only products. Epoxidation performed in the presence of chiral, nonracemic cinchona-alkaloid-based quaternary ammonium salts allowed the synthesis of enantiomerically enriched 2,3-epoxy-3-styrylchromanones, but with only moderate *ee* values.

Introduction

Chromones with styryl groups at their 2- or 3-positions represent a small and rare class of naturally occurring chromones. Some of these natural products and their synthetic analogues show marked biological activities.[1] A series of radioiodinated 2-styrylchromones as promising β-amyloidal imaging agents has recently been reported.[2] Syntheses and transformations including Diels–Alder reactions and 1,3-dipolar cycloadditions have also been reviewed.[3]

In comparison with the extensively studied methods for the synthesis of 2-styrylchromones, far fewer procedures have been developed for 3-styrylchromones. Heck reactions of 3-bromochromones offer an obvious approach, but up to now only one paper has been published, presenting the synthesis of the unsubstituted parent compound.[4] Two-step oxidative cyclizations of (*E*,*E*)-5-aryl-1-(2-hydroxyphenyl)-2,4-pentadien-1-ones give the desired backbone, but this method is limited to the preparation of 3-(α-alkylstyryl)chromones.[5] Another possibility is the disconnection of the C-α=C-β double bond; one possible synthetic path could be the Wittig reaction. (*E*)-2-Methyl-3-(3′,5′-dihydroxystyryl)chromone has been prepared from the appropriate benzaldehyde and a phosphonium salt generated from 3-(bromomethyl)chromone.[6] The main drawback of this approach is the troublesome selective monobromination of 3-methylchromone and the competitive nuclear bromination in the presence of hydroxy/alkoxy groups on the A-ring. The alternative Wittig route utilizes 3-formylchromones and benzylidenephosphoranes. These reactions give mixtures of (*Z*)- and (*E*)-3-styrylchromones, which are separable by chromatography on silica.[7] The major product in each case is the (*Z*) diastereomer, and this protocol provides the best method to prepare this isomer. The other synthetic route based on C-α=C-β disconnection is the Knoevenagel-type condensation of 3-formylchromones with activated methyl or methylene groups.[8] Recently, we have published a new and efficient method of this type. Treatment of 3-formylchromones with phenylacetic acids in pyridine solution and in the presence of potassium *tert*-butoxide either under conventional heating conditions or under microwave (MW) irradiation conditions resulted in a wide range of (*E*)-3-styrylchromones.[9] In this contribution we wish to disclose our newly developed solvent-free MW protocol using phenylmalonic acid as the source of the nucleophile. This method offers rapid and easy access to the target styryl derivatives.

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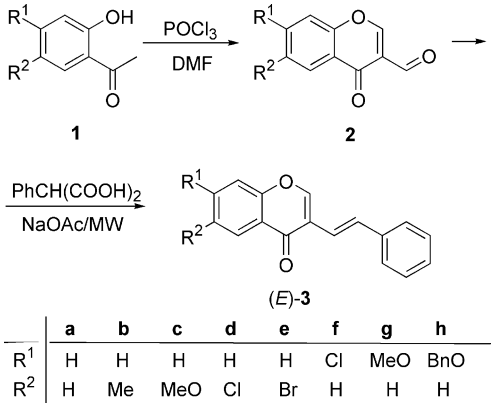
In continuation of our work on epoxidations of various oxygen heterocycles and their precursors with dioxiranes and other oxygen sources and on the use of (salen)manganese(III) complex (Jacobsen's complex) as a catalyst in these reactions,[10] we also started detailed studies on the oxidation of styrylchromones. Results on the oxidation of 2-styrylchromones with dimethyldioxirane (DMD) and also with hydrogen peroxide and iodosobenzene in the presence of Jacobsen's catalyst have recently been reported. Because of the low reactivities of these substrates and the highly unstable characters of the epoxides formed, oxidations should be quenched at low levels of conversion; thus, these transformations have only limited synthetic value.[11] In contrast, we have found that the epoxidation of 3-styrylchromones can be performed in a regio- and stereoselective manner and in good yields through the use of DMD or alkaline hydrogen peroxide (Weitz–Scheffer oxidation). Moreover, moderate enantioselectivities were observed when Weitz–Scheffer oxidation was conducted in the presence of cinchona-based quaternary ammonium salts as phase-transfer catalysts (Wynberg oxidation). The results of these experiments are also presented in this contribution.

Results and Discussion

Synthesis of (*E*)-Styrylchromones

In continuation of our work on the synthesis of (*Z*)-3-styrylchromones through the reactions of 3-formylchromones with phenylacetic acids in pyridine solution and in the presence of potassium *tert*-butoxide under microwave (MW) irradiation conditions[9] we have performed experiments using phenylmalonic acid as the precursor of the styryl unit. The choice of the reagent was based on the assumption that the incorporation of the second carboxyl group should enhance the C–H acidity and, therefore, promote the Knoevenagel condensation. The starting materials, 3-formylchromones **2** (Scheme 1), were prepared by Vilsmeier–Haack treatment of 2′-hydroxyacetophenones **1** according to literature procedures.[12,13] In the cases of acetophenones **1g** and **1h**, which contain strongly electron-donating methoxy or benzyloxy groups at their 4′-positions, the reactions took place with very low yields (7% and 26%, respectively). Similarly poor yields for chromone **2g** have been reported previously.[13,14] Product **2g** was obtained in better yield (24%) via the boron trifluoride complex of acetophenone **1g** by the modified protocol reported by Zúñiga and co-workers.[14] This approach was also tested for the development of an improved synthesis of benzyloxy derivative **2h**, but it failed due to the debenzylation of 4′-benzyloxy-2′-hydroxyacetophenone (**1h**) in the attempted synthesis of the borane intermediate.

To develop an environmentally benign approach to the MW-induced condensation of formyl derivatives **2** with phenylmalonic acid, we wished to investigate solvent-free transformations in the presence of various supports. Our first experiments were conducted in a simple domestic MW oven and indicated that reactions between aldehyde **2a** and



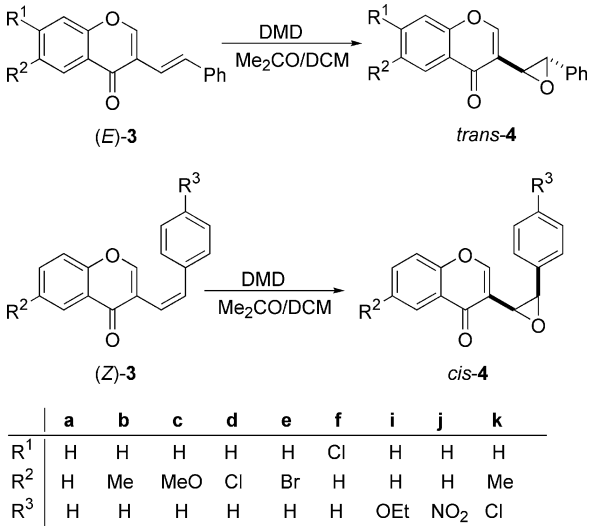
	a	b	c	d	e	f	g	h
R^1	H	H	H	H	H	Cl	MeO	BnO
R^2	H	Me	MeO	Cl	Br	H	H	H

Scheme 1.

2 equiv. of phenylmalonic acid performed on silica support could be useful. It was also found that two additional batches of phenylmalonic acid up to a total of 4 equiv. should be added to achieve acceptable (80–90%) levels of conversion and moderate (18–46%) yields. However, these results were not reproducible in a professional single-mode MW laboratory instrument, giving a further example of the drawbacks of the domestic apparatus in synthetic organic chemistry.[15] Of various supports (silica, sodium sulfate, sodium carbonate, sodium acetate, alumina, Montmorillonite K-10) tested in the single-mode MW apparatus, sodium acetate proved to be optimal. MW irradiation (100 °C interior temperature for 6 min) gave the desired 3-styrylchromones **3a**–**g** in moderate to good (47–61%) yields and with complete (*E*) diastereoselectivities, no (*Z*) diastereomers being detectable or isolable (Scheme 1). The simplicity of the aqueous workup and the fact that only very limited amounts of organic solvent were needed to provide analytically pure products (*E*)-**3a**–**g** make this procedure an efficient and "green" protocol for the synthesis of 3-styrylchromones.

Dimethyldioxirane Oxidation of 3-Styrylchromones

Treatment of dichloromethane (DCM) solutions of the prepared styrylchromones (*E*)-**3a**–**f** with 4 equiv. of dimethyldioxirane (DMD) in acetone[16] resulted in fast reactions and afforded good to excellent (55–95%) yields of single products that were identified as *trans*-3-(3-phenyloxiran-2-yl)chromones *trans*-**4a**–**f** (Scheme 2). Epoxidation took place with complete regio- and diastereoselectivity in all cases. The appearance of the α-H and β-H methine proton signals at δ = 3.82–3.84 ppm and δ = 4.13–4.16 ppm, respectively, in the ^{1}H NMR spectra, in addition to the appearance of the C-α and C-β methine carbon atom signals at δ = 55.9–56.2 ppm and δ = 54.0–54.6 ppm, respectively, in the ^{13}C NMR spectra, unequivocally confirmed that epoxidation had occurred at the styryl double bonds. The unchanged 2-H singlets in the ^{1}H NMR spectra, the C-2 and C-3 signals in the ^{13}C NMR spectra and the C=O stretching in the IR spectra clearly show that the C-2=C-3 double bonds remained intact.



	a	b	c	d	e	f	i	j	k
R^1	H	H	H	H	H	Cl	H	H	H
R^2	H	Me	MeO	Cl	Br	H	H	H	Me
R^3	H	H	H	H	H	H	OEt	NO_2	Cl

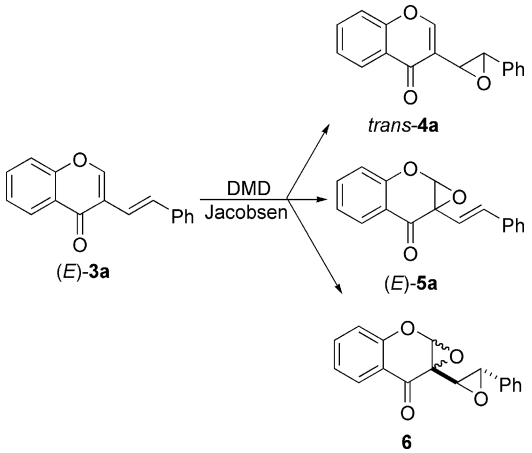
Scheme 2.

Epoxidation of the (*Z*) diastereomers gave similar results. DMD treatment of substrates (*Z*)-**3a**, (*Z*)-**3b** and (*Z*)-**3i**–**k** led to the formation of the *cis*-3-(3-phenyloxiran-2-yl)chromones *cis*-**4a**, *cis*-**4b** and *cis*-**4i**–**k** in excellent (80–96%) yields. Again, the epoxidations took place with complete regio- and diastereoselectivity. The relative configurations of the 2,3-disubstituted epoxides **4** were assigned on the basis of their $^3J_{2\text{-H},3\text{-H}}$ coupling constants: values of 1.5–2.1 Hz were measured for the *trans* isomers, whereas values of 3.9–4.3 Hz were found for the *cis* isomers.

Comparison of the ^{1}H NMR chemical shifts of the α-H and β-H methine proton signals revealed a difference of diagnostic value. While the α-H and β-H signals in the spectra of the *trans* isomers appeared at δ = 3.82–3.84 ppm and 4.13–4.16 ppm, the corresponding signals for the *cis* isomers showed marked downfield shifts: the α-H and β-H signals for these diastereomers were moved to δ = 4.40–4.47 ppm ($\Delta\delta \approx +0.6$ ppm) and 4.46–4.57 ppm ($\Delta\delta \approx +0.35$ ppm), respectively. This phenomenon could be interpreted in terms of the different conformations. In the dominant conformer of the *cis* isomers, both the α-H and the β-H hydrogen atoms are located in proximity to the carbonyl function of the chromone skeleton; thus, the anisotropic shift of the carbonyl group results in a downfield shift. In the *trans* diastereomers both hydrogen atoms are far from the carbonyl function.

The complete diastereoselectivity is in accordance with previously made observations during the DMD epoxidations. The (*E*) → *trans* vs. (*Z*) → *cis* selectivity could be interpreted on the basis of the concerted "butterfly" transition state of the dioxirane oxidations.[17,18] The exclusive attack of DMD at the styryl double bond can be explained in terms of the highly electrophilic character of the oxidizing agent.[18,19] Because of the electron-withdrawing effect of the C-4 carbonyl group, the C-2=C-3 double bond of the endocyclic α,β-enone system is electron-deficient; thus, it is less reactive toward electrophilic oxidants and tends to seek for nucleophilic oxidizing agents instead. Diminished reactivity of the chromone double bond toward DMD had previously been observed in the cases of the parent compound and of some derivatives substituted in their A-rings. In the oxidation of these substrates, very large amounts (12–25 equiv.) of DMD were required to obtain moderate (43–51%) levels of conversion in the epoxidation reactions.[20] Isoflavones (3-phenylchromones) showed somewhat higher reactivities but still needed large excesses (11–16 equiv.) of DMD for the completion of their epoxidations.[21] In contrast, a styryl group connected to the α-position of an α,β-enone system has normal or slightly increased electron density and is therefore sensitive to the attack of the electrophilic DMD. Similar discrimination has been reported in the case of methyl 2,6-octadienoate derivatives, in which the dioxirane exclusively attacked the electron-rich 6,7-double bond while the electron-poor 2,3-double bond remained intact.[22]

We have pointed out that the combination of DMD and Jacobsen's (salen)Mn^{III} complex represents a new, synthetically valuable enantioselective oxidizing system that works under mild and neutral conditions.[10e,10f,10h,23] This combination allowed us to synthesize enantiomerically enriched isoflavones in moderate (22–39%) yields, with the enantiomeric excesses varying over a wide range (21–90%) depending on the substitution patterns. It is noteworthy that large amounts of DMD (6–10 equiv.) were again needed to achieve these moderate yields. We also tested the DMD/(salen)Mn^{III} system in the epoxidation of (*E*)-3-styrylchromone [(*E*)-**3a**]. Unfortunately, the regioselectivity that we had observed in the reaction of DMD *in the absence of Mn^{III} complex* was completely lost, and only a mixture of the monoepoxides *trans*-**4a** and (*E*)-**5a** and the two diastereomers of diepoxide **6a** was detected by ^{1}H NMR spectroscopy. The ratio of the products depended on the amounts of the oxygen source used (Scheme 3). The attempted separation of the epoxides by column chromatography on silica failed, due to the complexities of the mixtures and the labile characters of the diepoxides. This loss of regioselectivity can be attributed to the enhanced reactivity of the actual oxidizing agent [i.e., the (oxido)Mn^V complex formed from the original Mn^{III} catalyst].



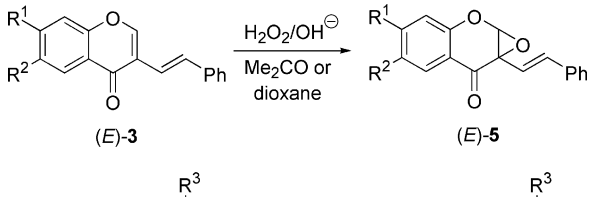
Scheme 3.

Weitz–Scheffer Oxidation of 3-Styrylchromones

To test the assumed reactivity of the 2,3-double bond of the chromone ring toward nucleophilic oxidizing agents, we initiated studies on the reactions of (*E*)- and (*Z*)-3-styrylchromones with alkaline hydrogen peroxide. Only a very few results on the Weitz–Scheffer epoxidation of chromones and isoflavones have so far been reported. In an early paper, the transformation of 2-methylisoflavone into its epoxide was reported as the only example.[24] Later, various 2-unsubstituted isoflavones were epoxidized by this methodology.[10g,25] The first synthesis of chromone epoxide under alkaline conditions by treatment either with hydrogen peroxide[26] or with cyclohexylidenebis(hydroperoxide)[27] was reported very recently. Bernini and co-workers[28] found that the Weitz–Scheffer epoxidation of chromones and isoflavones took place more rapidly in ionic liquid than in conventional solvents.

Treatment of 3-stryrylchromones (*E*)-**3a**–**f** and (*Z*)-**3a**,**b**,**i**–**k** with hydrogen peroxide and sodium hydroxide in various solvents (acetone, methanol, 1,4-dioxane and [bmim]PF_4 ionic liquid) afforded the expected 2,3-epoxy-3-styrylchromones (*E*)-**5a**–**f** and (*Z*)-**5a**,**b**,**j**,**k**, the best isolated yields [27–63% for the (*E*) and 69–82% for the (*Z*) derivatives] being obtained by using acetone or 1,4-dioxane (Scheme 4). Surprisingly, substrate (*Z*)-**3i** failed to give any oxidation product, with only the unreacted starting material being recoverable. The epoxidation again took place with complete regioselectivity, with only 2,3-epoxides being isolable or detectable. We were thus able to develop methods for the synthesis of either of the monoepoxides of the 3-styrylchromones simply by changing the electrophilicity/nucleophilicity of the oxidizing reagent. The structures of the obtained epoxides (*E*)-**5a**–**f** and (*Z*)-**5a**,**b**,**j**,**k** were confirmed by the marked upfield shifts of the 2-H signals to δ = 5.51–5.54 ppm in the cases of epoxides (*E*)-**5a**–**f** and to δ = 5.21–5.31 ppm in the cases of epoxides (*Z*)-**5a**,**b**,**j**,**k**. The different shifts can be attributed to the anisotropy effects of the styryl double bond and of the phenyl ring, which is in proximity to the 2-H atom in the (*Z*) compounds. The C-2, C-3 and C-4 atoms showed the expected chemical shifts (C-2 signal at δ = 61.1–62.4 ppm, C-3 signal at δ = 82.4–83.9 ppm and C-4 signal at δ = 187.1–188.7 ppm), characteristic of substituted chromanone rings. The C=O stretching in their IR spectra (1670–1688 cm^{-1}) provided further evidence of the presence of the chromanone units. The styryl double bonds and their relative configurations remained unchanged in all cases, as was confirmed by their chemical shifts in the ^1H and ^{13}C NMR spectra and their $^3J_{\alpha\text{-H},\beta\text{-H}}$ coupling constants. The weak cross-peaks in the COSY spectra between the signals of β-H and 2′,6′-H of derivative (*E*)-**5a** and of α-H and 2-H of derivative (*Z*)-**5a** gave further support for the stereochemistry. The complete assignment of the ^1H and ^{13}C NMR signals of isomers (*E*)- and (*Z*)-**5a** was carried out on the basis of their COSY and HETCORR spectra.

To make the assignment of the signals in the ^{13}C NMR spectra unambiguous we used the so-called J-echo (J-MOD, J-modulated spin-echo) technique in all cases. J-echo is a 1D method used for multiplicity editing. Through a judicious choice of delay periods in the spin-echo (set by the coupling constant), the experiment can be tuned to produce spectra in which different multiplicities produce differing responses. A typical experiment would provide spectra in which the quaternary and methylene signals would have the opposite phase to the methine and methyl resonances. However, in the ^{13}C NMR spectra of epoxides (*E*)-**5a**–**f** and (*Z*)-**5a**,**b**,**j**,**k** we observed an anomalous behaviour of the C-2 atoms, as they changed their phases and looked like quaternary or methylene signals. A probable explanation for this unique characteristic could be based on the difference in the $^1J_{C,H}$ coupling constant of C-2 in the epoxide ring and the average coupling constant (140 Hz) used in the J-echo experiment to set the measuring parameters. The smallest rings have much larger $^1J_{C,H}$ values (e.g. J = 160 Hz in cyclopropane[29]); thus, the C-2 signal has the opposite phase at the end of the experiment and appears as a methylene carbon atom.



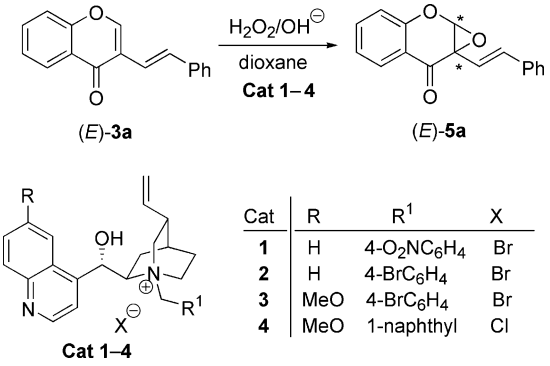
	a	b	c	d	e	f	i	j	k
R^1	H	H	H	H	H	Cl	H	H	H
R^2	H	Me	MeO	Cl	Br	H	H	H	Me
R^3	H	H	H	H	H	H	OEt	NO_2	Cl

Scheme 4.

Wynberg Oxidation of 3-Styrylchromones

One of the best enantioselective epoxidation methods for electron-poor alkenes such as α,β-enones and -enoates utilizes hydrogen peroxide or other organic peroxides in alkaline media and in the presence of chiral, nonracemic quaternary ammonium salts.[30] This methodology was invented and developed by Wynberg and co-workers,[31] who used ammonium salts derived from the cinchona alkaloids quinine and quinidine as phase-transfer catalysts (PTCs). Cinchoninium and cinchonidinium salts have also been found to be effective, although the details on the optimum conditions (substituents in the catalyst, solvent or base) are somewhat controversial.[32] Since we are strongly interested in the development of enantioselective epoxidation methods for oxygen-containing heterocycles, studies were commenced to evaluate the Wynberg oxidation in the 3-styrylchromone series.

We performed our experiments with PTCs **Cat 1**–**Cat 4** prepared from cinchonine and quinidine by standard methods using either benzyl bromides with strongly electron-withdrawing groups (EWGs) in their 4-positions or 1-naphthylmethyl chloride. The alkylating agents were chosen on the basis of the results published by Arai and co-workers;[32a,32b] the former family of catalysts had been found to be useful in the epoxidation of chalcones, whereas the latter was the PTC of choice in the case of 2-methyl-1,4-naphthoquinone (Scheme 5).



Cat	R	R^1	X
1	H	4-$O_2NC_6H_4$	Br
2	H	4-BrC_6H_4	Br
3	MeO	4-BrC_6H_4	Br
4	MeO	1-naphthyl	Cl

Scheme 5.

In the epoxidation of parent compound (*E*)-**3a**, two fractions of product (*E*)-**5a** were isolated. The first one precipitated directly from the reaction mixture, while the second was obtained by treatment of the mother liquor with water. The fractions were analyzed separately. Both were identified as pure epoxide (*E*)-**5a** by ^{1}H NMR spectroscopy, but their optical purities differed significantly. The first precipitate (Fraction 1) in all cases proved to be nearly racemic, showing only a marginal *ee* value, if any, whereas a moderate *ee* value was measured in most cases for the precipitate obtained from the mother liquor (Fraction 2) (Table 1). The best *ee* value was achieved with catalyst **Cat 1**, in which the strongly electron-withdrawing nitro group was attached at the 4-position of the benzyl group. This seems to support the observation of Arai and co-workers[32a,32b] on the beneficial effects of these types of substituents, although they found the bromo substituent to be superior to the nitro group. In contrast with their results, the incorporation of the bulkier naphthyl group did not improve the enantioselectivity.

Table 1. Results for the enantioselective epoxidation of (*E*)-3-styrylchromone [(*E*)-**3a**] in the presence of quaternary cinchona-based catalysts.

Cat	Fraction 1		Fraction 2		Weighted
	Yield (%)	*ee* (%)	Yield (%)	*ee* (%)	*ee* (%)[a]
1	33	0.6	31	46	23
2	20	0.9	32	25	16
3	37	0.9	26	33	14
4	31	0.6	42	27	16

[a] Defined as $(Y_1 \times ee_1 + Y_2 \times ee_2)/(Y_1 + Y_2)$; Y = Yield (%).

The moderate *ee* values (14–23%) are comparable with those (1–34%) found in the case of 2-methyl-1,4-naphthoquinone[32b] and provide further evidence for the conclusion that Wynberg oxidation works well only in the series of acyclic (*E*)-enones. At the same time, there is no effective metal-free method for the enantioselective epoxidation of the (*Z*) diastereomers or their endocyclic analogues yet.

Conclusion

Microwave-induced, solvent-free Knoevenagel condensation of phenylmalonic acid and various 3-formylchromones on sodium acetate support was found to be a convenient and environmentally benign method to produce (*E*)-3-styrylchromones in moderate to good yields and with complete diastereoselectivity.

Oxidation of 3-styrylchromones by DMD or hydrogen peroxide in alkaline medium were demonstrated to take place with complete regioselectivity; the former oxidant resulted in 3-(3-aryloxiran-2-yl)chromones exclusively, whereas the latter reagent led to the formation of 2,3-epoxy-3-styrylchromones as sole products. This selectivity could be interpreted in terms of the different electron density of the double bonds. In accordance with the previously postulated transition state of the dioxirane oxidations, the formation of 3-(3-aryloxiran-2-yl)chromones took place with complete diastereoselectivity, and the relative configuration was retained. Weitz–Scheffer oxidation in the presence of cinchona-based quaternary ammonium salts as phase-transfer catalysts provided the expected epoxides in poor enantiomeric excesses; this finding gives a further proof that this asymmetric oxidation works successfully only in the case of acyclic 2-alken-1-ones.

Experimental Section

General: Melting points: Boetius hot-stage, uncorrected values. IR: Perkin–Elmer 16 PC FT-IR; KBr pellets unless otherwise stated. NMR: Bruker AM 360 (360 MHz for ^{1}H; 90 MHz for ^{13}C). Recorded in $CDCl_3$ solution unless otherwise stated. Chemical shifts are given in δ relative to an internal standard TMS (δ = 0 ppm) or to the residual $CHCl_3$ (δ = 7.26 ppm for ^{1}H and δ = 77.0 ppm for ^{13}C). ^{13}C NMR assignments were supported by J-echo technique. MS: VG Trio-2 (EI, 70 eV). Optical rotations: Perkin–Elmer 341 (*l* = 1 dm), at 20 °C. Enantiomeric excesses (*ee*) were determined with a Jasco HPLC instrument (PU 980 solvent delivery system and pressure moderator, MD 910 diode array detector), Chiralcel OD column (hexane/propan-2-ol = 95:5, v = 1 mL min^{-1}). Elemental analysis: Carlo Erba. Microwave-induced syntheses: CEM Explorer. Thin-layer chromatography (TLC): Kieselgel 60 F_{254} (Merck) sheets, column chromatography: Kieselgel 60. Styrylchromones (*Z*)-**3a**,**b**,**i**–**k**[7] and DMD solution in acetone[16] were prepared according to literature procedures. $MgSO_4$ was used as drying agent.

Synthesis of 3-Formylchromones: 3-Formylchromones **2a**–**h** were synthesized by a modified Harnisch procedure.[12] Phosphorus oxychloride (1.9 mL, 3.126 g, 20.384 mmol) was added dropwise to a stirred and cooled (0–5 °C) solution of 2′-hydroxyacetophenone **1a**–**h** (10 mmol) in abs. DMF (5 mL) over 30 min, and the reaction mixture was then allowed to warm to room temperature and was kept at this temperature for 1 h. (If the stirring of the resulting slurry became difficult, a further 3–4 mL of abs. DMF was added.)

It was then poured onto crushed ice and stirred for 4 h, and the solid precipitate was filtered off, washed with water, dried and recrystallized from hexane/ethyl acetate. The products were identified by their melting points and ^{1}H NMR spectra. Compounds (yields): **2a**[12] (50%), **2b**[13] (71%), **2c**[13] (74%), **2d**[13] (55%), **2e**[33] (53%), **2g**[13] (7%).

7-Chloro-3-formylchromone (2f): Yield: 64%, m.p. 183–186 °C. ^{1}H NMR: δ = 7.5 (dd, $^3J_{H,H}$ = 8.5, 1.9 Hz, 1 H, 6-H), 7.6 (d, $^3J_{H,H}$ = 1.9 Hz, 1 H, 8-H), 8.2 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, 5-H), 8.5 (s, 1 H, 2-H), 10.4 (s, 1 H, 3-CHO) ppm. ^{13}C NMR: δ = 118.8 (C-8), 120.6 (C-4a), 123.9 (C-3), 127.6 (C-6), 135.1 (C-5), 141.2 (C-7), 156.4 (C-8a), 160.8 (C-2), 175.3 (C-4), 188.4 (CHO) ppm. IR: $\tilde{\nu}$ = 3081, 1655 (C=O), 1610 (C=C), 1554, 1433, 1341, 1300, 891, 780 cm^{-1}. MS: *m*/*z* (%) = 208 (2) $[M]^{+\cdot}$, 180 (100) [M – CO], 154 (17) [RDA fragment], 138 (25), 126 (12), 110 (7), 89 (14). $C_{10}H_5ClO_3$ (208.60): calcd. C 57.58, H 2.42; found C 57.77, H 2.29.

7-Benzyloxy-3-formylchromone (2h): Yield: 26%, m.p. 148–149 °C. ^{1}H NMR: δ = 5.2 (s, 2 H, 7-PhC**H**$_2$O), 7.0 (d, $^3J_{H,H}$ = 2.4 Hz, 1 H, 8-H), 7.1 (dd, $^3J_{H,H}$ = 8.9, 2.4 Hz, 1 H, 6-H), 7.3–7.4 (m, 5 H, Ph), 8.2 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, 5-H), 8.5 (s, 1 H, 2-H), 10.4 (s, 1 H, 3-CHO) ppm. ^{13}C NMR: δ = 70.8 (7-Ph**C**H$_2$O), 102.3 (C-8), 116.3 (C-6), 119.2, 120.4 (C-3, C-4a), 127.6, 127.7, 128.7, 129.0 (C-5, C-2′,6′, C-3′,5′, C-4′), 135.5 (C-1′), 158.1 (C-8a), 160.4 (C-2), 164.1 (C-7), 177.7 (C-4), 189.1 (CHO) ppm. IR: $\tilde{\nu}$ = 1642 (C=O), 1621 (C=C), 1556, 1441, 1303, 1270, 1242 (C–O–C), 994, 763 cm^{-1}. MS: *m*/*z* (%) = 280 (1) $[M]^{+\cdot}$, 252 (19) [M – CO], 91 (100) $[Bn]^+$, 65 (13). $C_{17}H_{12}O_4$ (280.27): calcd. C 72.85, H 4.32; found C 73.11, H 4.28.

3-Formyl-7-methoxychromone (**2g**) was also prepared by the procedure reported by Zúñiga.[14] The 2,2-difluoro-7-methoxy-4-methyl-4*H*-1,3,2-benzodioxaborin intermediate was obtained in 67% yield and transformed into chromone **2g**. The crude product was subjected to column chromatography (eluent: hexane/ethyl acetate, 1:1) to give a 24% yield (calculated based on the 1,3,2-dioxaborin intermediate).

Microwave-Induced Synthesis of (*E*)-3-Styrylchromones. General Procedure: A 3-formylchromone **2a**–**f** (0.804 mmol), phenylmalonic acid (288 mg, 1.599 mmol) and anhydrous sodium acetate (65 mg, 0.792 mmol) were thoroughly mixed without the use of any solvent in an MW tube and irradiated by using the MW program as follows. Power: 120 W, ramp time: 180 s; hold time: 240 s; temperature: 100 °C. After completion of the reaction, the mixture was treated with water (10 mL), and the solidified precipitate was washed with water (5 × 50 mL), then with diisopropyl ether (30 mL) and dried to give pure chromones **3a**–**f**. The known products were identified by their melting points and ^{1}H NMR spectra. Compounds (yields): **3a**[4] (61%), **3b**[7] (55%).

(*E*)-6-Methoxy-3-styrylchromone [(*E*)-3c]: Yellow crystals. Yield: 50%, m.p. 123–126 °C. ^{1}H NMR: δ = 3.9 (s, 3 H, 6-OMe), 7.1 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, α-H), 7.3 (m, 2 H, 3′,5′-H), 7.3–7.4 (m, 3 H, 2′,4′,6′-H), 7.5 (m, 2 H, 7-H, 8-H), 7.6 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, β-H), 7.6 (d, $^3J_{H,H}$ = 2.7 Hz, 1 H, 5-H), 8.1 (s, 1 H, 2-H) ppm. ^{13}C NMR: δ = 55.9 (6-OMe), 105.1 (C-5), 119.2, 119.4 (C-7, C-8), 120.9 (C-3), 123.6 (C-α), 124.6 (C-4a), 126.5 (C-2′,6′), 127.7 (C-4′), 128.6 (C-3′,5′), 131.4 (C-β), 137.3 (C-1′), 150.6 (C-8a), 152.8 (C-2), 157.0 (C-6), 176.3 (C-4) ppm. IR: $\tilde{\nu}$ = 1636 (C=O), 1620 (C=C), 1484, 1448, 1324, 1280, 1198 (C–O–C), 1144, 714 cm^{-1}. $C_{18}H_{14}O_3$ (278.30): calcd. C 77.68, H 5.07; found C 77.47, H 4.98.

(*E*)-6-Chloro-3-styrylchromone [(*E*)-3d]: Yellowish crystals. Yield: 48%, m.p. 198–201 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 7.1 (d, $^3J_{H,H}$ = 16.4 Hz, 1 H, α-H), 7.3 (m, 1 H, 4′-H), 7.4 (m, 2 H, 3′,5′-H), 7.5 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, 2′,6′-H), 7.6 (dd, $^3J_{H,H}$ = 8.9, 2.6 Hz, 1 H, 7-H), 7.7 (d, $^3J_{H,H}$ = 16.4 Hz, 1 H, β-H), 7.8 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, 8-H), 8.1 (d, $^3J_{H,H}$ = 2.6 Hz, 1 H, 5-H), 8.7 (s, 1 H, 2-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 119.3 (C-8), 120.5 (C-3), 121.0 (C-α), 124.2 (C-β), 124.5 (C-4a), 126.2 (C-2′,6′), 127.8 (C-4′), 128.8 (C-3′,5′), 130.0 (C-6), 131.1 (C-5), 133.9 (C-7), 137.1 (C-1′), 149.0 (C-2), 153.8 (C-8a), 174.4 (C-4) ppm. IR: $\tilde{\nu}$ = 1642 (C=O), 1608 (C=C), 1556, 1468, 1448, 1272, 1168, 966, 818, 744 cm^{-1}. $C_{17}H_{11}ClO_2$ (282.72): calcd. C 72.22, H 3.92; found C 72.45, H 4.09.

(*E*)-6-Bromo-3-styrylchromone [(*E*)-3e]: Yellow crystals. Yield: 60%, m.p. 192–195 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 7.1 (d, $^3J_{H,H}$ = 16.4 Hz, 1 H, α-H), 7.3 (m, 1 H, 4′-H), 7.4 (m, 2 H, 3′,5′-H), 7.6 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, 2′,6′-H), 7.7 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, 8-H), 7.8 (d, $^3J_{H,H}$ = 16.4 Hz, 1 H, β-H), 8.0 (dd, $^3J_{H,H}$ = 8.9, 2.4 Hz, 1 H, 7-H), 8.2 (d, $^3J_{H,H}$ = 2.4 Hz, 1 H, 5-H), 8.7 (s, 1 H, 2-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 117.9 (C-6), 119.3 (C-8), 120.5 (C-3), 121.1 (C-α), 124.8 (C-4a), 126.2 (C-2′,6′), 127.3, 127.8 (C-β, C-4′), 128.7 (C-3′,5′), 131.1 (C-5), 136.6 (C-7), 137.0 (C-1′), 154.1 (C-8a), 155.1 (C-2), 174.3 (C-4) ppm. IR: $\tilde{\nu}$ = 1604 (C=O), 1606 (C=C), 1554, 1464, 1436, 1272, 1152, 748 cm^{-1}. $C_{17}H_{11}BrO_2$ (327.17): calcd. C 62.41, H 3.39; found C 62.64, H 3.32.

(*E*)-7-Chloro-3-styrylchromone [(*E*)-3f]: Yellow crystals. Yield: 60%, m.p. 192–195 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 7.1 (d, $^3J_{H,H}$ = 16.3 Hz, 1 H, α-H), 7.3 (m, 1 H, 4′-H), 7.40 (m, 2 H, 3′,5′-H), 7.5 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, 2′,6′-H), 7.6 (dd, $^3J_{H,H}$ = 8.5, 1.9 Hz, 1 H, 6-H), 7.8 (d, $^3J_{H,H}$ = 16.3 Hz, 1 H, β-H), 7.9 (d, $^3J_{H,H}$ = 1.9 Hz, 1 H, 8-H), 8.1 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, 5-H), 8.7 (s, 1 H, 2-H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 120.0 (C-8), 121.0 (C-α), 123.4 (C-3), 124.6 (C-4a), 127.7 (C-6), 128.2 (C-2′,6′), 129.3, 129.6 (C-β, C-4′), 130.5 (C-3′,5′), 133.6 (C-5), 139.5 (C-1′), 140.7 (C-7), 156.5 (C-2), 157.7 (C-8a), 176.8 (C-4) ppm. IR: $\tilde{\nu}$ = 1644, 1626 (C=O), 1608 (C=C), 1556, 1428, 1150, 972, 892, 862, 778, 746, 690 cm^{-1}. $C_{17}H_{11}ClO_2$ (282.72): calcd. C 72.22, H 3.92; found C 72.13, H 3.99.

(*E*)-7-Methoxy-3-styrylchromone [(*E*)-3g]: This compound was purified by column chromatography (eluent: hexane/ethyl acetate, 1:1). Yellow crystals. Yield: 47%, m.p. 151–152 °C. ^{1}H NMR: δ = 3.9 (s, 3 H, 7-OMe), 6.8 (d, $^3J_{H,H}$ = 2.2 Hz, 1 H, 8-H), 6.9 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, α-H), 7.0 (dd, $^3J_{H,H}$ = 9.2, 2.2 Hz, 1 H, 6-H), 7.3 (m, 1 H, 4′-H), 7.4 (m, 2 H, 3′,5′-H), 7.5 (m, 2 H, 2′,6′-H), 7.6 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, β-H), 8.0 (s, 1 H, 2-H), 8.2 (d, $^3J_{H,H}$ = 9.2 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 55.8 (7-OMe), 100.1 (C-8), 114.7 (C-6), 118.3 (C-3), 119.2 (C-α), 121.7 (C-4a), 126.6 (C-2′,6′), 127.6, 127.8 (C-5, C-4′), 128.6 (C-3′,5′), 131.5 (C-β), 137.4 (C-1′), 152.5 (C-2), 157.6 (C-8a), 164.0 (C-7), 176.0 (C-4) ppm. IR: $\tilde{\nu}$ = 3060, 3003 (epoxide), 2942, 2838 (MeO), 1640 (C=O), 1616 (C=C), 1439, 1402, 1269, 1243, 1201 (C–O–C and epoxide), 1173, 1097, 1026, 970, 834, 747, 695 cm^{-1}. $C_{18}H_{14}O_3$ (278.30): calcd. C 77.68, H 5.07; found C 77.54, H 4.94.

Synthesis of 3-(3-Phenyloxiran-2-yl)chromones by Dimethyldioxirane Oxidation of 3-Styrylchromones. General Procedure: Dimethyldioxirane solution (40 mL, 0.078 M in acetone) was added to a stirred solution of a 3-styrylchromone [(*E*)-**3a**–**f** or (*Z*)-**3a**,**b**,**i**–**k**, 0.75 mmol] in dichloromethane (10 mL), and the mixture was allowed to react at room temperature. The reaction was complete within 2 h. The reaction mixture was concentrated, and the solid residue was treated with hexane, filtered and recrystallized from a solvent (indicated in parentheses) or purified by column chromatography (1,2-dichloroethane). The reactions of (*E*)-3-styrylchromones resulted in the formation of *trans*-3-(3-phenyloxiran-2-yl)chromones *trans*-**3a**–**f**, whereas the oxidation of (*Z*)-3-styryl-

chromones led exclusively to *cis*-3-(3-phenyloxiran-2-yl)chromones *cis*-**3a**,**b**,**i**–**k**. No other diastereomer was detected in the worked up reaction mixtures in any case.

***trans*-3-(3-Phenyloxiran-2-yl)chromone (*trans*-4a):** Off-white crystals. Yield: 88%, m.p. 110–112 °C (hexane/EtOAc). ^{1}H NMR: δ = 3.8 (d, $^3J_{H,H}$ = 1.9 Hz, 1 H, α-H), 4.2 (d, $^3J_{H,H}$ = 1.9 Hz, 1 H, β-H), 7.3–7.5 (m, 7 H, 6-H, 8-H, Ph), 7.7 (m, 1 H, 7-H), 7.9 (s, 1 H, 2-H), 8.2 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 56.1 (C-α), 62.4 (C-β), 118.2 (C-8), 121.1 (C-4a), 123.6 (C-3), 125.4, 125.6 (C-6, C-4′), 125.7 (C-2′,6′), 128.5 (C-5, C-3′,5′), 133.6 (C-7), 133.7 (C-1′), 153.4 (C-2), 156.2 (C-8a), 176.8 (C-4) ppm. IR: $\tilde{\nu}$ = 3066 (epoxide), 1632 (C=O), 1608 (C=C), 1574, 1468, 1432, 1390, 1350, 1318, 1224 (epoxide), 1168, 876, 856, 762, 732 cm^{-1}. $C_{17}H_{12}O_3$ (264.28): calcd. C 77.26, H 4.58; found C 77.39, H 4.76.

***cis*-3-(3-Phenyloxiran-2-yl)chromone (*cis*-4a):** Off-white crystals. Yield: 80%, m.p. 175–176.5 °C (hexane). ^{1}H NMR: δ = 4.4 (d, $^3J_{H,H}$ = 4.2 Hz, 1 H, α-H), 4.5 (d, $^3J_{H,H}$ = 4.2 Hz, 1 H, β-H), 7.2–7.4 (m, 7 H, 6-H, 8-H, Ph), 7.6 (m, 1 H, 7-H), 7.7 (s, 1 H, 2-H), 8.1 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 54.0 (C-α), 59.5 (C-β), 118.1 (C-8), 118.2 (C-4a), 123.3 (C-3), 125.2, 125.5 (C-6, C-4′), 126.6 (C-2′,6′), 127.8 (C-5), 128.0 (C-3′,5′), 133.8 (C-7), 136.3 (C-1′), 152.4 (C-2), 156.3 (C-8a), 176.9 (C-4) ppm. IR: $\tilde{\nu}$ = 3060 (epoxide), 1654 (C=O), 1612 (C=C), 1466, 1346, 1312, 1218 (epoxide), 1196, 854, 824, 760, 746 cm^{-1}. $C_{17}H_{12}O_3$ (264.28): calcd. C 77.26, H 4.58; found C 77.12, H 4.54.

***trans*-6-Methyl-3-(3-phenyloxiran-2-yl)chromone (*trans*-4b):** This compound was purified by column chromatography. Off-white crystals. Yield: 55%, m.p. 130–131 °C. ^{1}H NMR: δ = 2.5 (s, 3 H, 6-Me), 3.8 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, α-H), 4.2 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, β-H), 7.3–7.4 (m, 6 H, 8-H, Ph), 7.5 (dd, $^3J_{H,H}$ = 8.3, 1.4 Hz, 1 H, 7-H), 7.9 (s, 1 H, 2-H), 8.0 (d, $^3J_{H,H}$ = 1.4 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 20.9 (6-Me), 56.2 (C-α), 62.4 (C-β), 117.9 (C-8), 120.9 (C-4a), 123.3 (C-3), 124.9 (C-4′), 125.7 (C-2′,6′), 128.5 (C-5, C-3′,5′), 135.1 (C-7), 135.4, 136.9 (C-6, C-1′), 152.4 (C-2), 154.6 (C-8a), 176.9 (C-4) ppm. IR: $\tilde{\nu}$ = 3072 (epoxide), 1650 (C=O), 1616 (C=C), 1576, 1484, 1458, 1420, 1340, 1314, 1232 (epoxide), 1204, 1168, 1144, 870, 836, 782, 716 cm^{-1}. $C_{18}H_{14}O_3$ (278.30): calcd. C 77.68, H 5.07; found C 77.84, H 4.89.

***cis*-6-Methyl-3-(3-phenyloxiran-2-yl)chromone (*cis*-4b):** Off-white crystals. Yield: 80%, m.p. 146–147 °C (hexane). ^{1}H NMR: δ = 2.4 (s, 3 H, 6-Me), 4.4 (d, $^3J_{H,H}$ = 3.9 Hz, 1 H, α-H), 4.5 (d, $^3J_{H,H}$ = 3.9 Hz, 1 H, β-H), 7.1–7.3 (m, 6 H, 8-H, Ph), 7.4 (dd, $^3J_{H,H}$ = 8.3, 1.5 Hz, 1 H, 7-H), 7.7 (s, 1 H, 2-H), 7.9 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 20.8 (6-Me), 54.0 (C-α), 59.5 (C-β), 117.9 (C-8), 118.0 (C-4a), 123.0 (C-3), 124.7 (C-4′), 126.7 (C-2′,6′), 127.7 (C-5), 128.0 (C-3′,5′), 134.9 (C-7), 133.8, 135.2 (C-6, C-1′), 153.4 (C-2), 154.5 (C-8a), 176.9 (C-4) ppm. IR: $\tilde{\nu}$ = 3030 (epoxide), 1648 (C=O), 1616 (C=C), 1486, 1448, 1438, 1336, 1312, 1234 (epoxide), 1200, 1168, 884, 844, 818, 744, 700 cm^{-1}. $C_{18}H_{14}O_3$ (278.30): calcd. C 77.68, H 5.07; found C 77.59, H 5.00.

***trans*-6-Methoxy-3-(3-phenyloxiran-2-yl)chromone (*trans*-4c):** Off-white crystals. Yield: 71%, m.p. 134–138 °C (hexane). ^{1}H NMR: δ = 3.8 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, α-H), 3.9 (s, 3 H, 6-OMe), 4.2 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, β-H), 7.2 (dd, $^3J_{H,H}$ = 9.0, 2.9 Hz, 1 H, 7-H), 7.3–7.4 (m, 5 H, Ph), 7.5 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, 7-H), 7.6 (d, $^3J_{H,H}$ = 2.9 Hz, 1 H, 5-H), 7.9 (s, 1 H, 2-H) ppm. ^{13}C NMR: δ = 55.9, 56.2 (C-α, 6-MeO), 62.4 (C-β), 104.6 (C-5), 119.6 (C-8), 120.3 (C-4a), 124.0 (C-7), 124.2 (C-3), 125.7 (C-2′,6′), 128.5 (C-3′,5′), 136.3 (C-1′), 151.2 (C-8a), 152.3 (C-2), 157.1 (C-6), 176.7 (C-4) ppm. IR: $\tilde{\nu}$ = 3060 (epoxide), 2968, 2943, 2842 (OMe), 1646 (C=O), 1612 (C=C), 1484, 1470, 1439, 1313, 1248, 1202 (epoxide), 1183, 1141, 1127, 874, 787, 713 cm^{-1}. $C_{18}H_{14}O_4$ (294.30): calcd. C 73.46, H 4.79; found C 73.71, H 4.91.

***trans*-6-Chloro-3-(3-phenyloxiran-2-yl)chromone (*trans*-4d):** This compound was purified by column chromatography. Off-white crystals. Yield: 61%, m.p. 144.5–145.5 °C. ^{1}H NMR: δ = 3.8 (d, $^3J_{H,H}$ = 1.7 Hz, 1 H, α-H), 4.1 (d, $^3J_{H,H}$ = 1.7 Hz, 1 H, β-H), 7.3–7.4 (m, 5 H, Ph), 7.5 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, 8-H), 7.6 (dd, $^3J_{H,H}$ = 8.6, 2.2 Hz, 1 H, 7-H), 7.9 (s, 1 H, 2-H), 8.2 (d, $^3J_{H,H}$ = 2.2 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 55.9 (C-α), 62.5 (C-β), 120.0 (C-8), 121.3 (C-4a), 124.5 (C-3), 125.1 (C-4′), 125.8 (C-2′,6′), 128.5 (C-3′,5′), 128.6 (C-5), 131.4 (C-6), 134.1 (C-7), 136.1 (C-1′), 152.7 (C-2), 154.7 (C-8a), 175.7 (C-4) ppm. IR: $\tilde{\nu}$ = 3084 (epoxide), 1650 (C=O), 1606 (C=O), 1466, 1446, 1350, 1156, 826, 698 cm^{-1}. $C_{17}H_{11}ClO_3$ (298.72): calcd. C 68.35, H 3.71; found C 68.12, H 3.96.

***trans*-6-Bromo-3-(3-phenyloxiran-2-yl)chromone (*trans*-4e):** This compound was purified by column chromatography. Off-white crystals. Yield: 95%, m.p. 154–156 °C. ^{1}H NMR: δ = 3.8 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, α-H), 4.2 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, β-H), 7.3–7.4 (m, 6 H, 8-H, Ph), 7.8 (dd, $^3J_{H,H}$ = 9.0, 2.4 Hz, 1 H, 7-H), 7.9 (s, 1 H, 2-H), 8.3 (d, $^3J_{H,H}$ = 2.4 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 55.9 (C-α), 62.5 (C-β), 118.9 (C-6), 120.2 (C-8), 121.5 (C-4a), 124.9 (C-3), 125.8 (C-2′,6′), 128.5 (C-3′,5′), 128.3, 128.6 (C-4′, C-5), 136.1 (C-1′), 136.8 (C-7), 152.6 (C-2), 155.1 (C-8a), 175.7 (4-C) ppm. IR: $\tilde{\nu}$ = 3062 (epoxide), 1648 (C=O), 1604 (C=C), 1460, 1442, 1304, 1210 (epoxide), 1154, 878, 824, 780, 736, 696 746 cm^{-1}. $C_{17}H_{11}BrO_3$ (343.17): calcd. C 59.50, H 3.23; found C 59.55, H 3.40.

***trans*-7-Chloro-3-(3-phenyloxiran-2-yl)chromone (*trans*-4f):** Off-white crystals. Yield: 74%, m.p. 174–177 °C (hexane). ^{1}H NMR: δ = 3.8 (d, $^3J_{H,H}$ = 1.6 Hz, 1 H, α-H), 4.1 (d, $^3J_{H,H}$ = 1.6 Hz, 1 H, β-H), 7.3–7.4 (m, 6 H, 6-H, Ph), 7.5 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, 8-H), 7.9 (s, 1 H, 2-H), 8.2 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 55.9 (C-α), 62.5 (C-β), 118.3 (C-8), 121.7 (C-4a), 122.2 (C-3), 125.8 (C-2′,6′), 126.3 (C-4′), 127.1 (C-6), 128.5 (C-3′,5′), 128.6 (C-5), 136.1 (C-1′), 140.0 (C-7), 152.5 (C-2), 156.5 (C-8a), 176.1 (C-4) ppm. IR: $\tilde{\nu}$ = 3076 (epoxide), 1654 (C=O), 1608 (C=C), 1560, 1440, 1428, 1356, 1210 (epoxide), 1154, 870, 810, 790, 756, 702 cm^{-1}. $C_{17}H_{11}ClO_3$ (298.72): calcd. C 68.35, H 3.71; found C 68.49, H 3.77.

***cis*-3-[3-(4-Ethoxyphenyl)oxiran-2-yl]chromone (*cis*-4i):** Off-white crystals. Yield: 92%, m.p. 140–142 °C (*i*Pr_2O/hexane). ^{1}H NMR: δ = 1.4 (t, $^3J_{H,H}$ = 6.8 Hz, 1 H, Me), 3.9 (q, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH_2), 4.4 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, α-H), 4.5 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, β-H), 6.8 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, 3′,5′-H), 7.2 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, 2′,6′-H), 7.3–7.4 (m, 2 H, 6-H, 8-H), 7.6 (m, 1 H, 7-H), 7.7 (s, 1 H, 2-H), 8.2 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 14.7 (Me), 54.0 (C-α), 59.3 (C-β), 63.3 (CH_2), 114.1 (C-2′,6′), 118.1 (C-8), 118.3 (C-4a), 123.4 (C-3), 125.2, 125.5 (C-5, C-6), 125.6 (C-1′), 127.8 (C-3′,5′), 133.6 (C-7), 153.5 (C-2), 156.2 (C-8a), 158.5 (C-4′), 176.9 (C-4) ppm. IR: $\tilde{\nu}$ = 3074 (epoxide), 2874 (OEt), 1646 (C=O), 1610 (C=C), 1512, 1466, 1348, 1242 (C–O–Et), 1172, 1052 (C–O–Et), 820, 756 cm^{-1}. $C_{19}H_{16}O_4$ (308.33): calcd. C 74.01, H 5.23; found C 74.16, H 5.11.

***cis*-3-[3-(4-Nitrophenyl)oxiran-2-yl]chromone (*cis*-4j):** Off-white crystals. Yield: 93%, m.p. 185–187 °C (*i*Pr_2O/hexane). ^{1}H NMR: δ = 4.5 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, α-H), 4.6 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, β-H), 7.4 (m, 2 H, 6-H, 8-H), 7.5 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, 2′,6′-H), 7.6 (m, 1 H, 7-H), 7.8 (s, 1 H, 2-H), 8.1 (overlapping d's, 3 H, 5-H, 3′,5′-H) ppm. ^{13}C NMR: δ = 54.6 (C-α), 58.4 (C-β), 117.7 (C-4a), 118.2 (C-8), 123.2 (C-3), 123.3 (C-2′,6′), 125.4, 125.5 (C-5, C-6), 127.5 (C-3′,5′), 134.0 (C-7), 141.2 (C-1′), 147.6 (C-4′), 153.2 (C-2), 156.2 (C-8a), 176.5 (C-4) ppm. IR: $\tilde{\nu}$ = 1646 (C=O), 1610

(C=C), 1522 (NO_2), 1466, 1348 (NO_2), 1106, 860, 760 cm^{-1}. $C_{17}H_{11}NO_5$ (309.27): calcd. C 66.02, H 3.58, N 4.53; found C 65.87, H 3.42, N 4.75.

***cis*-3-[3-(4-Chlorophenyl)oxiran-2-yl]-6-methylchromone (*cis*-4k):** Off-white crystals. Yield: 96%, m.p. 144–147 °C (hexane). ^1H NMR: δ = 2.4 (s, 3 H, 6-Me), 4.4 (dd, $^3J_{H,H}$ = 4.3, 1.1 Hz, 1 H, α-H), 4.5 (d, $^3J_{H,H}$ = 4.3 Hz, 1 H, β-H), 7.2 (br. s, 4 H, 2′,3′,5′,6′-H), 7.3 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, 8-H), 7.4 (dd, $^3J_{H,H}$ = 8.6, 2.2 Hz, 1 H, 7-H), 7.7 (d, $^3J_{H,H}$ = 1.1 Hz, 1 H, 2-H), 7.9 (d, $^3J_{H,H}$ = 2.2 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 20.5 (6-Me), 54.1 (C-α), 58.7 (C-β), 117.9 (C-4a), 118.0 (C-8), 123.1 (C-3), 124.9 (C-5), 128.1, 128.4 (C-2′,6′, C-3′,5′), 132.6, 133.8 (C-6, C-4′), 135.2 (C-7), 135.5 (C-1′), 153.6 (C-2), 154.8 (C-8a), 177.2 (C-4) ppm. IR: $\tilde{\nu}$ = 1650 (C=O), 1619 (C=C), 1488, 1436, 1424, 1317, 1166, 1088, 843 cm^{-1}. $C_{18}H_{13}ClO_3$ (312.75): calcd. C 69.13, H 4.19; found C 68.97, H 4.03.

Synthesis of 2,3-Epoxy-3-styrylchroman-4-ones by Weitz–Scheffer Oxidation of 3-Styrylchromones. General Procedure: Hydrogen peroxide (30%, 0.5 mL) and then sodium hydroxide solution (8% 0.24 mL) were added to a cooled (0 °C) and stirred solution of a 3-styrylchromone [(*E*)-**3a**–**f** or (*Z*)-**3a**,**b**,**i**–**k** (0.400 mmol)] in acetone or 1,4-dioxane (5 mL), and the reaction was monitored by TLC (PhMe). After completion of the reaction (0.25–1.5 h), the mixture was poured onto crushed ice, and the precipitate was filtered off and crystallized from hexane or hexane/ethyl acetate. The reactions of (*E*)-3-styrylchromones resulted in the formation of (*E*)-2,3-epoxy-3-styrylchroman-4-ones (*E*)-**5a**–**f**, whereas the oxidation of (*Z*)-3-styrylchromones led exclusively to (*Z*)-2,3-epoxy-3-styrylchroman-4-ones (*Z*)-**5a**,**b**,**i**–**k**. No other diastereomer or regioisomer was detected in the worked up reaction mixture in any case.

(*E*)-2,3-Epoxy-3-styrylchroman-4-one [(*E*)-5a]: This reaction was performed in acetone solution. Yellowish crystals. Yield: 52%, m.p. 135–137 °C (hexane/ethyl acetate). ^1H NMR: δ = 5.5 (s, 1 H, 2-H), 6.8 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, β-H), 6.9 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, α-H), 7.1 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, 8-H), 7.2 (m, 1 H, 6-H), 7.3–7.4 (m, 3 H, 3′,5′-H, 4′-H), 7.5 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, 2′,6′-H), 7.6 (m, 1 H, 7-H), 8.0 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 62.3 (C-3), 83.6 (C-2), 117.5, 117.9 (C-6, C-8), 120.1 (C-1′), 123.4 (C-4′), 126.9 (C-2′,6′), 127.6 (C-α), 128.6 (C-β), 128.7 (C-3′,5′), 133.8 (C-5), 135.5 (C-4a), 136.0 (C-7), 155.1 (C-8a), 188.3 (C-4) ppm. IR: $\tilde{\nu}$ = 3060, 3034 (epoxide), 1678 (C=O), 1654, 1604 (C=C), 1584, 1478, 1464, 1350, 1330, 1304, 1278, 1208 (epoxide), 1148, 1102, 1080, 960, 908, 834, 762, 742 760 cm^{-1}. $C_{17}H_{12}O_3$ (264.28): calcd. C 77.26, H 4.58; found C 77.28, H 4.25. When the reaction was performed with benzyltrimethylammonium hydroxide (Triton B, 90 μL of a 40% methanolic solution), (*E*)-**5a** was obtained in 63% yield, m.p. 131–134 °C.

(*Z*)-2,3-Epoxy-3-styrylchroman-4-one [(*Z*)-5a]: This reaction was performed in acetone solution. Yellowish oil. Yield: 81%. ^1H NMR: δ = 5.2 (s, 1 H, 2-H), 6.0 (d, $^3J_{H,H}$ = 11.9 Hz, 1 H, α-H), 7.0 (d, $^3J_{H,H}$ = 11.9 Hz, 1 H, β-H), 7.1 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, 8-H), 7.2 (m, 6 H, 6-H, Ph), 7.6 (m, 1 H, 7-H), 8.0 (dd, $^3J_{H,H}$ = 8.0, 1.4 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 61.1 (C-3), 82.8 (C-2), 118.0 (C-8), 119.5 (C-1′), 120.0 (C-α), 123.4 (C-6), 127.5 (C-5), 128.3 (C-2′,6′), 128.4 (C-4′), 128.6 (C-3′,5′), 135.4 (C-4a), 136.2 (C-7), 137.2 (C-β), 155.2 (C-8a), 188.1 (C-4) ppm. IR: $\tilde{\nu}$ = 3028 (epoxide), 1688, 1682 (C=O), 1608 (C=C), 1464, 1336, 1208 (epoxide), 1120, 1082, 758, 700 cm^{-1}. $C_{17}H_{12}O_3$ (264.28): calcd. C 77.26, H 4.58; found C 77.39, H 4.43.

(*E*)-2,3-Epoxy-6-methyl-3-styrylchroman-4-one [(*E*)-5b]: This reaction was performed in dioxane solution. White crystals. Yield: 27%, m.p. 93–96 °C (hexane). ^1H NMR: δ = 2.4 (s, 3 H, 6-Me), 5.5 (s, 1 H, 2-H), 6.8 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, β-H), 6.9 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, α-H), 7.0 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, 8-H), 7.3–7.4 (m, 4 H, 7-H, 3′,5′-H, 4′-H), 7.5 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, 2′,6′-H), 7.8 (s, 1 H, 5-H) ppm. ^{13}C NMR: δ = 20.5 (6-Me), 62.3 (C-3), 83.6 (C-2), 117.7, 117.8 (C-8, C-4′), 119.7 (C-1′), 126.9 (C-2′,6′), 127.2 (C-α), 128.6 (C-β), 128.7 (C-3′,5′), 133.1 (C-6), 133.7 (C-5), 135.5 (C-4a), 137.1 (C-7), 153.2 (C-8a), 188.5 (C-4) ppm. IR: $\tilde{\nu}$ = 3060, 3026 (epoxide), 2920 (Me), 1678 (C=O), 1618 (C=C), 1488, 1450, 1424, 1318, 1296, 1216 (epoxide), 1204, 1130, 1104, 966, 922, 826, 800, 738 cm^{-1}. $C_{18}H_{14}O_3$ (278.30): calcd. C 77.68, H 5.07; found C 77.83, H 4.92.

(*Z*)-2,3-Epoxy-6-methyl-3-styrylchroman-4-one [(*Z*)-5b]: This reaction was performed in dioxane solution. White crystals. Yield: 69%, m.p. 93–96 °C (hexane). ^1H NMR: δ = 2.3 (s, 3 H, 6-Me), 5.2 (s, 1 H, 2-H), 6.0 (d, $^3J_{H,H}$ = 11.9 Hz, 1 H, α-H), 6.9 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, 8-H), 7.0 (d, $^3J_{H,H}$ = 11.9 Hz, 1 H, β-H), 7.1–7.3 (m, 5 H, Ph), 7.4 ($^3J_{H,H}$ = 7.9 Hz, 1 H, 7-H), 7.8 (dd, $^3J_{H,H}$ = 8.0, 1.4 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 20.5 (6-Me), 61.2 (C-3), 82.8 (C-2), 117.8 (C-8), 119.1 (C-1′), 120.1 (C-α), 127.2 (C-5), 128.2 (C-2′,6′), 128.3 (C-4′), 128.5 (C-3′,5′), 133.1 (C-6), 135.4 (C-4a), 137.0, 137.2 (C-7, C-β), 153.3 (C-8a), 188.3 (C-4) ppm. IR: $\tilde{\nu}$ = 3066, 3028 (epoxide), 1680 (C=O), 1618 (C=C), 1488, 1312, 1218 (epoxide), 1206, 1132, 1090, 934, 806 cm^{-1}. $C_{18}H_{14}O_3$ (278.30): calcd. C 77.68, H 5.07; found C 77.60, H 5.17.

(*E*)-2,3-Epoxy-6-methoxy-3-styrylchroman-4-one [(*E*)-5c]: This reaction was performed in dioxane solution. White crystals. Yield: 34%, m.p. 76–78 °C (hexane). ^1H NMR: δ = 3.8 (s, 3 H, 6-OMe), 5.5 (s, 1 H, 2-H), 6.8 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, β-H), 6.9 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, α-H), 7.1 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, 8-H), 7.2 (dd, $^3J_{H,H}$ = 9.0, 2.9 Hz, 1 H, 7-H), 7.3–7.4 (m, 4 H, 5-H, 3′,5′-H, 4′-H), 7.5 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, 2′,6′-H) ppm. ^{13}C NMR: δ = 56.2 (6-MeO), 62.4 (C-3), 83.9 (C-2), 108.1 (C-8), 118.1 (C-7), 119.5 (C-4′), 120.5 (C-1′), 125.5 (C-α), 127.3 (C-2′,6′), 128.9 (C-β), 129.0 (C-3′,5′), 134.1 (C-5), 135.9 (C-4a), 149.9 (C-8a), 155.8 (C-6), 188.7 (C-4) ppm. IR: $\tilde{\nu}$ = 3059, 3027 (epoxide), 2937, 2945, 2834 (MeO), 1680 (C=O), 1617 (C=C), 1490, 1443, 1431, 1292, 1274, 1201 (epoxide), 1142, 1077, 1030, 822, 757, 700 cm^{-1}. $C_{18}H_{14}O_4$ (294.30): calcd. C 73.46, H 4.79; found C 73.51, H 4.75.

(*E*)-6-Chloro-2,3-epoxy-3-styrylchroman-4-one [(*E*)-5d]: This reaction was performed in acetone solution. Brownish crystals. Yield: 51%, m.p. 119–122 °C (hexane/ethyl acetate). ^1H NMR: δ = 5.5 (s, 1 H, 2-H), 6.7 (d, $^3J_{H,H}$ = 16.6 Hz, 1 H, β-H), 6.8 (d, $^3J_{H,H}$ = 16.6 Hz, 1 H, α-H), 7.1 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, 8-H), 7.3–7.4 (m, 3 H, 3′,5′-H, 4′-H), 7.5 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, 2′,6′-H), 7.6 (dd, $^3J_{H,H}$ = 9.0, 2.5 Hz, 1 H, 7-H), 7.9 (d, $^3J_{H,H}$ = 2.5 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 62.1 (C-3), 83.6 (C-2), 116.9 (C-8), 119.6 (C-4′), 121.0 (C-1′), 127.0 (C-2′,6′,α), 128.7 (C-3′,5′,β), 129.0 (C-6), 134.2 (C-5), 135.3 (C-4a), 135.9 (C-7), 153.5 (C-8a), 187.3 (C-4) ppm. IR: $\tilde{\nu}$ = 3058, 3024 (epoxide), 1684 (C=O), 1608 (C=C), 1472, 1428, 1304, 1266, 1204 (epoxide), 1154, 1108, 968, 920, 820, 792, 746 cm^{-1}. $C_{17}H_{11}ClO_3$ (298.72): calcd. C 68.35, H 3.71; found C 68.55, H 3.87.

(*E*)-6-Bromo-2,3-epoxy-3-styrylchroman-4-one [(*E*)-5e]: This reaction was performed in dioxane solution. White crystals. Yield: 58%, m.p. 113–116 °C (hexane/ethyl acetate). ^1H NMR: δ = 5.5 (s, 1 H, 2-H), 6.7 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, β-H), 6.8 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, α-H), 7.0 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, 8-H), 7.3–7.4 (m, 3 H, 3′,5′-H, 4′-H), 7.5 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, 2′,6′-H), 7.7 (dd, $^3J_{H,H}$ = 8.6, 2.0 Hz, 1 H, 7-H), 8.1 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 62.2 (C-3), 83.6 (C-2), 116.2 (C-1′), 116.9 (C-8), 120.0 (C-4′), 121.5 (C-6), 127.0 (C-2′,6′), 128.5 (C-3′,5′,α), 130.0 (C-β),

134.2 (C-5), 135.3 (C-4a), 138.7 (C-7), 154.0 (C-8a), 187.1 (C-4) ppm. IR: $\tilde{\nu}$ = 3056 (epoxide), 1684 (C=O), 1636, 1602 (C=O), 1470, 1422, 1268, 1206 (epoxide), 1154, 1128, 1106, 820, 792, 746, 692 cm^{-1}. $C_{17}H_{11}BrO_3$ (343.17): calcd. C 59.50, H 3.23; found C 59.36, H 3.21.

(*E*)-7-Chloro-2,3-epoxy-3-styrylchroman-4-one [(*E*)-5f]: This reaction was performed in dioxane solution. White crystals. Yield: 61%, m.p. 75–77 °C (hexane/ethyl acetate). ^{1}H NMR: δ = 5.5 (s, 1 H, 2-H), 6.7 (d, $^3J_{H,H}$ = 16.3 Hz, 1 H, β-H), 6.8 (d, $^3J_{H,H}$ = 16.3 Hz, 1 H, α-H), 7.1 (s, 1 H, 8-H), 7.2 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, 6-H), 7.3–7.4 (m, 3 H, 3′,5′-H, 4′-H), (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, 2′,6′-H), 7.9 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 62.1 (C-3), 83.7 (C-2), 117.0, 118.1 (C-6, C-8), 118.6 (C-1′), 124.2 (C-4′), 127.0 (C-2′,6′,α), 128.7 (C-β), 128.8 (C-3′,5′), 134.2 (C-5), 135.3 (C-7), 142.1 (C-4a), 155.4 (C-8a), 187.3 (C-4) ppm. IR: $\tilde{\nu}$ = 3060, 3024 (epoxide), 2924, 1684 (C=O), 1604 (C=C), 1576, 1428, 1204 (epoxide), 1088, 964, 916, 798, 746 cm^{-1}. $C_{17}H_{11}ClO_3$ (298.72): calcd. C 68.35, H 3.71; found C 68.29, H 3.54.

(*Z*)-2,3-Epoxy-3-(4′-nitrostyryl)chroman-4-one [(*Z*)-5i]: This reaction was performed in dioxane solution. White crystals. Yield: 82%, m.p. 170–173 °C (hexane/ethyl acetate). ^{1}H NMR: δ = 5.3 (s, 1 H, 2-H), 6.2 (d, $^3J_{H,H}$ = 11.9 Hz, 1 H, α-H), 7.0 (d, $^3J_{H,H}$ = 11.9 Hz, 1 H, β-H), 7.1 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, 8-H), 7.2 (m, 1 H, 6-H), 7.4 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, 2′,6′-H), 7.6 (m, 1 H, 7-H), 8.0 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, 5-H), 8.2 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, 3′,5′-H) ppm. ^{13}C NMR: δ = 61.1 (C-3), 82.4 (C-2), 118.0 (C-8), 119.3 (C-1′), 123.6 (C-6), 123.7 (C-2′,6′,α), 127.7 (C-5), 129.0 (C-3′,5′), 134.9 (C-β), 136.5 (C-7), 141.9 (C-4a), 147.3 (C-4′), 155.0 (C-8a), 187.5 (C-4) ppm. IR: $\tilde{\nu}$ = 3054 (epoxide), 1670 (C=O), 1608 (C=C), 1518 (NO_2), 1480, 1464 (NO_2), 1346, 1314, 1206 (epoxide), 1150, 1100, 878, 856, 758 cm^{-1}. $C_{17}H_{11}NO_5$ (309.27): calcd. C 66.02, H 3.58; found C 65.87, H 3.35.

(*Z*)-3-(4′-Chlorostyryl)-2,3-epoxy-6-methylchroman-4-one [(*Z*)-5j]: This reaction was performed in dioxane solution. White crystals. Yield: 78%, m.p. 98–101 °C (hexane). ^{1}H NMR: δ = 2.4 (s, 3 H, 6-Me), 5.2 (s, 1 H, 2-H), 6.0 (d, $^3J_{H,H}$ = 11.9 Hz, 1 H, α-H), 6.9 (d, $^3J_{H,H}$ = 11.9 Hz, 1 H, β-H), 7.0 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, 8-H), 7.1 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, 2′,6′-H), 7.2 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, 3′,5′-H), 7.4 (dd, $^3J_{H,H}$ = 8.3, 1.8 Hz, 1 H, 7-H), 7.78 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 20.5 (6-Me), 61.1 (C-3), 82.6 (C-2), 117.8 (C-8), 119.1 (C-1′), 120.8 (C-α), 127.3 (C-5), 128.7, 129.5 (C-2′,6′, C-3′,5′), 133.2, 133.9, 134.2 (C-4a, C-6, C-4′), 135.8 (C-β), 137.4 (C-7), 153.2 (C-8a), 188.1 (C-4) ppm. IR: $\tilde{\nu}$ = 3064 (epoxide), 2920 (Me), 1680 (C=O), 1618 (C=C), 1490, 1432, 1320, 1212 (epoxide), 1136, 1088, 1078, 940, 826, 792 cm^{-1}. $C_{18}H_{13}ClO_3$ (312.75): calcd. C 69.13, H 4.19; found C 68.99, H 4.28.

Synthesis of Quaternary Quinidinium and Cinchoninium Phase-Transfer Catalysts: Catalysts **Cat 1**, **Cat 2** and **Cat 4** were synthesized according to a literature method.[32b] The same synthetic procedure (THF at reflux with 1 equiv. of alkylating agent) was used for the synthesis of the new compound **Cat 3**.

***N*-(4-Bromobenzyl)quinidinium Bromide (Cat 3):** Yield: 62%, m.p. 229–232 °C. $[\alpha]_D$ = +164.2 (*c* = 1.0, MeOH). ^{1}H NMR: δ = 0.9 (m, 1 H, one of 7-H), 1.7–1.9 (m, 2 H, 4-H, 5-H), 2.2–2.4 (m, 2 H, 3-H, 1 H of 7-H), 2.8 (m, 1 H of 6-H), 3.3 (m, 1 H of 2-H), 3.7 (s, 3 H, 6′-OMe), 4.2, 4.3, 4.5 (3 × m, 2 × 1 H, 6-H, 8-H, 1 H of 2-H), 5.2 (d, $^3J_{H,H}$ = 16.7 Hz, 1 H, =CH_2, H_{trans}), 5.3 (d, $^3J_{H,H}$ = 9.6 Hz, 1 H, =CH_2, H_{cis}), 5.6 (d, $^3J_{H,H}$ = 11.4 Hz, 9-H), 5.8–5.9 (m, 2 H, =CH, 9-OH), 6.4 (br. s, 1 H of CH_2), 6.6 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H of CH_2), 7.1 (d, $^3J_{H,H}$ = 9.2 Hz, 1 H, 7′-H), 7.4 (d, $^3J_{H,H}$ = 7.6 Hz, 2′′,6′′-H), 7.5–7.6 (m, 3 H, 5′-H, 3′′,5′′-H), 7.7 (br. s, 1 H, 3′-H), 7.8 (d, $^3J_{H,H}$ = 9.2 Hz, 1 H, 8′-H), 8.5 (br. s, 1 H, 2′-H) ppm.

Enantioselective Epoxidation of (*E*)-3-Styrylchromone in the Presence of Chiral, Nonracemic PTCs. General Procedure: Hydrogen peroxide (30%, 0.6 mL), then the catalyst (25 mol-%) and finally sodium hydroxide solution (8%, 0.1 mL) were added to a stirred solution of (*E*)-3-styrylchromone (*E*)-**3a** (100 mg, 0.403 mmol) in 1,4-dioxane (3 mL). The mixture was stirred at room temperature, and the reaction was monitored by TLC (PhMe). After ca. 20 min, a solid started to precipitate. When the reaction was complete, the solid was filtered off and washed with a copious amount of water. A second fraction of the precipitate was obtained from the mother liquor by treatment with water. The two precipitates were analyzed separately; the *ee* values were determined by CSP-HPLC. The results are shown in Table 1.

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