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Synthesis of 5-Aryl-1,4-naphthoquinone and 1-Aryl-9,10-anthraquinone Derivatives by Cycloaddition of 1-(Dimethoxyphenyl)-3-trimethylsiloxy-1,3-butadienes to 1,4-Benzoquinones and 1,4-Naphthoquinones

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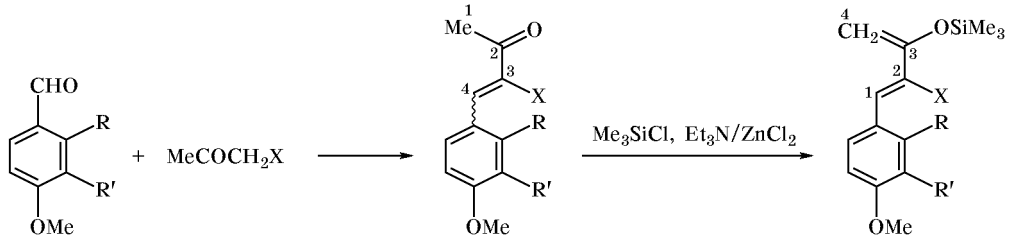
Abstract—The Diels–Alder reaction of new 1-(3,4-dimethoxyphenyl)- or 1-(2,4-dimethoxyphenyl)-2-R-3-trimethylsiloxy-1,3-butadienes with 2,5- and 2,6-dibromo-, and 2-bromo-6-methyl-1,4-benzoquinones regioselectively yields substituted 7-hydroxy-5-(dimethoxyphenyl)-1,4-naphthoquinones. By cycloaddition of the siloxydienes to naphthoquinone, bromonaphthoquinone, and juglone the corresponding substituted 3-hydroxy-1-(dimethoxyphenyl)-9,10-anthraquinones or their 4,4a-dihydro or 1,1a,4,4a-tetrahydro derivatives were obtained.

The presence of a polyhydroxy- or polymethoxy-aromatic substituent is a characteristic feature of many series of naturally occurring biologically active compounds. Introduction of these pharmacophoric fragments into quinone molecules is very interesting from the practical viewpoint, specifically with a view to create new pharmacological agents. For example, such substituted 1-[hydroxy(methoxy)aryl]-9,10-anthraquinones as knipholone and gaboroquinones A and B, isolated from plants of the *Bulbine*, *Bulbinella*, *Kniphofia* (*Asphodelacea*), and *Senna* (*Fabacea*) species, are known to exhibit antiplasmoid and wound healing activities [1].

The Diels–Alder reaction of siloxybutadienes with quinones underlies a generally accepted method for the synthesis of polyfunctional naphtho- and anthraquinones. We previously applied this approach to the preparation of 5-aryl-7-hydroxy-1,4-naphthoquinones and 1-aryl-3-hydroxy-9,10-anthraquinones [2]. Some products synthesized in such a way were found to exhibit a high activity as inhibitors of HIV reverse transcriptase [3].

In the present work we continued our studies on cycloaddition of 1-aryl-3-siloxydienes with quinones and showed that 2-substituted 1-(dimethoxyphenyl)-3-trimethylsiloxy-1,3-butadienes are convenient building

Scheme 1.



I–III **IV–VI**

I, **II**, **IV**, **V**, R = H; **III**, **VI**, R = OMe; **I**, **II**, **IV**, **V**, R′ = OMe; **III**, **VI**, R′ = H; **I**, **IV**, X = H; **II**, **III**, **V**, **VI**, X = CO_2Et.

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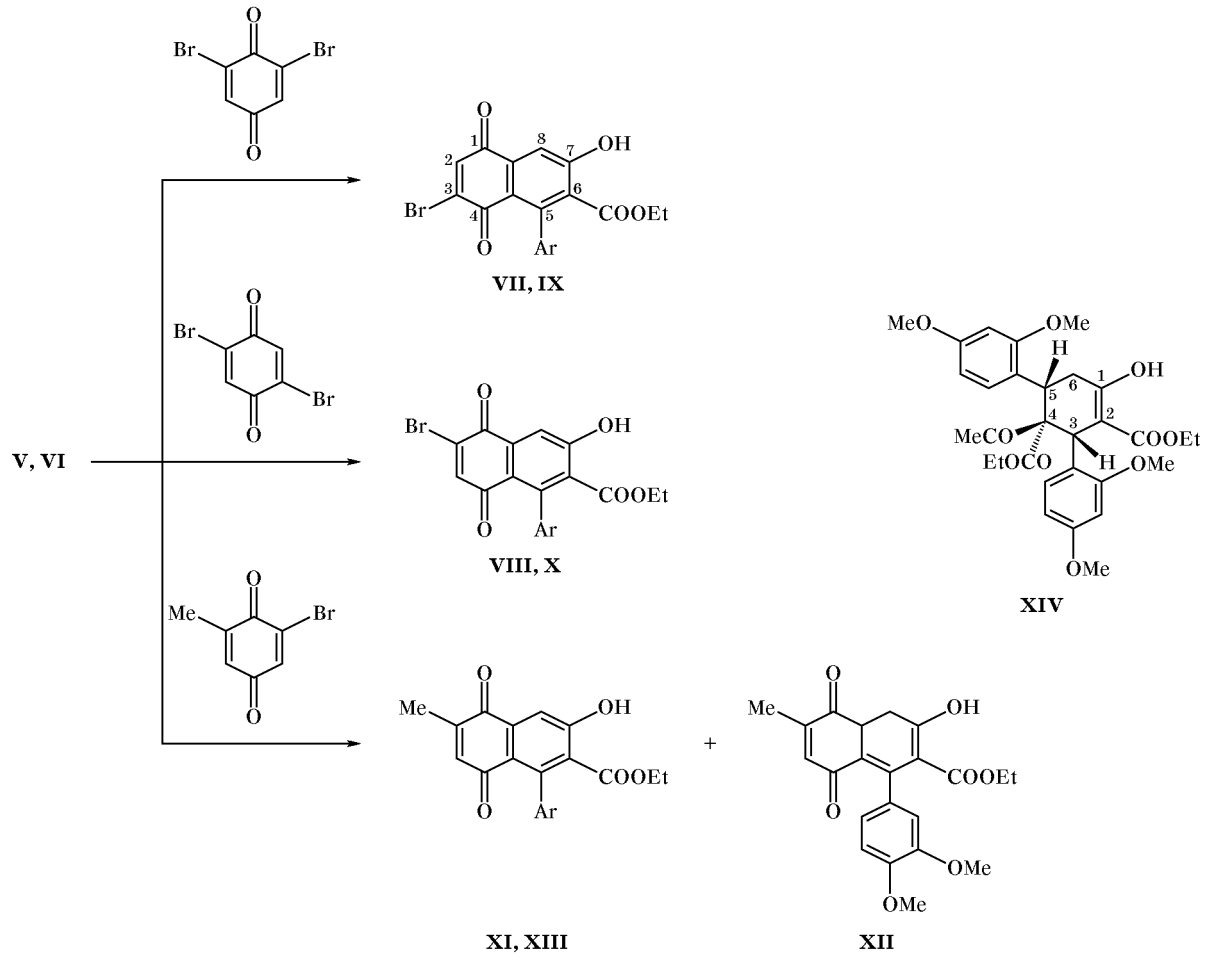
Scheme 2.



VII, **VIII**, **XI**, **XII**, Ar = 3,4-$(MeO)_2C_6H_3$; **IX**, **X**, **XIII**, 2,4-$(MeO)_2C_6H_3$.

blocks which make it possible to introduce hydroxy and dimethoxyphenyl groups into a quinone molecule in one step. The Diels–Alder reaction of siloxybutadienes with brominated benzo- and naphthoquinones involves successive cycloaddition and dehydrobromination, leading to 3-hydroxy-1-(dimethoxyphenyl)naphtho- and -anthraquinones, respectively.

Using the standard procedure [4], by crotonization of 3,4-dimethoxybenzaldehyde with acetone we obtained known (*E*)-4-(3,4-dimethoxyphenyl)-3-buten-2-one (**I**) [5, 6] (Scheme 1). The reactions of 3,4- and 2,4-dimethoxybenzaldehydes with ethyl acetoacetate afforded 4-(3,4- or 2,4-dimethoxyphenyl)-3-ethoxycarbonyl-3-buten-2-ones **II** and **III** in 63 and 78% yield, respectively. According to the ^{1}H NMR data, each product was a mixture of *Z* and *E* isomers at a ratio of (1.24–1.38) : 1.

Previously unknown 1-(3,4-dimethoxyphenyl)- and 1-(2,4-dimethoxyphenyl)-2-R-3-trimethylsiloxy-1,3-butadienes **IV**–**VI** were synthesized in 66, 92, and 40% yield, respectively, by reaction of methyl styryl ketones **I**–**III** with chlorotrimethylsilane in the presence of anhydrous zinc(II) chloride and triethylamine under argon (Scheme 1). Compounds **IV**–**VI** undergo decomposition on attempted distillation; therefore, the crude products were purified by passing through a layer of silica gel deactivated by microwave radiation. Siloxydienes **IV**–**VI** are yellow–brown oils which can be stored in an argon atmosphere.

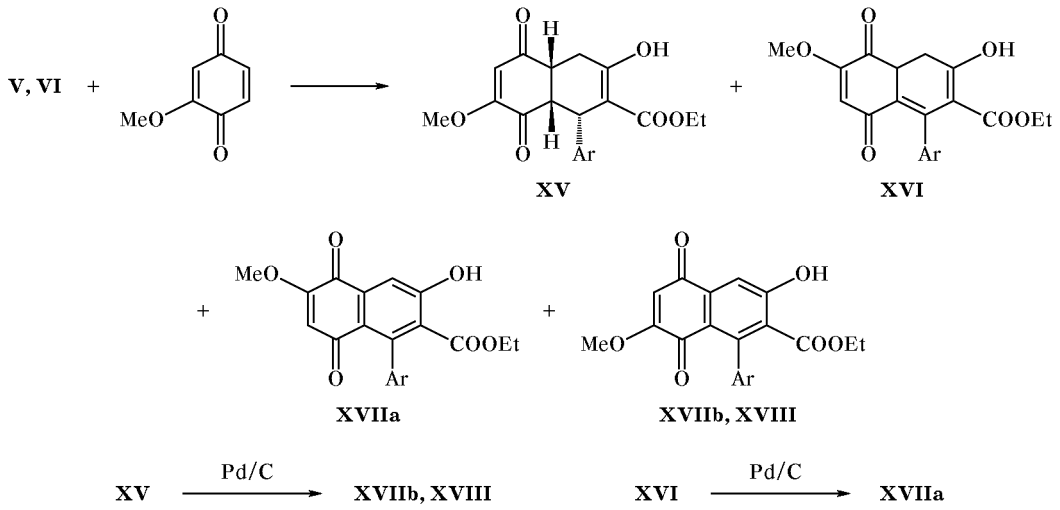
The reaction of siloxydiene **V** with 2,6-dibromobenzoquinone or 2,5-dibromobenzoquinone in boiling benzene occurs regioselectively and leads to formation of 3-bromo-6-ethoxycarbonyl-7-hydroxy-5-(3,4-dimethoxyphenyl)-1,4-naphthoquinone (**VII**) (38%) or 2-bromo-6-ethoxycarbonyl-7-hydroxy-5-(3,4-dimethoxyphenyl)-1,4-naphthoquinone (**VIII**) (36%), respectively (Scheme 2, Table 1). Siloxydiene **VI** reacts with dibromobenzoquinones at a lower rate;

Table 1. Reactions of siloxydienes **IV**–**VI** with quinones

Amounts of the reactants, g (mmol)		Reaction time, h	Product, yield, g (%)
diene	quinone		
V, 1.23 (3.51)	2,6-Dibromo-1,4-benzoquinone, 0.79 (2.98)	6	**VII**, 0.52 (38)
V, 1.28 (3.66)	2,5-Dibromo-1,4-benzoquinone, 0.79 (2.98)	7.5	**VIII**, 0.50 (36)
VI, 0.54 + 0.55 (0.77 + 0.79)	2,6-Dibromo-1,4-benzoquinone, 0.17 (0.63)	22.5 + 8.5	**IX**, 0.14 (49)
VI, 1.25 + 0.56 (1.71 + 0.76)	2,5-Dibromo-1,4-benzoquinone, 0.38 (1.43)	22.5 + 14	**X**, 0.22 (33)[a]
V, 1.06 (3.03)	2-Bromo-6-methyl-1,4-benzo-quinone, 0.60 (2.98)	8	**XII**, 0.22 (19) **XI**, 0.49 (42)
VI, 1.20 + 0.53 (1.71 + 0.76)	2-Bromo-6-methyl-1,4-benzo-quinone 0.29 (1.43)	21 + 14	**XIII**, 0.13 (23) **XIV**, 0.54 (39)
V, 1.14 (3.26)	2-Methoxy-1,4-benzoquinone, 0.41 (2.98)	7.5	**XVI**, 0.09 (7) **XV**, 0.22 (18) **XVIIa** + **XVIIb**, 0.25 (20) (1 : 2.15)
VI, 1.49 + 0.73 (2.13 + 1.04)	2-Methoxy-1,4-benzoquinone, 0.20 (1.43)	22.5 + 8.5	**XVIII**, 0.12 (20)[b] **XIV**, 0.29 (16)
IV, 0.93 (2.84)	2-Bromo-1,4-naphthoquinone, 0.83 (3.50)	8	**XX**, 0.74 (72)
IV, 1.24 (3.79)	Juglone, 0.61 (3.51)	8	**XXII**, 0.42 (31) **XXIII**, 0.08 (6) **XXIV**, 0.12 (9)
V, 1.25 (3.57)	1,4-Naphthoquinone, 0.47 (2.98)	7	**XXVII**, 0.10 (8) **XXVI**, 0.26 (20) **XXVIII**, 0.37 (29)
V, 1.28 (3.66)	Juglone, 0.52 (2.98)	7	**XXX**, 0.40 (30) **XXIX**, 0.09 (7) **XXXI**, 0.39 (29)
VI, 1.21 + 0.58 (1.73 + 0.83)	1,4-Naphthoquinone, 0.23 (1.43)	21 + 8.5	**XXXII**, 0.12 (20)[c] **XXXIII**, 0.06 (10)[d] **XIV**, 0.08 (9)
VI, 1.15 + 0.42 (1.64 + 0.60)	2-Bromo-1,4-naphthoquinone, 0.34 (1.43)	22.5 + 14	**XXXII**, 0.04 (6) **XXXIII**, 0.06 (9) **XIV**, 0.14 (11)
VI, 1.30 + 0.49 (1.86 + 0.70)	Juglone, 0.25 (1.43)	22.5 + 8.5	**XXXIV**, 0.10 (16) **XIV**, 0.25 (18)

[a] Yield on the reacted quinone 48%; conversion 68%.
[b] Yield on the reacted quinone 27%; conversion 75%.
[c] Yield on the reacted quinone 31%; conversion 65%.
[d] Yield on the reacted quinone 16%.

Scheme 3.



XV–**XVII**, Ar = 3,4-$(MeO)_2C_6H_3$; XVIII, Ar = 2,4-$(MeO)_2C_6H_3$; ratio **XVIIa**:**XVIIb** 1:2.5.

these reactions were carried out by heating 1 equiv of the quinone with 1.15–1.49 equiv of diene **VI** in boiling benzene for 22.5 h; an additional amount of diene **VI** (0.4–0.6 equiv) was then added, and the mixture was heated under reflux for 8.5–14 h more. Under these conditions, the only products were compounds **IX** (49%, from 2,6-dibromobenzoquinone) and **X** (48%, from 2,5-dibromobenzoquinone).

The reaction of siloxybutadiene **V** with 2-bromo-6-methyl-1,4-benzoquinone resulted in formation of 42% of 6-ethoxycarbonyl-5-(3,4-dimethoxyphenyl)-7-hydroxy-2-methyl-1,4-naphthoquinone (**XI**) and 19% of its 1a,8-dihydro derivative **XII**. Excess siloxydiene **VI** reacted with the same quinone to afford naphthoquinone **XIII** in 23% yield. Also, cycloaddition product of diene **VI** and ketone **III**, 4-acetyl-2,4-bis-(ethoxycarbonyl)-3,5-bis(2,4-dimethoxyphenyl)-1-cyclohexenol (**XIV**) was isolated (yield 39%) as a single stereoisomer.

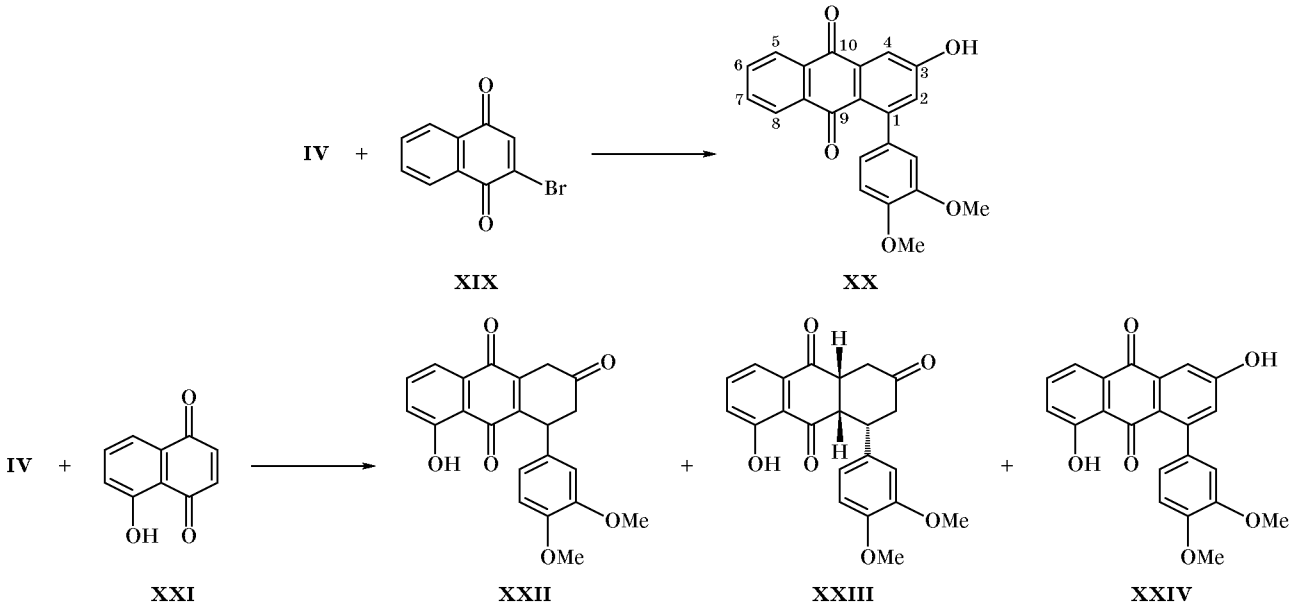
Thus the structure of the Diels–Alder adduct derived from siloxydienes **V** and **VI** and 2,6- and 2,5-dibromobenzoquinones corresponds to such mutual orientation of the diene and quinone in the transition state, at which the bromine atom appears in the *para* position with respect to the siloxy group (orbital control). An analogous pattern in the addition of 3-siloxydienes to haloquinones was observed in [7]. In the reactions of siloxydienes **V** and **VI** with 2-bromo-6-methyl-1,4-benzoquinone, the bromine atom appears in the *meta* position with respect to the siloxy group. Such orientation was typical of 1-(2-methoxyphenyl)-2-R-3-trimethylsiloxy-1,3-butadienes [2]. In the latter case, the opposite regioselectivity is likely to result from the predominant charge control of the reaction; here, the interaction between the positively charged C^2 atom in the quinone and C^4 in the siloxydiene (which has a partial negative charge) becomes crucial.

The reaction of siloxybutadiene **V** with methoxybenzoquinone in boiling benzene was not regioselective; the products were 2- and 3-methoxy-5-(3,4-dimethoxyphenyl)-6-ethoxycarbonyl-7-hydroxy-1,4-naphthoquinones **XVIIa** and **XVIIIb** (ratio 1:2.15), 3-methoxytetrahydronaphthoquinone **XV**, and 2-methoxydihydronaphthoquinone **XVI** (Scheme 3). The position of the methoxy group in compounds **XV** and **XVI** was established by converting them into naphthoquinones **XVIIb** and **XVIIa**, respectively, via dehydrogenation over Pd/C. The reaction of methoxybenzoquinone with excess siloxydiene **VI**, followed by dehydrogenation over Pd/C, led to formation of a mixture of 3-methoxynaphthoquinone **XVIII** (yield 27%) and cyclohexenol **XIV** (16%).

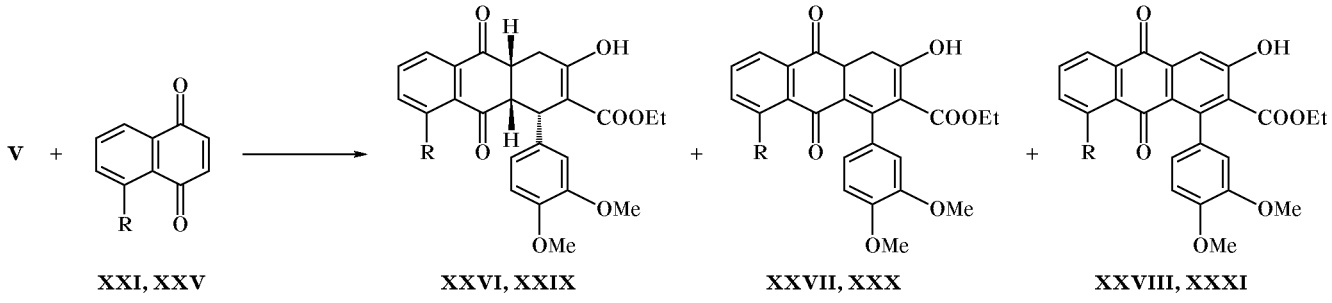
Diene **IV** reacted with 2-bromo-1,4-naphthoquinone (**XIX**) to give exclusively 3-hydroxy-1-(3,4-dimethoxyphenyl)-9,10-anthraquinone (**XX**) in 72% yield (Scheme 4). By reaction of diene **IV** with juglone (**XXI**) we obtained 31% of 8-hydroxy-1-(3,4-dimethoxyphenyl)-3-oxo-1,2,3,4-tetrahydro-9,10-anthraquinone (**XXII**). In addition, we succeeded in isolating primary adduct **XXIII** (6%) and anthraquinone **XXIV** (9%).

The reaction of siloxydiene **V** with 1,4-naphthoquinone (**XXV**) in boiling benzene afforded 20% of tetrahydroanthraquinone **XXVI**, 8% of dihydroanthraquinone **XXVII**, and 29% of anthraquinone **XXVIII**

Scheme 4.



Scheme 5.



XXV, **XXVI**–**XXVIII**, R = H; **XXI**, **XXIX**–**XXXI**, X = H.

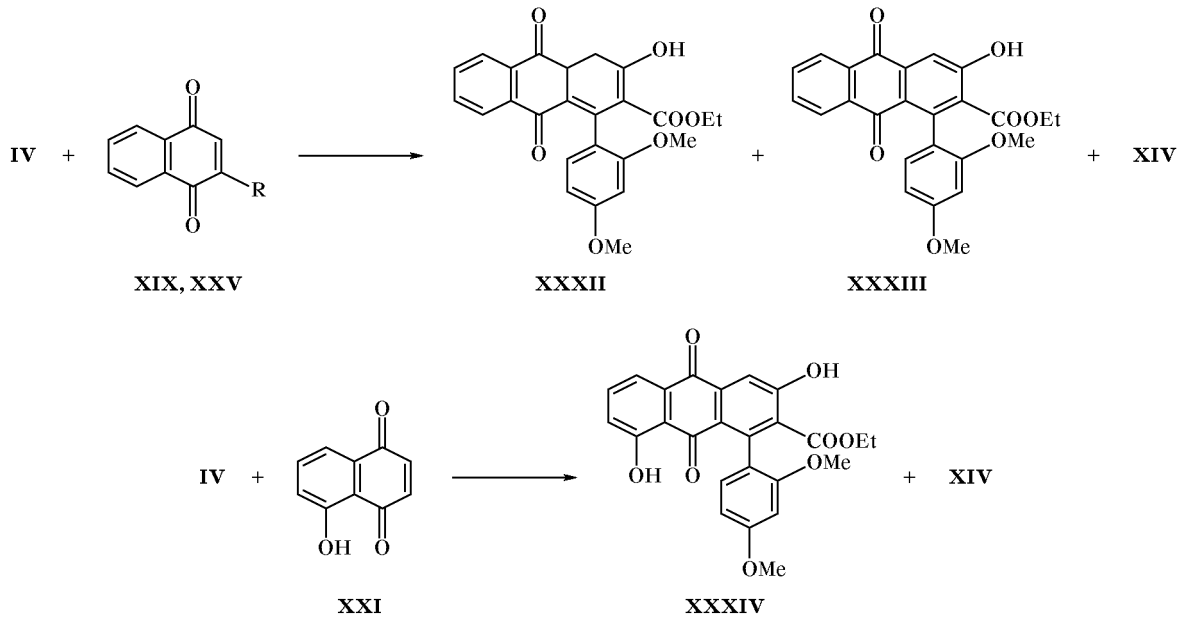
(Scheme 5). Under analogous conditions, diene **V** reacted with quinone **XXI** in a regioselective fashion; the products were anthraquinone derivatives **XXIX** (7%), **XXX** (30%), and **XXXI** (29%).

As noted above, the Diels–Alder reactions with diene **VI** require a longer time and larger excess of the diene, and the yields are lower than in the reactions with diene **V**. The reactions of **VI** with naphthoquinone (**XXV**) and 2-bromo-1,4-naphthoquinone (**XIX**) gave compounds **XXXII** (yield 31 and 6%, respectively) and **XXXIII** (16 and 9%) (Scheme 6). By reaction of siloxydiene **VI** with juglone (**XXI**) we obtained anthraquinone **XXXIV** in as low as 16% yield. In all these reactions, 9–18% of cyclohexenol **XIV** was also isolated.

The structure of the products was determined by analysis of their spectral data. We also performed assignment of the *Z* and *E* isomers of ketones **II** and **III** (Table 2). In the ^{1}H NMR spectrum of *Z*-**II**, the signal from 4-H (δ 7.43 ppm) is located in a stronger field than the corresponding signal of the *E* isomer (δ 7.53 ppm), which is consistent with the results of calculations based on the additivity schemes [8]. In the ^{13}C NMR spectrum of *Z*-**II**, recorded in the monoresonance mode, the signal from C^2 (CH_3**C**O) at δ_C 194.3 ppm is split due to coupling with 4-H ($^3J_{CH}$ = 7 Hz), indicating *cis* arrangement of C^2 and 4-H, while the ester carbonyl carbon atom is coupled with 4-H through a constant $^3J_{CH}$ of 12.5 Hz, which corresponds to *trans* arrangement of these atoms, in keeping with published data [9].

Mutual orientation of substituents in the molecule of cyclohexenol **XIV** was deduced from the ^{1}H NOESY spectrum. Protons of the acetyl group at C^4 showed NOE with 3-H and 5-H; this means that the latter are arranged *cis*. Therefore, compound **XIV** is

Scheme 6.



XIX, R = Br; **XXV**, R = H.

the product of *endo*-cycloaddition of the *Z* isomer of **III** to siloxydiene **VI**.

The IR and UV spectra and elemental analyses of naphthoquinones **VII**–**XIII** and **XV**–**XVIII** and anthraquinones **XX**, **XXII**–**XXIV**, and **XXVI**–**XXXIV** are given in Table 3, the ^{1}H NMR spectra are given in Table 4, and Tables 5 and 6 contain their ^{13}C NMR spectral parameters.

The ^{1}H NOESY spectra of tetrahydronaphthoquinone **XV** and tetrahydroanthraquinone **XXVI** revealed NOE between the 5-H and 4a-H protons and 1-H and 1a-H, respectively, indicating *cis* orientation of these protons. The doublet signal from 5-H in the spectrum of **XV** (δ 4.28 ppm) is characterized by a coupling constant $^3J_{5,4a}$ of 6 Hz. In the spectra of **XXVI** and **XXIX**, the 1-H signal is a doublet (δ 4.70–4.72 ppm) with a coupling constant $^3J_{1,1a}$ of 1–2 Hz; similar values of $^3J_{5,4a}$ and $^3J_{1,1a}$ were observed by us previously [2, 10, 11].

The chemical shift of 1a-H in the ^{1}H NMR spectra of dihydronaphthoquinones **XII** and **XVI** or of 4a-H in the spectra of dihydroanthraquinones **XXVII**, **XXX**, and **XXXII** ranges from 5.0 to 5.3 ppm; their signals are doublets of doublets with coupling constants of 5 and 3 Hz. The ^{1}H NMR spectra of the aromatic products, naphthoquinones **VII**–**XI**, **XIII**, **XVIIb**, and **XVIII** and anthraquinones **XX**, **XXIV**, **XXVIII**, **XXXI**, **XXXIII**, and **XXXIV** are characterized by downfield shift of the 8-H and 4-H signal, respectively, due to deshielding effect of the carbonyl group in the quinone fragment.

The position of the substituent (Br, Me, MeO) in molecules **VII**, **VIII**, **XI**–**XIII**, and **XVIIb** was determined on the basis of multiplicities of the carbonyl carbon signals in the ^{13}C NMR spectra recorded in the monoresonance mode. The corresponding values of J_{CH} (Tables 5, 6) are typical of quinone systems [12]: $^3J(C^1\text{–}3\text{-H})$ = 7–10 Hz, $^3J(C^1\text{–}8\text{-H})$ = 3.5–5 Hz, $^2J(C^1\text{–}2\text{-H})$ = 0.8–1.7 Hz. If the substituent is located in position *2* (compounds **VIII**, **XI**, and **XIII**), the signal from C^1 is a doublet of doublets with coupling constants of 7 and 4 Hz, while the C^4 signal is a doublet with J = 1.5 Hz. When the substuent occupies position *3* (**VII**, **XVIIb**), the C^1 signal appears as a doublet of doublets with J = 4, 1.5 Hz, while C^4 gives a doublet with J = 7 Hz. In addition, we determined the coupling constant $^4J(C^4\text{–}8\text{-H})$ in naphthoquinones **VII**, **VIII**, and **XVIIb** (0.7–1.0 Hz), as well as $^3J(C^1\text{–}2\text{-C}\mathbf{H}_3)$ = 0.9 Hz in **XI**.

The difference in the chemical shifts of the C^1 and C^4 carbonyl carbon atoms in 3-bromonaphthoquinones **VII** and **IX** is 6.0 to 6.1 ppm, whereas the corresponding difference for 2-bromo derivatives **VIII** and **X** is 2.9 to 2.7 ppm. The value of $\Delta(\delta_{C^1}, \delta_{C^4})$ for 3-methoxynaphthoquinone **XVIIb** is 5.7 ppm, and for 2-methoxy analog **XVIIa**, 3.6 ppm. The C^1 and C^4 carbonyl carbon signals in the spectrum of methoxynaphthoquinone **XVIII** differ by 6.3 ppm; therefore,

Table 2. ^{1}H and ^{13}C NMR spectra of ketones **I**–**III** and siloxydienes **IV**–**VI** in $CDCl_3$

Comp. no.	^{1}H NMR spectrum, δ, ppm (*J*, Hz)	^{13}C NMR spectrum, δ_C, ppm
I	2.29 s (3H, CH_3), 3.83 s (6H, OCH_3), 6.52 d (1H, 3-H, 16), 6.69 d (1H, 5′-H, 8), 7.00 d (1H, 2′-H, 2), 7.03 d.d (1H, 6′-H, 8; 2), 7.38 d (1H, 4-H, 16)	27.0 (C^1), 55.6, 55.7 (2 OCH_3), 109.5 ($C^{5'}$), 110.9 ($C^{2'}$), 122.7 ($C^{6'}$), 124.9 (C^3), 127.1 ($C^{1'}$), 143.1 ($C^{4'}$), 149.0 and 151.1 (C^3, $C^{4'}$), 198.2 (C^2)
II[a]	1.25 t (3H, CH_3), 2.32 s (3H, *Z*-CH_3), 2.34 s (3H, *E*-CH_3), 3.83, 3.85 s (6H, *Z*-OCH_3), 3.79, 3.80 s (6H, *E*-OCH_3), 4.23 q (2H, CH_2), 6.85 d (1H, *Z*-5′-H, 8), 6.77 d (1H, *E*-5′-H, 8), 7.01 d (1H, *Z*-2′-H, 2), 6.87 d (1H, *E*-2′-H, 2), 7.08 d.d (1H, *Z*-6′-H, 8; 2), 6.94 d.d (1H, *E*-6′-H, 8; 2), 7.43 (1H, *Z*-4-H), 7.53 (1H, *E*-4-H)	13.7 (*Z*-CH_3), 13.8 (*E*-CH_3), 26.1 (*Z*-C^1), 31.0 (*E*-C^1), 55.6, 55.7 (2 OCH_3), 61.4 (*Z*-CH_2), 61.1 (*E*-CH_2), 110.9 ($C^{5'}$), 111.7 (*Z*-$C^{2'}$), 112.0 (*E*-$C^{2'}$), 124.3 (*Z*-$C^{6'}$), 123.9 (*E*-$C^{6'}$), 125.4 (*Z*-C^3), 125.5 (*E*-C^3), 132.4 (*Z*-$C^{1'}$), 131.7 (*E*-$C^{1'}$), 140.9 (*Z*-C^4), 140.2 (*E*-C^4), 148.9, 151.0, 151.4 ($C^{3'}$, $C^{4'}$), 168.0 d.t (*Z*-CO_2, J_{CH} = 12.5, 3.0 Hz), 164.4 (*E*-CO_2), 194.3 d.q (*Z*-C^2, J_{CH} = 7.0, 6.0 Hz), 203.6 s (*E*-C^2)
III[b]	1.22 t (3H, *Z*-CH_3), 1.26 t (3H, *E*-CH_3), 2.34 s (3H, *Z*-CH_3), 2.67 s (3H, *E*-CH_3), 3.77, 3.79 s (6H, *Z*-OCH_3), 3.76 s and 3.78 s (6H, *E*-OCH_3), 4.23 q (2H, CH_2), 6.39 d (1H, 3′-H, 2), 6.40 d.d (1H, 5′-H, 8.5; 2), 7.17 d (1H, *E*-6′-H, 9), 7.33 d (1H, *Z*-6′-H, 8.5), 7.83 s (1H, *Z*-4-H), 7.85 s (1H, *E*-4-H)	13.7 (*Z*-CH_3), 14.0 (*E*-CH_3), 26.1 (*Z*-C^1), 30.8 (*E*-C^1), 55.1, 55.2, 55.1 (*Z*-OCH_3, *E*-OCH_3), 60.9 (*E*-CH_2), 61.1 (*Z*-CH_2), 104.9 (*E*-$C^{5'}$), 105.1 (*Z*-$C^{5'}$), 114.8 (*Z*-$C^{1'}$), 114.9 (*E*-$C^{1'}$), 130.2 (*Z*-$C^{6'}$), 131.2 (*E*-$C^{6'}$), 132.0 (C^3), 136.0 (*E*-C^4), 136.4 (*Z*-C^4), 159.2, 163.0 (*E*-$C^{2'}$, $C^{4'}$), 159.6, 163.3 (*Z*-$C^{2'}$, $C^{4'}$), 164.8 (*E*-CO_2), 168.2 (*Z*-CO_2), 195.0 (*Z*-C^2), 203.2 (*E*-C^2)
IV	0.26 s [9H, $(CH_3)_3SiO$], 3.85 s and 3.88 s (6H, OCH_3), 4.36 and 4.40 (2H, 4-H), 6.44 d (1H, 2-H, 15.5), 6.73 d (1H, 1-H, 15.5), 6.79 d (1H, 5′-H, 8), 6.93 d (1H, 2′-H, 2), 6.94 d.d (1H, 6′-H, 8, 2)	0.1 [$(CH_3)_3SiO$], 55.7, 55.8 (2 OCH_3), 95.8 (C^3), 109.2 ($C^{5'}$), 111.2 ($C^{2'}$), 120.0 ($C^{6'}$), 124.5, 128.9 (C^1, C^2), 129.8 ($C^{1'}$), 148.9, 149.0 (C^3, $C^{4'}$), 155.0 (C^4)
V	0.25 s [9H, $(CH_3)_3SiO$], 1.19 t (3H, CH_3), 3.81 s and 3.83 s (6H, OCH_3), 4.21 q (2H, CH_2), 4.41 (2H, 4-H), 6.86 m (3H, 1-H, 2′-H, 6′-H), 6.77 d (1H, 5′-H, 9)	0.2 [$(CH_3)_3SiO$], 13.7 (CH_3), 61.1 (CH_2), 55.6, 55.7 OCH_3), 94.2 (C^3), 110.9 ($C^{5'}$), 111.0 ($C^{2'}$), 121.7 ($C^{6'}$), 127.9 (C^2), 128.6 (C^1), 131.3 ($C^{1'}$), 148.6, 149.2 ($C^{3'}$, $C^{4'}$), 152.4 (C^4)
VI	0.26 s [9H, $(CH_3)_3SiO$], 1.16 t (3H, CH_3), 3.70 s and 3.78 s (6H, OCH_3), 4.16 q (2H, CH_2), 4.41 and 4.47 (2H, 4-H), 6.35 m (3H, 1-H, 3′-H, 5′-H), 7.17 m (1H, 6′-H)	

[a] *Z*:*E* isomer ratio 1.24:1. For the *Z*-CO_2 and *Z*-C^2 signals of **II,** *J*(C–4-H) values from the monoresonance spectrum are given.
[b] *Z*:*E* isomer ratio 1.38:1.

compound **XVIII** was assigned the structure of 3-methoxy derivative.

Signals from the C^9 and C^{10} carbonyl carbon atoms in the ^{13}C NMR spectra of tetrahydroanthraquinone **XXII** and dihydroanthraquinone **XXXII** were assigned as follows. In the spectrum of **XXII**, the signal at δ_C 182.9 ppm (C^{10}) is a doublet of triplets with $^3J(C^{10}$–5-H) = 3.8 Hz and $^3J(C^{10}$–4-H) = 1 Hz; the signal at δ_C 188.0 ppm (C^9) is a doublet with $^3J(C^9$–1-H) = 2.6 Hz. The carbonyl carbon signals of dihydroanthraquinone **XXXII** are split in the following manner: the signal at δ_C 183.0 ppm (C^{10}) is a doublet of triplets, $^3J(C^{10}$–5-H) = 8 Hz and $^3J(C^{10}$–4-H) = 1.3 Hz, and the signal at δ_C 184.2 ppm (C^9) is a doublet with $^3J(C^9$–8-H) = 8 Hz. The C^9 and C^{10} signals of anthraquinone **XXVIII** were identified by analysis of the COLOC spectrum. The signal at δ_C 182.4 ppm (C^{10}) showed a cross peak with 4-H, and the signal from C^9 (δ_C 180.9 ppm) was displaced upfield due to effect of the 1-aryl and 3-hydroxy groups [2, 12].

Thus the cycloaddition of 1-dimethoxyphenyl-3-trimethylsiloxy-1,3-butadienes to bromobenzoquinones and naphthoquinones provides a convenient and regio-

Table 3. Melting points, IR and UV spectra, elemental analyses, and molecular weights (mass spectral data) of naphthoquinones **VII**–**XIII** and **XV**–**XVIII**, anthraquinones **XX**, **XXII**–**XXIV**, and **XXVI**–**XXXIV**, and cyclohexenol **XIV**

Comp. no.	mp, °C	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	Found, % (M^+)		Formula	Calcd., % (M^+)	
				C	H		C	H
VII	248–251	3350, 1732, 1678, 1574, 1251	277 (4.01), 396 (3.00)	54.8	3.5	$C_{21}H_{17}O_7Br$[a]	54.7	3.7
VIII	240–243	3350, 1738, 1680, 1655, 1570, 1517, 1228	277 (4.04), 396 (3.01)	55.1	3.1	$C_{21}H_{17}O_7Br$[b]	54.7	3.7
IX	209–210	3439, 1714, 1679, 1613, 1573, 1510, 1208, 1028	278 (4.28), 393 (3.15), 520 (2.81)	460.01576		$C_{21}H_{17}O_7Br$	460.01581	
X	187–189	3429, 1654, 1612, 1250, 1209	276 (4.25), 398 (3.25)	53.8	3.5	$C_{21}H_{17}O_7Br$[c]	54.7	3.7
XI	240–242	3364, 1732, 1664, 1609, 1576, 1251, 1223	270 (4.39), 379 (3.31)	66.3	5.4	$C_{22}H_{20}O_7$	66.7	5.1
XII	187–185	3435, 1655, 1514, 1263	280 (3.84), 385 (3.38)	65.3	5.6	$C_{22}H_{22}O_7$	66.3	5.6
XIII	164–166	3366, 1734, 1666, 1575, 1210	270 (4.53), 307 (3.72), 380 (3.44)	66.1	5.2	$C_{22}H_{20}O_7$	66.7	5.1
XIV	80–82	3437, 1730, 1705, 1650, 1613, 1586, 1505, 1267, 1209	256 (4.12)	64.7	6.7	$C_{30}H_{36}O_{10}$	64.7	6.5
XV	154–155	3435, 1708, 1664, 1603, 1517, 1221	234 (4.15), 257 (4.15)	63.1	5.8	$C_{22}H_{24}O_8$	63.4	5.8
XVI	173–175	3468, 1690, 1642, 1608, 1514, 1246	235 (4.21), 275 (4.03), 335 (3.54), 518 (3.04)	414.13098		$C_{22}H_{22}O_8$	414.13145	
XVIIa/ **XVIIb**	253–257	3370, 1730, 1680, 1650, 1616, 1517, 1245, 1204	271 (4.36), 400 (3.26)	412.11657		$C_{22}H_{20}O_8$	412.11580	
XVIII	214–215	3522, 3408, 1732, 1674, 1636, 1615, 1570, 1210	281 (4.24), 327 (3.65)	412.11720		$C_{22}H_{20}O_8$	412.11580	
XX	310–312	3414, 1668, 1593, 1564, 1518, 1289, 1251	240 (4.37), 272 (4.45), 368 (3.49)	69.6	5.3	$C_{22}H_{16}O_5 \cdot C_4H_8O_2$	69.6	5.4
XXII	172–174	3428, 1717, 1638, 1615, 1515, 1258	278 (4.15), 420 (3.56), 510 (3.36), 660 (3.00)	69.8	4.8	$C_{22}H_{18}O_6$	69.8	4.4
XXIII	212–214	3420, 1711, 1592, 1516, 1262	231 (4.30), 275 (3.82), 344 (3.83), 654 (2.82)	380.12645		$C_{22}H_{20}O_6$	380.12598	
XXIV	225–230	3416, 1634, 1592, 1516, 1252	279 (4.20), 344 (3.71), 410 (3.55), 656 (1.54)	376.09433		$C_{22}H_{16}O_6$	376.09468	
XXVI	202–204	3482, 1695, 1651, 1515, 1239	226 (4.49), 250 (4.26), 306 (3.57), 337 (3.50)	436.15184		$C_{25}H_{24}O_7$	436.15219	
XXVII	185–187	3435, 1664, 1513, 1291, 1241	245 (4.41), 267 (4.13), 331 (3.54)	434.13575		$C_{25}H_{22}O_7$	434.13654	

Table 3. (Contd.)

Comp. no.	mp, °C	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	Found, % (M^+)		Formula	Calcd., % (M^+)	
				C	H		C	H
XXVIII	310–315	3374, 1731, 1670, 1563, 1518, 1251	240 (4.40), 270 (4.50), 370 (3.54)	432.12083		$C_{25}H_{20}O_7$	432.12089	
XXIX		3442, 1736, 1715, 1653, 1517, 1456, 1259	230 (4.19), 259 (3.76), 348 (3.49)	66.1	5.2	$C_{25}H_{24}O_8$	66.4	5.4
XXX	200–203	3444, 1654, 1618, 1512, 1455, 1238, 1219	250 (4.29), 278 (4.10), 349 (3.48), 422 (3.61)	65.8	4.9	$C_{25}H_{22}O_8$	66.7	4.9
XXXI	260–265	3311, 1733, 1663, 1638, 1571, 1516, 1250, 1223	218 (4.23), 273 (4.04), 337 (3.51), 408 (3.45)	448.11531		$C_{25}H_{20}O_8$	448.11580	
XXXII	215–219	3646, 1663, 1337, 1293, 1206	245 (4.41), 267 (4.13), 331 (3.54)	434.13920		$C_{25}H_{22}O_7$	434.13654	
XXXIII	220–221	3350, 1732, 1673, 1565, 1358, 1304, 1256, 1210, 1159	240 (4.36), 274 (4.52), 313 (3.87), 376 (3.51)	432.12095		$C_{25}H_{20}O_7$	432.12089	
XXXIV	245–247	3436, 1733, 1613, 1506, 1466, 1210	221 (4.53), 272 (4.32), 406 (3.49)	66.8	4.3	$C_{25}H_{20}O_8$	67.0	4.5

[a] Found Br: 17.1%. Calculated Br: 17.3%.
[b] Found Br: 17.7%. Calculated Br: 17.3%.
[c] Found Br: 17.2%. Calculated Br: 17.3%.

Table 4. ^{1}H NMR spectra of naphthoquinones **VII**–**XIII** and **XV**–**XVIII**, anthraquinones **XX**, **XXII**–**XXIV**, and **XXVI**–**XXXIV**, and cyclohexenol **XIV** in $CDCl_3$

Comp. no.	Chemical shifts δ, ppm (*J*, Hz)
VII	0.82 t (3H, C**H**$_3$CH$_2$), 3.78 s and 3.90 s (6H, CH$_3$O), 3.95 q (2H, CH$_3$C**H**$_2$), 7.44 s (1H, 2-H), 6.61 d (1H, 2′-H, 2), 6.59 d.d (1H, 6′-H, 8, 2), 6.86 d (1H, 5′-H, 8), 7.68 s (1H, 8-H), 10.71 s (1H, OH)
VIII	0.81 t (3H, C**H**$_3$CH$_2$), 3.60 s and 3.90 s (6H, CH$_3$O), 3.95 q (2H, CH$_3$C**H**$_2$), 7.25 s (1H, 3-H), 6.62 d (1H, 2′-H, 2), 6.58 d.d (1H, 6′-H, 8, 2), 6.66 d (1H, 5′-H, 8), 7.76 s (1H, 8-H), 10.75 s (1H, OH)
IX	0.83 t (3H, C**H**$_3$CH2), 3.66 s and 3.83 s (6H, CH$_3$O), 3.98 q (2H, CH$_3$C**H**$_2$), 7.68 s (1H, 2-H), 6.71 d.d (1H, 5′-H, 2, 8), 6.72 d (1H, 3′-H, 1), 6.71 d (1H, 6′-H, 8), 7.77 s (1H, 8-H), 11.01 s (1H, OH)
X	0.87 t (3H, C**H**$_3$CH$_2$), 3.66 s and 3.83 s (6H, CH$_3$O), 3.98 q (2H, CH$_3$C**H**$_2$), 7.24 s (1H, 3-H), 6.46 d.d (1H, 5′-H, 2, 8), 6.50 s (1H, 3′-H), 6.72 d (1H, 6′-H, 8), 7.76 s (1H, 8-H), 11.13 s (1H, OH)
XI	0.81 t (3H, C**H**$_3$CH$_2$), 2.00 s (3H, 2-CH$_3$), 3.79 s and 3.88 s (6H, CH$_3$O), 3.93 q (2H, CH$_3$C**H**$_2$), 6.74 s (1H, 3-H), 6.63 d (1H, 2′-H, 2), 6.61 d.d (1H, 6′-H, 8, 2), 6.85 d (1H, 5′-H, 8), 7.63 s (1H, 8-H), 10.47 s (1H, OH)
XII	1.20 t (3H, C**H**$_3$CH$_2$), 1.96 s (3H, 2-CH$_3$), 3.48 m (2H, 8-H), 3.79 s and 3.85 s (6H, CH$_3$O), 4.13 q (2H, CH$_3$CH$_3$C**H**$_2$), 5.02 d.d (1H, 1a-H, 3, 5), 6.54 s (1H, 3-H), 6.69 s (2H, 2′-H, 6′-H), 6.84 s (1H, 5′-H), 12.38 s (1H, OH)
XIII	0.83 t (3H, C**H**$_3$CH$_2$), 2.01 s (3H, 2-CH$_3$), 3.66 s and 3.83 s (6H, CH$_3$O), 3.97 q (2H, CH$_3$C**H**$_2$), 6.57 s (1H, 3-H), 6.49 d.d (1H, 5′-H, 2, 8.5), 6.50 s (1H, 3′-H), 6.73 d (1H, 6′-H, 8.5), 7.85 s (1H, 8-H), 10.81 s (1H, OH)

Table 4. (Contd.)

Comp. no.	Chemical shifts δ, ppm (*J*, Hz)
XIV	1.04 t (3H, C**H**$_3$CH$_2$OCO-2), 1.24 t (3H, C**H**$_3$CH$_2$OCO-4), 1.58 s (3H, CH$_3$CO), 2.68 d.d (1H, 6-H, 19.5, 12), 2.93 d.d (1H, 6-H, 19.5, 6.5), 3.70 s and 3.76 s (12H, CH$_3$O), 3.99 q (2H, CH$_3$C**H**$_2$OCO-2), 4.25 q and 4.38 q (2H, CH$_3$C**H**$_2$OCO-4), 4.25 m (1H, 5-H), 5.31 s (1H, 3-H), 6.32 s (1H, 3′-H), 6.29 d.d (1H, 5a′-H, 2, 8.5), 6.46 d.d (1H, 5b′-H, 2, 9), 7.08 d (1H, 6a′-H, 8.5), 7.33 d (1H, 6b′-H), 12.33 s (1H, OH)
XV	0.99 t (3H, C**H**$_3$CH$_2$), 2.45 d.d (1H, 8b-H, 20, 9.5), 3.12 d (1H, 1a-H, 9.5, 6), 3.45 t (1H, 4a-H, 6), 3.60 d (1H, 8a-H, 20), 3.35 s, 3.75 s, and 3.76 s (9H, CH$_3$O), 4.00 q (2H, CH$_3$C**H**$_2$), 4.28 d (1H, 5-H, 6), 5.36 s (1H, 2-H), 6.26 s(1H, 2′-H), 6.28 s (1H, 6′-H), 6.60 s (1H, 5′-H), 12.49 s (1H, OH)
XVI	1.18 t (3H, C**H**$_3$CH$_2$), 3.45 m and 3.60 m (2H, 8-H), 3.73 s, 3.78 s, and 3.84 s (9H, CH$_3$O), 4.11 q (2H, CH$_3$C**H**$_2$), 5.03 d.d (1H, 1a-H, 3, 5), 5.85 s (1H, 2-H), 6.68 s (2H, 2′-H, 6′-H), 6.86 s (1H, 5′-H), 12.38 s (1H, OH)
XVIIa	0.80 t (3H, C**H**$_3$CH$_2$), 3.80 s and 3.89 s (9H, CH$_3$O), 3.95 q (2H, CH$_3$C**H**$_2$), 5.90 s (1H, 2-H), 6.63 d (1H, 2′-H, 2), 6.57 d.d (1H, 6′-H, 8, 2), 6.84 d (1H, 5′-H, 8), 7.75 s (1H, 8-H), 10.45 s (1H, OH)
XVIIb	0.80 t (3H, C**H**$_3$CH$_2$), 3.80 s and 3.89 s (9H, CH$_3$O), 3.95 q (2H, CH$_3$C**H**$_2$), 6.10 s (1H, 2-H), 6.63 d (1H, 2′-H, 2), 6.57 d.d (1H, 6′-H, 8, 2), 6.84 d (1H, 5′-H, 8), 7.72 s (1H, 8-H), 10.86 s (1H, OH)
XVIII	0.83 t (3H, C**H**$_3$CH$_2$), 3.70 s, 3.79 s, and 3.83 s (9H, CH$_3$O), 3.98 q (2H, CH$_3$C**H**$_2$), 6.09 s (1H, 2-H), 6.45 d.d (1H, 5′-H, 2, 8), 6.47 s (1H, 3′-H), 6.69 d (1H, 6′-H, 8), 7.71 s (1H, 8-H), 11.13 s (1H, OH)
XX	3.85 s and 3.93 s (6H, CH$_3$O), 6.81 d (1H, 2′-H, 2), 6.83 d.d (1H, 6′-H, 8, 2), 6.93 d (1H, 5′-H, 8), 7.04 d (1H, 2-H, 3), 7.73 m and 7.76 m (2H, 6-H, 7-H), 7.78 d (1H, 4-H, 3), 8.11 m, 8.22 m (2H, 5-H, 8-H)
XXII	2.83 m (2H, 2-H), 3.34 d and 3.69 d (2H, 4-H, 23), 3.77 s and 3.81 s (6H, CH$_3$O), 4.78 d.d (1H, 1-H, 4, 3), 6.55 d.d (1H, 6′-H, 8, 1.5), 6.68 d (1H, 2′-H, 1.5), 6.70 d (1H, 5′-H, 8), 7.02 d.d (1H, 7-H, 8, 2), 7.60 m (2H, 5-H, 6-H), 11.93 s (1H, OH)
XXIII	2.55 d.d (1H, 4-H, 16, 5.5), 2.71 m (2H, 2-H), 3.10 d.d (1H, 4-H, 16, 5.5), 3.50 m (1H, 1a-H), 3.67 m (1H, 4a-H), 3.80 m (1H, 1-H), 3.77 s and 3.83 s (6H, CH$_3$O), 6.47 d (1H, 2′-H, 2), 6.58 d.d (1H, 6′-H, 8, 1.5), 6.77 d (1H, 5′-H, 8), 7.26 d.d (1H, 7-H, 8, 1), 7.55 d.d (1H, 5-H, 8, 1), 7.62 t (1H, 6-H, 8), 11.62 s (1H, OH)
XXIV	3.84 s and 3.93 s (6H, CH$_3$O), 6.87 d (1H, 2′-H, 1.5), 6.92 d.d (1H, 6′-H, 8, 1.5), 6.97 d (1H, 5′-H, 8), 7.08 d (1H, 2-H, 2.5), 7.22 d (7-H, 8), 7.56 t (6-H, 8), 7.73 d (1H, 5-H, 8), 7.79 d (4-H, 2.5), 11.57 s (1H, OH)
XXVI	1.02 t (3H, C**H**$_3$CH$_2$), 2.42 d.d (1H, 4-H, 19, 11), 2.65 d.d (1H, 4-H, 19, 6.5), 3.32 d.d (1H, 1a-H, 4, 2), 3.43 d.d.d (1H, 4a-H, 11, 6.5, 4), 3.92 s and 3.93 s (6H, CH$_3$O), 4.05 q (2H, CH$_3$C**H**$_2$), 4.70 d (1H, 1-H, 2), 6.63 d (1H, 6′-H, 8), 6.66 s (1H, 2′-H), 6.77 d (1H, 5′-H, 8), 7.74 m (2H, 6-H, 7-H), 8.03 m (2H, 5-H, 6-H), 12.45 s (1H, OH)
XXVII	1.22 t (3H, C**H**$_3$CH$_2$), 3.63 d (1H, 4-H, 4.5), 3.70 d (1H, 4-H, 3), 3.76 s and 3.84 s (6H, CH$_3$O), 4.18 q (2H, CH$_3$C**H**$_2$), 5.25 d.d (1H, 4a-H, 4.5, 3), 6.65 s and 6.69 s (2H, 2′-H, 6′-H), 6.90 s (1H, 5′-H), 7.68 m (2H, 6-H, 7-H), 8.04 m (2H, 5-H, 6-H), 12.45 s (1H, OH)
XXVIII	0.90 t (3H, CH$_3$C**H**$_2$), 3.92 s and 3.95 s (6H, CH$_3$O), 3.95 q (2H, CH$_3$C**H**$_2$), 6.72 d.d (1H, 6′-H, 8, 1.5), 6.74 d (1H, 2′-H, 1.5), 6.92 d (1H, 5′-H, 8), 7.71 s (1H, 4-H), 7.83 m (2H, 6-H, 7-H), 7.90 m and 8.10 m (2H, 5-H, 6-H), 11.48 s (1H, OH)
XXIX	1.02 t (3H, C**H**$_3$CH$_2$), 2.25 m and 2.59 m (2H, 4-H), 3.34 m (1H, 1a-H), 3.78 m (1H, 4a-H), 3.84 s and 3.85 s (6H, CH$_3$O), 4.03 q (2H, CH$_3$C**H**$_2$), 4.72 d (1H, 1-H, 1), 6.64 d (1H, 6′-H, 8), 6.68 s (1H, 2′-H), 6.80 d (1H, 5′-H, 8), 7.27 d.d (1H, 7-H, 8, 1), 7.53 d.d (1H, 5-H, 8, 1), 7.85 t (1H, 6-H, 8), 11.90, 12.48 s (2H, OH)
XXX	1.20 t (3H, C**H**$_3$CH$_2$), 3.63 m (2H, 4-H), 3.78 s and 3.85 s (6H, CH$_3$O), 4.16 q (2H, CH$_3$C**H**$_2$), 5.16 t (1H, 4a-H, 3.5), 6.70 s (2H, 2′-H, 6′-H), 6.90 s (1H, 5′-H), 7.15 d.d (1H, 7-H, 7.5, 2), 7.48 m (2H, 5-H, 6-H), 11.92 s and 12.39 s (2H, OH)

Table 4. (Contd.)

Comp. no.	Chemical shifts δ, ppm (*J*, Hz)
XXXI	0.85 t (3H, C**H**$_3$CH$_2$), 3.83 s and 3.93 s (6H, CH$_3$O), 3.95 q (2H, CH$_3$C**H**$_2$), 6.66 d (1H, 2′-H, 2), 6.70 d.d (1H, 6′-H, 9, 2), 6.89 d (1H, 5′-H, 9), 7.23 d.d (1H, 7-H, 8, 1.5), 7.58 t (1H, 6-H, 8), 7.74 d.d (1H, 5-H, 8, 1.5), 7.92 s (1H, 4-H), 10.47 s and 12.40 s (2H, OH)
XXXII	1.23 t (3H, C**H**$_3$CH$_2$), 3.53 d (1H, 4-H, 5), 3.59 d (1H, 4-H, 3.5), 3.68 s and 3.73 s (6H, CH$_3$O), 4.13 q (2H, CH$_3$C**H**$_2$), 5.27 d.d (1H, 4a-H, 3.5, 5), 6.31 d (1H, 3′-H, 2), 6.42 d.d (1H, 5′-H, 2.5, 8.5), 7.35 d (1H, 6′-H, 8.5), 7.63 m (2H, 6-H, 7-H), 7.95 m and 8.05 m (2H, 5-H, 8-H), 12.42 s (1H, OH)
XXXIII	0.85 t (3H, CH$_3$C**H**$_2$), 3.67 s and 3.80 s (6H, CH$_3$O), 3.99 q (2H, CH$_3$C**H**$_2$), 6.54 s (1H, 3′-H), 6.51 d.d (1H, 5′-H, 2, 8), 6.78 d (1H, 6′-H, 8), 7.70 m (2H, 6-H, 7-H), 7.70 m and 8.09 m (2H, 5-H, 8-H), 7.92 s (1H, 4-H), 10.81 s (1H, OH)
XXXIV	0.86 t (3H, C**H**$_3$CH$_2$), 3.68 s and 3.87 s (6H, CH$_3$O), 3.99 q (2H, CH$_3$C**H**$_2$), 6.53 s (1H, 3′-H), 6.51 d.d (1H, 5′-H, 8, 2), 6.78 d (1H, 6′-H, 8), 7.21 d.d (1H, 7-H, 8, 1.5), 7.57 t (1H, 6-H, 8), 7.75 d.d (1H, 5-H, 8, 1.5), 7.90 s (1H, 4-H), 10.74 s and 12.49 s (2H, OH)

selective one-step route to 7-hydroxy-5-(dimethoxyphenyl)-1,4-naphthoquinone and 3-hydroxy-1-(dimethoxyphenyl)-9,10-anthraquinone derivatives.

EXPERIMENTAL

The IR spectra were recorded on a Vector 22 spectrometer from samples prepared as KBr pellets. The UV spectra were measured on an HP 8453 UV-Vis spectrophotometer from solutions in ethanol with a concentration *c* of 10^{-4} M. The ^{1}H NMR spectra were recorded on Bruker AC-200 (200.13 MHz) and DRX-500 instruments (500.13 MHz). The ^{13}C NMR spectra were run on Bruker AC-200 (50.32 MHz; JMOD) and DRX-500 spectrometers (125.76 MHz; JMOD, monoresonance, COLOC, NOESY). Chloroform-*d* and DMSO-d_6 were used as solvents (*c* = 5–10%) and internal reference. The progress of reactions was monitored by TLC on Silufol UV-254 plates using chloroform–methanol (20:1) as eluent; spots were visualized under UV light or by treatment with gaseous ammonia. Column chromatography was performed on KSK silica gel, 60–100 μm, using petroleum ether (bp 70–100°C)–diethyl ether (3:1), diethyl ether, chloroform, or chloroform–methanol (100:1) as eluent. Dienes **IV**–**VI** were purified using KSK silica gel, 60–100 μm, which was preliminarily dried for 3 h at 120°C and deactivated by heating in a microwave oven for 10 min at a power of 300 W.

2-Methoxy-1,4-benzoquinone was prepared by the procedure described in [13]; 2,5- and 2,6-dibromo-1,4-benzoquinones and 2-bromo-1,4-naphthoquinone were synthesized by bromination of hydroquinone, phenol, or 1-naphthol, respectively, followed by oxidation according to the procedure reported in [14].

Methyl styryl ketones I–III. 4-(3,4-Dimethoxyphenyl-3-buten-2-one (**I**) was obtained by crotonization of acetone with 3,4-dimethoxybenzaldehyde. Ketones **II** and **III** were synthesized by the Knoevenagel condensation (Cope modification [4]) of ethyl acetoacetate with 3,4-dimethoxybenzaldehyde or 2,4-dimethoxybenzaldehyde, respectively.

Ketone **I**. Yield 45%, bp 140–142°C (2 mm), mp 95–98°C; published data: mp 85–86°C, 91–92°C [5]; 85–86°C [6].

Ketone **II**. Yield 63%, bp 190–195°C (1 mm); *Z*:*E* isomer ratio 1.24:1 (^{1}H NMR data); *Z*-**II**, mp 105–106°C (from diethyl ether); published data [15]: bp 190–196°C (0.8 mm), mp 82.5–84.5°C (with no regard to isomeric composition).

Ketone **III**. Yield 78%, bp 165–174°C (2 mm), *Z*:*E* isomer ratio 1.38:1 (^{1}H NMR data).

Typical procedure for the synthesis of siloxybutadienes IV–VI. A solution of 32 mmol of ketone **I**–**III** in 20 ml of anhydrous acetonitrile and 12.20 ml (96 mmol) of chlorotrimethylsilane were added in succession to a suspension of 0.44 g (3 mmol) of anhydrous zinc(II) chloride and 12.2 ml of triethylamine while stirring at 80°C under argon. The mixture was stirred for 5 h at 50°C, cooled, and diluted with 150 ml of dry diethyl ether. The precipitate was filtered off, the filtrate was evaporated under reduced pressure (water-jet pump), and the residue was treated with 30 ml of dry diethyl ether. The ether solution was passed through a layer of deactivated silica gel, and the solvent was removed to obtain compounds **IV**–**VI** as a light brown oily substances.

1-(3,4-Dimethoxyphenyl)-3-trimethylsiloxy-1,3-butadiene (IV). Yield 66%; according to the ^{1}H

Table 5. ^{13}C NMR spectra of naphthoquinones **VII**–**XIII**, **XV**, and **XVI**–**XVIII** in $CDCl_3$, δ, ppm (J_{CH}, Hz)

Atom no.	**VII**	**VIII**	**IX**	**X**	**XI**[a]	**XII**[a]
C^1	181.6 d.d (4.7, 0.8)	177.6 d.d (8.9, 4.7)	181.8	177.8	183.6 d.d.q (9.3, 3.4, 0.9)	185.6 m
C^{1a}	136.4	136.4	139.2	136.3[b]	137.0	39.3
C^2	138.3	135.7	138.3	135.8[b]	151.0	145.8
C^3	143.6	143.0	135.5	142.9	135.5	132.6
C^4	75.6 d.d (7.8, 1.0)	180.5 t (0.9)	175.7	180.5	183.8 d (5.1)	186.0 d (1.7)
C^{4a}	120.8[b]	120.4[b]	121.2	121.4	120.6[b]	134.9
C^5	147.6	147.0	145.1	144.1	146.0	142.4
C^6	122.5[b]	122.5[b]	121.6	122.4	122.5[b]	110.4
C^7	163.2	163.2	164.0	163.7	162.4	167.4
C^8	115.9	117.0	117.2	116.8	114.9	28.1
CO_2Et	169.3	169.6	169.7	169.8	169.4	170.8
CH_3CH_2	62.1, 13.1	62.1, 13.1	62.1, 13.1	62.0, 13.0	61.8, 13.0	60.6, 13.9
Ar**O**CH_3	55.8, 55.9	55.8, 55.9	55.3, 55.4	55.3, 55.4	55.7, 55.8	55.6, 55.8
$C^{1'}$	131.6	131.6	120.1	120.2	132.2	135.1
$C^{2'}$	111.8	111.7	157.4[b]	157.6[c]	111.8	112.5
$C^{3'}$	147.5[c]	148.6	98.4	98.2	148.3[c]	147.8[b]
$C^{4'}$	148.6[c]	148.6	160.9[b]	160.8[c]	148.4[c]	148.4[b]
$C^{5'}$	110.6	110.6	104.1	103.9	110.5	110.9
$C^{6'}$	119.8	119.8	128.1	128.1	119.9	120.3

Atom no.	**XIII**[b]	**XV**	**XVI**	**XVIIa**	**XVIIb**	**XVIII**
C^1	183.7 d.d (10, 3.5)	195.2	180.0	179.7	183.4 d.d (4.2, 1.7)	183.9
C^{1a}	137.3	41.6	39.0	135.6	137.2	137.5
C^2	151.1	111.7[b]	158.5	158.5	108.0	108.1
C^3	133.6	161.0	106.8	112.4	161.7	157.8
C^4	184.1 d (4.5)	195.1	185.9	183.3	177.7 d.d (7.3, 0.7)	177.6
C^{4a}	122.2	41.6	135.7	120.6[b]	119.5[b]	121.9
C^5	143.3	50.6	140.7	145.3	147.0	144.5
C^6	123.2	98.8	110.3	122.0[b]	121.3[b]	125.4
C^7	163.4	170.5	167.4	163.0	163.7	164.5
C^8	115.0	24.5	28.4	115.4	115.4	115.5
CO_2Et	170.0	170.9	170.8	169.1	169.7	170.1
CH_3CH_2	61.8, 13.1	60.4, 13.7	60.7, 13.9	61.9, 13.1	61.9, 13.1	61.9, 13.1
Ar**O**CH_3	55.2, 55.4	55.4, 55.6, 55.7	55.7, 55.8, 56.1	56.1, 58.8	55.8, 56.0, 56.4	55.3, 55.4, 55.5
$C^{1'}$	119.8	131.8	134.7	132.0	132.0	119.0
$C^{2'}$	157.8[b]	111.2[b]	112.7	111.8	111.4	160.8[b]
$C^{3'}$	98.3	148.0[c]	147.9[b]	148.4[c]	148.4[c]	98.3
$C^{4'}$	160.6[b]	148.5[c]	148.5[b]	148.5[c]	148.5[c]	161.8[b]
$C^{5'}$	103.9	110.8	111.0	110.4	110.6	104.0
$C^{6'}$	128.2	120.3	120.2	119.9	119.6	128.0

[a] δ(2-CH_3), ppm: 16.9 (**XI**), 15.7 (**XII**), 17.1 (**XIII**).
[b,c] Alternative assignment is possible.

Table 6. ^{13}C NMR spectra of anthraquinones **XX**, **XXII**–**XXIV**, and **XXVI**–**XXXIV** and cyclohexenol **XIV**[a] in $CDCl_3$, δ, ppm (*J*, Hz)

Atom no.	**XX**[b]	**XXII**	**XXIII**	**XXIV**	**XXVI**	**XXVII**	**XXVIII**[b]
C^1	147.2	37.8	41.0	147.7	42.8	144.8	142.9
C^{1a}	123.5	144.9	47.4[c]	123.6	53.9	137.5	123.0
C^2	124.9	45.2	45.8	125.2	98.8	100.4	130.0
C^3	161.7	205.2	211.2	160.2	169.6	167.5	157.8
C^4	113.0[c]	37.1	39.6	113.4	29.2	28.8	112.8
C^{4a}	137.2	142.3	43.7[c]	137.3	36.8	39.5	136.2
C^5	126.5[d]	124.5	124.3	124.8	127.4[c]	126.5[c]	126.1[c]
C^{5a}	134.9	131.8	132.4	132.8	135.9[d]	131.9[d]	134.5[d]
C^6	133.9[e]	136.4	137.2	135.6	134.5	133.5	133.5[e]
C^7	135.1[e]	118.5	118.5[d]	118.0	134.5	133.7	134.6[e]
C^8	127.0[d]	161.6	161.4	162.3	126.7[c]	126.1[c]	126.7[c]
C^{8a}	134.9	114.8	116.43	116.7	135.9[d]	131.8[d]	132.1[d]
C^9	181.9	188.0 d (2.6)	205.2	187.8 s	195.1	182.7	180.9
C^{10}	183.4	182.9 d.t (3.8, 1)	202.5	183.0 (4.2)	196.5	183.8	182.4
CO_2Et					171.6	170.9	165.5
CH_3CH_2					60.5, 13.7	60.7, 14.0	60.6, 13.6
Ar**O**CH_3	56.24	55.8	55.3, 55.8	55.8, 55.9	55.9	55.7, 55.8	55.6, 55.9
$C^{1'}$	132.8	132.4	136.1	134.3	132.6	134.9	130.9
$C^{2'}$	113.3[c]	110.9	111.4	111.8	111.2	112.6	112.6
$C^{3'}$	148.7[f]	148.5[c]	148.4[e]	147.7[c]	147.9[e]	147.9[e]	148.0[f]
$C^{4'}$	148.7[f]	149.4[c]	149.2[e]	148.4[c]	149.1[e]	148.5[e]	148.2[f]
$C^{5'}$	111.2	111.5	110.2	110.8	111.0	110.9	111.2
$C^{6'}$	120.6	119.1	118.9[d]	120.1	119.4	120.4	120.6

Atom no.	**XXIX**	**XXX**	**XXXI**	**XXXII**	**XXXIIII**	**XXXIV**
C^1	42.4	144.6	138.4	139.2	144.1	144.5
C^{1a}	53.2	138.8	121.2	143.0	122.8	122.7
C^2	99.5	100.3		98.6	124.9	124.0
C^3	168.8	167.3	163.2[c]	168.4	163.4	162.2
C^4	29.6	28.9	116.1	29.3	115.8	116.1
C^{4a}	36.5	39.1	132.8[d]	37.7	138.5	138.5
C^5	124.4	136.1	124.9	125.9[c]	126.5[c]	128.1
C^{5a}	135.4	131.6	132.6[d]	131.8[d]	132.6[d]	132.7
C^6	137.2	124.3	135.7	133.2[e]	133.0[e]	135.5
C^7	118.9[c]	118.8	118.8	133.5[e]	134.2[e]	118.7
C^8	161.4	161.4	162.4[c]	126.5[c]	127.4[c]	163.9
C^{8a}	116.7	114.8	117.1	132.1[d]	135.3[d]	117.2
C^9	201.0	188.0	187.4	184.2 d (8)	181.4	187.6
C^{10}	195.8	182.9	181.9	183.0 d.t (8, 1.3)	182.8	182.2
CO_2Et	171.6	170.7	169.8	171.3	170.0	169.9
CH_3CH_2	60.9, 14.0	60.8, 14.0	62.1, 13.2	60.5, 13.9	61.7, 13.1	62.0, 13.1
Ar**O**CH_3	55.9	55.7, 55.9	55.9	55.1, 55.5	55.3, 55.5	55.4, 55.5

Table 6. (Contd.)

Atom no.	XXIX	XXX	XXXI	XXXII	XXXIIII	XXXIV
$C^{1'}$	133.1	134.7	132.0[d]	121.3	120.6	120.9
$C^{2'}$	111.1	112.7	111.9	158.7[f]	157.7[f]	157.8[c]
$C^{3'}$	147.4	148.0[c]	148.6	98.3	98.4	98.3
$C^{4'}$	147.4	148.5[c]	148.6	159.9[f]	160.6[f]	160.7[c]
$C^{5'}$	111.8	111.0	110.6	104.4	103.9	103.8
$C^{6'}$	119.5[c]	120.4	119.9	133.5	128.3	124.7

[a] ^{13}C NMR spectrum of **XIV**, δ_C, ppm: 13.6, 13.8 ($\mathbf{C}H_3CH_2$); 28.2 ($\mathbf{C}H_3CO$); 31.7 (C^3); 33.7 (C^6); 38.6 (C^5); 54.8, 55.0, 55.1, 55.5 ($ArOCH_3$); 60.0, 60.7 ($CH_3\mathbf{C}H_2$); 68.0 (C^4); 97.6, 98.3 ($C^{3'}$); 100.4 (C^2); 103.7 ($C^{5'}$); 120.7, 121.6 ($C^{1'}$); 129.9, 130.8 ($C^{6'}$); 158.3, 158.5, 159.0, 160.0 ($C^{2'}$, $C^{4'}$); 171.4, 171.5 (COO); 172.4 (C^1); 203.7 (CO).

[b] In DMSO-d_6 at 80°C.

[c–f] Alternative assignment is possible.

NMR data, the product contained 19% of the initial ketone and 85 wt % of the main substance.

Ethyl 2-(3,4-dimethoxybenzylidene)-3-trimethylsiloxy-3-butenoate (V). Yield 92%, purity 100% (^1H NMR data).

Ethyl 2-(2,4-dimethoxybenzylidene)-3-trimethylsiloxy-3-butenoate (VI). Yield 40%, purity 50 wt % (^1H NMR data).

Typical procedure for the Diels–Alder reaction of siloxydienes IV–VI with quinones. A solution of 3–3.5 mmol of appropriate quinone and 1–1.25 equiv of diene **IV** or **V** in 10 ml of benzene was refluxed under argon for 5–8 h. In the reactions with diene **VI**, a solution of 1.43 mmol of quinone and 1.15–1.49 equiv of **VI** was refluxed under argon for 22.5 h, an additional 0.5 equiv of **VI** was added, and the mixture was heated for 8.5–14 h more. The progress of the reaction was monitored by TLC. The solvent was distilled off on a rotary evaporator, and the residue was recrystallized from diethyl ether to isolate naphthoquinones **VII**, **VIII**, and **XI** or anthraquinones **XX**, **XXVIII**, and **XXX**. The mother liquor was subjected to column chromatography with successive elution with petroleum ether (bp 70–100°C)–diethyl ether (3 : 1) and diethyl ether or chloroform and chloroform–methanol (100 : 1). Compounds **VIII**, **XX**, and **XXVIII** were recrystallized from ethyl acetate, and **VII**, **IX**–**XIII**, **XV**–**XVIII**, **XXII**–**XXIV**, **XXVI**, **XXVII**, and **XXIX**–**XXXIV**, from diethyl ether. The amounts of the reactants, reaction times, and yields of the products are given in Table 1.

a. A fraction (0.10 g) containing ketone **II** and compound **XVI** was dissolved in 20 ml of toluene, 14 mg of 10% Pd/C was added, and the mixture was heated for 3.5 h under reflux. It was then cooled, filtered, and evaporated, and the residue was separated by preparative thin-layer chromatography on silica gel to isolate 60 mg of ketone **II** and 20 mg of naphthoquinone **XVIIa**.

b. A fraction (0.20 g) containing ketone **II** and compound **XV** was dissolved in 20 ml of toluene, 11 mg of 10% Pd/C was added, and the mixture was heated for 3.5 h under reflux. The mixture was cooled and filtered, the filtrate was evaporated, and the residue was separated by preparative thin-layer chromatography on silica gel to isolate 103 mg of ketone **II** and 49 mg of naphthoquinone **XVIIb**.

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