Synthesis, Structures and Topochemistry of 2-Monovinyl-Substituted 1,4-Benzoquinones☆

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In the course of topochemical investigations of substituted quinones the 2-monovinyl-substituted 1,4-benzoquinones **1** were synthesized by electrochemical oxidation of the corresponding 1,4-dimethoxybenzene derivatives **3** to the quinone bisketals **4** and subsequent hydrolysis. In solution, the aryl-substituted vinylquinones **1a**−**1t** underwent unexpected Diels-Alder additions. The stereochemically unique course of the reaction was proved spectroscopically and by X-ray structure analysis of the dimer **8k**. As a basic requirement for the topochemical studies, the crystal structures of eight quinones **1** were determined by X-ray diffraction. In the crystals of **1a**, **1c**, **1e**, **1f**, **1i** and **1n** with an α-type packing arrangement, the vinylic double bonds have short contacts (< 4.4 Å) across a centre of symmetry. The quinone **1k** crystallizes in a β arrangement with short distances (< 4.0 Å) between molecules related by translation and in a γ arrangement without suitable contacts. The crystals of all quinones **1** were irradiated with UV light to perform [2+2] cycloadditions. The photoreactive quinones dimerized exclusively at the vinylic double bonds, resulting in the corresponding cyclobutanes **9**. Topochemically controlled the dimers **9a**−**9c**, **9e**, **9l**−**9n**, **9q**, **9r** and **9u** with molecular C_i symmetry were formed whereas the dimers **9k** and **9t** have C_s symmetry. The structures of the cyclobutanes were determined by spectroscopical investigations and in the case of **9b**, **9e** and **9r** additionally by X-ray analysis. Despite short contacts, crystals of **1f** and **1i** were photostable. This is probably because of insufficient lattice flexibility indicated by relatively high densities.

The topochemical investigations of 2,5-bisstyryl-substituted 1,4-benzoquinones were restricted by their pronounced insolubility[1]. We tried to avoid these difficulties by exchanging the aryl groups for ester substituents[2] or reducing the number of substituents on the benzoquinone system. We describe in this paper the topochemistry of 2-monovinyl-substituted 1,4-benzoquinones **1** (Scheme 1)[3].

These kinds of compounds combine the potential solid-state photoreactivity of quinones[4] and olefinic systems like stilbenes[5] or cinnamic acids[6].

Starting from an α-type packing arrangement, the quinones **1** can photochemically dimerize at the vinylic double bonds resulting in cyclobutane derivatives with molecular centres of inversion. Particularly interesting is a β-type packing with a 4 Å stacking axis, in order to obtain short contacts between all double bonds and therefore an increased variety of [2+2] cycloadditions, and also the possibility of undergoing polycycloadditions in the crystal.

The chlorine and methylenedioxy substituents on the phenyl ring of the quinones **1h**−**1s** and the ester groups of the derivatives **1t** and **1u** were chosen to generate the layered structures by principles of crystal engineering[7]. The compounds **1b**−**1g** with methyl substitution of the aromatic system were selected in order to prove whether they would crystallize with structures isomorphous to those of the correspondingly substituted chloro derivatives and therefore to ascertain the validity of chlorine-methyl interchangeability[8].

The parent compound of the aryl-substituted quinones **1a** was already described[9]. Irradiation in solution gave only amorphous products from which no pure material could be isolated.

Synthesis of the Quinones 1

The 2-monovinyl-substituted 1,4-benzoquinones **1**, with exception of quinones **1s** and **1u**, were synthesized following efficient procedures which were developed for the synthesis of the corresponding 2,5-bisvinyl-substituted 1,4-benzoquinones[1].

As shown in Scheme 2, the quinones **1a**−**1r**, **1t** and **1u** were prepared from the corresponding dimethoxybenzene derivatives **3**. In the case of the aryl substituents, the vinylic groups were generated by a Horner-Emmons reaction between 2,5-dimethoxybenzaldehyde and the corresponding phosphonates **2**, synthesized by a Michaelis-Arbuzov reaction of the analogous benzyl halides. The reactions were carried out in DMF solution with sodium methoxide, stirring for at least 4 h at room temperature. The resulting stilbene derivatives **3** could easily be detected from the blue fluorescence on irradiation with UV light (λ = 366 nm). After working up and purification the aryl-substituted *trans*-1,4-dimethoxy-2-vinylbenzenes **3a**−**3r** and **3t** were obtained, isomerically pure, in yields of 80−90%. The dimeth-

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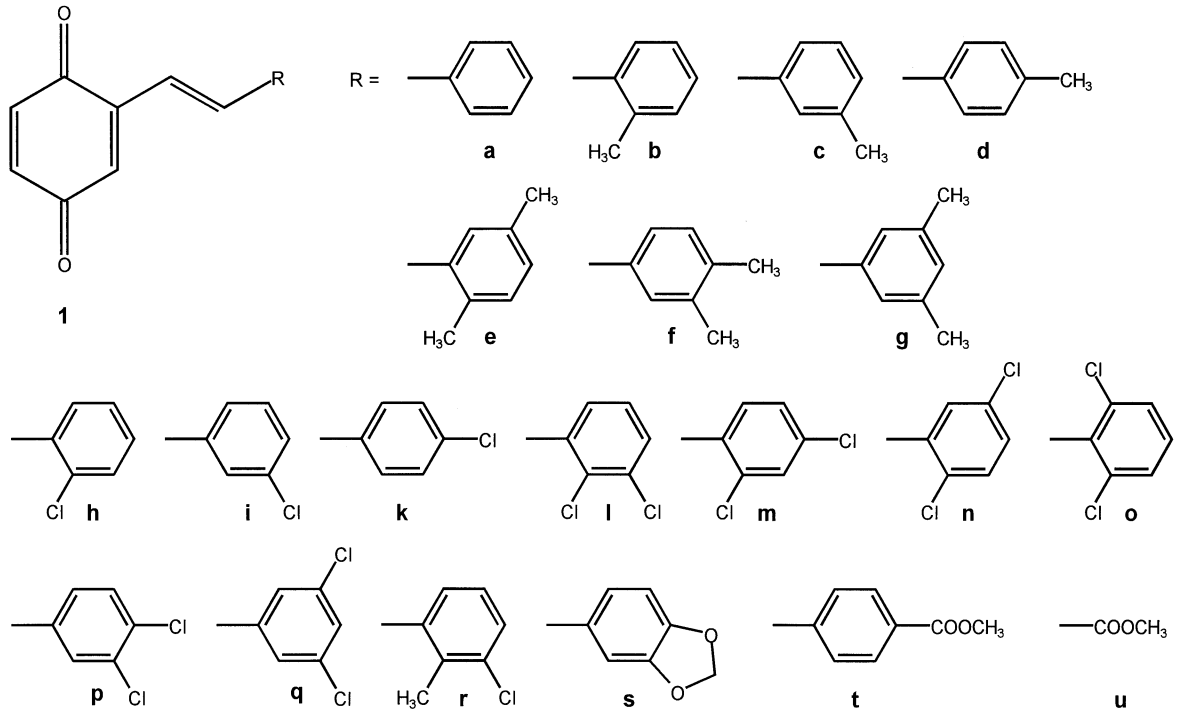
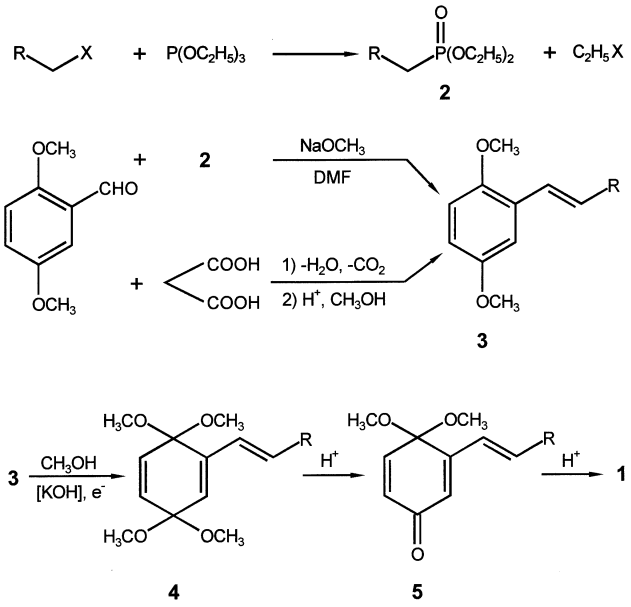
Scheme 1. Formula scheme of the 2-monovinyl-substituted 1,4-benzoquinones **1a**−**1u**



Scheme 2. Synthesis of the quinones **1a**−**1t** and **1u**



oxybenzene derivatives **3** were characterized spectroscopically by IR, UV, ^{1}H- and ^{13}C-NMR spectroscopy and by mass spectrometry.

The ester derivative **3u** could be obtained by a Knoevenagel-Doebner condensation of 2,5-dimethoxybenzaldehyde with malonic acid and a subsequent transformation of the resulting acid to the methyl ester[10].

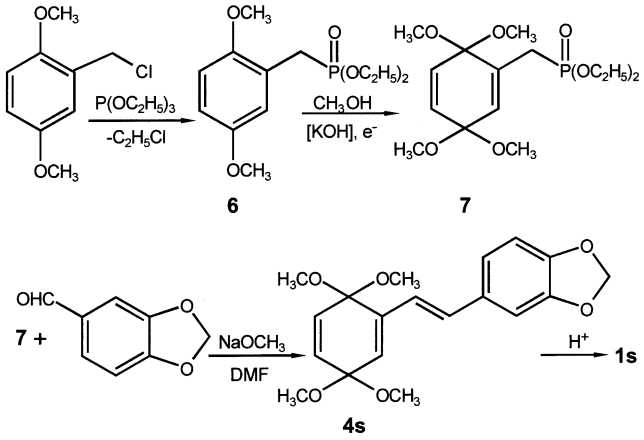
The dimethoxybenzene compounds **3a**−**3r**, **3t** and **3u** were electrochemically oxidized to the corresponding quinone bisketals **4** using Pt electrodes in dried methanol, with KOH as conducting salt. In a one-cell pot without diaphragm, the electrolysis was conducted for approximately 3 h at room temperature. The course and the end of the reaction were monitored by the decreasing UV fluorescence of the starting materials. The yields were 40−60% for the methylphenyl and 60−80% for the chlorophenyl derivatives. For the ester derivative **4u**, the yield was only 22% because of partial reduction of the conjugated methyl ester at the cathode[10b]. The quinone bisketals **4** were characterized by IR, UV, ^{1}H- and ^{13}C-NMR spectroscopy and mass spectrometry.

The protolytic hydrolysis of the quinone bisketals **4** at room temperature yielded the corresponding quinones **1**. Hydrolysis of the ester function and of the derivatives **1t** and **1u** was not observed under these conditions. From the acetone solvent, in which the quinone bisketals **4** and 2 N H_2SO_4 as catalyst are readily soluble, the generated quinones **1** crystallized with high purity in yields of 60−80%. Under hydrolytic conditions which are too mild (immediate cooling of the reaction solution to −30°C) the precipitation of the intermediate quinone monoketals **5** can be observed. For example, **5l** was isolated and characterized spectroscopically and by X-ray structure analysis[11].

For the quinone derivative **1s**, containing a heterocycle, a modified synthetic path had to be used, because the ether function of the methylenedioxyphenyl substituent is also electrochemically oxidized under the applied conditions. Therefore the oxidation must be carried out before introducing the methylenedioxyphenyl substituent. We thus oxidized the 2,5-dimethoxybenzylphosphonate **6**[12] (Scheme

3), obtained by a Michaelis-Arbuzov reaction of 2,5-dimethoxybenzyl chloride, to the quinone bisketal **7**, which was subsequently converted with 3,4-methylenedioxybenzaldehyde to the monovinyl-substituted quinone bisketal **4s**. This ketal was hydrolysed in acidic solution to the quinone **1s** by the same procedure as described above.

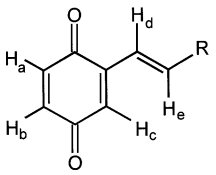
Scheme 3. Synthesis of the quinone **1s**



Spectroscopy of the Quinones 1

The NMR spectra of the derivatives **1a**−**1t** had to be recorded immediately after dissolving the compounds in $CDCl_3$, since these compounds undergo an unexpected Diels-Alder cycloaddition (see below). In the ^{1}H-NMR spectrum, the signal for proton H_a of the quinone ring (Figure 1) in the range $\delta = 6.75-6.88$ splits into a doublet ($^3J = 10.0-10.4$ Hz; except for **1u**: $^3J = 6.2$ Hz), because of *cis* coupling to proton H_b. The W arrangement of both protons H_b and H_c results in longe-range coupling which can be recognized in most cases by the appearance of doublets of doublets at $\delta = 6.75-6.80$ for H_b with coupling constants of $^4J = 1.8-2.3$ Hz. Alternatively, a doublet could be detected for H_b with the corresponding *cis* coupling constant. The proton H_c always gives singlets at $\delta = 6.80-6.95$. The protons H_d and H_e show the typical coupling constant of $^3J = 16.2-16.7$ Hz for a *trans* substitution. The chemical shifts of the olefinic protons H_d and H_e were assigned by using the corresponding increment system[13] (Table 1).

Figure 1. Characterization of the quinoid and olefinic protons H_a-H_e of the 2-monovinyl-substituted 1,4-benzoquinones **1**



In the ^{13}C-NMR spectrum, the signals for the carbonyl carbon atoms of the quinone rings appear at $\delta = 185.6-187.1$ and $\delta = 187.3-187.6$. The IR spectra are characterized by the typical absorptions of C=O and C=C stretching and bending vibrations (Table 2).

In the mass spectra, the $M^+ + 2$ peaks have relatively high intensities because of the addition of two hydrogen atoms to the quinone system of **1**, leading to the corresponding hydroquinones[14]. The absorption bands in the electronic spectra in the long-wavelength region ($\lambda = 520-640$ nm) are responsible for the visible colour of compounds **1** from orange-red to red-violet.

Table 1. ^{1}H-NMR-chemical shifts (δ values in ppm) and coupling constants (in Hz) for the quinoid and olefinic protons H_a-H_e of the 2-monovinyl-substituted 1,4-benzoquinones **1**

comp.	H_a	H_b	H_c	H_d	H_e
1a	6.80 (d, J = 10.3)	6.76 (d, J = 10.0)	6.88 (s)	7.45 (d, J = 16.5)	7.10 (d, J = 16.5)
1b	6.80 (d, J = 10.1)	6.76 (d, J = 10.1)	6.88 (s)	7.01 (d, J = 16.3)	7.74 (d, J = 16.3)
1c	6.79 (d, J = 10.3)	6.76 (dd, J = 2.3, 10.4)	6.87 (s)	7.42 (d, J = 16.5)	7.09 (d, J = 16.4)
1d	6.78 (d, J = 10.3)	6.75 (dd, J = 2.1, 10.3)	6.85 (s)	7.42 (d, J = 16.3)	7.06 (d, J = 16.5)
1e	6.80 (d, J = 10.1)	6.76 (dd, J = 2.0, 10.3)	6.88 (s)	7.01 (d, J = 16.4)	7.71 (d, J = 16.3)
1f	6.75 (d, J = 10.3)	6.75 (dd, J = 2.2, 10.3)	6.85 (s)	7.40 (d, J = 16.5)	7.06 (d, J = 16.5)
1g	6.79 (d, J = 10.3)	6.75 (dd, J = 1.9, 10.3)	6.86 (s)	7.38 (d, J = 16.5)	7.08 (d, J = 16.5)
1h	6.82 (d, J = 10.1)	6.78 (dd, J = 2.0, 10.2)	6.95 (s)	7.10 (d, J = 16.4)	7.85 (d, J = 16.5)
1i	6.81 (d, J = 10.3)	6.78 (s)	6.86 (s)	7.39 (d, J = 16.0)	7.04 (d, J = 16.5)
1k	6.80 (d, J = 10.3)	6.76 (dd, J = 1.8, 10.3)	6.86 (s)	7.40 (d, J = 16.5)	7.06 (d, J = 16.2)
1l	6.83 (d, J = 10.0)	6.79 (d, J = 10.2)	6.95 (s)	7.08 (d, J = 16.4)	7.84 (d, J = 16.4)
1m	6.82 (d, J = 10.0)	6.79 (dd, J = 1.8, 10.2)	6.94 (s)	7.07 (d, J = 16.5)	7.75 (d, J = 16.5)
1n	6.83 (d, J = 10.2)	6.80 (dd, J = 2.2, 10.4)	6.95 (s)	7.08 (d, J = 16.5)	7.75 (d, J = 16.5)
1o	6.82 (d, J = 10.3)	6.78 (dd, J = 2.0, 10.2)	6.92 (s)	7.17 (d, J = 16.6)	7.49 (d, J = 16.7)
1p	6.82 (d, J = 10.2)	6.77 (d, J = 10.0)	6.85 (s)	7.41 (d, J = 16.6)	7.05 (d, J = 16.5)
1q	6.82 (d, J = 10.2)	6.78 (dd, J = 2.1, 10.2)	6.85 (s)	7.33 (d, J = 16.4)	7.05 (d, J = 16.5)
1r	6.81 (d, J = 10.0)	6.78 (dd, J = 1.8, 10.2)	6.87 (s)	6.94 (d, J = 16.3)	7.75 (d, J = 16.2)
1s	6.85 (d, J = 10.3)	6.79 (d, J = 10.0)	6.77 (s)	7.37 (d, J = 16.5)	6.93 (d, J = 16.2)
1t	6.82 (d, J = 10.1)	6.78 (d, J = 10.2)	6.90 (s)	7.48 (d, J = 16.5)	7.18 (d, J = 16.5)
1u	6.88 (d, J = 6.2)	6.80 (d, J = 6.2)	6.80 (s)	7.50 (d, J = 16.5)	6.82 (d, J = 16.2)

Diels-Alder Reaction of the Quinones 1a−1t

As mentioned before, when recording NMR spectra, additional signals appeared (except in the case of **1u**), which were attributed to the corresponding Diels-Alder dimers **8** of the aryl-substituted quinones **1**. In the course of 24−30 h, 10−80% of the dimers may be identified by integration of the characteristic signals. The vinyl-substituted quinones **1a**−**1t** react as diene and dienophile to afford only dimer **8**, one of four possible isomers (Scheme 4).

For identification, we selected the bisaryl-substituted vinyltetrahydrophenanthrenetetraone **8k** and determined the structure by X-ray analysis (Figure 2).

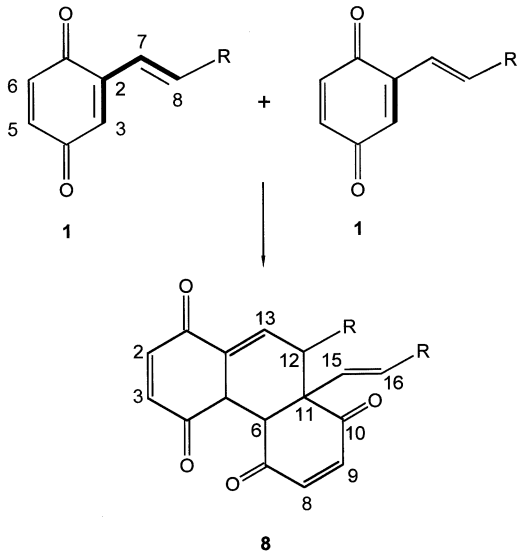
The tetrahydrophenanthrenetetraone skeleton is strongly strained at the vinyl-substituted quaternary carbon atom C11. Therefore, the corresponding bonds are elongated be-

Table 2. Selected IR-spectroscopical data of the 2-monovinyl-substituted 1,4-benzoquinones **1**; dimorphic crystal forms of **1k** and **1t**, respectively

comp.	stretching vibration $\tilde{\nu}$ [cm^{-1}] C=O	C=C (olefin)	C=C (quinone)	bending vibration $\tilde{\nu}$ [cm^{-1}] =C−H *(trans)*	=C−H	=C−H *(cis)*
1a	1657, 1642	1623	–	974	823	690
1b	1652	1616	–	968	821	–
1c	1658, 1648	1623	1603	973	827	689
1d	1659, 1633	1618	–	975	803	–
1e	1652	1623	1604	966	824, 806	–
1f	1659, 1645	1621	1604	973	809	–
1g	1663, 1645	1623	1608	966	816	689
1h	1660, 1646	1618	–	967	820	–
1i	1650	1622	1590	976	785	685
1k[a]	1657, 1641	1621	1593	977	834, 806	–
1k[b]	1655, 1642	1620	1605	976	838, 805	–
1l	1659, 1643	1620	1608	975, 966	821	705
1m	1664, 1651	1618	–	968	808	–
1n	1663	1621	–	972	820	–
1o	1657	1627	–	979, 964	787	706
1p	1650	1627	–	975	813	691
1q	1660, 1647	1622	1607	978	818, 799	672
1r	1661, 1645	1617	1589	975, 962	822, 783	701
1s	1657, 1641	1618	1604	970	827, 806	–
1t[c]	1656, 1642	1621	1604	973, 960	822	692
1t[d]	1659, 1642	1623	1605	980, 959	823	694
1u	1657	1607	1590	944	–	–

[a]Red prisms: γ arrangement. – [b]Dark-red needles: β modification. – [c]Dark-red needles. – [d]Orange-red plates.

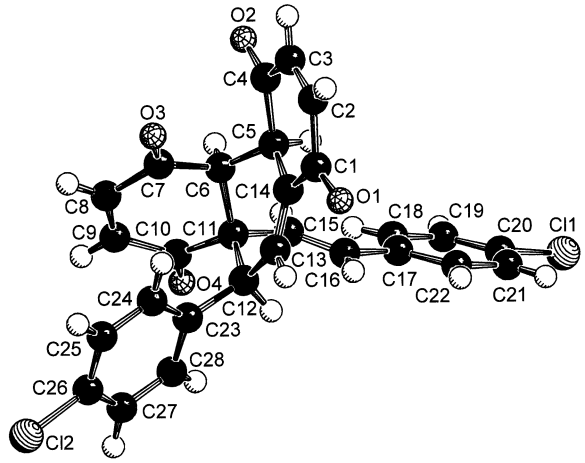
Scheme 4. Diels-Alder reactions of the quinones **1** to the dimers **8**



8

cause of non-bonding repulsions: C11−C6 = 1.560(3), C11−C10 = 1.535(3) and C11−C12 = 1.577(3) Å. The bond angles at the sp^2-hybridized carbon atoms C15 and C16 are enlarged because of 1···4 repulsive contacts: C11−C15−C16 = 128.1(2) and C15−C16−C17 = 127.2(2)°. Despite the short intermolecular contact C2···C3A (A: 1 − *x*, 2 − *y*, 2 − *z*) of 4.266(4) Å between the peripheral double bonds across a centre of symmetry the compound is not photoreactive in the crystal because an approach of both bulky molecules is contradictory to the principle of minimal atomic movement[16].

Figure 2. Molecular structure of the bisaryl-substituted vinyltetrahydrophenanthrenetetraone **8k** with labelling



The exclusive formation of isomer **8k** may be explained by semiempirical calculations (AM1) of coefficients of the frontier molecular orbitals[17]. The diene and the dienophile reactivities are represented by the HOMO and LUMO, respectively. The substituted and therefore sterically hindered quinoid double bond has the larger coefficients (LUMO) compared to the other one. Consequently the [4+2] cycloaddition is kinetically favoured at this double bond (Figure 3).

In the ^{1}H-NMR spectrum of **8k**, H12 couples only with H13 to give a doublet (δ = 4.15; ^3J = 4.5 Hz), since C11, substituted by the vinyl group, does not bear a hydrogen atom. Therefore, the substitution pattern of the regioisomer is established. Since two different *cis*-substituted double bonds can be detected in the ^{1}H-NMR spectrum as four doublets with *cis* coupling constants (δ = 6.09, 6.27, 6.97, 7.05; ^3J = 10.4 Hz) for H2, H3, H8 and H9, the dienophile reactivity of the double bond C5=C6 of **1k** can be excluded. Consequently, the regioselectivity is spectroscopically proved and in agreement with the results of the X-ray analysis. The chemical shifts and the multiplicity of the signals belonging to the tetrahydrophenanthrenetetraone skeleton look almost identical to those in the ^{1}H-NMR spectra of the other Diels-Alder dimers **8**. Therefore the stereochemistry of all dimers **8** is the same as determined unequivocally for **8k**.

A corresponding Diels-Alder dimerization could not be observed in the case of the ester-substituted derivative **1u**. The absence of the Diels-Alder reaction was also found in 2,5-bisacrylate-substituted 1,4-benzoquinones, which is explained by the *s-trans* conformation of the potentially reactive 4π-electron system, as determined by X-ray analysis[2].

Crystal Structures and Packing Arrangements of Some Quinones 1

The knowledge of the packing arrangements of the quinones in the crystal is a basic requirement for understanding their topochemical reactivity. Hence, the crystal and molecular structure of the quinones **1a**, **1c**, **1e**, **1f**, **1i**, **1k**

Figure 3. Frontier molecular orbitals of the 2-monovinyl-substituted 1,4-benzoquinone **1k** (HOMO: top; LUMO: bottom); selected coefficients of the HOMO: C2 0.144, C3 0.320, C7 −0.429, C8 −0.330; selected coefficients of the LUMO: C2 −0.356, C3 0.392, C5 0.283, C6 −0.289

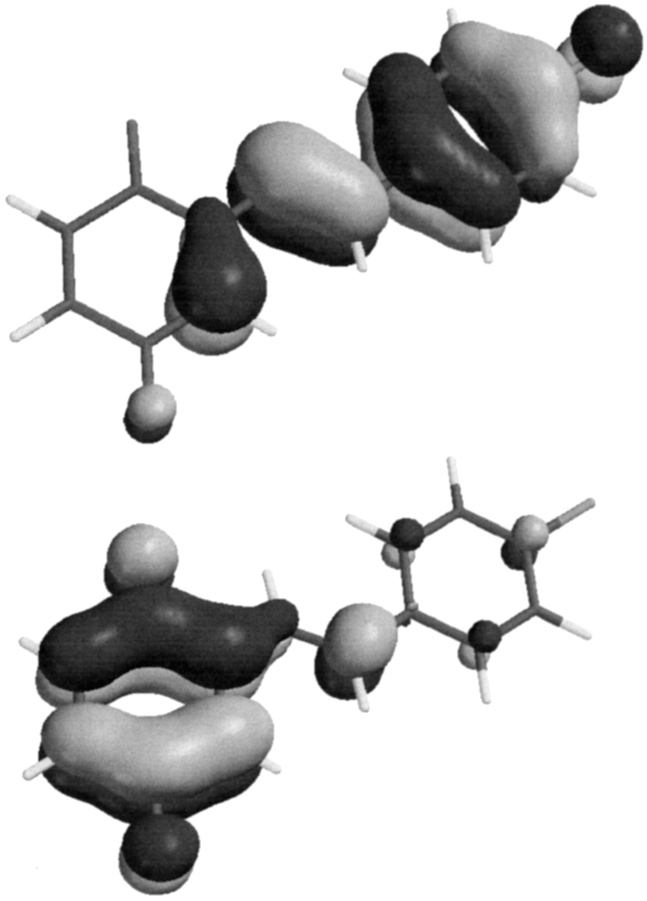
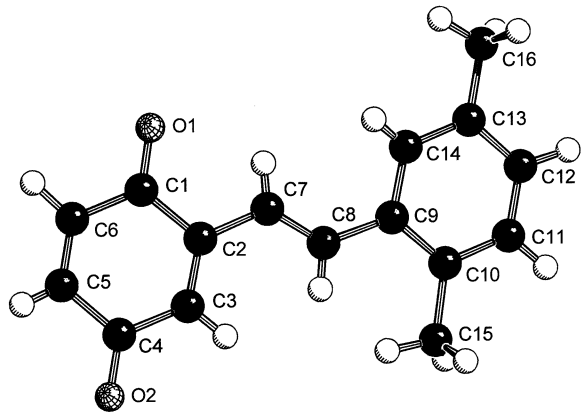


Figure 4. Molecular structure of the 2-monovinyl-substituted 1,4-benzoquinone **1e** with labelling exemplary for all the derivatives **1** investigated by X-ray analysis; selected averaged bond lengths [Å] for all derivatives **1**: C1−O1 1.219, C1−C2 1.499, C1−C6 1.475, C2−C3 1.344, C3−C4 1.461, C4−O2 1.225, C4−C5 1.476, C5−C6 1.319; averaged 1,4-distance [Å]: C7···O1 2.799

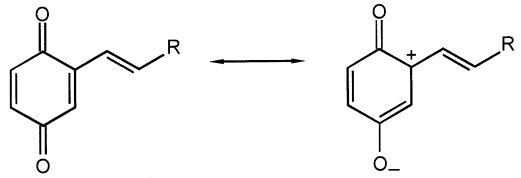


and **1n** were determined by X-ray studies. In the case of the derivative **1k**, we examined both dimorphic crystal forms. For the quinones **1r**−**1u** we derived the general packing type simply from the cell dimensions by comparison to the known crystal structures. The crystals of **1a**, **1e**, **1f**, **1i** and **1n** were grown by slow cooling in a cryostat, starting crystallization below room temperature. The crystals of **1c** and of both forms of **1k**, which crystallized simultaneously, were obtained directly by hydrolysis of the corresponding quinone bisketals **4**. For the quinones **1r**−**1u**, we obtained only very thin plates by slow cooling of the respective hydrolysis solution which were not suitable for complete structure analysis.

All the molecular structures of the investigated quinones show *s-cis* conformations of the 4π-electron system C3−C2−C7−C8 (Figure 4) which is essential for the observed [4+2] cycloadditions in solution.

The equivalence of the bond lengths in the quinone system is changed by the conjugation with the vinyl group. In all examined structures **1**, the bonds C1−C2, C2−C3 and C4−O2 are longer than the bonds C3−C4, C5−C6 and C1−O1, respectively (Figure 4), because of an essential contribution of the polar resonance form (Figure 5). Accordingly, C3−C4 is shorter than C1−C6 and C4−C5.

Figure 5. Polar resonance form of the 2-monovinyl-substituted 1,4-benzoquinones **1**



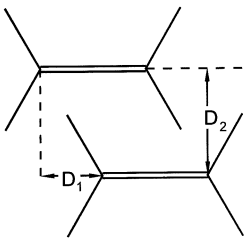
Similar electronic effects were also found in other monosubstituted 1,4-benzoquinones[18] and in 2,5-bisstyryl-substituted 1,4-benzoquinones[1]. The non-bonding 1,4-repulsive interactions C7···O1 are responsible for the significant elongation of the bond C1−C2.

We analysed the packing arrangement of the quinones **1** with respect to the topochemical criteria of the distances between parallel C=C double bonds, the parallel shift parameter D_1 and the perpendicular shift parameter D_2 in the projection (Table 3 and Table 4). Three different packing types were found:

1) In the α-type packing, vinylic double bonds C7=C8 of neighbouring molecules have short contacts (< 4.4 Å) across a centre of symmetry involving an antiparallel orientation of the molecules. This type was found for the quinones **1a**, **1c**, **1e**, **1f**, **1i** and **1n** (Table 3). The characteristics of the α-type packing arrangement is shown for the derivative **1e** in Figure 6 as an example.

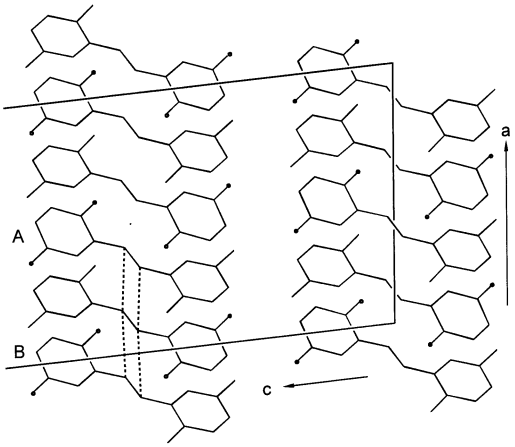
2) In the β-type packing, neighbouring molecules are related by translation along the short cell axis (< 4.0 Å) involving a parallel orientation of the molecules with the same short distance between all corresponding double bonds (Table 4 and Figure 7). This type was determined for the β modification of quinone **1k** [a = 3.938(1) Å]. For

Table 3. Intermolecular contacts of the quinones **1a**, **1c**, **1e**, **1f**, **1i** and **1n** with an α-type packing arrangement between the double bonds C7=C8 of neighbouring molecules related by centres of symmetry



comp.	contact no.	symmetry	distance [Å]	shift parameter D_1 [Å]	D_2 [Å]
1a	1	A: $-x, -y, 2-z$	4.305(2)	0.914	2.291
	2	B: $1-x, -y, 2-z$	4.160(2)	1.323	2.139
1c	1	A: $-x, -y, -1-z$	3.988(3)	0.597	1.932
	2	B: $1-x, -y, -1-z$	3.674(3)	1.277	0.102
	3	C: $-x, 1-y, -z$	3.623(4)	1.085	0.113
	4	D: $1-x, 1-y, -z$	3.801(3)	1.499	0.413
1e	1	A: $0.5-x, 0.5-y, 1-z$	3.553(6)	1.085	0.273
	2	B: $-x, 1-y, 1-z$	3.786(6)	1.489	0.675
1f	1	A: $1-x, -y, -z$	3.653(3)	1.250	0.037
	2	B: $2-x, -y, -z$	3.990(4)	0.868	1.797
1i	1	A: $1-x, -y, -z$	3.966(2)	1.351	1.704
	2	B: $2-x, -y, 1-z$	3.988(2)	1.059	2.232
1n	1	A: $-x, 1-y, 2-z$	4.084(3)	1.346	2.240

Figure 6. Projection of the crystal packing arrangement (α-type) of the 2-monovinyl-substituted 1,4-benzoquinone **1e** along axis *b* (topochemical contacts are indicated)

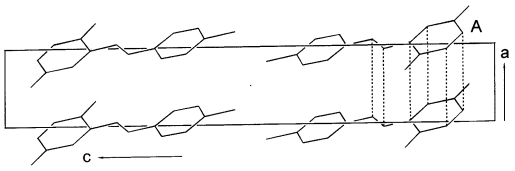


the quinone **1t** this packing pattern was deduced from the observed short cell axis [c = 3.81(2) Å].

Table 4. Intermolecular shift parameters *D1* and *D2* (as defined in Table 3) for the double bonds of quinone **1k** related by translation [A: $x-1, y, z$; C···C(A) 3.938(6) Å] in a β-type packing arrangement

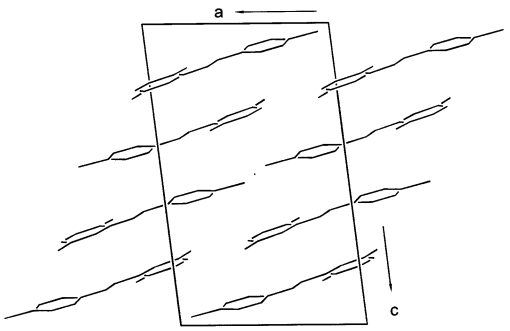
comp.	contact no.	atoms	shift parameter D_1 [Å]	D_2 [Å]
1k	1	C2−C3/C2A−C3A	2.101	1.230
	2	C5−C6/C5A−C6A	2.108	0.159
	3	C7−C8/C7A−C8A	0.915	1.906

Figure 7. Crystal packing arrangement of the 2-monovinyl-substituted 1,4-benzoquinone **1k** (β arrangement) along axis *b* (topochemical contacts are indicated)



3) For the second crystal form of quinone **1k**, we found a γ-type packing without topochemically suitable contacts between neighbouring molecules (Figure 8).

Figure 8. Crystal packing arrangement of the 2-monovinyl-substituted 1,4-benzoquinone **1k** (γ arrangement) along axis *b*



The substitution of planar aromatic molecules with halogens is known as a crystal-engineering device[7a][7c] to attain β-type-layered structures because of attractive halogen···halogen interactions. Therefore we attached chlorine substituents to the parent styryl quinone system **1a** and synthesized the derivatives **1h**−**1r** to favour β-type packing arrangements. Similar steering capabilities were discussed for methylenedioxy and ester substituents[7e][7f], so we applied this substitution pattern to the compounds **1s**−**1u**. Contrary to many reported examples[19], in our systems the introduced steering groups resulted only in the generation of a β-type structure in both cases, **1k** and **1t**. The repulsive dipole···dipole interactions between the quinone moieties can probably not be overcome by the specific steering forces and the antiparallel molecular orientation of the α-type packing arrangement is favoured. Even in the cases of **1k** and **1t**, where the application of intramolecular substitution with steering groups was successful, a second crystal arrangement was obtained in addition to the β-type form. This indicates that a close interplay between different types of interactions with the same order of magnitude determines the packing arrangements.

If we interchange the chloro substituents in the derivatives **1i** and **1n** by methyl groups, with almost the same space requirements, we obtain the same packing pattern in the analogous cases of **1c** and **1e**, indicating that steric requirements also have to be considered.

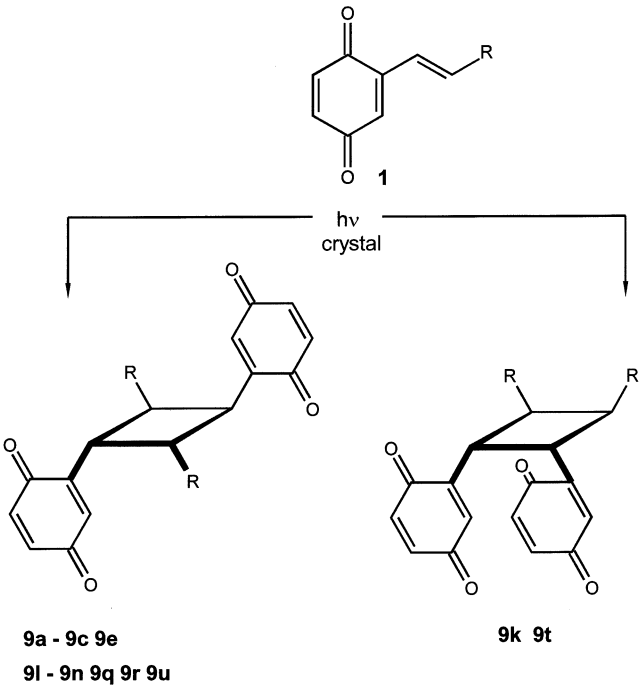
Photochemical Reactivity of the Quinones 1 in the Crystalline State

The crystals of the quinones **1** were powdered and irradiated with a high-pressure mercury lamp (1200 W) in a glass vessel which can be kept at constant temperature by water cooling. After five hours of irradiation time, we checked a small sample of each irradiated quinone **1** by ^{1}H-NMR ($CDCl_3$) and IR spectroscopy (KBr), to determine whether any reaction had taken place. Alternatively, the irradiation was carried on for a further 35 h, and the substance checked again, as above, to prove the photostability. The quinones **1d**, **1f**−**1k** (γ arrangement), **1p** and **1s** are not photoreactive in the crystalline state and under these conditions do not show any visible changes. The photostability of the γ form of **1k** corresponds to the packing arrangement determined by X-ray analysis. For the derivative **1s** only the cell dimensions are available, and for **1d**, **1g**, **1h** and **1p**, no structural information is accessible. Despite the short contacts between the vinylic double bonds below 4 Å and comparatively suitable shift parameters D_1 and D_2, (Table 3) the quinones **1f** and **1i** do not show any photocycloaddition in the crystal. We explain this photostability as being a consequence of insufficient flexibility of the molecules in the crystal lattice which is deduced from the relatively high density ($D_{calcd.}$ = 1.30 and 1.45 Mg m^{-3} for **1f** and **1i**, respectively) compared to the corresponding densities of the photoreactive quinones **1e** and **1k** bearing the same substituents ($D_{calcd.}$ = 1.28 and 1.42 Mg m^{-3} for **1e** and **1k**, respectively).

The crystals of the quinones **1a**−**1c**, **1e**, **1k** (β arrangement)−**1o**, **1q**, **1r**, **1t** and **1u** exhibit significant colour changes and continuous decomposition of the initial crystalline state after irradiation for five hours. Simultaneously, the melting range rises by 35−80°C. In the case of **1k** (β arrangement)−**1o**, **1q** and **1t**, too many decompositon products were formed during irradiation under the described conditions (dark colour, ^{1}H-NMR spectra). Therefore, the irradiation was repeated under more moderate conditions, using a filter (absorption edge 520 nm) to eliminate the short-wavelength range. The photochemically formed products were detected by IR and ^{1}H-NMR spectroscopy. From the spectroscopic and X-ray data (see below), only cyclobutanes **9** could be identified as resulting from [2+2] cycloadditions of the vinylic double bonds (Scheme 5).

The reaction products were treated with acetone or toluene at room temperature to remove the unreacted monomers. The remaining dimers of **1b**, **1c**, **1e** and **1r** could be recrystallized, isolated purely with yields of 28−59% and characterized. The irradiation products of **1a**, **1o** and **1u** obtained in yields of 22−52% could not be dissolved to perform NMR-spectroscopical studies. Therefore only IR and MS investigations were carried out. The reaction products of **1k** (β arrangement)−**1m**, **1q** and **1t** could not be isolated and consequently the spectroscopical data were obtained only from the reaction mixture. The irradiated sample of **1n** was treated in the same manner. Subsequently, the dimer could be isolated as an insoluble precipitate in a yield of 36%.

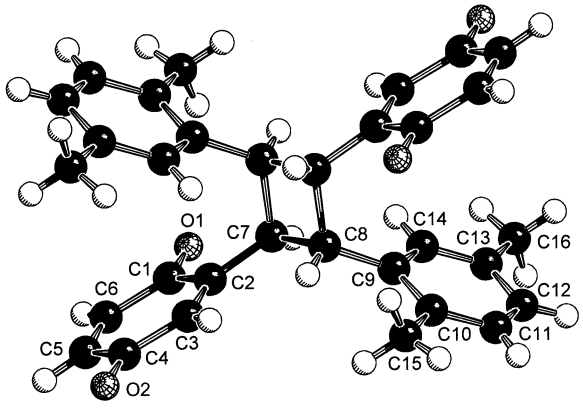
Scheme 5. Photoinduced dimerizations in the solid state of the quinones **1** to the cyclobutanes **9**



Crystal Structures of the Dimers 9b, 9e and 9r

For the topochemically generated dimers **9b**, **9e** and **9r**, crystals suitable for X-ray diffraction could be obtained and analysed. The molecules lie on crystallographic centres of symmetry (space group $P2_1/c$ with Z = 2). The cyclobutanes have *r-ctt* configurations with the quinone rings attached in the 1,3 position (Figure 9).

Figure 9. Molecular structure of the cyclobutane **9e** with labelling exemplary for all the derivatives **9** investigated by X-ray analysis



The molecular structure of the cyclobutane **9e** (Figure 9) corresponds precisely to the centrosymmetric head-to-tail orientation of monomeric quinone **1e** in the crystal (Figure 6), as unequivocally determined by X-ray analysis. The photoinduced [2+2] cycloaddition of the vinylic double bonds of **1e** in the solid state is, therefore, exclusively controlled

by topochemical aspects. By retrospective conclusions, assuming a topochemical course of the dimerizations, the centrosymmetric α-type packing arrangement can also be deduced for the crystal structures of quinones **1b** and **1r**, further supported the cell dimensions determined for **1r**. In the cyclobutane rings of **9b**, **9e** and **9r**, the repulsive forces between both substituents in the *cis* orientation with non-bonding 1,4-distances C2···C9′ of 2.970(2)−3.038(2) Å give rise to a stretching of the corresponding bond lengths in the four-membered rings C7−C8′ by up to 1.582(2)−1.593(2) Å. The steric hindrance is increased by the planar form of the cyclobutane rings required by the centres of symmetry in the crystal. Consequently, the eclipsed orientation of the substituents can not be relaxed by a folding of the four-membered ring system. The second cyclobutane ring bond C7−C8 is not sterically strained because of the *trans*-substitution pattern, and is much shorter with lengths of 1.549(2)−1.555(2) Å. The deformation of the quinone rings of the derivatives **1**, caused by conjugation with vinyl substituents, can not take place in the dimers **9**. Therefore the bond lengths C1−C6, C3−C4 and C4−C5 of 1.465(3)−1.480(3) Å have the same order of magnitude. The bonds C1−C2 are lengthened up to 1.493(2)−1.502(2) Å because of the non-bonding repulsive 1,4-interactions C7···O1 of 2.781(2)−2.795(2) Å.

The quinone rings of **9b**, **9e** and **9r** have short intermolecular contacts of 3.647(3)−3.837(2) Å between C=C double bonds of neighbouring molecules related by a centre of symmetry. Nevertheless, no photoinduced reactions could be performed in the solid state. Probably because of the rigid crystal lattice generated by strong interlocking of the bulky molecules, any movement necessary for reaction is prevented.

Spectroscopy of the Dimers 9

The ^{1}H- and ^{13}C-NMR signals of the aryl and quinone substituents of the dimers **9b**, **9c**, **9e** and **9r** can be assigned as discussed for the monomers. For the cyclobutane protons of these dimers, an AA′BB′ spin system was found at which the midpoint of the multiplets are the following: **9b**: δ = 4.48; **9c**: δ = 4.32; **9e**: δ = 4.45; **9r**: δ = 4.47. The habitus of the multiplets is unique for all four dimers with the highest intensities being in the central region. In the ^{13}C-NMR spectra, the two signals for the cyclobutane carbon atoms appear at δ = 39.4−41.2 and δ = 41.1−44.1 (Δδ = 1.7−2.9). Since the molecular structure of the dimers **9b**, **9e** and **9r** is known from X-ray analysis, it can be deduced that the cyclobutane ring of the dimer **9c** also has a centre of symmetry (Scheme 5). This correlates with the α-type packing arrangement determined for the monomer crystals, involving an antiparallel orientation of the molecules **1c**.

For these four dimers and for the insoluble dimers **9a**, **9n**, **9o** and **9u**, IR spectra were recorded. The characteristic absorptions of the stretching and bending vibrations of quinoid C=O and C=C bonds appear in the expected range (Table 5), comparable to the corresponding monomers **1** (Table 2), indicating that the quinoid double bonds are not involved in dimerization.

Table 5. Selected IR-spectroscopical data of the cyclobutanes **9a**, **9b**, **9c**, **9e**, **9n**, **9o**, **9r** and **9u**

comp.	stretching vibration $\tilde{\nu}$ [cm^{-1}] C=O	C=C (quinone)	bending vibration $\tilde{\nu}$ [cm^{-1}] =C−H	=C−H *(cis)*
9a	1684, 1664	1596	826	700
9b	1656	1596	–	730
9c	1657	1599	782	707
9e	1656	1598	840, 813	–
9n	1683, 1659	1603	813	–
9o	1708	1580	805	732, 681
9r	1656	1597	787	713
9u	1686, 1667	1602	840, 792	731

On the other hand, the IR absorptions of the *trans*-vinylic double bonds of the quinones **1** disappeared in the spectra of **9**, confirming the [2+2] cycloaddition at these bonds of **1b**, **1c**, **1e** and **1r**, already identified by X-ray analysis and NMR spectroscopy and proving at the same time the analogous reaction at the vinylic double bonds of **1a**, **1n**, **1o** and **1u** to the corresponding dimers **9**.

In the mass spectra (EI) of these eight dimers, the molecular-ion peaks were detected. There were no mass-spectrometrical indications for oligomers formed by radical reactions, which is in agreement with the determined melting points having the same order of magnitude (ΔT = + 15°C).

On the supposition of the topochemical principles a C_i symmetry can also be derived for the insoluble dimers **9a**, **9n** and **9u** (Scheme 5) from the crystal structure of the corresponding monomers, ascertained by X-ray investigations. For the insoluble dimer **9o**, only the cyclobutane structure can be deduced from IR and MS data, without establishing the substitution pattern of the four-membered ring.

The photoproducts of the monomeric quinones **1k** (β arrangement), **1l**, **1m**, **1q** and **1t** could not be isolated because of decomposition problems. Nevertheless, the structure of the dimers could be determined from the data of ^{1}H- and ^{13}C-NMR spectra and mass spectra of the crude irradiation samples, in comparison to the corresponding data of the known dimer structures.

In the ^{1}H-NMR spectra of the dimers **9l**, **9m** and **9q**, AA′BB′ spin systems were observed for the cyclobutane protons, comparable to the ^{1}H-NMR data of the dimers already discussed (midpoint of the multiplets: **9l**: δ = 4.57; **9m**: δ = 4.51; **9q**: δ = 4.30). The corresponding ^{13}C-NMR spectra of **9m** and **9q** reveal two signals for the cyclobutane carbon atoms in the expected range at δ = 39.8, 40.3 and δ = 40.9, 44.4 (Δδ = 1.1 and 4.1), respectively. In the mass spectra, the molecular ion peaks of the dimers **9l**, **9m** and **9q** could be detected. We can thus conclude centrosymmetric structures for the cyclobutanes **9l**, **9m** and **9q** (Scheme 5). Assuming a topochemical course of the dimerization reactions, an α-type packing arrangement with head-to-tail orientation of the molecules can be deduced retrospectively for the crystal structures of monomeric quinones **1l**, **1m** and **1q** from the C_i symmetry of the dimers. The dimers **9k** and **9t** were generated from monomers with a β-type packing pattern. Therefore, dimers with mirror symmetry are expected if the reaction course is topochemically controlled.

In the ^{1}H-NMR spectra of **9k** and **9t** one broad signal with the chemical shift in the range of cyclobutanes was detected (**9k**: δ = 4.48; **9t**: δ = 4.60). These chemical shifts are comparable to the data for our dimers resulting from vinylic [2+2] cycloadditions and far from the data for quinone dimers[4d][20] or oxetane systems[21]. We can derive from the chemical shift of the cyclobutane protons that dimerizations of the vinylic double bonds of **1k** and **1t** have taken place and from the β-type-layered structures of these monomers and the habitus of the ^{1}H-NMR signals which is different from the habitus of the C_i dimers that there is a mirror symmetry for the dimers **9k** and **9t** (Scheme 5). Since only one kind of cyclobutane signal was detected, consecutive cycloadditions to cage structures or oligomers were excluded. This conclusion is supported by the ^{13}C-NMR data of **9k**, with only two signals for cyclobutane carbon atoms (δ = 40.2 and 44.3).

Contrary to the photochemistry of these types of quinones in solution[9], we performed photoinduced, uniform dimerizations in the solid state of the 2-monovinyl-substituted 1,4-benzoquinones **1a**−**1c**, **1e**, **1l**−**1n**, **1q**, **1r** and **1u** to corresponding centrosymmetric dimers **9** by [2+2] cycloadditions of the vinylic double bonds. The irradiation of the crystals of **1k** and **1t**, with a β-type packing arrangement designed by crystal-engineering devices, resulted in the corresponding cyclobutanes **9** with mirror symmetry.

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Experimental Section

General: Melting points: Dr.Tottoli apparatus from Büchi, open capillary tubes, all melting points are uncorrected. − IR: Bruker IFS 66. − UV/Vis: HP 8452 A (diode array). − Fluorescence: Jobin Yvon Spectrofluo JY 3D. − NMR: Bruker AC 300 (300 and 75 MHz, for ^{1}H and ^{13}C, respectively); chemical shifts are relative to the solvent signal ($CDCl_3$: δ_H = 7.26; δ_C = 77.0). − MS: Finnigan 3200 (70 eV) and Vacuum Generators Micromass ZAB-2F (70 eV, high resolution). − Elemental analyses: Heraeus CHN-O-Rapid. − Precursors for the syntheses have already been reported in the literature and were prepared as described or according to literature procedures: ethyl 3,4-dimethylbenzoate[22][23], 3,4-dimethylbenzyl alcohol[24][25], 3,4-dimethylbenzyl chloride[26], ethyl 3,5-dimethylbenzoate[22][27], 3,5-dimethylbenzyl alcohol[24][28], 3,5-dimethylbenzyl chloride[26][29], 2,3-dichlorobenzoyl chloride[30][31], 2,3-dichlorobenzyl alcohol[24][32], 2,3-dichlorobenzyl chloride[33][34], 2,5-dichlorobenzyl alcohol[24][35], 2,5-dichlorobenzyl chloride[33][36], 3,5-dichlorobenzyl alcohol[24][33], 3,5-dichlorobenzyl chloride[33], 3-chloro-2-methylbenzyl alcohol[37], 3-chloro-2-methylbenzyl chloride[26][38], 4-bromomethylbenzoic acid[39], methyl 4-bromomethylbenzoate[39], 2,5-dimethoxybenzyl alcohol[40][41], 2,5-dimethoxybenzyl chloride[41], diethyl benzylphosphonates **2a**[42], **2b**[43], **2c**[44], **2d**[44][45], **2e**[46], **2g**[47], **2h**[43], **2i**[45], **2k**[45], **2m**[48], **2o**[49], **2p**[48], **2t**[44], diethyl (2,5-dimethoxybenzyl)phosphonate[50], 1,4-dimethoxy-2-[2-(phenyl)ethenyl]benzene (**3a**)[51], methyl 2,5-dimethoxycinnamate (**3u**)[10], methyl 3-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)acrylate (**4u**)[10b].

General Procedure for the Synthesis of the Diethyl Benzylphosphonates **2**: A mixture of the appropriately substituted benzyl halide (0.1 mol) and triethyl phosphite (0.11 mol) is heated at 180°C for at least 4 h. The excess triethyl phosphite is removed by distillation at 100°C under reduced pressure. The residue is distilled under vacuum to give the derivatives **2** as colourless, oily liquids.

Diethyl (3,4-Dimethylbenzyl)phosphonate (**2f**): Yield: 34.8 g (80%). − B.p. 142−145°C/0.6 Torr. − IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1} (m), 2908 (m, C−H), 1506 (m, C_{ar}=C_{ar}), 1455 (w), 1391 (w, C−H), 1249 (s, P=O), 1056 (s), 1029 (s, P−O−C). − ^{1}H NMR ($CDCl_3$): δ = 1.23 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 2.20 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 3.06 (d, $^2J_{HP}$ = 21.4 Hz, 2 H, CH_2P), 3.99 (quint, ^3J = 7.1 Hz, 4 H, CH_2CH_3), 7.00 (d, ^3J = 7.8 Hz, 1 H, 4-H or 5-H), 7.01 (d, ^4J = 1.6 Hz, 1 H, 2-H), 7.04 (d, ^3J = 8.8 Hz, 1 H, 4-H or 5-H). − ^{13}C NMR ($CDCl_3$): δ = 16.3, 16.4 (2 CH_2CH_3, ^3J = 5.9 Hz), 19.3, 19.3 (CH_3, ^5J = 0.9 Hz), 19.7 (CH_3), 32.3, 34.1 (CH_2P, ^1J = 138.2 Hz), 61.9, 62.0 (2 CH_2CH_3, ^2J = 6.8 Hz), 127.0, 127.1 (J = 6.7 Hz), 128.7, 128.8 (J = 9.1 Hz), 129.7, 129.8 (J = 3.1 Hz), 131.0, 131.0 (J = 6.5 Hz), 135.0, 135.0 (J = 3.7 Hz), 136.6, 136.6 (J = 3.1 Hz) (6 aromatic C). − MS (70 eV); *m/z* (%): 256 (32) [M$^+$], 228 (11) [M$^+$ − C_2H_4], 200 (10) [M$^+$ − 2 × C_2H_4], 119 (100), 91 (37) [$C_7H_7^+$], 77 (14) [$C_6H_5^+$], 65 (11) [$C_5H_5^+$]. − $C_{13}H_{21}O_3P$ (256.78): calcd. C 60.93, H 8.26, P 12.09; found C 61.01, H 8.39, P 12.12.

Diethyl (2,3-Dichlorobenzyl)phosphonate (**2l**): Yield: 36.7 g (83%). − B.p. 141−143°C/0.1 Torr. − IR (KBr): $\tilde{\nu}$ = 2983 cm^{-1} (m), 2930 (w), 2907 (w, C−H), 1585 (w, C_{ar}=C_{ar}), 1452 (m), 1425 (s), 1392 (m, C−H), 1251 (s, P=O), 1055 (s), 1027 (s, P−O−C). − ^{1}H NMR ($CDCl_3$): δ = 1.20 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3), 3.36 (d, $^2J_{HP}$ = 22.1 Hz, 2 H, CH_2P), 4.00 (quint, ^3J = 7.1 Hz, 4 H, CH_2CH_3), 7.10 (dd, ^3J = 7.9 Hz, ^3J = 7.8 Hz, 1 H, 5-H), 7.12 (d, ^3J = 7.8 Hz, 1 H, 6-H), 7.30 (dd, ^3J = 8.0 Hz, ^4J = 1.65 Hz, 1 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 16.3, 16.4 (2 CH_2CH_3, ^3J = 6.0 Hz), 30.9, 32.7 (CH_2P, ^1J = 139.3 Hz), 62.3, 62.4 (2 CH_2CH_3, ^2J = 6.7 Hz), 127.0, 127.1 (J = 3.5 Hz), 129.1, 129.2 (J = 3.6 Hz), 129.8, 129.8 (J = 5.4 Hz), 132.6, 132.7 (J = 8.9 Hz), 133.4, 133.4 (J = 3.5 Hz) (6 aromatic C). − MS (70 eV); *m/z* (%): 299 (0.2) [M$^+$ + 1, $C_{11}H_{15}{}^{37}Cl^{35}ClO_3P^+$ + 1], 297 (0.6) [M$^+$ + 1, $C_{11}H_{15}{}^{35}Cl_2O_3P^+$ + 1], 263 (25) [M$^+$ − Cl], 261 (70) [M$^+$ − Cl], 233 (22) [M$^+$ − Cl, − C_2H_4], 205 (98) [M$^+$ − Cl, − 2 × C_2H_4], 91 (34) [$C_7H_7^+$], 81 (100), 65 (38) [$C_5H_5^+$]. − $C_{11}H_{15}Cl_2O_3P$ (297.12): calcd. C 44.47, H 5.09, Cl 23.86, P 10.43; found C 44.47, H 5.22, Cl 24.14, P 10.56.

Diethyl (2,5-Dichlorobenzyl)phosphonate (**2n**): Yield: 27.3 g (96%). − B.p. 118−129°C/0.01 Torr. − M.p. 51°C. − IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1} (s), 2933 (m), 2912 (m, C−H), 1590 (m, C_{ar}=C_{ar}), 1469 (s), 1443 (m), 1396 (s, C−H), 1240 (s, P=O), 1063 (s), 1023 (s, P−O−C). − ^{1}H NMR ($CDCl_3$): δ = 1.26 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3), 3.31 (d, $^2J_{HP}$ = 22.1 Hz, 2 H, CH_2P), 4.06 (quint, ^3J = 7.05 Hz, 4 H, CH_2CH_3), 7.16 (dd, ^3J = 8.6 Hz, ^4J = 2.4 Hz, 1 H, 4-H), 7.30 (dd, ^3J = 8.6 Hz, ^5J = 0.9 Hz, 1 H, 3-H), 7.41 (d, ^4J = 2.6 Hz, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 16.3, 16.4 (2 CH_2CH_3, ^3J = 6.1 Hz), 29.9, 31.7 (CH_2P, ^1J = 139.3 Hz), 62.3, 62.4 (2 CH_2CH_3, ^2J = 6.7 Hz), 128.4, 128.4 (J = 3.7 Hz), 130.6, 130.6 (J = 3.0 Hz), 131.5, 131.5 (J = 5.1 Hz), 131.9, 132.0 (J = 9.1 Hz), 132.5, 132.6, 132.6 (J = 4.3 Hz, J = 3.3 Hz) (6 aromatic C). − MS (70 eV); *m/z* (%): 263 (31) [M$^+$ − Cl, $C_{11}H_{15}{}^{37}Cl^{35}ClO_3P^+$ − Cl], 261 (92) [M$^+$ − Cl, $C_{11}H_{15}{}^{35}Cl_2O_3P^+$ − Cl], 233 (28) [M$^+$ − Cl, − C_2H_4], 205 (100) [M$^+$ − Cl, − 2 × C_2H_4]. − $C_{11}H_{15}Cl_2O_3P$ (297.12): calcd. C 44.47, H 5.09, Cl 23.86, P 10.43; found C 44.79, H 5.22, Cl 23.21, P 10.65.

Diethyl (3,5-Dichlorobenzyl)phosphonate (**2q**): Yield: 24.1 g (90%). − B.p. 129−133°C/0.1 Torr. − IR (KBr): $\tilde{\nu}$ = 2983 cm^{-1}

(m), 2931 (w), 2908 (w, C−H), 1590 (m, C_{ar}=C_{ar}), 1433 (m), 1392 (m, C−H), 1249 (s, P=O), 1054 (s), 1028 (s, P−O−C). − ^{1}H NMR ($CDCl_3$): δ = 1.21 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3), 3.02 (d, $^2J_{HP}$ = 21.8 Hz, 2 H, CH_2P), 3.99 (quint, ^3J = 7.1 Hz, 4 H, CH_2CH_3), 7.13 (dd, ^4J = 1.95 Hz, ^4J = 1.95 Hz, 2 H, 2-H, 6-H), 7.18 (dd, ^4J = 1.9 Hz, ^4J = 1.85 Hz, 1 H, 4-H). − MS (70 eV); *m/z* (%): 298 (6) [M^+, $C_{11}H_{15}{}^{37}Cl^{35}ClO_3P^+$], 296 (10) [$M^+$, $C_{11}H_{15}{}^{35}Cl_2O_3P^+$], 240 (9) [$M^+ - 2 \times C_2H_4$], 109 (100), 91 (34) [$C_7H_7^+$], 65 (35) [$C_5H_5^+$]. − $C_{11}H_{15}Cl_2O_3P$ (297.12): calcd. C 44.47, H 5.09, Cl 23.86, P 10.43; found C 44.43, H 5.36, Cl 23.62, P 10.71.

Diethyl (3-Chloro-2-methylbenzyl)phosphonate (**2r**): Yield: 79.8 g (91%). − B.p. 135−142°C/0.15 Torr. − IR (KBr): $\tilde{\nu}$ = 2982 cm^{-1} (m), 2930 (w), 2907 (w, C−H), 1570 (m, C_{ar}=C_{ar}), 1443 (m), 1391 (m, C−H), 1249 (s, P=O), 1055 (s), 1027 (s, P−O−C). − ^{1}H NMR ($CDCl_3$): δ = 1.17 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 2.36 (s, 3 H, CH_3), 3.14 (d, $^2J_{HP}$ = 22.0 Hz, 2 H, CH_2P), 3.94 (quint, ^3J = 7.1 Hz, 4 H, CH_2CH_3), 6.99 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, 1 H, 5-H), 7.10 (dd, ^3J = 6.7 Hz, ^4J = 2.6 Hz, 1 H, 6-H), 7.18 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 1 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 16.1, 16.2 (2 CH_2CH_3, ^3J = 6.0 Hz), 16.4, 16.5 (CH_3, ^4J = 0.9 Hz), 30.8, 32.7 (CH_2P, ^1J = 138.6 Hz), 61.8, 61.9 (2 CH_2CH_3, ^2J = 6.8 Hz), 126.2, 126.2 (*J* = 3.6 Hz), 127.8, 127.9 (*J* = 3.9 Hz), 129.0, 129.1 (*J* = 5.6 Hz), 132.1, 132.2 (*J* = 9.3 Hz), 134.8, 134.9, 135.0 (*J* = 6.7 Hz, *J* = 5.1 Hz) (6 aromatic C). − MS (70 eV); *m/z* (%): 278 (36) [M^+, $C_{12}H_{18}{}^{37}ClO_3P^+$], 276 (100) [$M^+$, $C_{12}H_{18}{}^{35}ClO_3P^+$], 248 (33) [$M^+ - C_2H_4$], 220 (85) [$M^+ - 2 \times C_2H_4$], 185 (43) [$M^+ - 2 \times C_2H_4$, − Cl], 77 (52) [$C_6H_5^+$]. − $C_{12}H_{18}ClO_3P$ (276.70): calcd. C 52.09, H 6.56, Cl 12.81, P 11.19; found C 51.90, H 6.65, Cl 12.99, P 11.25.

General Procedure for the Synthesis of the Phenyl(ethenyl)benzenes **3**: 2,5-Dimethoxybenzaldehyde (16.6 g, 0.1 mol) and 0.13 mol of the corresponding phosphonates **2** were dissolved in 100 ml of absolute DMF. Methanolic sodium methoxide solution (25.6 g. 0.66 mol, 30%) was added dropwise at such a rate that the temperature did not exceed 60°C. The mixture was then stirred at room temperature at least for 4 h at which stage the resulting derivative **3** could easily be detected by the blue fluorescence on irradiation with UV light (λ = 366 nm). After addition to ice-cold water (300 ml), the resulting mixture was extracted with ether (3 × 200 ml). The combined ether extracts were washed with water (2 × 100 ml), then with saturated aqueous sodium chloride (100 ml) and dried with $MgSO_4$. After removal of the solvent, the crude products crystallized or they were crystallized from methanol. For purification, they were recrystallized twice from methanol to give the isomerically pure derivatives **3** as colourless or light-yellow crystals. − ^{1}H NMR: For characterization of the quinoid and olefinic protons H_a−H_e of the compounds **3**, see Figure 1. The aromatic protons H_f−H_k of the substituents were labelled clockwise. For yields, melting points, UV/Vis and fluorescence data, molecular formulae and masses, and elemental analyses of the phenyl(ethenyl)benzenes **3**, see Table 6.

1,4-Dimethoxy-2-[2-(2-methylphenyl)ethenyl]benzene (**3b**): IR (KBr): $\tilde{\nu}$ = 2947 cm^{-1} (m), 2911 (w), 2833 (m, C−H), 1500 (s, C_{ar}=C_{ar}), 1466 (m), 1451 (m, C−H), 1250 (m), 1218 (s), 1042 (s, C−O), 968 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 2.44 (s, 3 H, CH_3), 3.84 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.81 (dd, ^3J = 8.9 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.86 (d, ^3J = 8.8 Hz, 1 H, H_a), 7.19 (s, 1 H, H_C), 7.17−7.25 (m, 2 H, H_g, H_h), 7.27 (d, ^3J = 8.0 Hz, 1 H, H_i), 7.34 (s, 2 H, H_d, H_e), 7.65 (d, 1 H, ^3J = 6.9 Hz, H_f). − ^{13}C NMR ($CDCl_3$): δ = 19.9 (CH_3), 55.8, 56.4 (OCH_3), 112.3, 112.4, 113.4, 124.7, 125.6, 126.2, 127.4, 127.4, 127.9, 130.3, 135.8, 136.9 (10 aromatic C; 2 olefinic C), 151.6, 153.9 (C_{ar}−OCH_3). − MS (70 eV); *m/z* (%): 255 (19) [M^+ + 1], 254 (100) [M^+], 239 (9) [$M^+ - CH_3$], 211 (16) [$M^+ - C_2H_3O$], 105 (9) [$C_8H_9^+$], 91 (5) [$C_7H_7^+$], 77 (4) [$C_6H_5^+$], 65 (4) [$C_5H_5^+$], 51 (4) [$C_4H_3^+$].

1,4-Dimethoxy-2-[2-(3-methylphenyl)ethenyl]benzene (**3c**): IR (KBr): $\tilde{\nu}$ = 2964 cm^{-1} (m), 2944 (m), 2837 (m, C−H), 1601 (m), 1583 (w), 1498 (s, C_{ar}=C_{ar}), 1464 (m), 1453 (m), 1441 (m, C−H), 1271 (m), 1257 (m), 1233 (s), 1221 (s), 1043 (s, C−O), 975 (s), 961 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 6.80 (dd, ^3J = 8.9 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.85 (d, ^3J = 8.9 Hz, 1 H, H_a), 7.08 (d, ^3J = 16.4 Hz, 1 H, H_e), 7.08 (d, ^3J = 7.5 Hz, 1 H, H_h), 7.17 (d, ^4J = 2.8 Hz, 1 H, H_c), 7.25 (dd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, 1 H, H_g), 7.36 (d, ^3J = 8.6 Hz, 1 H, H_f), 7.37 (s, 1 H, H_k), 7.46 (d, ^3J = 16.5 Hz, 1 H, H_d). − ^{13}C NMR ($CDCl_3$): δ = 21.5 (CH_3), 55.8, 56.4 (OCH_3), 111.7, 112.5, 113.7, 123.2, 123.9, 127.3, 127.5, 128.4, 128.5, 129.5, 137.8, 138.1 (10 aromatic C; 2 olefinic C), 151.6, 153.9 (C_{ar}−OCH_3). − MS (70 eV); *m/z* (%): 255 (20) [M^+ + 1], 254 (100) [M^+], 239 (12) [$M^+ - CH_3$], 211 (15) [$M^+ - C_2H_3O$], 91 (3) [$C_7H_7^+$], 77 (3) [$C_6H_5^+$].

1,4-Dimethoxy-2-[2-(4-methylphenyl)ethenyl]benzene (**3d**): IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1} (w), 2836 (w, C−H), 1599 (w), 1498 (s, C_{ar}=C_{ar}), 1460 (m, C−H), 1252 (m), 1220 (s), 1043 (s, C−O), 976 (m), 960 (w, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 2.41 (s, 3 H, CH_3), 3.86 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 6.82 (dd, ^3J = 8.9 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.87 (d, ^3J = 8.8 Hz, 1 H, H_a), 7.13 (d, ^3J = 16.5 Hz, 1 H, H_e), 7.21 (d, ^4J = 3.0 Hz, 1 H, H_c), 7.21 (d, ^3J = 7.1 Hz, 2 H, H_g, H_i), 7.47 (d, ^3J = 7.5 Hz, 2 H, H_f, H_k), 7.48 (d, ^3J = 15.6 Hz, 1 H, H_d). − ^{13}C NMR ($CDCl_3$): δ = 21.3 (CH_3), 55.8, 56.3 (OCH_3), 111.8, 112.5, 113.6, 122.4, 126.6, 127.6, 129.1, 129.4, 135.2, 137.4 (10 aromatic C; 2 olefinic C), 151.6, 154.0 (C_{ar}−OCH_3). − MS (70 eV); *m/z* (%): 255 (17) [M^+ + 1], 254 (100) [M^+], 239 (10) [$M^+ - CH_3$], 211 (28) [$M^+ - C_2H_3O$], 105 (13) [$C_8H_9^+$], 91 (7) [$C_7H_7^+$], 77 (6) [$C_6H_5^+$], 65 (6) [$C_5H_5^+$], 51 (7) [$C_4H_3^+$].

1,4-Dimethoxy-2-[2-(2,5-dimethylphenyl)ethenyl]benzene (**3e**): IR (KBr): $\tilde{\nu}$ = 2961 cm^{-1} (w), 2945 (w), 2837 (w, C−H), 1607 (w), 1498 (s, C_{ar}=C_{ar}), 1467 (m), 1455 (m), 1442 (m, C−H), 1269 (m), 1257 (m), 1219 (s), 1046 (s, C−O), 969 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.80 (dd, ^3J = 8.9 Hz, ^4J = 2.8 Hz, 1 H, H_b), 6.85 (d, ^3J = 8.9 Hz, 1 H, H_a), 6.99 (d, ^3J = 7.6 Hz, 1 H, H_h), 7.06 (d, ^3J = 7.8 Hz, 1 H, H_i), 7.16 (d, ^4J = 2.8 Hz, 1 H, H_c), 7.31 (s, 1 H, H_d), 7.31 (s, 1 H, H_e), 7.45 (s, 1 H, H_f). − ^{13}C NMR ($CDCl_3$): δ = 19.5, 21.1 (CH_3), 55.8, 56.4 (OCH_3), 112.3, 112.4, 113.3, 124.3, 126.2, 127.5, 128.0, 128.3, 130.3, 132.8, 135.5, 136.6 (10 aromatic C; 2 olefinic C), 151.6, 153.9 (C_{ar}−OCH_3). − MS (70 eV); *m/z* (%): 269 (20) [M^+ + 1], 268 (100) [M^+], 253 (8) [$M^+ - CH_3$], 238 (6) [$M^+ - 2 \times CH_3$], 225 (14) [$M^+ - C_2H_3O$], 91 (3) [$C_7H_7^+$], 77 (3) [$C_6H_5^+$], 65 (2) [$C_5H_5^+$], 51 (2) [$C_4H_3^+$].

1,4-Dimethoxy-2-[2-(3,4-dimethylphenyl)ethenyl]benzene (**3f**): IR (film, melt): $\tilde{\nu}$ = 2939 cm^{-1} (m), 2832 (m, C−H), 1606 (m), 1581 (m), 1494 (s, C_{ar}=C_{ar}), 1464 (m), 1453 (m, C−H), 1283 (m), 1237 (m), 1218 (s), 1049 (m), 1026 (m, C−O), 969 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 2.32 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 3.86 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 6.82 (dd, ^3J = 8.9 Hz, ^4J = 2.8 Hz, 1 H, H_b), 6.87 (d, ^3J = 8.8 Hz, 1 H, H_a), 7.11 (d, ^3J = 16.5 Hz, 1 H, H_e), 7.17 (d, ^3J = 7.8 Hz, 1 H, H_g), 7.22 (d, ^4J = 2.7 Hz, 1 H, H_c), 7.35 (d, ^3J = 7.8 Hz, 1 H, H_f), 7.38 (s, 1 H, H_k), 7.48 (d, ^3J = 16.5 Hz, 1 H, H_d). − ^{13}C NMR ($CDCl_3$): δ = 19.9, 19.8 (CH_3), 55.8, 56.4 (OCH_3), 111.7, 112.5, 113.5, 122.2, 124.3, 127.7, 128.0, 129.5, 130.0, 135.6, 136.1, 136.7 (10 aromatic C; 2 olefinic C), 151.6, 154.0 (C_{ar}−OCH_3). − MS (70 eV); *m/z* (%): 269 (21)

Table 6. Yields, melting points, UV/Vis and fluorescence data, molecular formulae and masses, and elemental analyses of the phenyl(ethenyl)benzenes **3**

comp.	yield [%]	m.p.[a] [°C]	UV/Vis[b] λ_{max} (lg ε) [nm]	fluor.[c] λ_{max} [nm]	empirical formula	molecular mass	C calcd.	C found	H calcd.	H found	Cl calcd.	Cl found
3b	84	64	242 (3.68), 290 (3.88), 338 (3.79)	440	$C_{17}H_{18}O_2$	254.33	80.28	80.17	7.14	7.05		
3c	72	42	242 (3.99), 294 (4.22), 342 (4.12)	418	$C_{17}H_{18}O_2$	254.33	80.28	80.31	7.14	7.18		
3d	89	78	242 (3.94), 294 (4.16), 342 (4.09)	434	$C_{17}H_{18}O_2$	254.33	80.28	80.06	7.14	7.18		
3e	93	75	242 (4.18), 290 (4.16), 338 (4.09)	420	$C_{18}H_{20}O_2$	268.35	80.57	80.50	7.51	7.59		
3f	78	29	242 (4.07), 298 (4.23), 340 (4.19)	412	$C_{18}H_{20}O_2$	268.35	80.57	80.30	7.51	7.42		
3g	79	67	242 (4.10), 296 (4.24), 340 (4.16)	413	$C_{18}H_{20}O_2$	268.35	80.57	80.53	7.51	7.61		
3h	78	39	242 (4.05), 292 (4.18), 344 (4.05)	429	$C_{16}H_{15}ClO_2$	274.75	69.95	69.77	5.46	5.61	12.93	13.03
3i	76	54	240 (4.06), 294 (4.22), 344 (4.09)	424	$C_{16}H_{15}ClO_2$	274.75	69.95	70.10	5.46	5.57	12.93	13.20
3k	79	89	242 (4.12), 296 (4.38), 344 (4.26)	420	$C_{16}H_{15}ClO_2$	274.75	69.95	70.22	5.46	5.54	12.93	13.14
3l	93	76	244 (3.97), 294 (4.12), 348 (3.97)	436	$C_{16}H_{14}Cl_2O_2$	309.19	62.18	61.98	4.53	4.59	22.94	23.20
3m	95	79	242 (4.04), 296 (4.29), 348 (4.15)	432	$C_{16}H_{14}Cl_2O_2$	309.19	62.18	62.24	4.53	4.59	22.94	22.72
3n	89	119	244 (4.11), 292 (4.21), 348 (4.08)	436	$C_{16}H_{14}Cl_2O_2$	309.19	62.18	62.24	4.53	4.59	22.94	23.15
3o	88	57	244 (4.11), 286 (4.17), 338 (4.01)	382	$C_{16}H_{14}Cl_2O_2$	309.19	62.18	62.10	4.53	4.57	22.94	22.95
3p	82	88	242 (4.00), 296 (4.27), 348 (4.12)	425	$C_{16}H_{14}Cl_2O_2$	309.19	62.18	62.12	4.53	4.57	22.94	23.10
3q	92	102	242 (4.12), 296 (4.26), 350 (4.10)	434	$C_{16}H_{14}Cl_2O_2$	309.19	62.18	62.17	4.53	4.63	22.94	23.09
3r	92	60	242 (4.30), 288 (4.22), 338 (4.03)	424	$C_{17}H_{17}ClO_2$	288.77	70.71	70.89	5.93	6.09	12.28	12.22
3t	65	81	244 (3.95), 310 (4.36), 356 (4.28)	450	$C_{18}H_{18}O_4$	298.34	72.47	72.51	6.08	6.13		

[a] Solvent: methanol. – [b] Solvent: $CHCl_3$. – [c] Solvent: $CHCl_3$.

[M^+ + 1], 268 (100) [M^+], 253 (7) [$M^+ - CH_3$], 238 (4) [$M^+ - 2 \times CH_3$], 225 (10) [$M^+ - C_2H_3O$], 91 (2) [$C_7H_7^+$], 77 (2) [$C_6H_5^+$].

1,4-Dimethoxy-2-[2-(3,5-dimethylphenyl)ethenyl]benzene (**3g**): IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (m), 2914 (m), 2835 (w, C–H), 1601 (m), 1494 (s, C_{ar}=C_{ar}), 1467 (m), 1450 (m, C–H), 1259 (m), 1242 (m), 1218 (s), 1047 (s, C–O), 969 (m, =C–H). – ^{1}H NMR ($CDCl_3$): δ = 2.34 (s, 6 H, CH_3), 3.83 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 6.79 (dd, ^3J = 8.9 Hz, ^4J = 2.9 Hz, 1 H, H_b), 6.85 (d, ^3J = 8.9 Hz, 1 H, H_a), 6.91 (s, 1 H, H_h), 7.04 (d, ^3J = 16.5 Hz, 1 H, H_e), 7.15 (d, ^4J = 2.9 Hz, 2 H, H_f, H_k), 7.17 (s, 1 H, H_c), 7.43 (d, ^3J = 16.5 Hz, 1 H, H_d). – ^{13}C NMR ($CDCl_3$): δ = 21.3 (CH_3), 55.8, 56.4 (OCH_3), 111.7, 112.5, 113.6, 122.9, 124.6, 127.6, 129.3, 129.6, 137.7, 138.0 (10 aromatic C; 2 olefinic C), 151.6, 153.9 (C_{ar}–OCH_3). – MS (70 eV); *m/z* (%): 269 (20) [M^+ + 1], 268 (100) [M^+], 253 (8) [$M^+ - CH_3$], 238 (7) [$M^+ - 2 \times CH_3$], 225 (21) [$M^+ - C_2H_3O$], 91 (3) [$C_7H_7^+$], 77 (3) [$C_6H_5^+$].

1-Chloro-2-[2-(2,5-dimethoxyphenyl)ethenyl]benzene (**3h**): IR (KBr): $\tilde{\nu}$ = 2952 cm^{-1} (m), 2906 (w), 2833 (m, C–H), 1501 (s, C_{ar}=C_{ar}), 1466 (s), 1452 (m), 1441 (m, C–H), 1249 (s), 1219 (s), 1043 (s), 1024 (m, C–O), 961 (m, =C–H). – ^{1}H NMR ($CDCl_3$): δ = 3.84 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 6.85 (s, 2 H, H_a, H_b), 7.17–7.30 (m, 3 H, H_c, H_g, H_h), 7.41 (d, ^3J = 7.8 Hz, 1 H, H_i), 7.47 (d, ^3J = 16.4 Hz, 1 H, H_d or H_e), 7.56 (d, ^3J = 16.4 Hz, 1 H, H_d or H_e), 7.76 (d, ^3J = 7.7 Hz, 1 H, H_f). – ^{13}C NMR ($CDCl_3$): δ = 55.9, 56.3 (OCH_3), 112.2, 112.4, 114.2, 125.4, 125.9, 126.7, 126.9, 127.1, 128.4, 129.7, 133.4, 135.9 (10 aromatic C; 2 olefinic C), 151.7, 153.9 (C_{ar}–OCH_3). – MS (70 eV); *m/z* (%): 276 (35) [M^+, $C16H15^{37}ClO_2^+$], 275 (19) [M^+ + 1], 274 (100) [M^+, $C16H15^{35}ClO_2^+$], 259 (12) [$M^+ - CH_3$], 239 (16) [M^+ – Cl], 231 (15) [$M^+ - C_2H_3O$], 196 (57) [M^+ – Cl, $- C_2H_3O$], 91 (5) [$C_7H_7^+$], 77 (11) [$C_6H_5^+$], 51 (10) [$C_4H_3^+$].

1-Chloro-3-[2-(2,5-dimethoxyphenyl)ethenyl]benzene (**3i**): IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1} (w), 2945 (w), 2835 (w, C–H), 1602 (w), 1590 (m), 1498 (s, C_{ar}=C_{ar}), 1469 (m), 1445 (w, C–H), 1269 (m), 1254 (m), 1245 (m), 1222 (s), 1047 (s, C–O), 970 (m, =C–H). – ^{1}H NMR ($CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.82 (dd, ^3J = 9.1 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.85 (d, ^3J = 9.4 Hz, 1 H, H_a), 7.02 (d, ^3J = 16.5 Hz, 1 H, H_e), 7.13 (d, ^4J = 2.4 Hz, 1 H, H_c), 7.21 (d, ^3J = 7.9 Hz, 1 H, H_h), 7.27 (dd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, 1 H, H_g), 7.39 (d, ^3J = 7.5 Hz, 1 H, H_f), 7.46 (d, ^3J = 16.5 Hz, 1 H, H_d), 7.53 (s, 1 H, H_k). – ^{13}C NMR ($CDCl_3$): δ = 55.8, 56.2 (OCH_3), 111.9, 112.3, 114.2, 124.9, 126.4, 126.7, 127.3, 127.9, 129.8, 134.6, 139.8 (10 aromatic C; 2 olefinic C), 151.7, 153.8 (C_{ar}–OCH_3). – MS (70 eV); *m/z* (%): 276 (33) [M^+, $C_{16}H_{15}{}^{37}ClO_2^+$], 275 (18) [$M^+$ + 1], 274 (100) [M^+, $C_{16}H_{15}{}^{35}ClO_2^+$], 259 (20) [$M^+ - CH_3$], 231 (19) [$M^+ - C_2H_3O$], 196 (88) [$M^+$ – Cl, $- C_2H_3O$], 91 (9) [$C_7H_7^+$], 77 (26) [$C_6H_5^+$], 51 (16) [$C_4H_3^+$], 36 (19) [HCl^+].

1-Chloro-4-[2-(2,5-dimethoxyphenyl)ethenyl]benzene (**3k**): IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2938 (m), 2907 (w), 2835 (m, C–H), 1609 (w), 1582 (m), 1497 (s, C_{ar}=C_{ar}), 1462 (m), 1453 (m), 1443 (m), 1428 (m, C–H), 1286 (m), 1242 (s), 1214 (s), 1050 (m), 1025

(m, C−O), 965 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.81 (dd, ^3J = 8.9 Hz, ^4J = 2.4 Hz, 1 H, H_b), 6.85 (d, ^3J = 8.9 Hz, 1 H, H_a), 7.04 (d, ^3J = 16.4 Hz, 1 H, H_e), 7.14 (d, ^4J = 2.4 Hz, 1 H, H_c), 7.31 (d, ^3J = 8.5 Hz, 2 H, H_g, H_i), 7.43 (d, ^3J = 16.2 Hz, 1 H, H_d), 7.46 (d, ^3J = 8.6 Hz, 2 H, H_f, H_k). − ^{13}C NMR ($CDCl_3$): δ = 55.7, 56.1 (OCH_3), 111.7, 112.2, 113.9, 123.9, 126.8, 127.7, 127.9, 128.7, 132.9, 136.3 (10 aromatic C; 2 olefinic C), 151.5, 153.7 (C_{ar}−OCH_3). − MS (70 eV); *m/z* (%): 276 (33) [M^+, $C_{16}H_{15}{}^{37}ClO_2{}^+$], 275 (18) [$M^+$ + 1], 274 (100) [M^+, $C_{16}H_{15}{}^{35}ClO_2{}^+$], 259 (14) [$M^+$ − CH_3], 231 (28) [M^+ − C_2H_3O], 196 (35) [M^+ − Cl, − C_2H_3O], 91 (2) [$C_7H_7{}^+$], 77 (8) [$C_6H_5{}^+$], 51 (7) [$C_4H_3{}^+$].

1,2-Dichloro-3-[2-(2,5-dimethoxyphenyl)ethenyl]benzene (**3l**): IR (KBr): $\tilde{\nu}$ = 2951 cm^{-1} (m), 2934 (m), 2905 (m), 2831 (m, C−H), 1581 (m), 1494 (s, C_{ar}=C_{ar}), 1461 (m), 1451 (m), 1441 (m), 1429 (m, C−H), 1282 (s), 1244 (s), 1214 (s), 1059 (m), 1044 (m), 1033 (m, C−O), 964 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.83 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.84 (s, 1 H, H_b), 6.85 (s, 1 H, H_a), 7.18 (d, ^4J = 1.7 Hz, 1 H, H_c), 7.21 (d, ^3J = 8.2 Hz, 1 H, H_g), 7.36 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1 H, H_h), 7.41 (d, ^3J = 16.4 Hz, 1 H, H_d or H_e), 7.50 (d, ^3J = 16.3 Hz, 1 H, H_d or H_e), 7.63 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1 H, H_f). − ^{13}C NMR ($CDCl_3$): δ = 55.9, 56.3 (OCH_3), 112.3, 112.4, 114.5, 124.9, 125.4, 126.7, 127.1, 127.2, 128.9, 131.5, 133.4, 138.3 (10 aromatic C; 2 olefinic C), 151.8, 153.8 (C_{ar}−OCH_3). −MS (70 eV); *m/z* (%): 312 (12) [M^+, $C_{16}H_{14}{}^{37}Cl_2O_2{}^+$], 311 (13) [$M^+$ + 1], 310 (72) [M^+, $C_{16}H_{14}{}^{37}Cl_{35}ClO_2{}^+$], 309 (19) [$M^+$ + 1], 308 (100) [M^+, $C_{16}H_{14}{}^{35}Cl_2O_2{}^+$], 293 (15) [$M^+$ − CH_3], 258 (8) [M^+ − CH_3, − Cl], 238 (10) [M^+ − 2 × Cl], 230 (37) [M^+ − C_2H_3O, − Cl], 229 (22) [M^+ − C_2H_3O, −HCl], 195 (29) [M^+ − C_2H_3O, −2 × Cl].

1,3-Dichloro-4-[2-(2,5-dimethoxyphenyl)ethenyl]benzene (**3m**): IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1} (m), 2939 (m), 2864 (m, C−H), 1604 (w), 1586 (w), 1499 (s, C_{ar}=C_{ar}), 1470 (s), 1439 (m, C−H), 1260 (m), 1243 (s), 1218 (s), 1040 (s), 1022 (m, C−O), 965 (s, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.83 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.83 (s, 1 H, H_b), 6.84 (s, 1 H, H_a), 7.18 (d, ^4J = 1.7 Hz, 1 H, H_c), 7.23 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1 H, H_g), 7.37 (d, ^3J = 8.5 Hz, 1 H, H_f), 7.39 (d, ^4J = 2.1 Hz, 1 H, H_i), 7.42 (s, 2 H, H_d, H_e). − ^{13}C NMR ($CDCl_3$): δ = 55.8, 56.2 (OCH_3), 112.2, 112.3, 114.4, 124.2, 126.4, 126.7, 127.2, 127.4, 129.5, 133.2, 133.8, 134.6 (10 aromatic C; 2 olefinic C), 151.7, 153.8 (C_{ar}−OCH_3). − MS (70 eV); *m/z* (%): 312 (11) [M^+, $C_{16}H_{14}{}^{37}Cl_2O_2{}^+$], 311 (11) [$M^+$ + 1], 310 (68) [M^+, $C_{16}H_{14}{}^{37}Cl_{35}ClO_2{}^+$], 309 (18) [$M^+$ + 1], 308 (100) [M^+, $C_{16}H_{14}{}^{35}Cl_2O_2{}^+$], 293 (13) [$M^+$ − CH_3], 265 (15) [M^+ − C_2H_3O], 258 (10) [M^+ − CH_3, − Cl], 238 (18) [M^+ − 2 × Cl], 230 (39) [M^+ − C_2H_3O, − Cl], 229 (44) [M^+ − C_2H_3O, − HCl], 195 (65) [M^+ − C_2H_3O, − 2 × Cl], 91 (5) [$C_7H_7{}^+$], 77 (7) [$C_6H_5{}^+$], 51 (13) [$C_4H_3{}^+$].

1,4-Dichloro-2-[2-(2,5-dimethoxyphenyl)ethenyl]benzene (**3n**): IR (KBr): $\tilde{\nu}$ = 2965 cm^{-1} (w), 2947 (w), 2837 (w, C−H), 1581 (w), 1496 (s, C_{ar}=C_{ar}), 1459 (m, C−H), 1265 (m), 1244 (m), 1220 (s), 1046 (s, C−O), 959 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.83 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 6.84 (s, 1 H, H_b), 6.85 (s, 1 H, H_a), 7.14 (dd, ^3J = 8.6 Hz, ^4J = 2.5 Hz, 1 H, H_h), 7.17 (s, 1 H, H_c), 7.30 (d, ^3J = 8.5 Hz, 1 H, H_i), 7.41 (s, 1 H, H_d or H_e), 7.41 (s, 1 H, H_d or H_e), 7.70 (d, ^4J = 2.4 Hz, 1 H, H_f). − ^{13}C NMR ($CDCl_3$): δ = 55.8, 56.2 (OCH_3), 112.2, 112.3, 114.6, 124.1, 126.3, 126.4, 127.1, 128.1, 130.7, 131.5, 132.8, 137.4 (10 aromatic C; 2 olefinic C), 151.8, 153.7 (C_{ar}−OCH_3). − MS (70 eV); *m/z* (%): 312 (10) [M^+, $C_{16}H_{14}{}^{37}Cl_2O_2{}^+$], 311 (11) [$M^+$ + 1], 310 (60) [M^+, $C_{16}H_{14}{}^{37}Cl_{35}ClO_2{}^+$], 309 (16) [$M^+$ + 1], 308 (100) [M^+, $C_{16}H_{14}{}^{35}Cl_2O_2{}^+$], 293 (13) [$M^+$ − CH_3], 273 (13) [M^+ − Cl], 265 (10) [M^+ − C_2H_3O], 258 (11) [M^+ − CH_3, − Cl], 238 (16) [M^+ − 2 Cl], 230 (40) [M^+ − C_2H_3O, − Cl], 229 (25) [M^+ − C_2H_3O, − HCl], 195 (35) [M^+ − C_2H_3O, − 2 × Cl], 91 (2) [$C_7H_7{}^+$], 77 (2) [$C_6H_5{}^+$], 51 (3) [$C_4H_3{}^+$].

1,3-Dichloro-2-[2-(2,5-dimethoxyphenyl)ethenyl]benzene (**3o**): IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1} (w), 2940 (w), 2833 (m, C−H), 1583 (m), 1495 (s, C_{ar}=C_{ar}), 1460 (m), 1440 (m, C−H), 1244 (s), 1213 (s), 1050 (s), 1023 (m, C−O), 967 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.84 (s, 6 H, OCH_3), 6.85 (s, 1 H, H_b), 6.86 (s, 1 H, H_a), 7.09 (dd, ^3J = 8.0 Hz, ^3J = 8.0 Hz, 1 H, H_h), 7.12 (d, ^3J = 17.1 Hz, 1 H, H_d or H_e), 7.20 (s, 1 H, H_c), 7.34 (d, ^3J = 8.1 Hz, 2 H, H_g, H_i), 7.50 (d, ^3J = 16.7 Hz, 1 H, H_d or H_e). − ^{13}C NMR ($CDCl_3$): δ = 56.0, 56.6 (OCH_3), 112.4, 112.8, 114.6, 123.4, 127.0, 128.0, 128.6, 132.2, 134.7, 135.2 (10 aromatic C; 2 olefinic C), 152.0, 154.0 (C_{ar}−OCH_3). − MS (70 eV); *m/z* (%): 312 (11) [M^+, $C_{16}H_{14}{}^{37}Cl_2O_2{}^+$], 311 (11) [$M^+$ + 1], 310 (68) [M^+, $C_{16}H_{14}{}^{37}Cl_{35}ClO_2{}^+$], 309 (16) [$M^+$ + 1], 308 (100) [M^+, $C_{16}H_{14}{}^{35}Cl_2O_2{}^+$], 293 (12) [$M^+$ − CH_3], 273 (13) [M^+ − Cl], 265 (10) [M^+ − C_2H_3O], 238 (30) [M^+ − 2 × Cl], 230 (53) [M^+ − C_2H_3O, − Cl], 229 (71) [M^+ − C_2H_3O, − HCl], 195 (67) [M^+ − C_2H_3O, − 2 × Cl], 91 (6) [$C_7H_7{}^+$], 77 (7) [$C_6H_5{}^+$], 65 (5) [$C_5H_5{}^+$], 51 (14) [$C_4H_3{}^+$].

1,2-Dichloro-4-[2-(2,5-dimethoxyphenyl)ethenyl]benzene (**3p**): IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1} (m), 2939 (m), 2908 (m), 2836 (m, C−H), 1608 (w), 1580 (m), 1495 (s, C_{ar}=C_{ar}), 1462 (m), 1427 (m, C−H), 1244 (s), 1216 (s), 1050 (m), 1022 (s, C−O), 967 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.83 (s, 1 H, H_b), 6.84 (s, 1 H, H_a), 6.98 (d, ^3J = 16.5 Hz, 1 H, H_e), 7.11 (d, ^4J = 1.9 Hz, 1 H, H_c), 7.34 (dd, ^3J = 8.4 Hz, ^4J = 1.85 Hz, 1 H, H_f), 7.40 (d, ^3J = 8.3 Hz, 1 H, H_g), 7.43 (d, ^3J = 16.4 Hz, 1 H, H_d), 7.60 (d, ^4J = 1.8 Hz, 1 H, H_k). − ^{13}C NMR ($CDCl_3$): δ = 55.8, 56.2 (OCH_3), 111.9, 112.3, 114.4, 125.4, 125.7, 126.4, 126.8, 128.1, 130.5, 130.9, 132.7, 138.1 (10 aromatic C; 2 olefinic C), 151.7, 153.8 (C_{ar}−OCH_3). − MS (70 eV); *m/z* (%): 312 (12) [M^+, $C_{16}H_{14}{}^{37}Cl_2O_2{}^+$], 311 (12) [$M^+$ + 1], 310 (68) [M^+, $C_{16}H_{14}{}^{37}Cl_{35}ClO_2{}^+$], 309 (15) [$M^+$ + 1], 308 (100) [M^+, $C_{16}H_{14}{}^{35}Cl_2O_2{}^+$], 293 (22) [$M^+$ − CH_3], 265 (26) [M^+ − C_2H_3O], 230 (45) [M^+ − C_2H_3O, − Cl], 229 (8) [M^+ − C_2H_3O, − HCl], 195 (53) [M^+ − C_2H_3O, − 2 × Cl], 91 (2) [$C_7H_7{}^+$], 77 (4) [$C_6H_5{}^+$], 65 (2) [$C_5H_5{}^+$], 51 (7) [$C_4H_3{}^+$].

1,3-Dichloro-5-[2-(2,5-dimethoxyphenyl)ethenyl]benzene (**3q**): IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1} (w), 2939 (w), 2834 (w, C−H), 1581 (s), 1495 (s, C_{ar}=C_{ar}), 1440 (m), 1429 (m, C−H), 1251 (m), 1240 (m), 1218 (m), 1053 (m), 1026 (m, C−O), 955 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 6.84 (s, 1 H, H_b), 6.85 (s, 1 H, H_a), 6.95 (d, ^3J = 16.4 Hz, 1 H, H_e), 7.10 (s, 1 H, H_c), 7.22 (dd, ^4J = 1.8 Hz, ^4J = 1.8 Hz, 1 H, H_h), 7.39 (d, ^4J = 1.8 Hz, 2 H, H_f, H_k), 7.45 (d, ^3J = 16.4 Hz, 1 H, H_d). − ^{13}C NMR ($CDCl_3$): δ = 55.8, 56.2 (OCH_3), 112.0, 112.3, 114.7, 124.8, 126.2, 126.3, 126.5, 127.0, 135.1, 141.0 (10 aromatic C; 2 olefinic C), 151.8, 153.8 (C_{ar}−OCH_3). − MS (70 eV); *m/z* (%): 312 (10) [M^+, $C_{16}H_{14}{}^{37}Cl_2O_2{}^+$], 311 (10) [$M^+$ + 1], 310 (61) [M^+, $C_{16}H_{14}{}^{37}Cl_{35}ClO_2{}^+$], 309 (18) [$M^+$ + 1], 308 (100) [M^+, $C_{16}H_{14}{}^{35}Cl_2O_2{}^+$], 293 (20) [$M^+$ − CH_3], 258 (9) [M^+ − CH_3, − Cl], 230 (39) [M^+ − C_2H_3O, − Cl], 195 (29) [M^+ − C_2H_3O, − 2 × Cl], 91 (1) [$C_7H_7{}^+$], 77 (2) [$C_6H_5{}^+$], 51 (2) [$C_4H_3{}^+$].

1-Chloro-3-[2-(2,5-dimethoxyphenyl)ethenyl]-2-methylbenzene (**3r**): IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1} (w), 2934 (w), 2835 (w, C−H), 1602 (w), 1586 (w), 1498 (s, C_{ar}=C_{ar}), 1465 (m), 1450 (m), 1420 (m, C−H), 1269 (m), 1249 (m), 1223 (s), 1047 (s, C−O), 967 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 2.46 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 6.81 (dd, ^3J = 8.9 Hz, ^4J = 2.6 Hz,

1 H, H_b), 6.86 (d, ^3J = 8.7 Hz, 1 H, H_a), 7.15 (d, ^4J = 2.8 Hz, 1 H, H_c), 7.10−7.29 (m, 2 H, H_g, H_h), 7.26 (d, ^3J = 16.3 Hz, 1 H, H_d or H_e), 7.33 (d, ^3J = 16.3 Hz, 1 H, H_d or H_e), 7.60 (d, ^3J = 7.6 Hz, 1 H, H_f). − ^{13}C NMR ($CDCl_3$): δ = 16.3 (CH_3), 55.8, 56.3 (OCH_3), 112.4, 112.5, 113.8, 124.6, 126.4, 126.7, 127.3, 127.4, 128.2, 133.6, 135.0, 139.3 (10 aromatic C; 2 olefinic C), 151.7, 153.8 (C_{ar}−OCH_3). − MS (70 eV); *m/z* (%): 290 (35) [M^+, $C_{17}H_{17}{}^{37}ClO_2{}^+$], 289 (20) [$M^+$ + 1], 288 (100) [M^+, $C_{17}H_{17}{}^{35}ClO_2{}^+$], 273 (8) [$M^+ - CH_3$], 245 (8) [$M^+ - C_2H_3O$], 238 (8) [$M^+ - CH_3$, − Cl], 210 (40) [$M^+ - C_2H_3O$, − Cl], 91 (2) [$C_7H_7{}^+$], 77 (2) [$C_6H_5{}^+$], 51 (3) [$C_4H_3{}^+$].

Methyl 4-[2-(2,5-Dimethoxyphenyl)ethenyl]benzoate (**3t**): IR (KBr): $\tilde{\nu}$ = 2949 cm^{-1} (w), 2836 (w, C−H), 1717 (s, C=O), 1606 (m), 1497 (m, C_{ar}=C_{ar}), 1466 (w), 1439 (w, C−H), 1282 (s), 1254 (w), 1219 (m), 1044 (m, C−O), 974 (w), 964 (w, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 3.92 (s, 3 H, $COOCH_3$), 6.83 (s, 1 H, H_b), 6.84 (s, 1 H, H_a), 7.11 (d, ^3J = 16.5 Hz, 1 H, H_e), 7.15 (d, ^4J = 2.1 Hz, 1 H, H_c), 7.57 (d, ^3J = 16.7 Hz, 1 H, H_d), 7.58 (d, ^3J = 8.3 Hz, 2 H, H_f, H_k.), 8.01 (d, ^3J = 8.4 Hz, 2 H, H_g, H_i). − ^{13}C NMR ($CDCl_3$): δ = 52.0 ($COOCH_3$), 55.8, 56.3 (OCH_3), 111.9, 112.4, 114.5, 126.0, 126.4, 126.7, 128.2, 128.8, 130.0, 142.4 (10 aromatic C; 2 olefinic C), 151.8, 153.8 (C_{ar}−OCH_3), 166.9 ($COOCH_3$). − MS (70 eV); *m/z* (%): 299 (20) [M^+ + 1], 298 (100) [M^+], 283 (10) [$M^+ - CH_3$], 255 (10) [$M^+ - C_2H_3O$], 196 (42) [$M^+ - C_2H_3O$, − $C_2H_3O_2$], 105 (12) [$C_8H_9{}^+$], 91 (18) [$C_7H_7{}^+$], 77 (23) [$C_6H_5{}^+$], 59 (63) [$C_2H_3O_2{}^+$], 51 (16) [$C_4H_3{}^+$].

Synthesis of the Tetramethoxycyclohexadienyl(ethenyl)benzenes **4**. − *General Procedure:* In a one-cell pot with a plane ground joint and two annealed cylindric Pt electrodes, 0.01 mol of the derivatives **3** and 1.8 g (0.03 mol) of KOH were dissolved by stirring in 500 ml of absolute methanol. The stirred solution was electrolysed at 4.0 V (direct current) and 0.15 A for 3−3.5 h at room temperature. The course and the end of the reaction were monitored by the decreasing UV fluorescence (λ = 366 nm) of the starting materials **3**. After conducting the electrolysis, three reaction mixtures were combined and the solution was concentrated in a rotary evaporator at < 35°C. The residual oil was washed with water (200 ml) and extracted with ether (200 ml), and the water layer was subsequently extracted with ether (2 × 200 ml). The combined ether extracts were washed with water (2 × 100 ml), to remove traces of KOH, then with saturated brine solution (100 ml) and dried with $MgSO_4$. Concentration in vacuo afforded the viscous crude products **4**, to which a small amount of methanol was added for crystallization. The derivatives **4** were purified by recrystallization from methanol to yield **4** as colourless or light-yellow crystals. − ^{1}H NMR: For characterization of the quinoid and olefinic protons H_a−H_e of the compounds **4** see Figure 1. The aromatic protons H_f−H_k of the substituents were labelled clockwise. For yields, melting points, molecular formulae and masses, and elemental analyses of the tetramethoxycyclohexadienyl(ethenyl)benzenes **4** see Table 7.

[2-(3,3,6,6-Tetramethoxycyclohexa-1,4-dienyl)ethenyl]benzene (**4a**): IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1} (m), 2819 (w, C−H), 1493 (w, C_{ar}=C_{ar}), 1465 (w), 1444 (w, C−H), 1108 (m), 1097 (s), 1059 (s, C−O), 975 (m), 963 (m), 958 (s), 692 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.19 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.92 (d, ^3J = 10.4 Hz, 1 H, H_a), 6.31 (dd, ^3J = 10.4 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.37 (d, ^4J = 2.6 Hz, 1 H, H_c), 6.73 (d, ^3J = 16.0 Hz, 1 H, H_e), 7.26 (d, ^3J = 16.3 Hz, 1 H, H_d), 7.25−7.36 (m, 3 H, H_g, H_h, H_i), 7.48 (d, 2 H, H_f, H_k). − ^{13}C NMR ($CDCl_3$): δ = 49.9, 51.0 (OCH_3), 93.6, 96.9 [$C(OCH_3)_2$), 123.9, 126.7, 127.8, 128.5, 128.8, 131.0, 131.8, 132.2, 137.2, 138.5 (6 aromatic C; 6 olefinic C). − MS (70 eV); *m/z* (%): 302 (1) [M^+], 271 (7) [$M^+ - CH_3O$], 240 (9) [$M^+ - 2 \times CH_3O$], 105 (100) [$C_8H_9{}^+$], 91 (51) [$C_7H_7{}^+$], 77 (19) [$C_6H_5{}^+$], 75 (47) [$C_3H_7O_2{}^+$], 65 (5) [$C_5H_5{}^+$], 51 (16) [$C_4H_3{}^+$], 45 (13) [$C_2H_5O^+$].

Table 7. Yields, melting points, molecular formulae and masses, and elemental analyses of the tetramethoxycyclohexadienyl-(ethenyl)benzenes **4**

comp.	yield [%]	m.p.[a] [°C]	empirical formula	molecular mass	C calcd. found	H calcd. found	Cl calcd. found
4a	62	84	$C_{18}H_{22}O_4$	302.37	71.49 71.24	7.34 7.38	
4b	58	91	$C_{19}H_{24}O_4$	316.39	72.13 71.93	7.64 7.69	
4c	39	65	$C_{19}H_{24}O_4$	316.39	72.13 72.29	7.64 7.75	
4d	54	92	$C_{19}H_{24}O_4$	316.39	72.13 72.07	7.64 7.76	
4e	60	47	$C_{20}H_{26}O_4$	330.42	72.70 72.66	7.93 8.00	
4f	47	75	$C_{20}H_{26}O_4$	330.42	72.70 72.63	7.93 7.94	
4g	39	47	$C_{20}H_{26}O_4$	330.42	72.70 72.47	7.93 7.92	
4h	61	85	$C_{18}H_{21}ClO_4$	336.81	64.26 64.40	6.30 6.32	10.40 10.56
4i	76	57	$C_{18}H_{21}ClO_4$	336.81	64.26 64.08	6.30 6.25	10.40 10.62
4k	67	59	$C_{18}H_{21}ClO_4$	336.81	64.26 63.99	6.30 6.23	10.40 10.58
4l	56	68	$C_{18}H_{20}Cl_2O_4$	371.26	58.23 58.09	5.43 5.37	19.10 19.37
4m	72	35	$C_{18}H_{20}Cl_2O_4$	371.26	58.23 57.99	5.43 5.42	19.10 19.29
4n	84	85	$C_{18}H_{20}Cl_2O_4$	371.26	58.23 58.28	5.43 5.47	19.10 19.32
4o	82	56	$C_{18}H_{20}Cl_2O_4$	371.26	58.23 58.19	5.43 5.53	19.10 18.94
4p	56	78	$C_{18}H_{20}Cl_2O_4$	371.26	58.23 58.12	5.43 5.39	19.10 19.00
4q	72	72	$C_{18}H_{20}Cl_2O_4$	371.26	58.23 58.26	5.43 5.38	19.10 19.21
4r	75	150	$C_{19}H_{23}ClO_4$	350.84	65.05 64.80	6.60 6.65	10.11 10.00
4s	67	77	$C_{19}H_{22}O_6$	346.37	65.89 65.93	6.40 6.41	
4t	55	72	$C_{20}H_{24}O_6$	360.40	66.65 66.83	6.71 6.66	

[a] Solvent: methanol.

1-Methyl-2-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4b**): IR (KBr): $\tilde{\nu}$ = 2942 cm^{-1} (m), 2829 (m, C−H), 1480 (m, C_{ar}=C_{ar}), 1457 (m), 1414 (m, C−H), 1108 (s), 1083 (s), 1066 (s, C−O), 987 (s), 951 (s), 713 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 3.21 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.92 (d, ^3J = 10.2 Hz, 1 H, H_a), 6.32 (dd, ^3J = 10.2 Hz, ^4J = 2.8 Hz, 1 H, H_b), 6.35 (d, ^4J = 2.8 Hz, 1 H, H_c), 6.60 (d, ^3J = 16.2 Hz, 1 H, H_d), 7.17 (d, ^3J = 16.2 Hz, 1 H, H_e), 7.17 (dd, ^3J = 6.9 Hz, ^4J = 2.25 Hz, 2 H, H_f, H_i), 7.53−7.58 (m, 2 H, H_g, H_h). − ^{13}C NMR ($CDCl_3$): δ = 19.8 (CH_3), 49.9, 51.0 (OCH_3), 93.6, 97.0 [$C(OCH_3)_2$], 125.3, 125.4, 126.1, 127.8, 129.1, 130.3, 130.5, 131.1, 131.8, 136.1, 136.4, 138.7 (6 aromatic C; 6 olefinic C). − MS (70 eV); *m/z* (%): 317 (1) [M^+ + 1], 316 (1) [M^+], 285 (9) [$M^+ - CH_3O$], 254 (10) [$M^+ - 2 \times CH_3O$], 181 (100), 105 (15) [$C_8H_9{}^+$], 91 (11) [$C_7H_7{}^+$], 77 (3) [$C_6H_5{}^+$], 65 (4) [$C_5H_5{}^+$], 51 (2) [$C_4H_3{}^+$].

1-Methyl-3-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4c**): IR (KBr): $\tilde{\nu}$ = 2967 cm^{-1} (m), 2942 (m), 2829 (m, C−H), 1600 (w), 1581 (w, C_{ar}=C_{ar}), 1462 (m, C−H), 1152 (m),

1107 (s), 1073 (s, C−O), 986 (s), 953 (s), 781 (m), 698 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 3.19 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.92 (d, ^3J = 10.5 Hz, 1 H, H_a), 6.32 (dd, ^3J = 10.4 Hz, ^4J = 2.8 Hz, 1 H, H_b), 6.37 (d, ^4J = 2.8 Hz, 1 H, H_c), 6.73 (d, ^3J = 16.2 Hz, 1 H, H_e), 7.06−7.30 (m, 4 H, H_d, H_f, H_g, H_h), 7.32 (s, 1 H, H_k). − ^{13}C NMR ($CDCl_3$): δ = 21.4 (CH_3), 49.9, 51.0 (OCH_3), 93.6, 96.9 [*C*(OCH_3)$_2$], 123.7, 124.0, 127.4, 128.5, 128.6, 128.8, 131.1, 132.0, 132.4, 137.2, 138.1, 138.6 (6 aromatic C; 6 olefinic C). − MS (70 eV); *m/z* (%): 316 (1) [M^+], 285 (6) [$M^+ - CH_3O$], 254 (9) [$M^+ - 2 \times CH_3O$], 105 (100) [$C_8H_9^+$], 91 (14) [$C_7H_7^+$], 77 (10) [$C_6H_5^+$], 75 (66) [$C_3H_7O_2^+$], 65 (8) [$C_5H_5^+$], 51 (6) [$C_4H_3^+$], 45 (12) [$C_2H_5O^+$], 31 (25) [CH_3O^+].

1-Methyl-4-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4d**): IR (KBr): $\tilde{\nu}$ = 2943 cm^{-1} (m), 2827 (w, C−H), 1607 (w), 1511 (m, C_{ar}=C_{ar}), 1461 (w), 1411 (m, C−H), 1123 (m), 1108 (s), 1084 (s), 1068 (s, C−O), 987 (s), 950 (s), 805 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 2.34 (s, 3 H, CH_3), 3.19 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.91 (d, ^3J = 10.4 Hz, 1 H, H_a), 6.30 (dd, ^3J = 10.4 Hz, ^4J = 2.8 Hz, 1 H, H_b), 6.34 (d, ^4J = 2.8 Hz, 1 H, H_c), 6.69 (d, ^3J = 16.4 Hz, 1 H, H_e), 7.12 (d, ^3J = 8.0 Hz, 2 H, H_g, H_i), 7.23 (d, ^3J = 16.4 Hz, 1 H, H_d), 7.37 (d, ^3J = 8.1 Hz, 2 H, H_f, H_k). − ^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_3), 49.9, 51.0 (OCH_3), 93.6, 96.9 [*C*(OCH_3)$_2$], 122.9, 126.7, 128.4, 129.3, 131.1, 132.0, 132.2, 134.5, 137.8, 138.6 (6 aromatic C; 6 olefinic C). − MS (70 eV); *m/z* (%): 316 (2) [M^+], 285 (16) [$M^+ - CH_3O$], 254 (24) [$M^+ - 2 \times CH_3O$], 135 (100), 105 (37) [$C_8H_9^+$], 91 (19) [$C_7H_7^+$], 77 (6) [$C_6H_5^+$], 75 (22) [$C_3H_7O_2^+$], 65 (5) [$C_5H_5^+$], 51 (3) [$C_4H_3^+$].

1,4-Dimethyl-2-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4e**): IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (m), 2831 (w, C−H), 1494 (w, C_{ar}=C_{ar}), 1459 (w), 1392 (w, C−H), 1102 (m), 1078 (s, C−O), 972 (w), 952 (m), 807 (w, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 3.21 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.92 (d, ^3J = 10.3 Hz, 1 H, H_a), 6.32 (dd, ^3J = 10.3 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.35 (d, ^4J = 2.6 Hz, 1 H, H_c), 6.60 (d, ^3J = 16.2 Hz, 1 H, H_d), 6.98 (d, ^3J = 8.8 Hz, 1 H, H_h), 7.04 (d, ^3J = 7.7 Hz, 1 H, H_i), 7.37 (s, 1 H, H_f), 7.51 (d, ^3J = 16.4 Hz, 1 H, H_e). − ^{13}C NMR ($CDCl_3$): δ = 19.2, 20.9 (CH_3), 49.9, 51.0 (OCH_3), 93.5, 96.9 [*C*(OCH_3)$_2$], 124.8, 125.9, 128.5, 128.7, 130.2, 130.4, 131.1, 131.8, 133.0, 135.4, 136.0, 138.7 (6 aromatic C; 6 olefinic C). − MS (70 eV); *m/z* (%): 331 (12) [M^+ + 1], 330 (35) [M^+], 315 (11) [$M^+ - CH_3$], 300 (21) [$M^+ - 2 \times CH_3$], 299 (95) [$M^+ - CH_3O$], 268 (100) [$M^+ - 2 \times CH_3O$], 105 (87) [$C_8H_9^+$], 91 (6) [$C_7H_7^+$], 77 (3) [$C_6H_5^+$], 75 (29) [$C_3H_7O_2^+$], 45 (3) [$C_2H_5O^+$].

1,2-Dimethyl-4-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4f**): IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (m), 2827 (m, C−H), 1605 (w), 1504 (m, C_{ar}=C_{ar}), 1452 (m, C−H), 1157 (m), 1124 (m), 1107 (s), 1084 (s), 1069 (s, C−O), 985 (s), 951 (s), 810 (m), 792 (w), 707 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 2.25 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 3.18 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.91 (d, ^3J = 10.4 Hz, 1 H, H_a), 6.31 (dd, ^3J = 10.4 Hz, ^4J = 2.8 Hz, 1 H, H_b), 6.36 (d, ^4J = 2.6 Hz, 1 H, H_c), 6.69 (d, ^3J = 16.4 Hz, 1 H, H_e), 7.10 (d, ^3J = 7.8 Hz, 1 H, H_g), 7.21 (d, ^3J = 16.4 Hz, 1 H, H_d), 7.22 (d, ^3J = 8.2 Hz, 1 H, H_f), 7.28 (s, 1 H, H_k). − ^{13}C NMR ($CDCl_3$): δ = 19.5, 19.7 (CH_3), 49.9, 51.0 (OCH_3), 93.6, 97.0 [*C*(OCH_3)$_2$], 122.7, 124.4, 128.0, 128.1, 129.9, 131.1, 132.0, 132.3, 134.9, 136.6, 136.7, 138.7 (6 aromatic C; 6 olefinic C). − MS (70 eV); *m/z* (%): 331 (2) [M^+ + 1], 330 (9) [M^+], 299 (33) [$M^+ - CH_3O$], 268 (24) [$M^+ - 2 \times CH_3O$], 105 (100) [$C_8H_9^+$], 91 (12) [$C_7H_7^+$], 77 (12) [$C_6H_5^+$], 75 (53) [$C_3H_7O_2^+$], 51 (6) [$C_4H_3^+$], 45 (14) [$C_2H_5O^+$], 31 (11) [CH_3O^+].

1,3-Dimethyl-5-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4g**): IR (KBr): $\tilde{\nu}$ = 2939 cm^{-1} (s), 2911 (m), 2829 (m, C−H), 1620 (w), 1596 (m, C_{ar}=C_{ar}), 1462 (m, C−H), 1120 (s), 1079 (s, C−O), 975 (s), 953 (s), 844 (m), 824 (m), 741 (m), 685 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 2.32 (s, 6 H, CH_3), 3.19 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.92 (d, ^3J = 10.4 Hz, 1 H, H_a), 6.31 (dd, ^3J = 10.4 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.36 (d, ^4J = 2.7 Hz, 1 H, H_c), 6.72 (d, ^3J = 16.4 Hz, 1 H, H_e), 6.90 (s, 1 H, H_h), 7.12 (s, 2 H, H_f, H_k), 7.19 (d, ^3J = 16.4 Hz, 1 H, H_d). − ^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_3), 49.9, 51.0 (OCH_3), 93.6, 96.9 [*C*(OCH_3)$_2$], 123.5, 124.7, 128.4, 129.7, 131.1, 132.0, 132.4, 137.1, 138.0, 138.6 (6 aromatic C; 6 olefinic C). − MS (70 eV); *m/z* (%): 330 (2) [M^+], 299 (10) [$M^+ - CH_3O$], 268 (8) [$M^+ - 2 \times CH_3O$], 105 (100) [$C_8H_9^+$], 91 (17) [$C_7H_7^+$], 77 (15) [$C_6H_5^+$], 75 (46) [$C_3H_7O_2^+$], 65 (5) [$C_5H_5^+$], 51 (6) [$C_4H_3^+$], 45 (12) [$C_2H_5O^+$], 31 (14) [CH_3O^+].

1-Chloro-2-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4h**): IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (m), 2903 (m), 2826 (m, C−H), 1588 (w, C_{ar}=C_{ar}), 1469 (m), 1440 (m, C−H), 1124 (s), 1109 (s), 1084 (s), 1071 (s, C−O), 989 (s), 951 (s), 754 (s), 730 (m), 695 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.21 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.95 (d, ^3J = 10.5 Hz, 1 H, H_a), 6.31 (dd, ^3J = 10.5 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.42 (d, ^4J = 2.6 Hz, 1 H, H_c), 6.71 (d, ^3J = 16.1 Hz, 1 H, H_d), 7.14−7.25 (m, 2 H, H_g, H_h), 7.35 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1 H, H_i), 7.62 (dd, ^3J = 7.6 Hz, ^4J = 1.9 Hz, 1 H, H_f), 7.63 (d, ^3J = 16.3 Hz, 1 H, H_e). − ^{13}C NMR ($CDCl_3$): δ = 49.9, 51.0 (OCH_3), 93.5, 96.6 [*C*(OCH_3)$_2$], 126.4, 126.7, 126.8, 128.4, 128.8, 129.2, 129.7, 130.8, 131.9, 133.7, 135.4, 138.6 (6 aromatic C; 6 olefinic C). − MS (70 eV); *m/z* (%): 338 (1) [M^+, $C_{18}H_{21}{}^{37}ClO_4^+$], 336 (2) [$M^+$, $C_{18}H_{21}{}^{35}ClO_4^+$], 307 (10) [$M^+ - CH_3O$], 306 (29) [$M^+ - CH_2O$], 305 (27) [$M^+ - CH_3O$], 291 (13) [$M^+ - CH_2O$, $- CH_3$], 276 (37) [$M^+ - 2 \times CH_3O$], 274 (100) [$M^+ - 2 \times CH_3O$], 239 (26) [$M^+ - 2 \times CH_3O$, − Cl], 127 (44) [$C_7H_{11}O_2^+$], 105 (31) [$C_8H_9^+$], 91 (13) [$C_7H_7^+$], 77 (22) [$C_6H_5^+$], 75 (37) [$C_3H_7O_2^+$], 51 (18) [$C_4H_3^+$].

1-Chloro-3-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4i**): IR (KBr): $\tilde{\nu}$ = 2939 cm^{-1} (m), 2899 (w), 2830 (m, C−H), 1589 (m, C_{ar}=C_{ar}), 1462 (m), 1426 (m, C−H), 1156 (w), 1116 (s), 1094 (s), 1081 (s, C−O), 987 (m), 973 (s), 788 (m), 738 (m), 697 (m), 688 (w), 676 (w, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.18 (s, 6 H, OCH_3), 3.35 (s, 6 H, OCH_3), 5.92 (d, ^3J = 10.4 Hz, 1 H, H_a), 6.32 (dd, ^3J = 10.5 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.37 (d, ^4J = 2.6 Hz, 1 H, H_c), 6.71 (d, ^3J = 16.4 Hz, 1 H, H_e), 7.17−7.34 (m, 4 H, H_d, H_f, H_g, H_h), 7.47 (s, 1 H, H_k). − ^{13}C NMR ($CDCl_3$): δ = 49.9, 51.0 (OCH_3), 93.4, 96.8 [*C*(OCH_3)$_2$), 125.0, 125.4, 126.5, 127.8, 129.8, 129.8, 130.9, 130.9, 131.9, 134.6, 138.2, 139.2 (6 aromatic C; 6 olefinic C). − MS (70 eV); *m/z* (%): 338 (0.4) [M^+, $C_{18}H_{21}{}^{37}ClO_4^+$], 336 (1) [$M^+$, $C_{18}H_{21}{}^{35}ClO_4^+$], 305 (2) [$M^+ - CH_3O$], 290 (3) [$M^+ - CH_3O$, $- CH_3$], 274 (3) [$M^+ - 2 \times CH_3O$], 127 (19) [$C_7H_{11}O_2^+$], 105 (43) [$C_8H_9^+$], 101 (6) [$C_5H_9O_2^+$], 91 (6) [$C_7H_7^+$], 77 (15) [$C_6H_5^+$], 75 (100) [$C_3H_7O_2^+$], 51 (9) [$C_4H_3^+$], 45 (37) [$C_2H_5O^+$], 36 (16) [HCl^+], 31 (25) [CH_3O^+].

1-Chloro-4-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4k**): IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1} (m), 2935 (m), 2898 (w), 2824 (m, C−H), 1588 (w, C_{ar}=C_{ar}), 1459 (w), 1400 (m, C−H), 1152 (w), 1117 (m), 1084 (s), 1063 (s, C−O), 949 (s), 848 (m), 833 (w), 821 (w), 804 (m), 722 (w), 710 (w), 688 (w, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.18 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.93 (d, ^3J = 10.4 Hz, 1 H, H_a), 6.31 (dd, ^3J = 10.4 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.35 (d, ^4J = 2.7 Hz, 1 H, H_c), 6.68 (d, ^3J = 16.4 Hz, 1 H, H_e), 7.21 (d, ^3J = 16.4 Hz, 1 H, H_d), 7.26 (dd, ^3J = 8.8 Hz, ^4J = 2.3 Hz, 2 H, H_g, H_i), 7.38 (dd, ^3J = 8.8 Hz, ^4J = 2.0 Hz, 2

H, H_f, H_k). – ^{13}C NMR ($CDCl_3$): δ = 49.9, 51.3 (OCH_3), 93.5, 96.9 [*C*(OCH_3)$_2$], 124.5, 127.9, 128.7, 129.3, 130.8, 130.9, 131.8, 133.4, 135.7, 138.2 (6 aromatic C; 6 olefinic C). – MS (70 eV); *m/z* (%): 339 (0.2) [M^+ + 1], 338 (0.9) [M^+, C18H21^{37}ClO$_4^+$], 337 (0.6) [M^+ + 1], 336 (2) [M^+, C18H21^{35}ClO$_4^+$], 305 (8) [M^+ – CH_3O], 290 (3) [M^+ – CH_3O, – CH_3], 274 (6) [M^+ – 2 × CH_3O], 127 (20) [$C_7H_{11}O_2^+$], 105 (100) [$C_8H_9^+$], 101 (5) [$C_5H_9O_2^+$], 91 (5) [$C_7H_7^+$], 77 (11) [$C_6H_5^+$], 75 (58) [$C_3H_7O_2^+$], 51 (8) [$C_4H_3^+$], 45 (14) [$C_2H_5O^+$], 31 (8) [CH_3O^+].

1,2-Dichloro-3-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4l**): IR (KBr): $\tilde{\nu}$ = 2939 cm^{-1} (m), 2902 (m), 2827 (m, C–H), 1580 (w, C_{ar}=C_{ar}), 1453 (m, C–H), 1158 (m), 1123 (m), 1102 (s), 1073 (s, C–O), 976 (m), 953 (s), 775 (m), 709 (w), 694 (w, =C–H). – ^{1}H NMR ($CDCl_3$): δ = 3.21 (s, 6 H, OCH_3), 3.37 (s, 6 H, OCH_3), 5.96 (d, ^3J = 10.5 Hz, 1 H, H_a), 6.33 (dd, ^3J = 10.5 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.43 (d, ^4J = 2.6 Hz, 1 H, H_c), 6.68 (d, ^3J = 16.3 Hz, 1 H, H_d), 7.17 (dd, ^3J = 7.9 Hz, ^3J = 7.9 Hz, 1 H, H_g), 7.36 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1 H, H_h), 7.53 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1 H, H_f), 7.64 (d, ^3J = 16.4 Hz, 1 H, H_e). – ^{13}C NMR ($CDCl_3$): δ = 49.9, 51.0 (OCH_3), 93.3, 96.6 [*C*(OCH_3)$_2$), 124.9, 127.0, 127.6, 128.6, 129.3, 129.9, 130.7, 131.7, 131.8, 133.4, 137.8, 138.2 (6 aromatic C; 6 olefinic C). – MS (70 eV); *m/z* (%): 371 (0.8) [M^+ + 1], 370 (0.7) [M^+, $C_{18}H_{20}{}^{35}Cl_2O_4^+$], 339 (3) [$M^+$ – CH_3O], 308 (3) [M^+ – 2 × CH_3O], 105 (100) [$C_8H_9^+$], 77 (2) [$C_6H_5^+$], 75 (45) [$C_3H_7O_2^+$], 45 (6) [$C_2H_5O^+$], 36 (12) [HCl^+], 31 (27) [CH_3O^+].

1,3-Dichloro-4-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4m**): IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1} (m), 2937 (m), 2832 (w, C–H), 1581 (w, C_{ar}=C_{ar}), 1467 (m, C–H), 1157 (w), 1122 (m), 1101 (s), 1079 (m, C–O), 983 (m), 962 (m), 813 (w, =C–H). – ^{1}H NMR ($CDCl_3$): δ = 3.21 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.96 (d, ^3J = 10.5 Hz, 1 H, H_a), 6.31 (dd, ^3J = 10.6 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.41 (d, ^4J = 2.7 Hz, 1 H, H_c), 6.68 (d, ^3J = 16.3 Hz, 1 H, H_d), 7.21 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1 H, H_g), 7.38 (d, ^4J = 2.1 Hz, 1 H, H_i), 7.55 (d, ^3J = 8.5 Hz, 1 H, H_f), 7.56 (d, ^3J = 16.3 Hz, 1 H, H_e). – ^{13}C NMR ($CDCl_3$): δ = 49.9, 51.0 (OCH_3), 93.4, 96.6 [*C*(OCH_3)$_2$], 126.8, 127.1, 127.3, 127.4, 129.4, 129.6, 130.6, 131.8, 133.7, 134.0, 134.1, 138.3 (6 aromatic C; 6 olefinic C). – MS (70 eV); *m/z* (%): 372 (0.5) [M^+, $C_{18}H_{20}{}^{37}Cl_{35}ClO_4^+$], 371 (0.2) [$M^+$ + 1], 370 (0.8) [M^+, $C_{18}H_{20}{}^{35}Cl_2O_4^+$], 339 (4) [$M^+$ – CH_3O], 105 (100) [$C_8H_9^+$], 91 (2) [$C_7H_7^+$], 77 (3) [$C_6H_5^+$], 75 (53) [$C_3H_7O_2^+$], 51 (5) [$C_4H_3^+$], 45 (9) [$C_2H_5O^+$], 36 (13) [HCl^+], 31 (3) [CH_3O^+].

1,4-Dichloro-2-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4n**): IR (KBr): $\tilde{\nu}$ = 2939 cm^{-1} (m), 2831 (m, C–H), 1584 (w, C_{ar}=C_{ar}), 1461 (m, C–H), 1157 (m), 1122 (m), 1107 (s), 1095 (s), 1075 (s, C–O), 972 (s), 956 (s), 820 (m, =C–H). – ^{1}H NMR ($CDCl_3$): δ = 3.21 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.96 (d, ^3J = 10.6 Hz, 1 H, H_a), 6.32 (dd, ^3J = 10.5 Hz, ^4J = 2.6 Hz, 1 H, H_b), 6.44 (d, ^4J = 2.6 Hz, 1 H, H_c), 6.69 (d, ^3J = 16.2 Hz, 1 H, H_d), 7.15 (dd, ^3J = 8.5 Hz, ^4J = 2.5 Hz, 1 H, H_h), 7.29 (d, ^3J = 8.5 Hz, 1 H, H_i), 7.56 (d, ^3J = 16.3 Hz, 1 H, H_e), 7.60 (d, ^4J = 2.5 Hz, 1 H, H_f). – ^{13}C NMR ($CDCl_3$): δ = 49.9, 51.0 (OCH_3), 93.3, 96.6 [*C*(OCH_3)$_2$], 126.4, 127.3, 127.6, 128.5, 130.1, 130.6, 130.7, 131.7, 131.8, 132.7, 136.9, 138.1 (6 aromatic C; 6 olefinic C). – MS (70 eV); *m/z* (%): 341 (0.3) [M^+ – CH_3O, $C_{18}H_{20}{}^{37}Cl_{35}ClO_4^+$ – CH_3O], 339 (0.5) [M^+ – CH_3O, $C_{18}H_{20}{}^{35}Cl_2O_4^+$ – CH_3O], 308 (0.5) [M^+ – 2 × CH_3O], 105 (100) [$C_8H_9^+$], 91 (2) [$C_7H_7^+$], 77 (3) [$C_6H_5^+$], 75 (43) [$C_3H_7O_2^+$], 51 (3) [$C_4H_3^+$], 45 (7) [$C_2H_5O^+$], 36 (9) [HCl^+], 31 (11) [CH_3O^+].

1,3-Dichloro-2-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4o**): IR (KBr): $\tilde{\nu}$ = 2939 cm^{-1} (m), 2904 (w), 2828 (m, C–H), 1555 (w, C_{ar}=C_{ar}), 1428 (m, C–H), 1147 (w), 1109 (m), 1081 (s), 1067 (s, C–O), 984 (m), 956 (m), 787 (w), 717 (w, =C–H). – ^{1}H NMR ($CDCl_3$): δ = 3.22 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.91 (d, ^3J = 10.4 Hz, 1 H, H_a), 6.33 (dd, ^3J = 10.4 Hz, ^4J = 2.8 Hz, 1 H, H_b), 6.36 (d, ^4J = 2.6 Hz, 1 H, H_c), 6.65 (d, ^3J = 16.6 Hz, 1 H, H_d), 7.08 (dd, ^3J = 8.0 Hz, ^3J = 8.0 Hz, 1 H, H_h), 7.31 (d, ^3J = 8.1 Hz, 2 H, H_g, H_i), 7.31 (d, ^3J = 16.6 Hz, 1 H, H_e). – ^{13}C NMR ($CDCl_3$): δ = 49.9, 51.0 (OCH_3), 93.3, 96.9 [*C*(OCH_3)$_2$], 126.9, 128.2, 128.4, 130.8, 131.2, 131.6, 132.5, 134.5, 134.9, 137.9 (6 aromatic C; 6 olefinic C). – MS (70 eV); *m/z* (%): 373 (1) [M^+ + 1], 372 (3) [M^+, $C_{18}H_{20}{}^{37}Cl_{35}ClO_4^+$], 371 (1) [$M^+$ + 1], 370 (4) [M^+, $C_{18}H_{20}{}^{35}Cl_2O_4^+$], 341 (12) [$M^+$ – CH_3O], 339 (20) [M^+ – CH_3O], 310 (6) [M^+ – 2 × CH_3O], 308 (9) [M^+ – 2 × CH_3O], 231 (6) [M^+ – 2 × CH_3O, – C_6H_5], 105 (100) [$C_8H_9^+$], 101 (8) [$C_5H_9O_2^+$], 91 (3) [$C_7H_7^+$], 77 (5) [$C_6H_5^+$], 75 (46) [$C_3H_7O_2^+$], 52 (9) [$C_4H_4^+$], 45 (11) [$C_2H_5O^+$], 36 (8) [HCl^+], 31 (10) [CH_3O^+].

1,2-Dichloro-4-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4p**): IR (KBr): $\tilde{\nu}$ = 2958 cm^{-1} (w), 2930 (m), 2822 (m, C–H), 1548 (w, C_{ar}=C_{ar}), 1467 (m), 1434 (w), 1396 (m, C–H), 1152 (w), 1106 (m), 1141 (w), 1099 (s), 1057 (s) 1047 (s, C–O), 975 (m), 953 (s), 809 (m), 684 (m), 675 (m, =C–H). – ^{1}H NMR ($CDCl_3$): δ = 3.18 (s, 6 H, OCH_3), 3.35 (s, 6 H, OCH_3), 5.93 (d, ^3J = 10.4 Hz, 1 H, H_a), 6.32 (dd, ^3J = 10.5 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.37 (d, ^4J = 2.6 Hz, 1 H, H_c), 6.68 (d, ^3J = 16.3 Hz, 1 H, H_e), 7.16 (d, ^3J = 16.3 Hz, 1 H, H_d), 7.28 (dd, ^3J = 8.4 Hz, ^4J = 1.9 Hz, 1 H, H_f), 7.38 (d, ^3J = 8.3 Hz, 1 H, H_g), 7.55 (d, ^4J = 1.9 Hz, 1 H, H_k). – ^{13}C NMR ($CDCl_3$): δ = 49.9, 51.0 (OCH_3), 93.4, 96.8 [*C*(OCH_3)$_2$], 125.9, 128.3, 129.0, 129.9, 130.2, 130.5, 130.8, 131.5, 131.9, 132.8, 137.4, 138.0 (6 aromatic C; 6 olefinic C). – MS (70 eV); *m/z* (%): 372 (0.5) [M^+, $C_{18}H_{20}{}^{37}Cl_{35}ClO_4^+$], 370 (0.6) [$M^+$, $C_{18}H_{20}{}^{35}Cl_2O_4^+$], 339 (3) [$M^+$ – CH_3O], 308 (2) [M^+ – 2 × CH_3O], 105 (100) [$C_8H_9^+$], 91 (2) [$C_7H_7^+$], 77 (4) [$C_6H_5^+$], 75 (60) [$C_3H_7O_2^+$], 51 (7) [$C_4H_3^+$], 45 (11) [$C_2H_5O^+$], 36 (3) [HCl^+], 31 (4) [CH_3O^+].

1,3-Dichloro-5-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzene (**4q**): IR (KBr): $\tilde{\nu}$ = 2941 cm^{-1} (m), 2907 (w), 2829 (w, C–H), 1584 (w, C_{ar}=C_{ar}), 1461 (w), 1438 (w, C-H), 1159 (w), 1106 (m), 1081 (s), 1061 (s, C–O), 980 (m), 953 (m), 796 (m, =C–H). – ^{1}H NMR ($CDCl_3$): δ = 3.18 (s, 6 H, OCH_3), 3.35 (s, 6 H, OCH_3), 5.93 (d, ^3J = 10.4 Hz, 1 H, H_a), 6.32 (dd, ^3J = 10.5 Hz, ^4J = 2.6 Hz, 1 H, H_b), 6.37 (d, ^4J = 2.5 Hz, 1 H, H_c), 6.69 (d, ^3J = 16.2 Hz, 1 H, H_e), 7.14 (d, ^3J = 16.3 Hz, 1 H, H_d), 7.22 (dd, ^4J = 1.8 Hz, ^4J = 1.8 Hz, 1 H, H_h), 7.33 (d, ^4J = 1.8 Hz, 2 H, H_f, H_k). – ^{13}C NMR ($CDCl_3$): δ = 49.9, 51.0 (OCH_3), 93.3, 96.8 [*C*(OCH_3)$_2$), 125.0, 126.8, 127.5, 129.8, 130.7, 130.7, 131.9, 135.1, 137.8, 140.3 (6 aromatic C; 6 olefinic C). – MS (70 eV); *m/z* (%): 372 (0.4) [M^+, $C_{18}H_{20}{}^{37}Cl_{35}ClO_4^+$], 371 (0.2) [$M^+$ + 1], 370 (0.7) [M^+, $C_{18}H_{20}{}^{35}Cl_2O_4^+$], 339 (4) [$M^+$ – CH_3O], 308 (5) [M^+ – 2 × CH_3O], 105 (100) [$C_8H_9^+$], 91 (2) [$C_7H_7^+$], 77 (2) [$C_6H_5^+$], 75 (41) [$C_3H_7O_2^+$], 51 (2) [$C_4H_3^+$], 45 (6) [$C_2H_5O^+$], 36 (8) [HCl^+], 31 (12) [CH_3O^+].

1-Chloro-2-methyl-3-[2-(3,3,6,6-tetramethoxycyclohexa-1,4-dienyl)ethenyl]benzene (**4r**): IR (KBr): $\tilde{\nu}$ = 2938 cm^{-1} (m), 2898 (w), 2823 (w, C–H), 1645 (s, C=C), 1457 (m), 1439 (m, C–H), 1163 (s), 1098 (s), 1075 (s, C–O), 973 (m), 956 (w), 834 (m), 786 (w, =C–H). – ^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 3.20 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 5.93 (d, ^3J = 10.2 Hz, 1 H, H_a), 6.31 (d, ^4J = 2.8 Hz, 1 H, H_b or H_c), 6.34 (s, 1 H, H_b or H_c), 6.53 (d, ^3J = 16.1 Hz, 1 H, H_d), 7.06–7.29 (m, 2 H, H_g, H_h), 7.40 (d, ^3J = 7.8 Hz, 1 H, H_f), 7.56 (d, ^3J = 16.1 Hz, 1 H, H_e). – ^{13}C NMR ($CDCl_3$): δ = 16.2 (CH_3), 49.9, 51.0 (OCH_3), 93.4, 96.9

[$C(OCH_3)_2$], 124.3, 126.6, 126.9, 128.4, 130.0, 130.7, 131.0, 131.8, 133.9, 135.0, 138.3, 138.8 (6 aromatic C; 6 olefinic C). − MS (70 eV); *m/z* (%): 352 (1) [M^+, $C_{19}H_{23}{}^{37}ClO_4^+$], 350 (3) [$M^+$, $C_{19}H_{23}{}^{35}ClO_4^+$], 321 (4) [$M^+ - CH_3O$], 319 (13) [$M^+ - CH_3O$], 290 (4) [$M^+ - 2 \times CH_3O$], 288 (11) [$M^+ - 2 \times CH_3O$], 105 (100) [$C_8H_9^+$], 91 (4) [$C_7H_7^+$], 77 (6) [$C_6H_5^+$], 75 (51) [$C_3H_7O_2^+$], 51 (5) [$C_4H_3^+$], 45 (9) [$C_2H_5O^+$], 36 (10) [$HCl^+$], 31 (18) [$CH_3O^+$].

5-[2-(3,3,6,6-Tetramethoxycyclohexa-1,4-dienyl)ethenyl]-1,3-benzodioxole (**4s**): Diethyl (2,5-dimethoxybenzyl)phosphonate (2.0 g, 0.07 mol) was electrochemically oxidized as described above. The crude oxidation product was not isolated because decomposition took place during distillation. The subsequent Horner-Emmons reaction of 5.3 g (0.035 mol) of 3,4-methylenedioxybenzaldehyde and 16.1 g (0.05 mol) of the crude oxidation product of diethyl (2,5-dimethoxybenzyl)phosphonate was performed according to the general procedure described above for the derivatives **3**. The compound **4s** was obtained with satisfactory analytical data. − IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (w), 2900 (w), 2828 (w, C−H), 1602 (w), 1503 (m), 1490 (m, C_{ar}=C_{ar}), 1446 (m, C−H), 1100 (s), 1078 (s, C−O), 962 (m), 928 (m), 822 (w), 800 (w, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.17 (s, 6 H, OCH_3), 3.35 (s, 6 H, OCH_3),), 5.90 (d, ^3J = 10.7 Hz, 1 H, H_a), 5.96 (s, 2 H, OCH_2O), 6.28 (d, ^4J = 2.7 Hz, 1 H, H_b or H_c), 6.32 (s, 2 H, H_b or H_c), 6.55 (d, ^3J = 16.3 Hz, 1 H, H_e), 6.76 (d, ^3J = 8.0 Hz, 1 H, H_g), 6.91 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1 H, H_f), 7.03 (d, ^4J = 1.6 Hz, 1 H, H_k), 7.17 (d, ^3J = 16.3 Hz, 1 H, H_d). − ^{13}C NMR ($CDCl_3$): δ = 49.9, 51.0 (OCH_3), 93.6, 96.9 [$C(OCH_3)_2$], 101.1 (OCH_2O), 105.8, 108.3, 121.9, 122.3, 128.3, 128.6, 131.1, 131.8, 131.9, 138.5, 147.6, 148.1 (6 aromatic C; 6 olefinic C). − MS (70 eV); *m/z* (%): 347 (0.4) [M^+ + 1], 346 (2) [M^+], 315 (8) [$M^+ - CH_3O$], 284 (10) [$M^+ - 2 \times CH_3O$], 241 (7) [$M^+ - 2 \times CH_3O$, $- C_2H_3O$], 127 (8) [$C_7H_{11}O_2^+$], 105 (100) [$C_8H_9^+$], 91 (14) [$C_7H_7^+$], 77 (16) [$C_6H_5^+$], 75 (50) [$C_3H_7O_2^+$], 65 (19) [$C_5H_5^+$], 51 (12) [$C_4H_3^+$], 45 (8) [$C_2H_5O^+$].

Methyl 4-[2-(3,3,6,6-Tetramethoxycyclohexa-1,4-dienyl)-ethenyl]benzoate (**4t**): IR (KBr): $\tilde{\nu}$ = 2944 cm^{-1} (w), 2906 (w), 2831 (w, C−H), 1721 (s, C=O), 1605 (w, C_{ar}=C_{ar}), 1437 (m, C−H), 1109 (s), 1079 (s, C−O), 982 (m), 961 (m, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.20 (s, 6 H, OCH_3), 3.36 (s, 6 H, OCH_3), 3.91 (s, 3 H, $COOCH_3$), 5.94 (d, ^3J = 10.5 Hz, 1 H, H_a), 6.32 (dd, ^3J = 10.5 Hz, ^4J = 2.7 Hz, 1 H, H_b), 6.40 (d, ^4J = 2.6 Hz, 1 H, H_c), 6.82 (d, ^3J = 16.2 Hz, 1 H, H_e), 7.29 (d, ^3J = 16.2 Hz, 1 H, H_d), 7.53 (d, ^3J = 8.3 Hz, 2 H, H_f, H_k), 7.99 (d, ^3J = 8.4 Hz, 2 H, H_g, H_i). − ^{13}C NMR ($CDCl_3$): δ = 49.9, 51.0 (OCH_3), 52.0 ($COOCH_3$), 93.4, 96.8 [$C(OCH_3)_2$], 126.5, 129.2, 129.9, 130.1, 130.2, 130.9, 131.3, 131.9, 138.2, 141.7 (6 aromatic C; 6 olefinic C), 166.8 ($COOCH_3$). − MS (70 eV); *m/z* (%): 361 (0.5) [M^+ + 1], 360 (2) [M^+], 329 (10) [$M^+ - CH_3O$], 298 (14) [$M^+ - 2 \times CH_3O$], 127 (8) [$C_7H_{11}O_2^+$], 105 (100) [$C_8H_9^+$], 91 (7) [$C_7H_7^+$], 77 (7) [$C_6H_5^+$], 75 (46) [$C_3H_7O_2^+$], 59 (27) [$C_2H_3O_2^+$], 45 (8) [$C_2H_5O^+$], 31 (63) [CH_3O^+].

General Procedure for the Synthesis of the 2-Ethenyl-1,4-benzoquinones **1**: For protolytic hydrolysis, about 500−1000 mg of the corresponding derivatives **4** was dissolved in 10−50 ml of acetone at a temperature < 40°C. To the stirred acetone solution, 2−3 drops of sulfuric acid (2 N) were added at room temperature. The reaction mixture was immediately cooled and stored at a temperature of 4°C or −30°C at which stage the solution darkened, and the products **1** crystallized. The crystalline solids were filtered off and recrystallized in acetone, again at a temperature < 40°C because of decomposition of **1** in solution, especially at high temperatures. − ^{1}H NMR: For characterization, ^{1}H-NMR chemical shifts and coupling constants of the quinoid and olefinic protons H_a−H_e of the compounds **1** see Figure 1 and Table 1. The aromatic protons H_f−H_k of the substituents were identified labelled clockwise. IR: For selected IR-spectroscopical data of the compounds **1** see Table 2. For yields, melting points, UV/Vis data, molecular formulae and masses, and elemental analyses of the ethenyl-1,4-benzoquinones **1**, see Table 8.

2-[2-(Phenyl)ethenyl]-1,4-benzoquinone (**1a**): Red needles. − Yield 0.13 g (20%). − M.p. 115−119°C [acetone, dec., ref.[9] 117−120°C (light petroleum ether)]. − ^{1}H NMR ($CDCl_3$): δ = 7.34 (s, 1 H, H_h), 7.38 (d, ^3J = 7.7 Hz, 2 H, H_g, H_i), 7.55 (d, ^3J = 7.7 Hz, 2 H, H_f, H_k).

2-[2-(2-Methylphenyl)ethenyl]-1,4-benzoquinone (**1b**): Orange-red plates and needles. − ^{1}H NMR ($CDCl_3$): δ = 2.44 (s, 3 H, CH_3), 7.20−7.24 (m, 3 H, H_g, H_h, H_i), 7.63 (d, ^3J = 8.8 Hz, 1 H, H_f). − MS (70 eV); *m/z* (%): 225 (3) [M^+ + 1], 224 (17) [M^+], 209 (2) [$M^+ - CH_3$], 181 (29) [$M^+ - CH_3$, − CO], 153 (23) [$M^+ - CH_3$, $-2 \times$ CO], 115 (100), 91 (21) [$C_7H_7^+$], 77 (23) [$C_6H_5^+$], 65 (25) [$C_5H_5^+$], 52 (12) [$C_4H_4^+$], 51 (36) [$C_4H_3^+$].

2-[2-(3-Methylphenyl)ethenyl]-1,4-benzoquinone (**1c**): Light-red plates and needles. − ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 7.16 (d, ^3J = 7.4 Hz, 1 H, H_h), 7.25 (dd, ^3J = 7.6 Hz, ^3J = 7.7 Hz, 1 H, H_g), 7.29 (d, ^3J = 7.4 Hz, 1 H, H_f), 7.37 (s, 1 H, H_k). − ^{13}C NMR ($CDCl_3$): δ = 21.3 (CH_3), 118.9, 124.9, 127.5, 128.2, 129.3, 132.1, 135.9, 136.4, 136.7, 138.0, 138.5, 141.9 (6 aromatic C; 6 olefinic C), 186.9, 187.5 (C=O). − MS (70 eV); *m/z* (%): 225 (15) [M^+ + 1], 224 (100) [M^+], 209 (4) [$M^+ - CH_3$], 196 (9) [M^+ − CO], 181 (32) [$M^+ - CH_3$, − CO], 153 (12) [$M^+ - CH_3$, $- 2 \times$ CO], 91 (3) [$C_7H_7^+$], 77 (2) [$C_6H_5^+$], 65 (2) [$C_5H_5^+$], 51 (2) [$C_4H_3^+$].

2-[2-(4-Methylphenyl)ethenyl]-1,4-benzoquinone (**1d**): Light-red plates. − ^{1}H NMR ($CDCl_3$): δ = 2.37 (s, 3 H, CH_3), 7.19 (d, ^3J = 8.0 Hz, 2 H, H_g, H_i), 7.45 (d, ^3J = 8.1 Hz, 2 H, H_f, H_k). − ^{13}C NMR ($CDCl_3$): δ = 21.4 (CH_3), 118.2, 127.2, 127.6, 129.4, 129.6, 136.4, 136.7, 137.9, 140.0, 142.1 (6 aromatic C; 6 olefinic C), 187.0, 187.6 (C=O). − MS (70 eV); *m/z* (%): 226 (8) [M^+ + 2], 225 (17) [M^+ + 1], 224 (100) [M^+], 209 (6) [$M^+ - CH_3$], 196 (10) [M^+ − CO], 181 (43) [$M^+ - CH_3$, − CO], 153 (19) [$M^+ - CH_3$, $- 2 \times$ CO], 91 (5) [$C_7H_7^+$], 77 (3) [$C_6H_5^+$], 65 (4) [$C_5H_5^+$], 51 (5) [$C_4H_3^+$].

2-[2-(2,5-Dimethylphenyl)ethenyl]-1,4-benzoquinone (**1e**): Red prisms. − ^{1}H NMR ($CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 7.09 (d, ^3J = 8.2 Hz, 2 H, H_h, H_i), 7.45 (s, 1 H, H_f). − ^{13}C NMR ($CDCl_3$): δ = 19.2, 20.9 (CH_3), 119.9, 126.5, 127.6, 130.3, 130.6, 134.0, 134.7, 135.7, 135.8, 136.5, 136.7, 142.2 (6 aromatic C; 6 olefinic C), 187.0, 187.6 (C=O). − MS (70 eV); *m/z* (%): 240 (19) [M^+ + 2], 238 (45) [M^+], 223 (12) [$M^+ - CH_3$], 195 (36) [$M^+ - CH_3$, − CO], 167 (17) [$M^+ - CH_3$, $- 2 \times$ CO], 152 (25) [$M^+ - 2 \times CH_3$, $- 2 \times$ CO], 105 (10) [$C_8H_9^+$], 91 (22) [$C_7H_7^+$], 78 (15) [$C_6H_6^+$], 77 (37) [$C_6H_5^+$], 65 (18) [$C_5H_5^+$], 54 (100), 52 (14) [$C_4H_4^+$], 51 (39) [$C_4H_3^+$].

2-[2-(3.4-Dimethylphenyl)ethenyl]-1,4-benzoquinone (**1f**): Red needles. − ^{1}H NMR ($CDCl_3$): δ = 2.28 (s, 6 H, CH_3), 7.15 (d, ^3J = 7.7 Hz, 1 H, H_g), 7.29 (d, ^3J = 7.7 Hz, 1 H, H_f), 7.34 (s, 1 H, H_k). − ^{13}C NMR ($CDCl_3$): δ = 19.8 (CH_3), 118.0, 125.4, 127.1, 128.8, 130.2, 133.8, 136.5, 136.8, 137.2, 138.2, 138.8, 142.2 (6 aromatic C; 6 olefinic C), 187.1, 187.6 (C=O). − MS (70 eV); *m/z* (%): 240 (17) [M^+ + 2], 239 (19) [M^+ + 1], 238 (97) [M^+], 223 (25) [$M^+ - CH_3$], 195 (100) [$M^+ - CH_3$, − CO], 167 (39) [$M^+ - CH_3$, $- 2 \times$ CO], 152 (50) [$M^+ - 2 \times CH_3$, $- 2 \times$ CO], 105 (14) [$C_8H_9^+$], 91 (45) [$C_7H_7^+$], 78 (17) [$C_6H_6^+$], 77 (63) [$C_6H_5^+$], 65 (25) [$C_5H_5^+$], 52 (14) [$C_4H_4^+$], 51 (54) [$C_4H_3^+$].

2-[2-(3,5-Dimethylphenyl)ethenyl]-1,4-benzoquinone (**1g**): Dark-red needles. − ^{1}H NMR ($CDCl_3$): δ = 2.34 (s, 6 H, CH_3), 6.99 (s,

Table 8. Yields, melting points, UV/Vis data, molecular formulae and masses, and elemental analyses of the ethenyl-1,4-benzoquinones **1**

comp.	yield [%]	m.p.[a] [°C]	UV/Vis[b] λ_{max} (lg ε) [nm]	empirical formula	molecular mass	C calcd.	C found	H calcd.	H found	Cl calcd.	Cl found
1b	63	77	234 (4.10), 268 (4.01), 282 (4.00), 412 (3.53)	$C_{15}H_{12}O_2$	224.25	80.34	80.16	5.39	5.38		
1c	84	109−112	232 (4.16), 272 (4.18), 292 (4.20), 442 (3.78)	$C_{15}H_{12}O_2$	224.25	80.34	80.12	5.39	5.46		
1d	52	135−137	234 (4.14), 270 (4.13), 296 (4.24), 454 (3.84)	$C_{15}H_{12}O_2$	224.25	80.34	80.11	5.39	5.50		
1e	71	79−87	234 (4.21), 264 (4.16), 290 (4.07), 446 (3.68)	$C_{16}H_{14}O_2$	238.28	80.67	80.53	5.88	5.77		
1f	77	142−145	230 (4.20), 268 (4.19), 298 (4.24), 456 (3.85)	$C_{16}H_{14}O_2$	238.28	80.67	80.33	5.88	5.97		
1g	69	110−115	233 (4.32), 272 (4.26), 296 (4.26), 450 (3.87)	$C_{16}H_{14}O_2$	238.28	80.67	80.25	5.88	6.01		
1h	64	95−99	264 (4.21), 284 (4.17), 422 (3.73)	$C_{14}H_9ClO_2$	244.68	68.72	68.70	3.71	3.76	14.49	14.56
1i	81	138	226 (4.16), 270 (4.16), 284 (4.16), 418 (3.70)	$C_{14}H_9ClO_2$	244.68	68.72	68.54	3.71	3.81	14.49	14.60
1k	86	130−133	222 (3.96), 268 (4.05), 290 (4.06), 420 (3.64)	$C_{14}H_9ClO_2$	244.68	68.72	68.58	3.71	3.83	14.49	14.89
1l	70	134−136	264 (4.14), 288 (4.09), 412 (3.65)	$C_{14}H_8Cl_2O_2$	279.12	60.25	60.20	2.89	2.96	25.40	25.31
1m	72	114−117	242 (3.62), 270 (3.75), 292 (3.75), 424 (3.31)	$C_{14}H_8Cl_2O_2$	279.12	60.25	60.21	2.89	3.01	25.40	25.30
1n	71	140−145	232 (4.02), 264 (4.07), 292 (4.01), 442 (3.62)	$C_{14}H_8Cl_2O_2$	279.12	60.25	60.00	2.89	2.92	25.40	25.40
1o	61	97−103	232 (4.30), 258 (4.24), 396 (3.60)	$C_{14}H_8Cl_2O_2$	279.12	60.25	60.19	2.89	2.99	25.40	25.20
1p	83	113−115	228 (4.24), 274 (4.27), 290 (4.27), 420 (3.85)	$C_{14}H_8Cl_2O_2$	279.12	60.25	59.96	2.89	3.03	25.40	24.87
1q	70	119−124	232 (4.33), 268 (4.26), 284 (4.24), 410 (3.75)	$C_{14}H_8Cl_2O_2$	279.12	60.25	60.21	2.89	3.02	25.40	25.55
1r	75	92−95	242 (4.15), 262 (4.24), 296 (4.06), 424 (3.71)	$C_{15}H_{11}ClO_2$	258.70	69.64	69.37	4.29	4.33	13.70	13.67
1s	56	128−135	236 (4.21), 310 (4.16), 492 (3.86)	$C_{15}H_{10}O_4$	254.24	70.86	70.87	3.97	4.04		
1t	80	154−159	296 (4.38), 420 (3.78)	$C_{16}H_{12}O_4$	268.27	71.64	71.39	4.51	4.50		
1u	69	105	242 (4.39), 350 (3.44)	$C_{10}H_8O_4$	192.17	62.50	62.42	4.20	4.24		

[a] Solvent: acetone, all compounds melt under decomposition. − [b] Spectra of **1b−1i**, **1l−1o** and **1q−1u** were recorded in $CHCl_3$, of **1k** and **1p** in CH_2Cl_2.

1 H, H_h), 7.17 (s, 2 H, H_f, H_k). − ^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_3), 118.7, 125.6, 127.3, 131.5, 135.9, 136.4, 136.7, 138.2, 138.4, 142.1 (6 aromatic C; 6 olefinic C), 186.9, 187.6 (C=O). − MS (70 eV); *m/z* (%): 240 (13) [M^+ + 2], 239 (17) [M^+ + 1], 238 (92) [M^+], 223 (9) [M^+ − CH_3], 195 (73) [M^+ − CH_3, − CO], 167 (32) [M^+ − CH_3, − 2 × CO], 152 (46) [M^+ − 2 × CH_3, − 2 × CO], 105 (9) [$C_8H_9^+$], 91 (29) [$C_7H_7^+$], 78 (17) [$C_6H_6^+$], 77 (51) [$C_6H_5^+$], 65 (24) [$C_5H_5^+$], 54 (100), 52 (11) [$C_4H_4^+$], 51 (48) [$C_4H_3^+$].

2-[2-(2-Chlorophenyl)ethenyl]-1,4-benzoquinone (**1h**): Orange-red needles. − ^{1}H NMR ($CDCl_3$): δ = 7.25−7.72 (m, 3 H, H_g, H_h, H_i), 7.71 (d, ^3J = 7.4 Hz, 1 H, H_f). − ^{13}C NMR ($CDCl_3$): δ = 121.5, 127.1, 127.2, 128.3, 130.0, 130.3, 133.4, 134.0, 134.4, 136.4, 136.8, 141.7 (6 aromatic C; 6 olefinic C), 186.6, 187.5 (C=O). − MS (70 eV); *m/z* (%): 246 (7) [M^+, $C_{14}H_9{}^{37}ClO_2^+$], 245 (3) [M^+ + 1], 244 (17) [M^+, $C_{14}H_9{}^{35}ClO_2^+$], 209 (13) [M^+ − Cl], 181 (32) [M^+ − Cl, − CO], 153 (30) [M^+ − Cl, − 2 × CO], 152 (25) [M^+ − HCl, − 2 × CO], 77 (26) [$C_6H_5^+$], 54 (100), 51 (26) [$C_4H_3^+$], 38 (12) [HCl^+].

2-[2-(3-Chlorophenyl)ethenyl]-1,4-benzoquinone (**1i**): Light-red plates and prisms. − ^{1}H NMR ($CDCl_3$): δ = 7.27−7.40 (m, 3 H, H_f, H_g, H_h), 7.53 (s, 1 H, H_k). − ^{13}C NMR ($CDCl_3$): δ = 120.8, 125.8, 127.3, 128.5, 129.4, 130.1, 135.0, 136.4, 136.6, 136.8, 137.8, 141.5 (6 aromatic C; 6 olefinic C), 186.7, 187.5 (C=O). − MS (70 eV); *m/z* (%): 247 (5) [M^+ + 1], 246 (39) [M^+, $C_{14}H_9{}^{37}ClO_2^+$], 245 (14) [M^+ + 1], 244 (99) [M^+, $C_{14}H_9{}^{35}ClO_2^+$], 216 (10) [M^+ − CO], 209 (21) [M^+ − Cl], 181 (100) [M^+ − Cl, − CO], 153 (37) [M^+ − Cl, − 2 × CO], 152 (27) [M^+ − HCl, − 2 × CO], 77 (10) [$C_6H_5^+$], 51 (7) [$C_4H_3^+$].

2-[2-(4-Chlorophenyl)ethenyl]-1,4-benzoquinone (**1k**): Red plates (**γ-1k**), dark-red needles (**β-1k**). − ^{1}H NMR ($CDCl_3$): δ = 7.35 (d, ^3J = 8.4 Hz, 2 H, H_g, H_i), 7.47 (d, ^3J = 8.4 Hz, 2 H, H_f, H_k). − ^{13}C NMR ($CDCl_3$): δ = 119.9, 127.9, 128.1, 128.7, 129.0, 134.5, 135.4, 136.5, 136.6, 141.7 (6 aromatic C; 6 olefinic C), 186.8, 187.5 (C=O). − MS (70 eV); *m/z* (%): 248 (3) [M^+ + 2], 247 (5) [M^+ + 1], 246 (26) [M^+, $C_{14}H_9{}^{37}ClO_2^+$], 245 (10) [M^+ + 1], 244 (53) [M^+, $C_{14}H_9{}^{35}ClO_2^+$], 209 (21) [M^+ − Cl], 181 (79) [M^+ − Cl, −CO], 153 (62) [M^+ − Cl, − 2 × CO], 152 (51) [M^+ − HCl, − 2 × CO], 77 (45) [$C_6H_5^+$], 54 (100], 51 (34) [$C_4H_3^+$], 36 (10) [HCl^+].

2-[2-(2,3-Dichlorophenyl)ethenyl]-1,4-benzoquinone (**1l**): Orange-red plates. − ^{1}H NMR ($CDCl_3$): δ = 7.22 (d, ^3J = 8.0 Hz, 1 H, H_g), 7.45 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1 H, H_h), 7.60 (dd, ^3J = 7.9 Hz, ^4J = 1.2 Hz, 1 H, H_f). − ^{13}C NMR ($CDCl_3$): δ = 122.8, 125.4, 127.4, 128.9, 130.8, 132.4, 133.4, 133.8, 136.4, 136.5, 136.8, 141.3 (6 aromatic C; 6 olefinic C), 186.4, 187.4 (C=O). − MS (70 eV); *m/z* (%): 282 (2) [M^+, $C_{14}H_8{}^{37}Cl_2O_2^+$], 280 (8) [$M^+$, $C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2^+$], 279 (2) [$M^+$ + 1], 278 (13) [M^+, $C_{14}H_8{}^{35}Cl_2O_2^+$], 243 (7) [$M^+$ − Cl], 215 (22) [M^+ − Cl, − CO], 187 (6) [M^+ − Cl, − 2 × CO], 152 (28) [M^+ − 2 × Cl, − 2 × CO], 54 (100), 51 (15) [CH_2Cl^+], 38 (8) [HCl^+].

2-[2-(2,4-Dichlorophenyl)ethenyl]-1,4-benzoquinone (**1m**): Dark-red needles. − ^{1}H NMR ($CDCl_3$): δ = 7.27 (dd, ^3J = 8.4 Hz, ^4J = 1.8 Hz, 1 H, H_g), 7.42 (d, ^4J = 2.1 Hz, 1 H, H_i), 7.64 (d, ^3J = 8.5 Hz, 1 H, H_f). − ^{13}C NMR ($CDCl_3$): δ = 122.0, 127.6, 127.9, 128.6, 129.8, 132.2, 132.6, 134.9, 135.5, 136.4, 136.8, 141.4 (6 aromatic C; 6 olefinic C), 186.5, 187.4 (C=O). − MS (70 eV); *m/z* (%): 282 (3) [M^+, $C_{14}H_8{}^{37}Cl_2O_2^+$], 281 (3) [$M^+$ + 1], 280 (18) [M^+, $C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2^+$], 279 (4) [$M^+$ + 1], 278 (27) [M^+, $C_{14}H_8{}^{35}Cl_2O_2^+$], 243 (15) [$M^+$ − Cl], 215 (27) [M^+ − Cl, − CO], 187 (11) [M^+ − Cl, − 2 × CO], 152 (49) [M^+ − 2 × Cl, − 2 × CO], 82 (100), 51 (12) [CH_2Cl^+], 38 (13) [HCl^+], 36 (31) [HCl^+].

2-[2-(2,5-Dichlorophenyl)ethenyl]-1,4-benzoquinone (**1n**): Orange-red plates and needles. − ^{1}H NMR ($CDCl_3$): δ = 7.24 (dd, ^3J = 8.7 Hz, ^4J = 2.45 Hz, 1 H, H_h), 7.34 (d, ^3J = 8.6 Hz, 1 H, H_i), 7.67 (d, ^4J = 2.4 Hz, 1 H, H_f). − ^{13}C NMR ($CDCl_3$): δ = 122.9, 127.0, 129.1, 130.1, 131.1, 132.3, 132.5, 133.2, 135.6, 136.6, 136.8, 141.3 (6 aromatic C; 6 olefinic C), 186.4, 187.4 (C=O). − MS (70 eV); *m/z* (%): 282 (5) [M^+, $C_{14}H_8{}^{37}Cl_2O_2^+$], 281 (5) [$M^+$ + 1], 280 (31) [M^+, $C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2^+$], 278 (41) [$M^+$, $C_{14}H_8{}^{35}Cl_2O_2^+$], 250 (11) [$M^+$ − CO], 243 (42) [M^+ − Cl], 215 (61) [M^+ − Cl, − CO], 187 (19) [M^+ − Cl, − 2 × CO], 152 (76) [M^+ − 2 × Cl, − 2 × CO], 82 (100), 54 (100), 51 (29) [CH_2Cl^+], 38 (14) [HCl^+], 36 (5) [HCl^+].

2-[2-(2,6-Dichlorophenyl)ethenyl]-1,4-benzoquinone (**1o**): Orange-red cubes. − ^{1}H NMR ($CDCl_3$): δ = 7.17 (d, ^3J = 7.6 Hz, 1 H, H_h), 7.35 (d, ^3J = 8.1 Hz, 2 H, H_g, H_i). − MS (70 eV); *m/z* (%): 282 (5) [M^+, $C_{14}H_8{}^{37}Cl_2O_2^+$], 280 (23) [$M^+$, $C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2^+$],

279 (5) [M^+ + 1], 278 (29) [M^+, $C_{14}H_8{}^{35}Cl_2O_2{}^+$], 243 (20) [$M^+$ − Cl], 215 (26) [M^+ − Cl, − CO], 187 (13) [M^+ − Cl, − 2 × CO], 152 (49) [M^+ − 2 × Cl, − 2 × CO], 82 (100), 51 (17) [CH_2Cl^+], 38 (12) [HCl^+], 36 (23) [HCl^+].

2-[2-(3,4-Dichlorophenyl)ethenyl]-1,4-benzoquinone (**1p**): Orange-red plates. − ^{1}H NMR ($CDCl_3$): δ = 7.36 (d, ^3J = 8.4 Hz, 1 H, H_g), 7.45 (d, ^3J = 8.3 Hz, 1 H, H_f), 7.62 (d, ^4J = 1.9 Hz, 1 H, H_k). − ^{13}C NMR ($CDCl_3$): δ = 121.3, 126.5, 128.4, 128.8, 129.1, 130.7, 130.8, 135.3, 136.1, 136.6, 136.8, 141.2 (6 aromatic C; 6 olefinic C), 186.6, 187.4 (C=O). − MS (70 eV); *m/z* (%): 283 (0.8) [M^+ + 1], 282 (5) [M^+, $C_{14}H_8{}^{37}Cl_2O_2{}^+$], 281 (5) [$M^+$ + 1], 280 (27) [M^+, $C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2{}^+$], 279 (7) [$M^+$ + 1], 278 (48) [M^+, $C_{14}H_8{}^{35}Cl_2O_2{}^+$], 215 (65) [$M^+$ − Cl, − CO], 187 (17) [M^+ − Cl, − 2 × CO], 152 (54) [M^+ − 2 × Cl, − 2 × CO], 54 (100), 51 (16) [CH_2Cl^+], 38 (10) [HCl^+], 36 (20) [HCl^+].

2-[2-(3,5-Dichlorophenyl)ethenyl]-1,4-benzoquinone (**1q**): Dark-red needles. − ^{1}H NMR ($CDCl_3$): δ = 7.31 (d, ^4J = 1.8 Hz, 1 H, H_h), 7.39 (d, ^4J = 1.7 Hz, 2 H, H_f, H_k). − ^{13}C NMR ($CDCl_3$): δ = 122.3, 125.7, 129.1, 129.3, 135.1, 135.6, 136.6, 136.7, 139.0, 141.0 (6 aromatic C; 6 olefinic C), 186.5, 187.3 (C=O). − MS (70 eV); *m/z* (%): 282 (1) [M^+, $C_{14}H_8{}^{37}Cl_2O_2{}^+$], 281 (1) [$M^+$ + 1], 280 (7) [M^+, $C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2{}^+$], 279 (2) [$M^+$ + 1], 278 (10) [M^+, $C_{14}H_8{}^{35}Cl_2O_2{}^+$], 215 (23) [$M^+$ − Cl, − CO], 187 (6) [M^+ − Cl, − 2 × CO], 152 (29) [M^+ − 2 × Cl, − 2 × CO], 54 (100), 51 (13) [CH_2Cl^+], 38 (6) [HCl^+], 36 (6) [HCl^+].

2-[2-(3-Chloro-2-methylphenyl)ethenyl]-1,4-benzoquinone (**1r**): Light-red plates and needles. − ^{1}H NMR ($CDCl_3$): δ = 2.46 (s, 3 H, CH_3), 7.15 (dd, ^3J = 7.9 Hz, ^3J = 7.9 Hz, 1 H, H_g), 7.36 (d, ^3J = 7.7 Hz, 1 H, H_h), 7.48 (d, ^3J = 7.6 Hz, 1 H, H_f). − ^{13}C NMR ($CDCl_3$): δ = 16.2 (CH_3), 122.2, 124.8, 126.9, 127.3, 128.6, 129.5, 130.0, 134.7, 135.8, 136.6, 137.3, 141.7 (6 aromatic C; 6 olefinic C), 186.8, 187.6 (C=O). − MS (70 eV); *m/z* (%): 260 (8) [M^+, $C_{15}H_{11}{}^{37}ClO_2{}^+$], 259 (3) [$M^+$ + 1], 258 (20) [M^+, $C_{15}H_{11}{}^{35}ClO_2{}^+$], 223 (9) [$M^+$ − Cl], 195 (37) [M^+ − Cl, − CO], 167 (19) [M^+ − Cl, − 2 × CO], 166 (11) [M^+ − HCl, − 2 × CO], 77 (11) [$C_6H_5{}^+$], 65 (11) [$C_5H_5{}^+$], 54 (100), 52 (9) [$C_4H_4{}^+$], 51 (28) [$C_4H_3{}^+$], 38 (10) [HCl^+].

2-[2-(1,3-Benzodioxol-5-yl)ethenyl]-1,4-benzoquinone (**1s**): Dark-red plates. − ^{1}H NMR ($CDCl_3$): δ = 6.01 (s, 2 H, OCH_2O), 7.01 (d, ^3J = 8.1 Hz, 1 H, H_g), 7.01 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1 H, H_f), 7.11 (d, ^4J = 1.8 Hz, 1 H, H_k). − ^{13}C NMR ($CDCl_3$): δ = 101.5 (OCH_2O), 106.1, 108.6, 117.4, 123.8, 127.0, 130.8, 136.5, 136.8, 137.7, 142.1 (6 aromatic C; 6 olefinic C), 186.7, 187.6 (C=O). − MS (70 eV); *m/z* (%): 256 (4) [M^+ + 2], 255 (3) [M^+ + 1], 254 (17) [M^+], 196 (6) [M^+ − CO, − CH_2O], 172 (21) [M^+ − 2 × CO, − C_2H_2], 168 (34) [M^+ − 2 × CO, − CH_2O], 114 (100), 77 (15) [$C_6H_5{}^+$], 65 (17) [$C_5H_5{}^+$], 51 (50) [$C_4H_3{}^+$], 45 (33) [$C_2H_5O^+$].

Methyl 4-[2-(3,6-Dioxocyclohexa-1,4-dienyl)ethenyl]benzoate (**1t**): Orange-red plates. − MS (70 eV); *m/z* (%): 269 (7) [M^+ + 1], 268 (38) [M^+], 237 (10) [M^+ − CH_3O], 225 (10) [M^+ − CH_3, − CO], 209 (20) [M^+ − CH_3O, − CO], 208 (10) [M^+ − CH_4O, − CO], 181 (74) [M^+ − CH_3O, − 2 × CO], 180 (17) [M^+ − CH_4O, − 2 × CO], 91 (12) [$C_7H_7{}^+$], 82 (100), 78 (17) [$C_6H_6{}^+$], 77 (66) [$C_6H_5{}^+$], 74 (18) [$C_3H_6O_2{}^+$], 59 (42) [$C_2H_3O_2{}^+$], 54 (100), 51 (32) [$C_4H_3{}^+$]. − Dark-red needles (**β-1t**): ^{1}H NMR ($CDCl_3$): δ = 3.93 (s, 3 H, $COOCH_3$), 7.61 (d, ^3J = 8.4 Hz, 2 H, H_g, H_i), 8.05 (d, ^3J = 8.4 Hz, 2 H, H_f, H_k). − ^{13}C NMR ($CDCl_3$): δ = 52.2 (COOCH_3), 121.8, 127.4, 128.7, 129.9, 130.1, 130.7, 136.6, 136.7, 140.2, 141.5 (6 aromatic C; 6 olefinic C), 166.5 ($COOCH_3$), 186.6, 187.5 (C=O). − MS (70 eV); *m/z* (%): 269 (11) [M^+ + 1], 268 (55) [M^+], 237 (19) [M^+ − CH_3O], 225 (17) [M^+ − CH_3, − CO], 209 (36) [M^+ − CH_3O, − CO], 208 (16) [M^+ − CH_4O, − CO], 181 (100) [M^+ − CH_3O, − 2 × CO], 180 (21) [M^+ − CH_4O, − 2 × CO], 152 (100), 127 (100), 91 (15) [$C_7H_7{}^+$], 87 (14) [$C_4H_7O_2{}^+$], 82 (100), 78 (19) [$C_6H_6{}^+$], 77 (93) [$C_6H_5{}^+$], 74 (23) [$C_3H_6O_2{}^+$], 59 (86) [$C_2H_3O_2{}^+$], 54 (100), 52 (11) [$C_4H_4{}^+$], 51 (69) [$C_4H_3{}^+$], 31 (13) [CH_3O^+].

Methyl 3-(3,6-Dioxocyclohexa-1,4-dienyl)acrylate (**1u**): Yellow cubes. − ^{1}H NMR ($CDCl_3$): δ = 3.81 (s, 3 H, $COOCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 52.1 (COOCH_3), 127.5, 133.3, 135.5, 136.6, 137.0, 139.5 (6 olefinic C), 166.0 ($COOCH_3$), 185.6, 187.0 (C=O). − MS (70 eV); *m/z* (%): 192 (3) [M^+], 161 (24) [M^+ − CH_3O], 133 (100) [M^+ − CH_3O, − CO], 105 (59) [M^+ − CH_3O, − 2 × CO], 59 (92) [$C_2H_3O_2{}^+$], 31 (7) [CH_3O^+].

For yields, melting points, UV/Vis data, molecular formulae and masses, elemental analyses or high-resolution MS data of the derivatives **5l**, **8k**, **9a**, **9b**, **9c**, **9e**, **9n**, **9o**, **9r** and **9u** see Table 9.

3-[2-(2,3-Dichlorophenyl)ethenyl]-4,4-dimethoxycyclohexa-2,5-dienone (**5l**): Protolytic hydrolysis of **4l** (500 mg, 1.3 ×·10^{-3} mol) in 10 ml of acetone with 2 drops of sulfuric acid (2 N) at room temperature and immediate cooling of the reaction mixture at −30°C yielded, besides the quinone **1l**, the compound **5l** as light-yellow plates. − IR (KBr): $\tilde{\nu}$ = 2947 cm^{-1} (m), 2938 (m), 2904 (w), 2833 (w, C−H), 1664 (s, C=O), 1626 (s, C=C), 1590 (s, C_{ar}=C_{ar}), 1449 (m), 1411 (s, C−H), 1158 (m), 1081 (s, C−O), 979 (m), 814 (w), 781 (m), 729 (w, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.27 (s, 6 H, OCH_3), 6.48 (dd, ^3J = 10.3 Hz, ^4J = 2.1 Hz, 1 H, H_b), 6.58 (d, ^4J = 1.9 Hz, 1 H, H_c), 6.75 (d, ^3J = 10.3 Hz, 1 H, H_a), 6.79 (d, ^3J = 16.1 Hz, 1 H, H_d), 7.22 (dd, ^3J = 7.9 Hz, ^3J = 7.9 Hz, 1 H, H_g), 7.43 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1 H, H_h), 7.58 (dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1 H, H_f), 7.95 (d, ^3J = 16.3 Hz, 1 H, H_e). − ^{13}C NMR ($CDCl_3$): δ = 51.2 (OCH_3), 96.0 [$C(OCH_3)_2$], 125.2, 126.3, 127.2, 128.2, 130.4, 132.2, 132.4, 133.5, 133.8, 136.8, 143.9, 151.3 (6 aromatic C; 6 olefinic C), 185.3 (C=O). − MS (70 eV); *m/z* (%): 328 (10) [M^+, $C_{16}H_{14}{}^{37}Cl_2O_3{}^+$], 327 (11) [$M^+$ + 1], 326 (61) [M^+, $C_{16}H_{14}{}^{37}Cl_{35}ClO_3{}^+$], 325 (16) [$M^+$ + 1], 324 (92) [M^+, $C_{16}H_{14}{}^{35}Cl_2O_3{}^+$], 309 (13) [$M^+$ − CH_3], 295 (33) [M^+ − CH_3O], 293 (48) [M^+ − CH_3O], 280 (11) [M^+ − CH_3, − CH_3O], 278 (16) [M^+ − CH_3, − CH_3O], 243 (23) [M^+ − CH_3, − CH_3O, − Cl], 215 (42) [M^+ − CH_3, − CH_3O, − Cl, − CO], 152 (100), 75 (12) [$C_3H_7O_2{}^+$], 51 (11) [$C_4H_3{}^+$].

9-(4-Chlorophenyl)-8a-[2-(4-chlorophenyl)ethenyl]-4a,4b,8a,9-tetrahydrophenanthrene-1,4,5,8-tetraone (**8k**): Freshly prepared quinone **1k** (226.8 mg, 0.93 × 10^{-3} mol) was dissolved in 20 ml of toluene at room temperature. After one week at 4°C, the yellow crystals of **8k** were precipitated, filtered off and purified by recrystallization from toluene. ^{1}H NMR and ^{13}C NMR: The labelling of the protons and carbon atoms is in accordance with the molecular structure labelling of **8k** (see Figure 2). − IR (KBr): $\tilde{\nu}$ = 3049 cm^{-1} (w, C_{ar}−H), 1681 (s, C=O), 1623 (m), 1606 (m, C=C), 1490 (m, C_{ar}=C_{ar}), 1409 (w), 1374 (w, C−H), 966 (w), 841 (m), 811 (w), 790 (w, =C−H). − ^{1}H NMR ($CDCl_3$): δ = 3.43 (dd, ^3J = 7.7 Hz, ^4J = 3.0 Hz, 1 H, 6-H), 4.15 (d, ^3J = 4.5 Hz, 1 H, 12-H), 4.23 (m, 1 H, 5-H), 6.09 (d, ^3J = 10.4 Hz, 1 H, 3-H), 6.27 (d, ^3J = 10.4 Hz, 1 H, 2-H), 6.43 (d, ^3J = 16.3 Hz, 1 H, 15-H), 6.50 (d, ^3J = 16.3 Hz, 1 H, 16-H), 6.72 (d, ^3J = 6.6 Hz, 1 H, 13-H), 6.97 (d, ^3J = 10.4 Hz, 1 H, 8-H or 9-H), 7.03 (d, ^3J = 6.8 Hz, 2 H, 24-H, 28-H), 7.05 (d, ^3J = 10.4 Hz, 1 H, 8-H or 9-H), 7.18 (d, ^3J = 8.7 Hz, 2 H, 25-H, 27-H), 7.31 (d, ^3J = 8.8 Hz, 2 H, 19-H, 21-H), 7.35 (d, ^3J = 8.8 Hz, 2 H, 18-H, 22-H). − ^{13}C NMR ($CDCl_3$): δ = 43.1, 46.1, 52.4 (5-C, 6-C, 12-C), 58.6 (11-C), 128.0, 129.0, 129.0, 130.6, 131.2, 131.8, 132.6, 133.9, 134.5, 135.2, 135.4, 139.4, 139.6, 140.7, 142.2 (12 aromatic C; 8 olefinic C), 184.1, 193.7, 194.8, 199.1 (C=O). − MS (70 eV); *m/z* (%): 490 (0.4) [M^+, $C_{28}H_{18}{}^{37}Cl\,{}^{35}ClO_4{}^+$], 488

Table 9. Yields, melting points, UV/Vis data, molecular formulae and masses, elemental analyses or high-resolution MS data of the derivatives **5l**, **8k**, **9a**, **9b**, **9c**, **9e**, **9n**, **9o**, **9r** and **9u**

comp.	yield [%]	m.p.[a] (solvent) [°C]	UV/Vis λ_{max} (lg ε) [nm]	empirical formula	molecular mass	C calcd.	C found	H calcd.	H found	Cl calcd.	Cl found
5l		107 (acetone)	232 (4.14), 252 (4.09), 344 (4.29)	$C_{16}H_{14}Cl_2O_3$	325.19	59.10	58.90	4.34	4.34	21.80	22.07
9b	42	206–207 (ethyl acetate)	230 (4.19), 252 (4.45), 334 (3.26)	$C_{30}H_{24}O_4$	448.50	80.34	79.96	5.39	5.45		
9e	59	215–216 (acetone)	244 (4.02), 252 (4.09), 280 (3.10), 306 (2.85)	$C_{32}H_{28}O_4$	476.56	80.67	80.36	5.88	5.84		
9r	29	213–214 (ethyl acetate)	232 (4.23), 252 (4.47), 332 (3.38)	$C_{30}H_{22}Cl_2O_4$	517.40	69.64	69.45	4.29	4.27	13.70	13.51
9u	52	190–195 (acetone)		$C_{20}H_{16}O_8$	384.34	62.50	62.17	4.20	4.35		

					MS (high resolution, 70 eV); *m/z* (%) calcd.	found	
8k	46	175 (toluene)	234 (4.25), 260 (4.20), 290 (3.69), 298 (3.58)	$C_{28}H_{18}Cl_2O_4$	492.0523	492.0582 (7.7)	$[C_{28}H_{18}{}^{37}Cl_2O_4{}^+]$
					490.0553	490.0548 (35.6)	$[C_{28}H_{18}{}^{37}Cl^{35}ClO_4{}^+]$
					488.0582	488.0540 (59.0)	$[C_{28}H_{18}{}^{35}Cl_2O_4{}^+]$
9a	22	180–185 (acetone)		$C_{28}H_{20}O_4$	420.1362	420.1383 (21.5)	$[C_{28}H_{20}O_4{}^+]$
9c	28	209–210 (ethyl acetate)	252 (4.30), 304 (3.15), 332 (3.13)	$C_{30}H_{24}O_4$	448.1675	448.1700 (26.8)	$[C_{30}H_{24}O_4{}^+]$
9n	36	197–200 (ethyl acetate)		$C_{28}H_{16}Cl_4O_4$	563.9685	563.9923 (1.0)	$[C_{28}H_{16}{}^{37}Cl_4O_4{}^+]$
					561.9714	561.9840 (5.7)	$[C_{28}H_{16}{}^{37}Cl_0{}^{35}ClO_4{}^+]$
					559.9744	559.9872 (11.5)	$[C_{28}H_{16}{}^{37}Cl_0{}^{35}Cl_2O_4{}^+]$
					557.9773	557.9839 (16.1)	$[C_{28}H_{16}{}^{37}Cl^{35}Cl_3O_4{}^+]$
					555.9803	555.9842 (11.0)	$[C_{28}H_{16}{}^{35}Cl_4O_4{}^+]$
9o	24	221–223 ($CHCl_3$)		$C_{28}H_{16}Cl_4O_4$	279.9872	279.9907 (60.1)	$[C_{14}H_8{}^{37}Cl^{35}ClO_2{}^+]$
					277.9901	277.9869 (49.7)	$[C_{14}H_8{}^{35}Cl_2O_2{}^+]$

[a] Compounds **9** melt under decomposition. – [b] Spectra were recorded in $CHCl_3$.

(0.5) [M^+, $C_{28}H_{18}{}^{35}Cl_2O_4{}^+$], 247 (5) [$C_{14}H_9{}^{37}ClO_2{}^+$ + 1], 246 (27) [$C_{14}H_9{}^{37}ClO_2{}^+$], 245 (3) [$C_{14}H_9{}^{35}ClO_2{}^+$ + 1], 244 (2) [$C_{14}H_9{}^{35}ClO_2{}^+$], 183 (8) [$C_{14}H_9{}^{37}ClO_2{}^+$ – Cl, – CO], 181 (10) [$C_{14}H_9{}^{35}ClO_2{}^+$ – Cl, – CO], 78 (8) [$C_6H_6{}^+$], 77 (19) [$C_6H_5{}^+$], 65 (11) [$C_5H_5{}^+$], 55 (100), 52 (32) [$C_4H_4{}^+$], 51 (80) [$C_4H_3{}^+$], 36 (9) [HCl^+].

General Procedure for Irradiation: The irradiations of 200–400 mg of the powdered derivatives **1**, were carried out with a 1200-W high-pressure mercury lamp (Q 1200, Heraeus, Hanau) in a glass vessel at 20°C for 5 h with continuous stirring[2]. The melting range of the irradiated quinones **1a**–**1c**, **1e**, **1n**, **1o**, **1r** and **1u** was raised by 35–70°C. For removal of unreacted starting materials and isolation of the generated photoproducts, the mixture was treated with a suitable solvent at room temperature. After recrystallization, the yellow cyclobutanes were obtained in analytical purity. – ^{1}H NMR: The characterization of the protons is in accordance with the proton characterization of the compounds **1**; however the protons H_d and H_e represent the cyclobutane protons. IR: For selected IR-spectroscopical data of the compounds **9**, see Table 5.

r-1,t-3-Bis(3,6-dioxocyclohexa-1,4-dienyl)-c-2,t-4-bis(phenyl)cyclobutane (**9a**): The irradiated quinone **1a** was treated twice with acetone at room temperature for 12 h. – MS (70 eV); *m/z* (%): 424 (6) [M^+ + 4], 423 (31) [M^+ + 3], 422 (93) [M^+ + 2], 421 (4) [M^+ + 1], 420 (9) [M^+], 418 (9) [M^+ – 2], 344 (15) [M^+ + 2, – $C_6H_6{}^+$], 213 (17) [$C_{14}H_{10}O_2{}^+$ + 3], 212 (100) [$C_{14}H_{10}O_2{}^+$ + 2], 211 (48) [$C_{14}H_{10}O_2{}^+$ + 1], 210 (70) [$C_{14}H_{10}O_2{}^+$], 183 (10) [$C_{14}H_{10}O_2{}^+$ + 1, – CO], 181 (20) [$C_{14}H_{10}O_2{}^+$ – 1, – CO], 153 (16) [$C_{14}H_{10}O_2{}^+$ – 1, – 2 × CO], 128 (14) [$C_{14}H_{10}O_2{}^+$ – 2 × CO, – C_2H_2], 127 (10) [$C_{14}H_{10}O_2{}^+$ – 1, – 2 × CO, – C_2H_2], 105 (15) [$C_8H_9{}^+$], 91 (24) [$C_7H_7{}^+$], 78 (14) [$C_6H_6{}^+$], 77 (20) [$C_6H_5{}^+$], 51 (18) [$C_4H_3{}^+$].

r-1,t-3-Bis(3,6-dioxocyclohexa-1,4-dienyl)-c-2,t-4-bis(2-methylphenyl)cyclobutane (**9b**): The irradiated quinone **1b** was stirred for 12 h in toluene at room temperature. The remaining cyclobutane **9b** was recrystallized twice from ethyl acetate. – ^{1}H NMR ($CDCl_3$): δ = 2.29 (s, 6 H, CH_3), 4.38–4.58 (m, 4 H, H_d, H_e), 6.49 (d, ^3J = 10.3 Hz, 2 H, H_a), 6.55 (d, ^3J = 11.1 Hz, 2 H, H_b), 6.56 (s, 2 H, H_c), 7.08–7.19 (m, 6 H, H_g, H_h, H_i), 7.29 (d, ^3J = 7.5 Hz, 2 H, H_f). – ^{13}C NMR ($CDCl_3$): δ = 19.8 (CH_3), 39.4, 41.3 (C_{tert}), 126.1, 126.2, 127.3, 130.7, 132.3, 135.8, 136.1, 136.4, 136.9, 147.2 (6 aromatic C; 4 olefinic C), 186.2, 187.0 (C=O). – MS (70 eV); *m/z* (%): 448 (1) [M^+], 446 (0.5) [M^+ – 2], 226 (19) [$C_{15}H_{14}O_2{}^+$], 225 (18) [$C_{15}H_{13}O_2{}^+$], 224 (100) [$C_{15}H_{12}O_2{}^+$], 209 (9) [$C_{15}H_{12}O_2{}^+$ – CH_3], 196 (15) [$C_{15}H_{12}O_2{}^+$ – CO], 181 (57) [$C_{15}H_{12}O_2{}^+$ – H_3, – CO], 153 (72) [$C_{15}H_{12}O_2{}^+$ – CH_3, – 2 × CO], 77 (19) [$C_6H_5{}^+$], 65 (20) [$C_5H_5{}^+$], 51 (21) [$C_4H_3{}^+$].

r-1,t-3-Bis(3,6-dioxocyclohexa-1,4-dienyl)-c-2,t-4-bis(3-methylphenyl)cyclobutane (**9c**): The irradiated quinone **1c** was stirred for 20 h in toluene at room temperature. The isolated cyclobutane derivative **9c** was purified by double recrystallization from ethyl acetate. – ^{1}H NMR ($CDCl_3$): δ = 2.27 (s, 6 H, CH_3), 4.22–4.41 (m, 4 H, H_d, H_e), 6.50 (d, ^3J = 10.0 Hz, 2 H, H_a), 6.56 (dd, ^3J = 10.1 Hz, ^4J = 2.2 Hz, 2 H, H_b), 6.64 (s, 2 H, H_c), 6.96–6.98 (m, 6 H, H_f, H_h, H_k), 7.12 (dd, ^3J = 8.1 Hz, ^3J = 8.1 Hz, 2 H, H_g). – ^{13}C NMR ($CDCl_3$): δ = 21.4 (CH_3), 41.2, 44.1 (C_{tert}), 125.0, 128.0, 128.4, 128.8, 132.1, 136.0, 136.4, 137.9, 138.2, 147.6 (6 aromatic C; 4 olefinic C), 186.6, 187.0 (C=O). – MS (70 eV); *m/z* (%): 448 (1) [M^+], 446 (3) [M^+ – 2], 226 (39) [$C_{15}H_{14}O_2{}^+$], 225 (20) [$C_{15}H_{13}O_2{}^+$], 224 (100) [$C_{15}H_{12}O_2{}^+$], 196 (11) [$C_{15}H_{12}O_2{}^+$ – CO], 181 (32) [$C_{15}H_{12}O_2{}^+$ – CH_3, – CO], 153 (15) [$C_{15}H_{12}O_2{}^+$ – CH_3, – 2 × CO], 91 (36) [$C_7H_7{}^+$], 77 (15) [$C_6H_5{}^+$], 65 (16) [$C_5H_5{}^+$], 51 (17) [$C_4H_3{}^+$].

c-2,t-4-Bis(2,5-dimethylphenyl)-r-1,t-3-bis(3,6-dioxocyclohexa-1,4-dienyl)cyclobutane (**9e**): The irradiated quinone **1e** was treated with toluene for 12 h at room temperature. The resulting cyclobutane **9e** was recrystallized twice from acetone. – ^{1}H NMR ($CDCl_3$): δ = 2.23 (s, 6 H, CH_3), 2.28 (s, 6 H, CH_3), 4.34–4.55 (m, 4 H, H_d, H_e), 6.49 (d, ^3J = 9.9 Hz, 2 H, H_a), 6.55 (d, ^3J = 9.6 Hz, 2 H, H_b), 6.58 (s, 2 H, H_c), 6.90 (d, ^3J = 7.7 Hz, 2 H, H_h), 6.97 (d, ^3J = 7.7 Hz, 2 H, H_i), 7.06 (s, 2 H, H_f). – ^{13}C NMR ($CDCl_3$):

Table 10. Crystallographic data for compounds **1a**, **1c**, **1e**, **1f**, **1i**, **1k** and **1n**

compound	**1a**	**1c**	**1e**	**1f**	**1i**	**γ-1k**	**β-1k**	**1n**
formula	$C_{14}H_{10}O_2$	$C_{15}H_{12}O_2$	$C_{16}H_{14}O_2$	$C_{16}H_{14}O_2$	$C_{14}H_9ClO_2$	$C_{14}H_9ClO_2$	$C_{14}H_9ClO_2$	$C_{14}H_8Cl_2O_2$
M_r	210.2	224.2	238.3	238.3	244.7	244.7	244.7	279.1
crystal habit	red prisms	light-red plates	red prisms	red needles	light-red prisms	red prisms	dark-red needles	orange-red needles
crystal size [mm]	0.5 × 0.35 × 0.25	0.5 × 0.5 × 0.25	0.15 × 0.35 × 0.4	0.12 × 0.2 × 0.45	0.4 × 0.2 × 0.18	0.5 × 0.5 × 0.4	0.45 × 0.4 × 0.25	0.45 × 0.3 × 0.15
solvent	acetone	acetone/ethyl acetate	toluene	ethyl acetate	ethyl acetate	acetone	acetone	acetone
crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	8.460(1)	7.416(1)	12.026(2)	7.423(1)	7.483(1)	10.400(2)	3.938(1)	7.525(1)
b [Å]	6.029(1)	25.566(4)	8.404(1)	13.609(2)	12.485(2)	6.638(1)	5.953(1)	12.303(2)
c [Å]	21.106(2)	6.811(1)	24.569(3)	6.870(1)	6.755(1)	16.891(4)	24.658(6)	7.268(1)
α [°]	90.0	97.14(1)	90.0	93.77(1)	103.47(1)	90.0	91.50(2)	99.60(1)
β [°]	96.96(1)	115.39(1)	95.95(1)	116.49(1)	112.55(1)	97.14(1)	90.26(2)	114.79(1)
γ [°]	90.0	84.54(1)	90.0	77.86(2)	76.38(1)	90.0	98.05(1)	78.90(1)
Z	4	4	8	2	2	4	2	2
$D_{calcd.}$ [Mg m^{-3}]	1.31	1.29	1.28	1.30	1.45	1.41	1.42	1.55
μ [mm^{-1}]	0.08	0.08	0.08	0.08	0.322	0.312	0.315	0.532
no. of reflections:								
measured	2715	5939	3096	3125	2873	2911	3120	3067
unique	2551	5514	2958	2901	2670	2764	2727	2853
observed [$I > 2.5\sigma(I)$]	1291	3773	1062	1297	1688	1816	1245	2004
no. of variables	185	307	187	219	190	190	190	195
min./max. transmission	–	–	–	–	0.92/0.95	0.86/0.91	0.89/0.93	0.85/0.93
$(\Delta/\sigma)_{max}$	0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01
R	0.041	0.060	0.054	0.044	0.038	0.042	0.062	0.053
wR (F)	0.048	0.089	0.070	0.048	0.045	0.060	0.068	0.063
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.151	0.305	0.281	0.169	0.240	0.206	0.358	0.556
$(\Delta\rho)_{min}$ [e Å^{-3}]	−0.197	−0.114	−0.311	−0.092	−0.135	−0.217	0.346	0.399

δ = 19.3, 21.3 (CH_3), 39.4, 41.1 (C_{tert}), 127.0, 127.9, 130.6, 132.2, 133.7, 135.6, 135.6, 136.0, 136.5, 147.5 (6 aromatic C; 4 olefinic C), 186.2, 187.0 (C=O). − MS (70 eV); *m/z* (%): 476 (2) [M^+], 240 (13) [$C_{16}H_{14}O_2^+ + 2$], 239 (19) [$C_{16}H_{14}O_2^+ + 1$], 238 (100) [$C_{16}H_{14}O_2^+$], 223 (16) [$C_{16}H_{14}O_2^+ - CH_3$], 195 (34) [$C_{16}H_{14}O_2^+ - CH_3$, − CO], 167 (15) [$C_{16}H_{14}O_2^+ - CH_3$, − 2 × CO], 152 (19) [$C_{16}H_{14}O_2^+ - 2 \times CH_3$, − 2 × CO], 91 (13) [$C_7H_7^+$], 77 (12) [$C_6H_5^+$].

c-2,t-4-Bis(2,5-dichlorophenyl)-r-1,t-3-bis(3,6-dioxocyclohexa-1,4-dienyl)cyclobutane (**9n**): The irradiated **1n** was extracted twice with ethyl acetate by stirring for 12 h at room temperature. − MS (70 eV); *m/z* (%): 282 (2) [$C_{14}H_8{}^{37}Cl_2O_2^+$], 281 (2) [$C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2^+ + 1$], 280 (10) [$C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2^+$], 279 (2) [$C_{14}H_8{}^{35}Cl_2O_2^+ + 1$], 278 (15) [$C_{14}H_8{}^{35}Cl_2O_2^+$], 243 (15) [$C_{14}H_8{}^{35}Cl_2O_2^+ - Cl$], 215 (22) [$C_{14}H_8{}^{35}Cl_2O_2^+ - Cl$, − CO], 187 (8) [$C_{14}H_8{}^{35}Cl_2O_2^+ - Cl$, − 2 × CO], 152 (39) [$C_{14}H_8{}^{35}Cl_2O_2^+ - 2 \times Cl$, − 2 × CO], 54 (100), 51 (14) [CH_2Cl^+], 38 (11) [HCl^+], 36 (20) [HCl^+].

Bis(2,6-dichlorophenyl)bis(3,6-dioxocyclohexa-1,4-dienyl)-cyclobutane (**9o**): The irradiated quinone **1o** (filter λ_c = 520 nm) was twice stirred in $CHCl_3$ at room temperature for 24 h. − MS (70 eV); *m/z* (%): 562 (0.2) [M^+, $C_{28}H_{16}{}^{37}Cl_3{}^{35}ClO_4^+$], 561 (0.1) [$M^+ + 1$], 560 (0.6) [$M^+$, $C_{28}H_{16}{}^{37}Cl_2{}^{35}Cl_2O_4^+$], 558 (1) [$M^+$, $C_{28}H_{16}{}^{37}Cl\,{}^{35}Cl_3O_4^+$], 556 (1) [$M^+$, $C_{28}H_{16}{}^{35}Cl_4O_4^+$], 284 (12) [$C_{14}H_8{}^{37}Cl_2O_2^+ + 2$], 283 (11) [$C_{14}H_8{}^{37}Cl_2O_2^+ + 1$], 282 (73) [$C_{14}H_8{}^{37}Cl_2O_2^+$], 281 (19) [$C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2^+ + 1$], 280 (100) [$C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2^+$], 279 (5) [$C_{14}H_8{}^{35}Cl_2O_2^+ + 1$], 278 (25) [$C_{14}H_8{}^{35}Cl_2O_2^+$], 245 (28) [$C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2^+ - Cl$], 215 (22) [$C_{14}H_8{}^{35}Cl_2O_2^+ - Cl$, − CO], 210 (91) [$C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2^+ - 2 \times Cl$], 189 (10) [$C_{14}H_8{}^{37}Cl\,{}^{35}ClO_2^+ - Cl$, − 2 × CO], 152 (60) [$C_{14}H_8{}^{35}Cl_2O_2^+ - 2 \times Cl$, − 2 × CO], 91 (10) [$C_7H_7^+$], 77 (17) [$C_6H_5^+$], 65 (11) [$C_5H_5^+$], 51 (21) [$C_4H_3^+$; CH_2Cl^+], 36 (8) [HCl^+].

c-2,t-4-Bis(3-chloro-2-methylphenyl)-r-1,t-3-bis(3,6-dioxocyclohexa-1,4-dienyl)cyclobutane (**9r**): After stirring the irradiated quinone **1r** (filter λ_c = 520 nm) for 20 h in toluene at room temperature, the cyclobutane **9r** was formed. It was subsequently purified by recrystallization from ethyl acetate. − ^{1}H NMR ($CDCl_3$): δ = 2.29 (s, 6 H, CH_3), 4.36−4.58 (m, 4 H, H_d, H_e), 6.48 (s, 2 H, H_c), 6.56 (d, ^3J = 10.0 Hz, 2 H, H_a), 6.60 (d, ^3J = 10.2 Hz, 2 H, H_b), 7.11 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, 2 H, H_g), 7.18−7.23 (m, 4 H, H_f, H_h). − ^{13}C NMR ($CDCl_3$): δ = 16.3 (CH_3), 39.5, 42.3 (C_{tert}), 124.6, 126.8, 128.5, 132.4, 135.0, 135.7, 136.2, 136.5, 137.6, 146.5 (6 aromatic C; 4 olefinic C), 186.2, 187.0 (C=O). − MS (70 eV); *m/z* (%): 516 (0.4) [M^+, $C_{30}H_{22}{}^{35}Cl_2O_4^+$], 260 (25) [$C_{15}H_{11}{}^{37}ClO_2^+$], 259 (11) [$C_{15}H_{11}{}^{35}ClO_2^+ + 1$], 258 (50) [$C_{15}H_{11}{}^{35}ClO_2^+$], 223 (22) [$C_{15}H_{11}{}^{35}ClO_2^+ - Cl$], 195 (57) [$C_{15}H_{11}{}^{35}ClO_2^+ - Cl$, − CO], 167 (26) [$C_{15}H_{11}{}^{35}ClO_2^+ - Cl$, − 2 × CO], 166 (17) [$C_{15}H_{11}{}^{35}ClO_2^+ - HCl$, − 2 × CO], 91 (9) [$C_7H_7^+$], 77 (13) [$C_6H_5^+$], 65 (8) [$C_5H_5^+$], 54 (100), 52 (8) [$C_4H_4^+$], 51 (17) [$C_4H_3^+$], 38 (8) [$HCl^+$], 36 (7) [$HCl^+$].

r-1,t-3-Bis(3,6-dioxocyclohexa-1,4-dienyl)-c-2,t-4-bis-(methoxycarbonyl)cyclobutane (**9u**): For the isolation of the compound **9u**, the irradiated quinone **1u** was treated twice with acetone at room temperature for 12 h. − MS (70 eV); *m/z* (%): 384 (4) [M^+], 382 (2) [$M^+ - 2$], 133 (24) [$C_{10}H_8O_4^+ - CH_3O$, − CO], 105 (25) [$C_{10}H_8O_4^+ - CH_3O$, − 2 × CO], 87 (10) [$C_4H_7O_2^+$], 74 (16) [$C_3H_6O_2^+$], 59 (100) [$C_2H_3O_2^+$].

X-ray Diffraction Analyses: Data collection was performed with a Nonius CAD4 diffractometer (*Mo-K*$_\alpha$ radiation, graphite monochromator, ω-2θ scan with θ = 2−28°) at 293 K (**1e**: 263 K). Ab-

Table 11. Crystallographic data for compounds **1r**, **1s**, **1t**, **1u**, **8k**, **9b**, **9e** and **9r**

compound	**1r**	**1s**	**1t**	**1u**	**8k**	**9b**	**9e**	**9r**
formula	$C_{15}H_{11}ClO_2$	$C_{15}H_{10}O_4$	$C_{16}H_{12}O_4$	$C_{10}H_8O_4$	$C_{28}H_{18}Cl_2O_4$	$C_{30}H_{24}O_4$	$C_{32}H_{28}O_4$	$C_{30}H_{22}Cl_2O_4$
M_r	258.7	254.2	268.3	192.2	489.4	448.5	476.6	517.4
crystal habit	light-red needles	dark-red plates	dark-red needles	yellow cubes	yellow prisms	yellow prisms	yellow polyhedrons	yellow plates
crystal size [mm]					0.15 × 0.35 × 0.35	×0.35 × 0.35 × 0.15	0.3 × 0.4 × 0.5	0.5 × 0.48 × 0.08
solvent	acetone	acetone/ethyl acetate	ethyl acetate	acetone	ethyl acetate	ethyl acetate	acetone	ethyl acetate
crystal system	monoclinic	triclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group		$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	7.361(1)	7.242(3)	5.948(2)	10.510(1)	11.932(3)	10.781(2)	6.659(1)	11.880(2)
b [Å]	23.120(2)	13.911(3)	28.31(2)	10.791(2)	12.229(2)	8.343(1)	19.900(4)	8.268(1)
c [Å]	7.430(3)	6.607(2)	3.881(2)	8.055(3)	8.135(2)	13.111(2)	9.951(1)	13.053(2)
α [°]	90.0	102.56(2)	90.47(4)	90.02(2)	95.73(1)	90.0	90.0	90.0
β [°]	100.9(1)	116.74(2)	98.73(3)	90.50(2)	94.69(1)	99.73(1)	105.29(1)	101.49(1)
γ [°]	90.0	83.12(2)	85.92(3)	90.01(1)	72.92(1)	90.0	90.0	90.0
Z	4	2	2	4	2	2	2	2
$D_{calcd.}$ [Mg m^{-3}]	1.39	1.46	1.39	1.40	1.44	1.28	1.24	1.37
μ [mm^{-1}]					0.320	0.08	0.08	0.29
no. of reflections:	25	25	16	24				
measured					5649	2913	3294	3149
unique					5391	2773	3046	3012
observed [$I > 2.5\sigma(I)$]					3211	1694	1933	1889
no. of variables					379	202	207	207
min./max. transmission					0.88/1.00	–	–	0.89/0.99
$(\Delta/\sigma)_{max}$					0.01	0.01	0.02	0.02
R					0.042	0.043	0.046	0.037
wR (F)					0.047	0.049	0.061	0.047
$(\Delta\rho)_{max}$ [e Å^{-3}]					0.241	0.188	0.212	0.257
$(\Delta\rho)_{min}$ [e Å^{-3}]					−0.098	−0.176	−0.201	−0.12

sorption correction was carried out numerically[52] for **1i**, **1k** (β and γ arrangements) and **1n**; semiempirically[53] for **8k** and **9r**. The structures were solved by direct methods SHELXS-86[54] for **1a**, **1c**, **1e**, **1f**, **1i**, **1k** (β arrangement) and **9b**; MULTAN[55] for **1k** (γ arrangement), **8k**, **9e** and **9r**; and SIR-88[56] for **1n**. The structural parameters of non-hydrogen atoms were refined anisotropically and of hydrogen atoms isotropically on F^2 by full-matrix least-squares technique (**1c**: coordinates of hydrogen atoms and their thermal parameters were fixed during refinement; **1e**: coordinates of hydrogen atoms of the methyl groups and thermal parameters of all hydrogen atoms were fixed during refinement; **9e**: coordinates of hydrogen atoms of the methyl groups and their thermal parameters were fixed during refinement). Structure solution and refinement were performed with the MolEN[57] program system. More details on the structure determination are given in Table 10 and Table 11[58].

☆ Dedicated to Professor *Bernhard Schramm* on the occasion of his 60th birthday.

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