Photooxygenation of chiral 1,3-cyclohexadienes: strong influence of substituents on the stereo- and mode selectivities

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Dedicated to Professor Waldemar Adam on the occasion of his 70th birthday

Abstract
Four different chiral 1,3-cyclohexadienes were synthesized and investigated in photooxygenations with singlet oxygen. A strong influence of substituents at the double bond was observed for the mode selectivity of the reactions. Phenyl and alkyl groups afford mixtures of ene and [4 + 2] products, whereas a trimethylsilyl group yields exclusively hydroperoxides, presumably due to a "large group effect". Additionally, the same diastereoselectivity for both reaction modes gives evidence for common perepoxide intermediates. Finally, the photooxygenation of a methylensulfonyl substituted 1,3-cyclohexadiene proceeds with very high diastereoselectivity, which can be explained by an intramolecular hydrogen bridge, shielding one face of the compound.

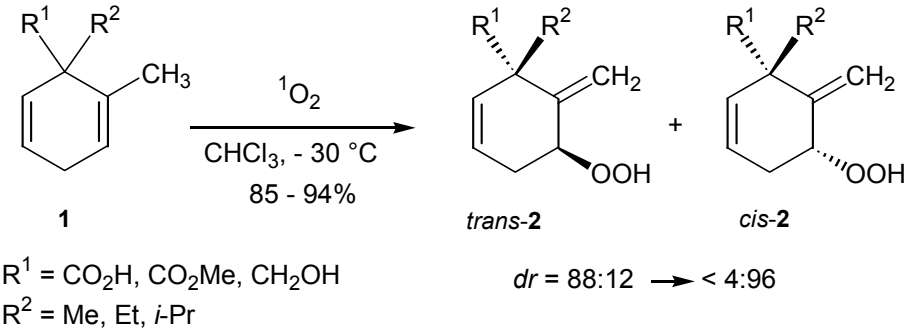
Keywords: Cyclohexadienes, singlet oxygen, mode selectivity, stereoselectivity, reaction mechanisms

Introduction

Singlet oxygen ($^1O_2$) represents a powerful and atom-economic oxidant, which has found numerous applications in organic synthesis.[1] The most convenient method for the generation of $^1O_2$ is the dye-sensitized photoreaction of molecular oxygen with visible light (photooxygenation). Alkenes react with $^1O_2$ by an ene-reaction to allylic hydroperoxides, whereas 1,3-dienes undergo predominantly [4 + 2]-cycloadditions to provide endoperoxides.[2] Singlet-oxygen ene reactions with high diastereoselectivities are based on the pioneering work of

Adam.[3] On the other hand, the stereochemical course of [4 + 2]-cycloadditions of $^1O_2$ to cyclic 1,3-dienes was studied less intensively, although this reaction is known for many years.[4] More recently, auxiliary controlled[5] and even organocatalytic[6] enantioselective photooxygenations were realized. Finally, singlet oxygen was applied for reversible light and air-driven lithography.[7]

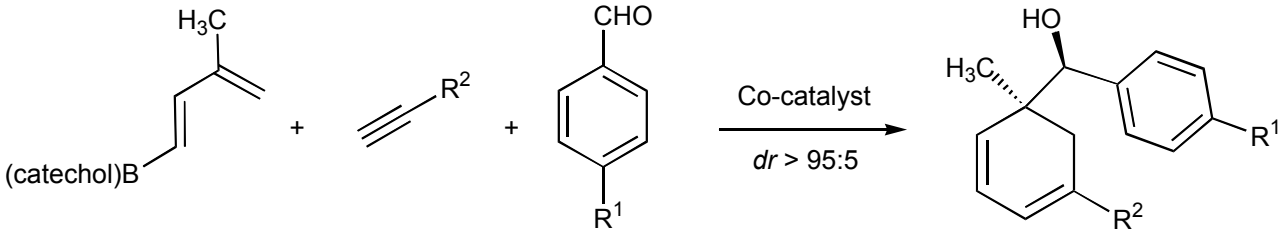
During our work on synthetic applications of singlet oxygen,[8] we found excellent regio- and high diastereoselectivities in the photooxygenation of 1,4-cyclohexadienes **1**, which are easily available by Birch reduction, to afford hydroperoxides **2** (Scheme 1). However, a direct comparison of ene-reaction *versus* [4 + 2]-cycloaddition was not possible with such systems. Therefore, we became interested in the photooxygenation of chiral 1,3-cylohexadienes, which allow the examination of stereo- and mode selectivities within the same molecule. Herein, we present our results on the addition of singlet oxygen to 1,3-cylohexadienes, which exhibits strong substituent effects.



Scheme 1

Results and Discussion

For the convenient synthesis of cyclohexadienes, we developed a new cobalt-catalyzed Diels-Alder methodology, starting from a boron-functionalized 1,3-diene **3** and various alkynes **4**.[9] Very recently, we succeeded in a one-pot combination of this reaction with an allylboration in the presence of aldehydes **5**, which afforded the desired 1,3-cyclohexadienes **6** from three simple precursors in moderate to good yields (Scheme 2). Furthermore, the reactions exhibit a high degree of diastereoselectivity and even asymmetric induction was achieved by chiral ligands.[10]



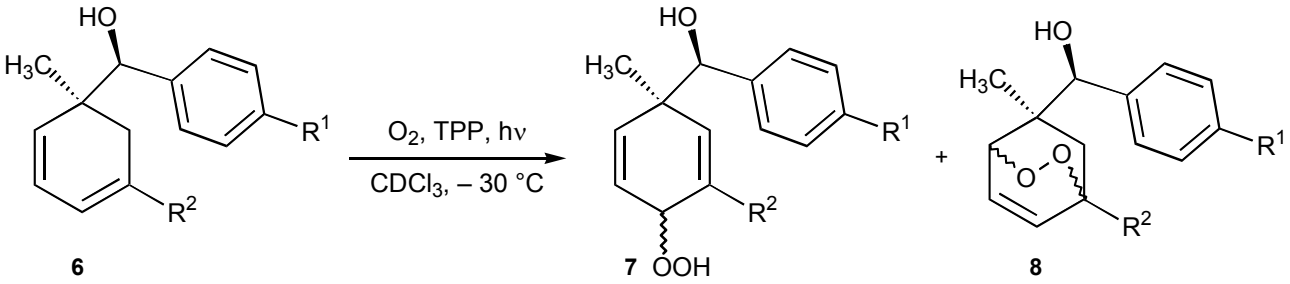
3 **4** **5**

R^1 = Cl, R^2 = Ph **6a** (36%)
R^1 = CF_3, R^2 = Ph **6b** (30%)
R^1 = NO_2, R^2 = $SiMe_3$ **6c** (84%)
R^1 = CF_3, R^2 = CH_2SO_2Ph **6d** (50%)

Scheme 2

For the photooxygenations, four differently substituted 1,3-cyclohexadienes **6a-d** were chosen in racemic form, since only the diastereo- and mode selectivities were examined. Singlet oxygen was conveniently generated at – 30 °C from molecular oxygen by irradiation with two sodium lamps in the presence of catalytic amounts of tetraphenylporphine (TPP) as sensitizer. Complete conversion was achieved after 10 min in deuterochloroform as solvent and the product ratios were directly determined from the ^{1}H NMR spectra (500 MHz) of the crude reaction mixture. The photooxygenations afforded hydroperoxides **7** and endoperoxides **8** in various ratios and the labile products were directly isolated by column chromatography in high yields and in analytically pure form (Table 1).

Table 1. Photooxygenation of the 1,3-cyclohexadienes **6**



6 **7** **8**

					Yield (%)[b]	
Entry	1,3-Diene	R^1	R^2	**7** : **8** [a]	**7** (*dr*)[a]	**8** (*dr*)[a]
1	**6a**	Cl	Ph	70:30	63 (*64:36*)	21 (*66:34*)
2	**6b**	CF_3	Ph	75:25	69 (*65:35*)	27 (*65:35*)
3	**6c**	NO_2	$SiMe_3$	>95:5	80 (*65:35*)	--
4	**6d**	CF_3	CH_2SO_2Ph	30:70	21 (*>95:5*)	63 (*>95:5*)

[a] Product and diastereomeric ratios (*dr*) were determined by ^{1}H NMR of the crude product (500 MHz). [b] Yield of isolated products after silica gel chromatography.

The first reactions were performed with the phenyl substituted 1,3-cyclohexadiene **6a** (R^2 = Ph) (entry 1), affording the hydroperoxides **7a** as main products in 63% yield. On the other hand, the endoperoxides **8a** were isolated only as minor products in 21% yield. Thus, the photooxygenation of diene **6a** proceeds with moderate mode selectivity. This result can be rationalized by the "large-group-effect" of the phenyl group,[1a] activating the adjacent methylene group for an ene-reaction. Even more interesting are the diastereoselectivities of the photooxygenation, since stereoisomers of hydroperoxide **7a** and endoperoxide **8a** were obtained in almost the same ratio (*dr* 64:36 and 66:34) (entry 1). The relative configurations of the newly formed stereocenters were determined by NOE measurements (Figure 1)

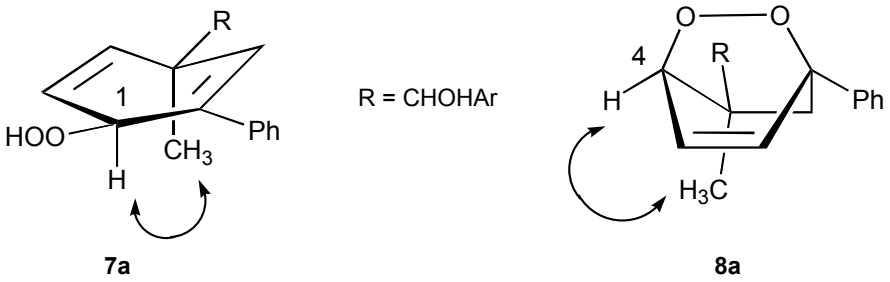


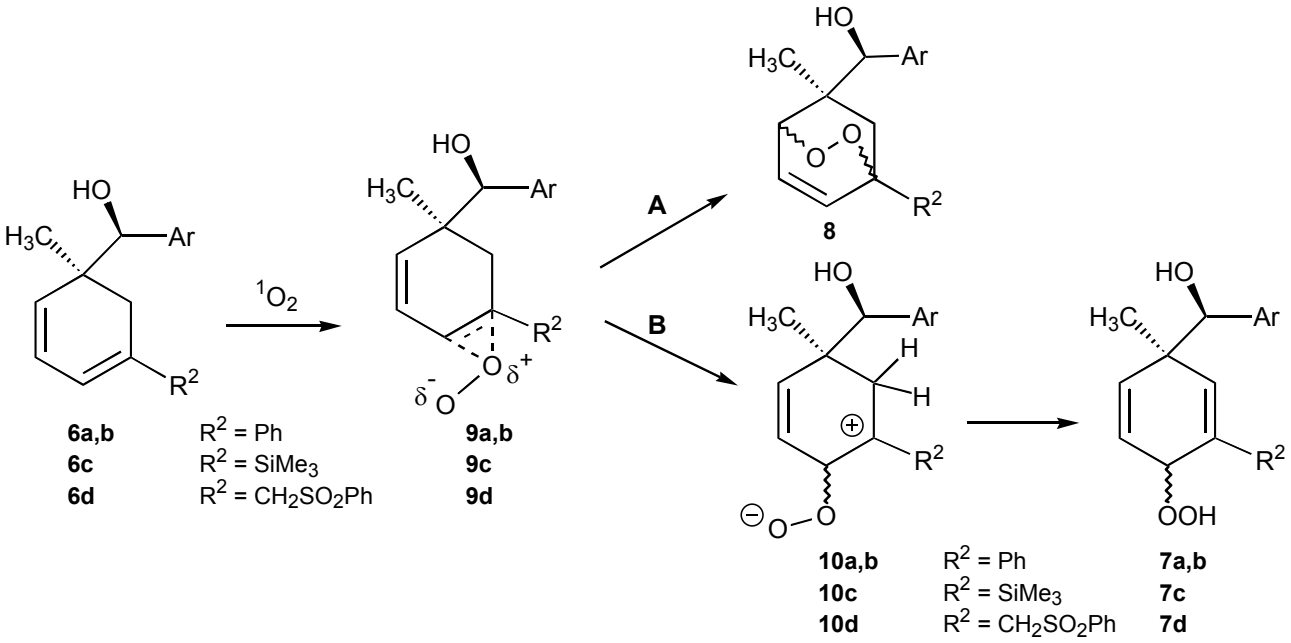
Figure 1. Characteristic NOE contacts in the main hydroperoxide **7a** and endoperoxide **8a**.

Distinct NOE contacts between the methyl group and H-1 of the main hydroperoxide **7a** and H-4 of the main endoperoxide **8a** indicate the preferential attack of $^1O_2$ from the side of the benzylic alcohol. This result can be rationalized by a stabilizing hydrogen bridge between the OH group and the negatively charged oxygen in a perepoxide intermediate, which is in accordance with the photooxygenation of allylic[3a] and homoallylic[8b] alcohols. However, due to the flexibility of 1,3-cyclohexadienes,[11] the diastereomeric ratio (*dr*) of the products are only 64:36 and 66:34 (Table 1, entry 1).

To further increase the stereoselectivities, we subsequently investigated the influence of *para* substituents at the aromatic ring of the benzylic alcohol (entry 2). Thus, an electron acceptor (R^1 = CF_3) should strengthen the postulated hydrogen bridge to singlet oxygen, resulting in a preferential attack *syn* to the OH group. However, almost the same stereo- and mode selectivity was observed in the photooxygenation (entry 2), which might be due to the remote position of the substituent.

On the other hand, a remarkable result is the almost identical diastereoselectivity (*dr* 65:35) for all products **7a**, **8a**, **7b** and **8b**, irrespective of an ene-reaction or [4 + 2]-cycloaddition (Table 1, entries 1 and 2). This gives clear evidence for a common perepoxide intermediate in both reaction modes, which is interesting for the mechanism of $^1O_2$ reactions and is in accordance with our studies on the photooxygenation of 1,2-dihydronaphthalenes.[12] Thus, in the first step the perepoxides **9a**,**b** are formed by attack of the electrophilic $^1O_2$ to the phenyl substituted double bond (Scheme 3). This step controls the stereoselectivities of all further

pathways and explains the similar diastereomeric ratios for all products.



Scheme 3

The perepoxide intermediates **9** can directly react to the endoperoxides **8** by attack of the terminal oxygen atom to the adjacent double bond (pathway **A**). However, heterolysis to the zwitterions **10** might compete (pathway **B**), which is favored by the stabilizing propensity of the phenyl group (R^2 = Ph) on the positively charged carbon atom. Finally, tautomerization affords the hydroperoxides **7a,b**. This mechanistic rational explains the mode selectivity in favor of the hydroperoxides (**7**:**8** = 70:30, entry 1 and 75:25, entry 2, Table 1).

To shift the mode selectivity to the side of the hydroperoxides, we investigated the photooxygenation of the silyl substituted 1,3-cyclohexadiene **6c** (R^2 = $SiMe_3$), since the "large group effect" of the silyl group strongly activates the geminal position.[1a] Indeed, now pathway **B** afforded only hydroperoxides **7c** as sole oxidation products (Table 1, entry 3) and the formation of endoperoxides **8c** (pathway **A**) could not compete, which is in accordance to our mechanistic rational. The diastereomeric ratio (*dr*) is again 65:35 in favor of a *syn* attack of $^1O_2$ to the OH group.

Finally, alkyl substitutents should stabilize the zwitterions **10** less effectively than phenyl groups. Therefore, we investigated the photooxygenation of 1,3-cyclohexadiene **6d** (R^2 = CH_2SO_2Ph), which bears an additional acceptor. Indeed, the mode selectivity is now in favor of the endoperoxide (**7d**:**8d** = 30:70, Table 1, entry 4). Thus, different substituents strongly influence the product distribution from >95:5 (R^2 = $SiMe_3$) to 30:70 (R^2 = CH_2SO_2Ph).

A very interesting result is the high diastereoselectivity of the photooxygenation of the 1,3-cyclohexadiene **6d** (entry 4) in contrast to all other substrates (entries 1-3). Thus, the

hydroperoxide **7d** and endoperoxide **8d** were isolated in high yields in diastereomerically pure form. Furthermore, $^1O_2$ attacks the diene from exactly the opposite face (*anti* to the OH group), which was confirmed by NOESY and distinct NOE contacts between the benzylic proton and H-1 of the hydroperoxide **7d** and H-4 of the endoperoxide **8d** (Figure 2).

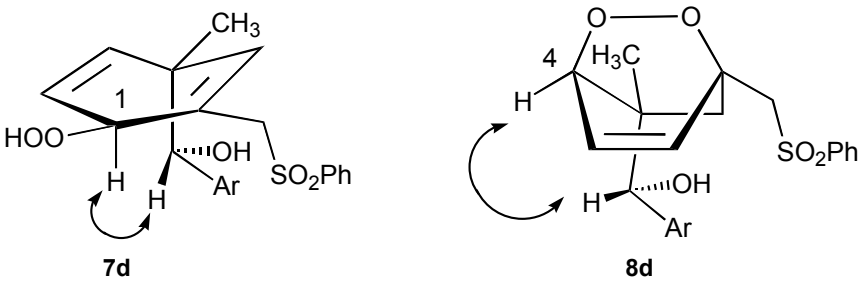


Figure 2. Characteristic NOE contacts in the hydroperoxide **7d** and endoperoxide **8d**.

Therefore, the high stereoselectivity cannot be due to the interaction of $^1O_2$ with the benzylic alcohol during the photooxygenation. We explain this remarkable result by the conformation of the starting material **6d**. The OH group and the phenyl sulfone can form an *intramolecular* hydrogen bridge, which was established by X-ray analysis (Figure 3).[10]

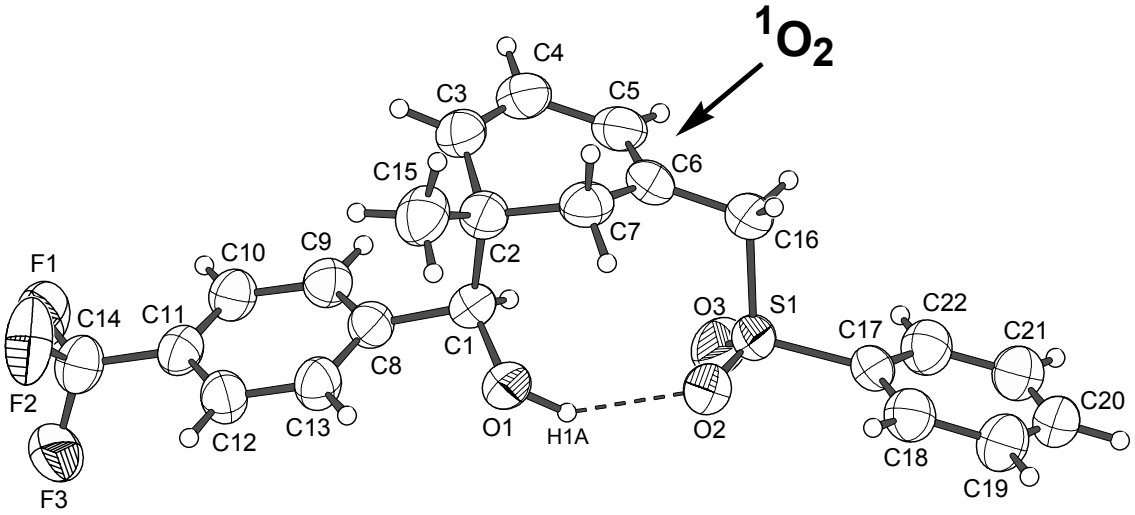


Figure 3. Crystal structure of 1,3-cyclohexadiene **6d**[10] and preferred attack of $^1O_2$.

This does not only block the alcohol for coordination with singlet oxygen, but also shields one face of the 1,3-cyclohexadiene **6d** efficiently. Therefore, the photooxygenation can occur only from the less hindered side, irrespective of the reaction mode. Such severe steric interactions by hydrogen bonding were hitherto unknown in singlet oxygen reactions. Finally,

especially the endoperoxide **8d** is not only of mechanistic but also of synthetic interest, since starting from the boron-functionalized 1,3-diene **3** and other simple precursors, four stereogenic centers are constructed in only few steps with high selectivity.

In summary, the photooxygenation of chiral 1,3-cyclohexadienes affords hydroperoxides and endoperoxides in high yields. Substituents at the double bond strongly influence the mode selectivity of the reactions. The same diastereoselectivity for ene-reaction and [4 + 2]-cycloaddition gives evidence for common perepoxide intermediates. Finally, the photooxygenation of a methylensulfonyl substituted 1,3-cyclohexadiene proceeds with very high diastereoselectivity, which can be explained by an intramolecular hydrogen bridge, shielding one face of the compound. Future work will focus on synthetic applications of these new oxidation reactions, generating four stereogenic centers in only few steps from simple precursors.

Experimental Section

General Procedures. Commercially available compounds were used without further purification; solvents were dried according to standard procedures. Flash chromatography was performed using Merck Kieselgel 60 silica. TLC analysis was carried out on Alugram silica gel 60 F_{254} plates (Macherey-Nagel). Potassium iodide was used as developing reagent for the peroxide products. NMR spectra were measured on a Bruker AC 300 (300 MHz) and AC 500 (500 MHz) spectrometer using deuterochloroform ($CDCl_3$) as internal standard. IR spectra were recorded on a Perkin Elmer 1600 FT-IR and elemental analysis were performed on a Vario El 3 instrument (Elementar).

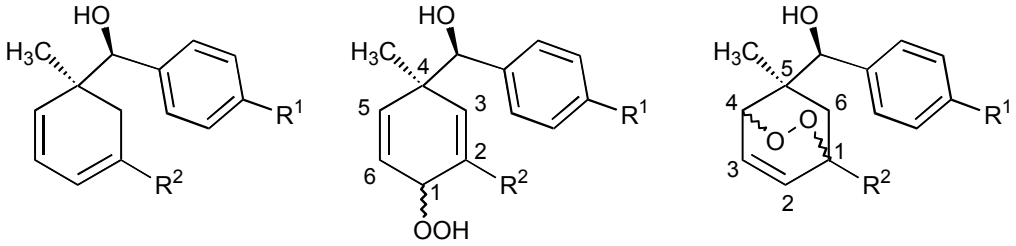
General procedure for the cobalt-catalyzed Diels-Alder / allylboration reaction sequence

Anhydrous zinc iodide (60 mol%), zinc dust (60 mol%) and $CoBr_2$(dppe) (10 mol%) were stirred under argon in 0.5 mL DCM until the green suspension turned brown (5-10 min). Then, the boron diene **1** (1.0 eq.) in DCM (c = 200 mg / mL) and the appropriate alkyne **2** (1.0 eq.) were added and the mixture was stirred at room temperature. After 30 min the aldehyde (1.0 eq.) was added and the reaction was stirred at room temperature for 15 h. The suspension was diluted with MTBE and washed with 1 M aqueous NaOH and saturated $NaHSO_3$ solution. After drying with $MgSO_4$ the solution was filtered over a short pad of silica gel and then the solvent was removed under vacuum. The residue was then purified by flash column chromatography (pentane/MTBE). For analytical data see reference 10.

General photooxygenation procedure

The 1,3-cyclohexadienes **1a-d** and tetraphenylporphin (1 mg) were dissolved in $CDCl_3$ (3 mL) in a glass tube. A slow stream of oxygen was bubbled through the solution and the tube was irradiated at – 30 °C with two sodium lamps (250 W). After 10 min tlc (hexane / ethyl acetate 2:1) showed complete conversion. The ratio of the isomers was directly determined from the NMR spectra (500 MHz) of the crude reaction mixture and the oxidation products were isolated by column chromatography.

Numbering of compounds and ring carbon atoms



R^1 = Cl, R^2 = Ph	**6a**	**7a**	**8a**
R^1 = CF_3, R^2 = Ph	**6b**	**7b**	**8b**
R^1 = NO_2, R^2 = $SiMe_3$	**6c**	**7c**	**8c**
R^1 = CF_3, R^2 = CH_2SO_2Ph	**6d**	**7d**	**8d**

Photooxygenation of 1,3-cyclohexadiene (6a). The photooxygenation of 1,3-cyclohexadiene **6a** (132 mg, 0.42 mmol) afforded a crude product mixture (140 mg) of hydroperoxides **7a** (*dr* = 64:36) and endoperoxides **8a** (*dr* = 66:34) in a ratio of 70:30. Column chromatography (hexane / ethyl acetate 4 : 1) yielded 20 mg (14 %) of the main endoperoxide **8a** (R_f = 0.61), 10 mg (7 %) of the minor endoperoxide **8a** (R_f = 0.46), 30 mg (21%) of the minor hydroperoxide **7a** (R_f = 0.36) and 60 mg (42%) of the main hydroperoxide **7a** (R_f = 0.25) as colorless oils.

Main hydroperoxide 7a. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.15 (s, 3H, CH_3), 1.59, 2.08 (each bs, 1H, OH, OOH), 4.58 (bs, 1H, CHOH), 5.11 (dd, *J* = 3.0, 1.2 Hz, 1H, H-1), 6.05 (d, *J* = 1.2 Hz, 1H, 3-H), 6.08 (dt, *J* = 9.9, 1.2 Hz, 1H, 5-H), 6.18 (dd, *J* = 9.9, 3.0 Hz, 1H, 6-H), 7.20-7.50 (m, 9H, H-arom.); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 23.6 (q, CH_3), 44.5 (s, C-4), 76.3 (d, CHOH), 80.2 (d, C-1), 124.4 (q, CF_3), 126.2, 126.4, 127.7, 128.0, 128.5, 133.8, 134.6, 135.7 (each d, C-3, C-5, C-6, C-arom.), 124.9, 128.2, 139.3, 145.0 (each s, C-2, C-arom.); IR (KBr) 3420, 2982, 2940, 1740, 1445, 1395, 1221, 1127, 1022, 939 cm^{-1}; Anal. Calcd for $C_{20}H_{19}ClO_3$: C, 70.07; H, 5.59; Found: C, 70.32; H, 5.80.

Minor hydroperoxide 7a. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.07 (s, 3H, CH_3), 1.63, 3.34 (each bs, 1H, OH, OOH), 4.58 (bs, 1H, CHOH), 5.41 (d, *J* = 3.8, 1.2 Hz, 1H, H-1), 5.97 (d, *J* = 1.8 Hz, 1H, 3-H), 6.11 (dd, *J* = 9.9, 1.2 Hz, 1H, 5-H), 6.22 (dd, *J* = 9.9, 3.9 Hz, 1H, 6-H), 7.20-7.60 (m, 9H, H-arom.); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 24.5 (q, CH_3), 44.0 (s, C-4), 77.2 (d, CHOH), 79.7 (d, C-1), 125.2 (q, CF_3), 125.8, 126.0, 127.4, 127.7, 128.2, 133.8, 134.6, 135.8 (each d, C-3, C-5, C-6, C-arom.), 133.8, 135.6, 138.5 (each s, C-2, C-arom.); IR (KBr) 3420, 2982, 2940, 1740, 1445, 1395, 1221, 1127, 1022, 939 cm^{-1}.

Main endoperoxide 8a. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.82 (s, 3H, CH_3), 1.67 (d, *J* = 13.2 Hz, 1H, 6-H), 2.75 (d, *J* = 2.5 Hz, 1H, OH), 2.84 (d, *J* = 13.2 Hz, 1H, 6′-H), 4.22 (dd, *J* = 5.4, 1.8 Hz, 1H, 4-H), 5.18 (d, *J* = 2.5 Hz, 1H, CHOH), 6.69 (dd, *J* = 7.8, 5.4 Hz, 1H, 3-H), 6.71 (dd, *J* = 7.8, 1.8 Hz, 1H, 2-H), 7.20-7.60 (m, 9H, H-arom.); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.0 (q, CH_3), 29.7 (t, C-6), 40.9 (s, C-5), 77.4 (d, CHOH), 78.4 (d, C-4), 79.1 (s, C-1), 124.9 (q, CF_3), 126.0, 126.7, 128.3, 128.7, 132.4, 134.6, 135.7 (each d, C-2, C-3, C-arom.), 128.1, 139.3, 145.0 (each s,

C-arom.); IR (KBr) 3420, 2982, 2940, 1740, 1445, 1395, 1221, 1127, 1022, 939 cm^{-1}; Anal. Calcd for $C_{20}H_{19}ClO_3$: C, 70.07; H, 5.59; Found: C, 70.33; H, 5.34.

Minor endoperoxide 8a. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 3H, CH_3), 1.85 (bs, 1H, OH), 2.18 (d, *J* = 13.3 Hz, 1H, 6-H), 2.21 (d, *J* = 13.3 Hz, 1H, 6´-H), 3.88 (dd, *J* = 5.8, 1.3 Hz, 1H, 4-H), 4.44 (bs, 1H, CHOH), 6.78 (dd, *J* = 8.3, 1.3 Hz, 1H, 2-H), 6.93 (dd, *J* = 8.3, 5.8 Hz, 1H, 3-H), 7.20-7.60 (m, 9H, H-arom.); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.0 (q, CH_3), 29.7 (t, C-6), 40.9 (s, C-5), 77.4 (d, CHOH), 78.4 (d, C-4), 79.1 (s, C-1), 124.9 (q, CF_3), 126.0, 126.7, 128.3, 128.7, 132.4, 134.6, 135.7 (each d, C-2, C-3, C-arom.), 128.1, 139.3, 145.0 (each s, C-arom.); IR (KBr) 3420, 2982, 2940, 1740, 1445, 1395, 1221, 1127, 1022, 939 cm^{-1}.

Photooxygenation of 1,3-cyclohexadiene 6b. The photooxygenation of 1,3-cyclohexadiene **6b** (67 mg, 0.19 mmol) afforded a crude product mixture (75 mg) of hydroperoxides **7b** (*dr* = 65:35) and endoperoxides **8b** (*dr* = 65:35) in a ratio of 75:25. Column chromatography (hexane / ethyl acetate 4 : 1) yielded 20 mg (27 %) of the main endoperoxide **8b** (R_f = 0.43), 32 mg (44%) of a mixture of both hydroperoxides **7b** (R_f = 0.2-0.3) and 18 mg (25%) of the pure main hydroperoxide **7b** (R_f = 0.16) as colorless oils.

Main hydroperoxide 7b. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.17 (s, 3H, CH_3), 3.35, 3.60 (each bs, 1H, OH, OOH), 4.65 (bs, 1H, CHOH), 5.08 (ddd, *J* = 3.1, 2.0, 1.5 Hz, 1H, H-1), 6.03 (d, *J* = 1.5 Hz, 1H, 3-H), 6.09 (dd, *J* = 10.0, 2.0 Hz, 1H, 5-H), 6.19 (dd, *J* = 10.0, 3.1 Hz, 1H, 6-H), 7.20-7.60 (m, 9H, H-arom.); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 23.6 (q, CH_3), 44.5 (s, C-4), 76.3 (d, CHOH), 80.2 (d, C-1), 124.4 (q, CF_3), 126.2, 126.4, 127.7, 128.0, 128.5, 133.8, 134.6, 135.7 (each d, C-3, C-5, C-6, C-arom.), 124.9, 128.2, 139.3, 145.0 (each s, C-2, C-arom.); IR (KBr) 3423, 2855, 1620, 1460, 1326, 1166, 1124, 1066, 759, 698, 608 cm^{-1}; Anal. Calcd for $C_{21}H_{19}F_3O_3$: C, 67.02; H, 5.09; Found: C, 66.82; H, 5.12.

Minor hydroperoxide 7b. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.07 (s, 3H, CH_3), 3.41, 3.70 (each bs, 1H, OH, OOH), 4.49 (bs, 1H, CHOH), 5.39 (dd, *J* = 4.0, 1.9 Hz, 1H, H-1), 5.94 (d, *J* = 1.9 Hz, 1H, 3-H), 6.05 (d, *J* = 10.0 Hz, 1H, 5-H), 6.22 (dd, *J* = 10.0, 4.0 Hz, 1H, 6-H), 7.20-7.60 (m, 9H, H-arom.); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 24.5 (q, CH_3), 44.0 (s, C-4), 77.2 (d, CHOH), 79.7 (d, C-1), 125.2 (q, CF_3), 125.8, 126.0, 127.4, 127.7, 128.2, 133.8, 134.6, 135.8 (each d, C-3, C-5, C-6, C-arom.), 133.8, 135.6, 138.5 (each s, C-2, C-arom.); IR (KBr) 3431, 2971, 1620, 1419, 1327, 1166, 1124, 1067, 851, 760, 698, 609 cm^{-1}.

Endoperoxide 8b. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.82 (s, 3H, CH_3), 1.66 (d, *J* = 13.4 Hz, 1H, 6-H), 2.80 (d, *J* = 2.5 Hz, 1H, OH), 2.85 (d, *J* = 13.4 Hz, 1H, 6´-H), 4.21 (dd, *J* = 6.1, 1.5 Hz, 1H, 4-H), 5.25 (d, *J* = 2.5 Hz, 1H, CHOH), 6.69 (dd, *J* = 8.3, 6.1 Hz, 1H, 3-H), 6.71 (dd, *J* = 8.3, 1.5 Hz, 1H, 2-H), 7.20-7.70 (m, 9H, H-arom.); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.0 (q, CH_3), 29.7 (t, C-6), 40.9 (s, C-5), 77.4 (d, CHOH), 78.4 (d, C-4), 79.1 (s, C-1), 124.9 (q, CF_3), 126.0, 126.7, 128.3, 128.7, 132.4, 134.6, 135.7 (each d, C-2, C-3, C-arom.), 128.1, 139.3, 145.0 (each s, C-arom.); IR (KBr) 3494, 2928, 1618, 1449, 1326, 1163, 1113, 1016, 698 cm^{-1}; HRMS Calcd. $C_{21}H_{19}F_3O_3Na$: 399.1184; Found: 399.1184.

Photooxygenation of 1,3-cyclohexadiene 6c. The photooxygenation of 1,3-cyclohexadiene **6c** (160 mg, 0.50 mmol) afforded a crude product mixture (150 mg) of hydroperoxides **7c** (*dr* = 65:35) and *no* endoperoxide **8c** could be detected. Column chromatography (hexane / ethyl acetate 6 : 1) yielded 20 mg (11 %) of the pure minor hydroperoxide **7c** (R_f = 0.57) and 120 mg (69%) of a mixture of both hydroperoxides **7c** (R_f = 0.43) as a white solid (mp 67-68 °C).

Main hydroperoxide 7c. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 9H, $SiMe_3$), 1.17 (s, 3H, CH_3), 2,71, 3.60 (each bs, 1H, OH, OOH), 4.45 (bs, 1H, CHOH), 4.57 (dd, *J* = 2.8, 2.1 Hz, 1H, H-1), 5.86 (t, *J* = 2.1 Hz, 1H, 3-H), 5.93 (dd, *J* = 10.1, 2.1 Hz, 1H, 5-H), 6.13 (dd, *J* = 10.1, 2.8 Hz, 1H, 6-H), 7.36 (d, *J* = 8.7 Hz, 2H, H-arom.), 8.08 (d, *J* = 8.7 Hz, 2H, H-arom.); ^{13}C-NMR (75 MHz, $CDCl_3$) δ –1.5 (q, $SiMe_3$), 23.7 (q, CH_3), 43.5 (s, C-4), 77.5 (d, CHOH), 79.6 (d, C-1), 122.2, 128.6 (each d, C-arom.), 127.8, 133.5, 143.5 (each d, C-3, C-5, C-6), 137.2, 147.1, 147.7 (each s, C-2, C-arom.); IR (KBr) 3433, 2958, 2872, 1606, 1519, 1348, 1267, 1047, 840 cm^{-1}; Anal. Calcd for $C_{17}H_{23}NSiO_5$: C, 58.43; H, 6.63; N, 4.01; Found: C, 58.60; H, 6.91; N 4.05.

Minor hydroperoxide 7c. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.15 (s, 9H, $SiMe_3$), 1.01 (s, 3H, CH_3), 1.64, 3.35 (each bs, 1H, OH, OOH), 4.61 (d, *J* = 2.8 Hz, 1H, CHOH), 4.95 (dd, *J* = 3.6 Hz, 1H, H-1), 5.83 (d, *J* = 1.4 Hz, 1H, 3-H), 6.05 (dd, *J* = 10.1, 1.4 Hz, 1H, 5-H), 6.18 (dd, *J* = 10.1, 3.6 Hz, 1H, 6-H), 7.46 (d, *J* = 8.8 Hz, 2H, H-arom.), 8.20 (d, *J* = 8.8 Hz, 2H, H-arom.); ^{13}C-NMR (75 MHz, $CDCl_3$) δ –1.5 (q, $SiMe_3$), 24.4 (q, CH_3), 42.8 (s, C-4), 77.1 (d, CHOH), 78.9 (d, C-1), 122.7, 128.6 (each d, C-arom.), 123.3, 126.9, 130.5 (each d, C-3, C-5, C-6), 137.9, 143.6, 147.6 (each s, C-2, C-arom.); IR (KBr) 3445, 2943, 2864, 1612, 1519, 1344, 1258, 1044, 838 cm^{-1}; Anal. Calcd for $C_{17}H_{23}NSiO_5$: C, 58.43; H, 6.63; N, 4.01; Found: C, 58.86; H, 6.31; N 4.23.

Photooxygenation of 1,3-cyclohexadiene 6d. The photooxygenation of 1,3-cyclohexadiene **6d** (266 mg, 0.63 mmol) afforded a crude product mixture (285 mg) of hydroperoxide **7d** (*dr* > 95:5) and endoperoxides **8d** (*dr* = 90:10) in a ratio of 30:70. Column chromatography (hexane / ethyl acetate 4 : 1) yielded 180 mg (63 %) of the main endoperoxide **8d** (R_f = 0.47) as white crystals (mp 64–65 °C) and 60 mg (21%) of the hydroperoxide **7d** (R_f = 0.27) as white crystals (mp 45-46 °C). The minor endoperoxide **8d** (< 10%) could not be isolated.

Hydroperoxide 7d. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.03 (s, 3H, CH_3), 2.03, 2.43 (each bs, 1H, OH, OOH), 3.75 (d, *J* = 13.9 Hz, 1H, CH_2S), 4.17 (d, *J* = 13.9 Hz, 1H, $CH_2'S$), 4.53 (bs, 1H, CHOH), 4.55 (d, *J* = 3.0 Hz, 1H, H-1), 5.78 (d, *J* = 1.5 Hz, 1H, 3-H), 5.89 (dd, *J* = 10.1, 1.5 Hz, 1H, 5-H), 6.02 (dd, *J* = 10.1, 3.0 Hz, 1H, 6-H), 7.25-7.95 (m, 9H, H-arom.); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 22.8 (q, CH_3), 44.4 (s, C-4), 59.1 (t, CH_2S), 76.7 (d, CHOH), 79.7 (d, C-1), 123.9 (q, C-2), 124.6 (q, CF_3), 125.4, 126.1, 127.4, 128.4, 129.3, 134.0, 135.8, 141.2 (each d, C-3, C-5, C-6, C-arom.), 138.8, 143.5 (each s, C-arom.); IR (KBr) 3412, 2929, 1448, 1327, 1162, 1128, 747, 526 cm^{-1}; Anal. Calcd for $C_{22}H_{21}F_3SO_5$: C, 58.14; H, 4.66; S, 7.05; Found: C, 58.14; H, 4.70; S 7.03.

Main endoperoxide 8d. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.20 (s, 3H, CH_3), 1.82 (d, *J* = 13.5 Hz, 1H, 6-H), 2.15 (d, *J* = 13.5 Hz, 1H, 6′-H), 2.69 (bs, 1H, OH), 3.39 (d, *J* = 14.4 Hz, 1H, CH_2S), 3.46 (d, *J* = 14.4 Hz, 1H, $CH_2'S$), 3.71 (dd, *J* = 5.8, 0.9 Hz, 1H, 4-H), 4.36 (bs, 1H, CHOH), 6.80

(dd, *J* = 8.5, 5.8 Hz, 1H, 3-H), 7.03 (dd, *J* = 8.5, 0.9 Hz, 1H, 2-H), 7.40-7.90 (m, 9H, H-arom.); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.2 (q, CH_3), 40.1 (t, C-6), 41.2 (s, C-5), 59.5 (t, CH_2S), 75.8 (s, C-1), 77.4 (d, CHOH), 78.1 (d, C-4), 125.2 (q, CF_3), 127.4, 128.0, 129.1, 129.4, 131.8, 132.7, 134.1 (each d, C-2, C-3, C-arom.), 140.3, 144.5 (each s, C-arom.); IR (KBr) 3514, 2976, 1448, 1327, 1156, 1128, 566 cm^{-1}; Anal. Calcd for $C_{22}H_{21}F_3SO_5$: C, 58.14; H, 4.66; S, 7.05; Found: C, 58.06; H, 4.65; S 7.17.

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