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Synthesis of the novel conjugated ω,ω′-diaryl/heteroaryl hexatriene system with the central double bond in a heteroaromatic ring: photochemical transformations of 2,3-divinylfuran derivatives

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Abstract—New β,β′-aryl/heteroaryl 2,3-divinylfuran derivatives (**9a–d**) in which a hexatriene system is a part of heteroaromatic ring have been synthesized and their photochemical properties were investigated. The primary process observed was the isomerization to *trans*,*trans*-isomers **9a–d** followed by photochemical rearrangement of the furan ring giving the phototransposition products (**I–IV**). Stilbenes (**20**, **21**) and phenanthrenes (**22**, **25**, and **26**), formed as secondary products from the competitive intermolecular cycloadditions, were also observed.

1. Introduction

In our first paper about a photochemical approach to heteropolycyclic compounds from hexatriene systems in which the central double bond is placed in a benzene ring (**1**), we described the furan derivative of *o*-divinylbenzene (**2a**) and its transformation into the fused bicyclo[3.2.1]octadiene structure **3** (Fig. 1).[1]

The investigation was extended to many modified furan,[2–9] pyrrole,[10–16] and sydnone[17,18] analogues (**1a**,**b**; **2b–e**), where their photochemical behavior was examined. We have observed that the photochemistry of furan derivatives of *o*-divinylbenzene[1,2,4,6,7,9] results in a [2+2] cycloaddition and formation of intramolecular cycloadducts **3** or **4** (Fig. 1), obtained via 1,6- or 1,4-biradical ring closure, respectively (Scheme 1). In the case of β-(3-substituted-2-furyl)-*o*-divinylbenzenes (**2b–d**),[7] the 1,4-biradical ring closure leading to benzobicyclo[2.1.1]hexene derivatives (**4**) was preferred due to steric reasons. The same benzobicyclo-[2.1.1]hexene structure was obtained on irradiation of β-aryl *o*-divinylbenzenes (**1c**).[19–31]

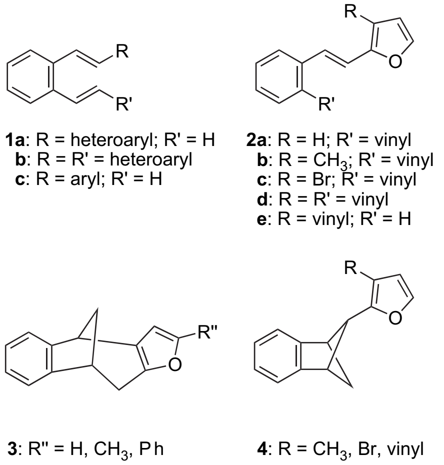

Figure 1.

On irradiation of compound **2d** (unsaturated system with the vinyl group on benzene and on the furan ring) the benzobicyclo[2.1.1]hexene structure **5** was isolated.[7] The furobicyclo[2.1.1]hexene derivative **6** (Fig. 2), formed as a result of the vinyl-furan group participating in a cycloaddition, was not isolated. If the cycloadduct **6** was formed, further [π^2+σ^2] cycloaddition[19] and formation of tricyclic structure **7** via the excited state of the styryl group would be expected. The tricyclic structure **8** was not obtained due to the nonabsorption of the vinyl-furan derivative **5** under the experimental

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Keywords: Oxygen heterocycles; Pericyclic reaction; Photochemistry; Rearrangement; Synthesis.

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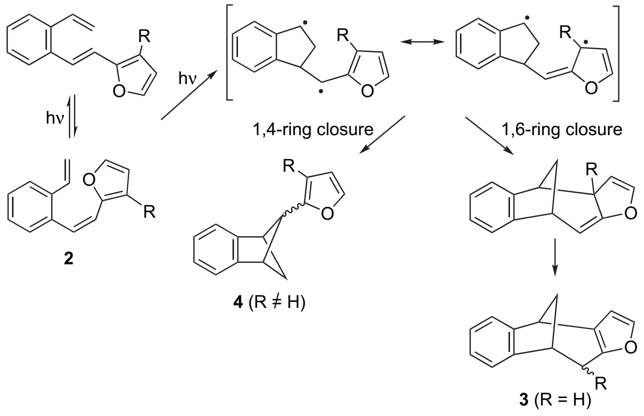


Scheme 1.

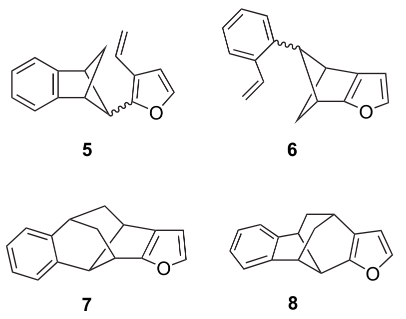


Figure 2.

conditions. On irradiation of **2e** (hexatriene system in which the central double bond is a part of only a furan ring) mostly high-molecular-weight material was obtained.[7]

In order to get a deeper understanding of the photochemical behavior of the hexatriene system with the central double bond in a heteroaromatic ring, we describe herein for the first time the synthesis and photochemistry of β,β′-aryl/heteroaryl 2,3-divinylfurans **9** (Fig. 3), compounds with carefully chosen aryl/heteroaryl substituents were used. There are examples of β,β′-disubstituted 2,3-divinylfurans[32–42] in the literature but to the best of our knowledge, there are no examples with aryl/heteroaryl substituents.

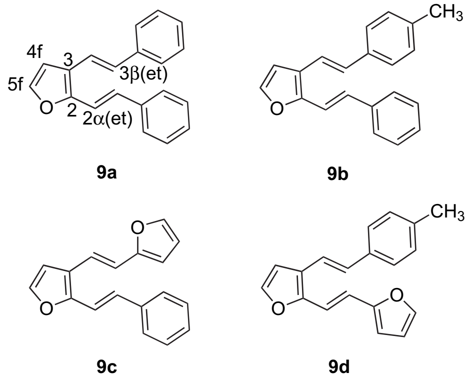


Figure 3.

2. Results and discussion

Introduction of the second aromatic moiety to the β-position of the vinyl group of **2e** to give compounds **9a–d** could result in intramolecular complexation[9] and formation of the bicyclic structures (Scheme 2). In such a way the access to a variety of differently functionalized heteropolycyclic compounds could be enabled.

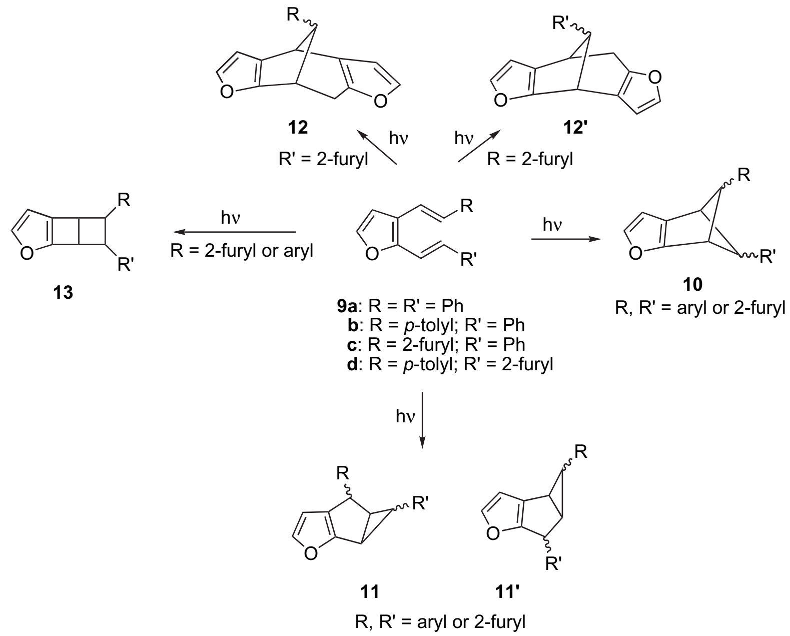
If we consider the 2,3-divinylfurans **9** as heteroaromatic analogues of disubstituted *o*-divinylbenzenes (**1b**),[9] we might expect the formation of several furobicyclo structures (**10–13**) on irradiation of **9**. The furobicyclo[2.1.1]hexene (**10**) and furobicyclo[3.1.0]hexene (**11**, **11′**) derivatives might be formed by initial [2+2] cycloaddition via 1,4-biradicals **14** and/or **14′** (Fig. 4), followed by ring closure.

In the formation of products **10**, the aromatic character of the furan ring is pronounced while in the case of **11/11′**, through the participation of two of the furan π electrons and vinylcyclopropane–cyclopentene rearrangement,[43,44] the diene character of the furan ring is prevailing. If one of the β-substituents is a furan ring (**9c**,**d**), then 1,6-biradical ring closure[1,2,4,6,7,9] may occur leading to furobicyclo-[3.2.1]octadiene structures (**12**, **12′**) by the mechanism described therein. If the head-to-head [2+2] cycloaddition took place, the furobicyclo[2.2.0]hexene **13** would be formed (Scheme 2).

Novel β,β′-aryl/heteroaryl-substituted 2,3-divinylfurans **9a–d**, were prepared by a series of reactions according to Scheme 3. The corresponding *cis*- and *trans*-aryl/heteroaryl-2-vinylfurans **16** are prepared by a Wittig reaction from aldehydes **15** in moderate-to-good yields (47–82%). To reduce the number of isomers of the final products **9a–d**, the isomers **16a–c** were separated by column chromatography on silica gel. The *trans*-**16b** and *trans*-**16c** were transformed to *trans*-**17a** and *trans*-**17b**, respectively, by formylation with *n*-butyl lithium and DMF (∼50% yield). The *trans*-**16a** was converted to **9e**,**f** (Scheme 3) in three steps giving a mixture of *cis*,*trans*- and *trans*,*trans*-isomers. After column chromatography, the *trans*,*trans*-**9e** and *trans*,*trans*-**9f** were debrominated to *trans*,*trans*-**9b** and *trans*,*trans*-**9c**, respectively. By using a Wittig reaction with formyl derivatives *trans*-**17a**,**b**, the corresponding triphenylphosphonium salts, **9a–d** were prepared as mixtures of *cis*,*trans*- and *trans*,*trans*- isomers (65–95%). All isolated compounds were identified and characterized spectroscopically. The ratios of the isomers were determined from the NMR spectra and by GC–MS measurements.

Diaryl-substituted 2,3-divinylfurans **9a**,**b** (Fig. 3) have very similar patterns in their respective ^{1}H NMR. Generally, all *cis*,*trans*- and *trans*,*trans*-**9** derivatives show ethylenic doublets at 6.6–7.1 ppm. Within this region for all *trans*,*trans*-**9** derivatives considerable shifts of one of the ethylenic doublets to higher fields are observed compared to the other three ethylenic protons. The 4f proton of the furan ring A of all *trans*,*trans*-**9** is found at 6.6–6.7 ppm while the 4f proton of the furan ring B (**9c**,**d**) is shifted by 0.2 ppm to the higher field and is well recognizable.

Compounds **9a–d** are the starting materials for irradiation experiments and show strong absorption maxima at



Scheme 2. Hypothetic photochemical products of intramolecular [2+2] cycloaddition of ethylenic bonds.

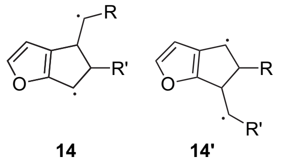
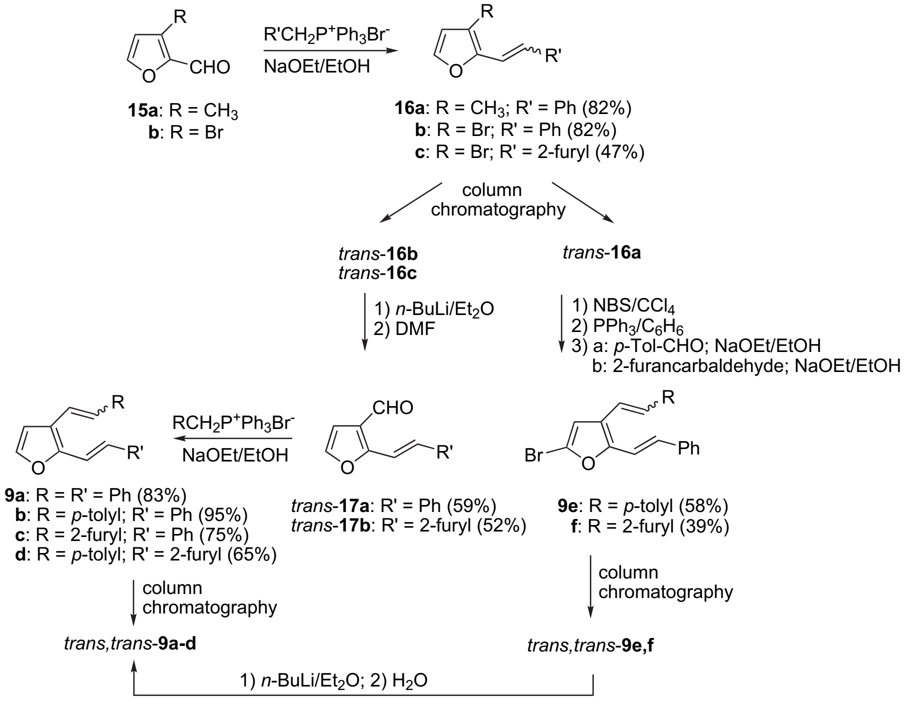


Figure 4. Possible 1,4-biradicals.

350–360 nm with similar molar absorption coefficients. The furan derivatives *trans*,*trans*-**9c** and *trans*,*trans*-**9d** demonstrate bathochromic shifts of 5 and 6 nm, respectively, in comparison to the corresponding aryl analogues (*trans*,*trans*-**9a**, *trans*,*trans*-**9b**) due to the conjugation from the oxygen lone pair through the furan ring. The ethanolic solution of *cis*,*trans*-**9a** (UV concentration) was irradiated and the process was followed by UV measurements (Fig. 5). After 15 s, the shift of the absorption maximum to the longer wavelength (359 nm) with concomitant formation of another maximum at 275 nm was observed. The new maxima (275 and 359 nm) correspond to the *trans*,*trans*-**9** isomer. These maxima decrease on further irradiation as it is comparable with the results of the pure *trans*,*trans*-**9a** irradiations (Fig. 6).



Scheme 3.

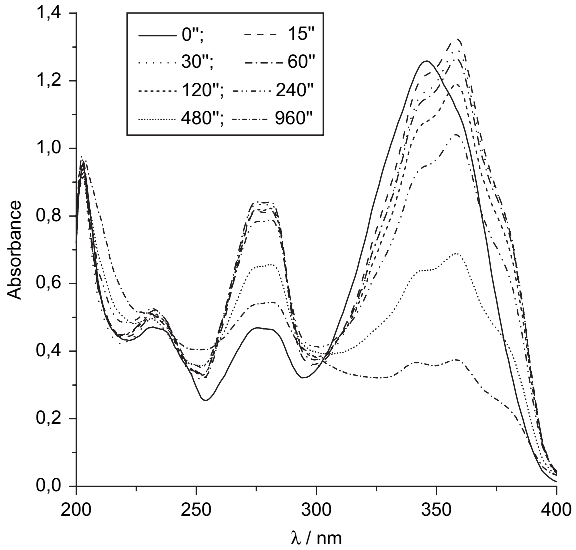


Figure 5.

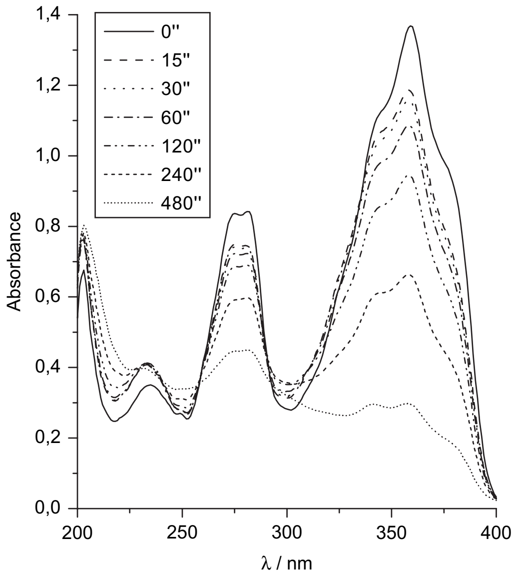


Figure 6.

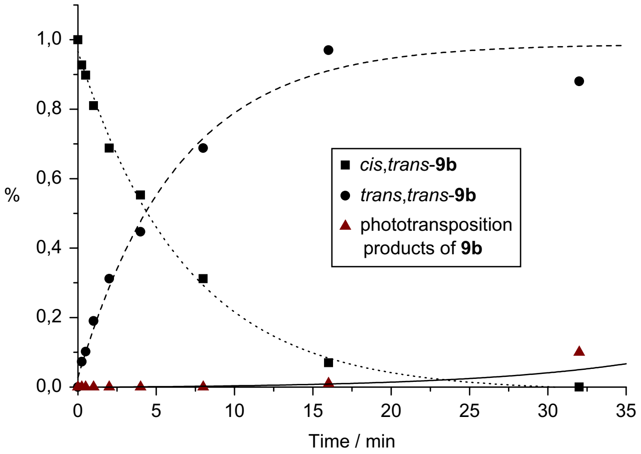


Figure 7.

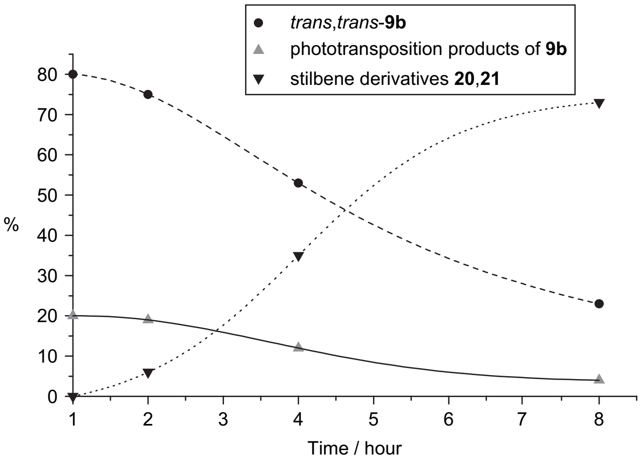
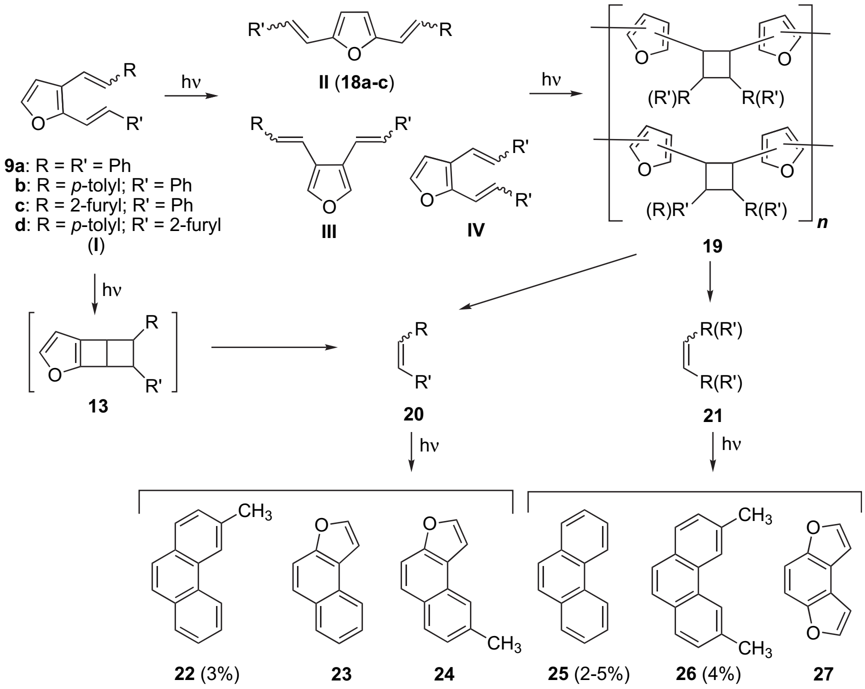


Figure 8.

Compounds **9a–d** with concentrations of 10^{-3} M were irradiated in benzene solutions under anaerobic conditions in Rayonet reactor at 350 nm. The reaction course of all these substituted divinylfurans **9** was followed by GC–MS measurements and the results were similar. In the first 15 min of irradiation, only the isomerization of *cis*,*trans*- to *trans*,*trans*-isomers **9** was detected (Fig. 7; **9b** presented).

On further irradiation for 30 min (Fig. 7), the new signals appeared having similar retention times with molecular ions identical to the starting compounds. The ratios of the sums of these new signals (see Section 4) in the experiments with **9a–d** to the signals of the corresponding starting compounds *trans*,*trans*-**9** were ca. 1:4. After 1 h of irradiation, the ratio of the signals remained the same (Fig. 8) and did not change on further irradiation. After 2 h of irradiation, besides already described signals, the signals, which correspond to stilbenes and styrylfurans (**20**, **21**; Scheme 4) appeared and become more intensive on further irradiation. The ^{1}H NMR spectra of all photomixtures showed neither signals for the aliphatic protons of the furobicyclic structures (**10–13**) nor cyclobutane dimeric structures as in the case of irradiation experiments of β,β′-disubstituted *o*-divinylbenzenes.[9] In a lower magnetic field, the signals of new aromatic protons at 7.5–8.0 ppm have been observed along with new ethylenic protons at 6.5–7.0 ppm, having characteristic coupling constants for *cis*- and *trans*-isomers. In the case of the methyl derivatives (**9b** and **9d**) several new methyl signals appear.

When the irradiation of **9a–d** was performed at higher concentrations (~10^{-1} M), the appearance of stilbenes and styrylfurans (**20**, **21**; Scheme 4) was observed by GC–MS already after 30 min. On further irradiation, the signals of **20** and **21** increase faster than at lower concentrations and on prolonged irradiation time, regardless of concentration, they are the only detectable compounds besides phenanthrenes (**22**, **25**, and **26**) and a high amount of tarry material. The naphthofurans **23** and **24** and furobenzofuran **27** are not detected in the reaction mixture, although their corresponding precursors **20** and **21** are found, and this is not a surprising fact. Electrocyclization reactions of styrylfurans[4] are not efficient reactions and compete with the formation of high-molecular-weight products.



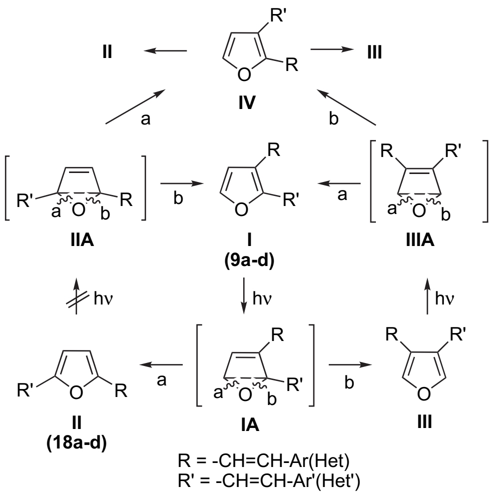
Scheme 4.

From the NMR spectra of the photomixtures, combined with the GC data, one can conclude that the signals observed in GC–MS correspond to the phototransposition products, the constitutional isomers **I**–**IV** of distyrylfurans **9a**–**d** (Scheme 4).

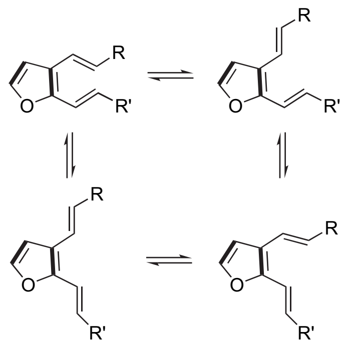
To confirm this assumption one of these constitutional isomers, the substituted 2,5-divinylfuran **II** (**18a**–**c**; Scheme 4) was prepared by independent synthesis (Section 4). The retention times of synthesized **18a**–**c**, as mixtures of configurational isomers (*cis*,*cis*-, *cis*,*trans*-, and *trans*,*trans*-**18**), were compared to the signals of the photomixtures of irradiation experiments of **9a**–**c**. Only the signal for *trans*,*trans*-2,5-divinylfuran derivative **II** (**18a**–**c**) coincides to one of the signals of the irradiation mixture of **I** (**9a**–**c**). After addition of *trans*,*trans*-2,5-divinylfuran **II** to the photomixture the coincident signal increases. It is not unexpected that *cis*,*cis*- or *cis*,*trans*-isomers **II** have not been found in the photomixture because they undergo fast cis–trans isomerization and that is confirmed by independent irradiation of **II**. The remaining GC-signals in the photomixture of **9**, having similar retention times and the same molecular ions, could correspond to the structures **III** and/or **IV**.[45]

The formation of phototransposition furan derivatives (**I**–**IV**) can be explained by formal [2+2] cycloaddition of the π systems in the furan ring and rearrangements of the obtained epoxy-furan derivatives (**IA**–**IIIA**; Scheme 5).[46–48] The anticipated dienic character of the furan ring might be a reason for their formation and mutual rearrangement. This process of cycloaddition is prevailing due to the more convenient and rigid conformation of furan double bonds compared to ethylenic π system (Scheme 6).

The existence of compounds **20** on irradiation of **9** can be explained by thermal cleavage of the intra- (**13**) or



Scheme 5. Schematic representation of the possible phototransposition products.



Scheme 6. Possible conformations of *trans*,*trans*-**9** derivatives.

intermolecular cycloadducts (**19**), formed by intra- or intermolecular [2+2] cycloaddition of the ethylenic bonds (Scheme 4). Since in the irradiation mixture of unsymmetrically substituted 2,3-divinylfuran derivatives **9b–d** besides **20** (Scheme 4) the symmetrically substituted stilbene derivatives **21** were found; it is concluded that the stilbene derivatives were derived from the intermolecular cycloadduct **19**, although the formation of **20** and the intramolecular process via unstable **13** cannot be excluded. Moreover, on irradiation of 2,5-divinylfuran derivatives **18a–c** no phototransposition products were detected showing that **II** (**18a–c**) does not undergo an intramolecular furan rearrangement process to the constitutional isomers (Scheme 5). Instead, they polymerize by intermolecular cycloaddition reactions of ethylenic bonds (**19**). Even though no evidence of a cyclobutane structure was found in the ^{1}H NMR spectra, we are sure of its formation due to the detection of all combination of ethene derivatives **20** and **21** in GC–MS measurements. Only some of their corresponding phenanthrenes (**22**, **25**, and **26**) are the isolated products from the photoreaction mixture after prolonged irradiation and complete conversion of the starting compounds **9**. The phenanthrene derivatives are formed by electrocyclization reaction of stilbenes via oxidation of dihydrophenanthrenes, as a result of imperfect anaerobic reaction conditions.[49]

3. Conclusion

The conjugated hexatriene systems with a central double bond placed in a furan ring (**9a–d**) have been studied. They behave completely different from the hexatriene system with the central double bond incorporated in benzene ring (**1**) under the same reaction conditions. Compared to diheteroaryl systems (**1b**) in which the intramolecular cycloaddition and cis–trans isomerization were the competitive processes it is obvious that in this system the primary process is cis–trans isomerization to *trans*,*trans*-isomers. Because of dienic character of the furan ring and prevailing conformation of the furan double bonds, the excitation of the hexatriene causes the [2+2] cycloaddition within the furan ring followed by rearrangement, rather than the [2+2] cycloaddition of ethylenic bonds. The photochemical process within the furan ring is competitive with the intermolecular cycloaddition processes and leads to the formation of phototransposition (**I–IV**) and high-molecular-weight products, respectively. The phototransposition process is confirmed by independent synthesis of one of the representatives (**18a–c**).

4. Experimental

4.1. General

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-600 Spectrometer at 300 or 600 MHz and 75 or 150 MHz, respectively. All NMR spectra were measured in $CDCl_3$ using tetramethylsilane as reference. The assignment of the signals is based on 2D CH-correlation and 2D HH-COSY, LRCOSY, and NOESY experiments. UV spectra were measured on a Varian Cary 50 UV–vis Spectrophotometer. IR spectra were recorded on Perkin–Elmer Spectrum One. Mass spectra were obtained on a GC–MS (Varian CP-3800 Gas Chromatograph–Varian Saturn 2200) equipped with FactorFour Capillary Column VF-5ms. Irradiations were performed in a Pyrex vessel in benzene solutions in a Rayonet reactor equipped with RPR 3500 Å lamps. All irradiation experiments were carried out in deoxygenated solutions by bubbling a stream of argon prior to irradiation. Melting points were obtained using an Original Kofler Mikroheitztisch apparatus (Reichert, Wien) and are uncorrected. Elemental analyses were carried out on Perkin–Elmer, Series II, CHNS Analyzer 2400. Silica gel (Merck 0.063–0.2 mm) was used for chromatographic purifications. Thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60 F_{254} plates. Solvents were purified by distillation. Boiling range of petroleum ether, used for chromatographic separation, was 40–70 °C.

Furan-2-carbaldehyde was obtained from a commercial source. Benzyltriphenylphosphonium bromide, *p*-methylbenzyltriphenylphosphonium bromide, and 2-furylmethyltriphenylphosphonium bromide were synthesized from the corresponding bromides[50] and triphenylphosphine in benzene solution.

3-Methyl-2-furancarbaldehyde (**15a**)[51] was prepared by oxidation of 3-methyl-2-furfurylalcohol[52] that was obtained from 3-methyl-2-furoate[53] with $LiAlH_4$. 3-Bromo-2-furancarbaldehyde (**15b**) was prepared from 2-furancarboxylic acid according to a described procedure.[54] Compound **17a** was prepared as described in the literature.[7]

4.2. Preparation of 16a and 16c

Starting compounds **16a** and **16c** were prepared from benzyltriphenylphosphonium bromide and the corresponding aldehydes, 3-methyl-2-furancarbaldehyde (**15a**) and 3-bromo-2-furancarbaldehyde (**15b**), respectively. Starting compound 3-bromo-2-(2-phenylethenyl)furan (**16b**) was obtained according to the described procedure.[7]

A solution of sodium ethoxide (0.12 g, 5.2 mmol in 10 mL ethanol) was added dropwise to a stirred solution of benzyltriphenylphosphonium bromide (1.69 g, 4.0 mmol) and 3-methyl-2-furancarbaldehyde (**15a**) (4.0 mmol) in absolute ethanol (100 mL). Stirring was continued under a stream of nitrogen for 1 day at room temperature. After removal of the solvent, the residue was worked up with water and benzene. The benzene extracts were dried with $MgSO_4$ and concentrated. The crude reaction mixture was purified and the isomers of **16a** were separated by repeated column chromatography on silica gel using petroleum ether/diethyl ether (0–3%) mixture as eluent. The first fractions yielded *trans*-isomer and the last fractions yielded *cis*-isomer. Starting compound **16c** was prepared also by Wittig reaction from 2-furylmethyltriphenylphosphonium bromide and 3-bromo-2-furancarbaldehyde (**15b**). Characterization data of the new compounds **16a** and **16c** are given below.

4.2.1. 3-Methyl-2-(2-phenylethenyl)furan (16a). Yield 82.0%; according to ^{1}H NMR spectroscopy, a mixture of 45% *cis* and 55% *trans* isomers was obtained.

trans-**16a**: R_f 0.61 (petroleum ether); colorless crystals; mp 50–51 °C; UV (EtOH) λ_{max} ($\log \varepsilon$) 340 (4.37, sh), 322

(4.50), 310 (4.43, sh) nm; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H 7.47 (d, J=7.8 Hz, 2H), 7.33 (m, 3H), 7.22 (t, J=7.2 Hz, 1H), 6.97 (d, J=16.5 Hz, H-et, 1H), 6.89 (d, J=16.5 Hz, H-et, 1H), 6.27 (s, H-4f, 1H), 2.12 (s, CH$_3$, 3H); ^{13}C NMR (CDCl$_3$) δ_C 148.70 (s), 141.20 (d), 137.33 (s), 128.52 (2d), 127.11 (d), 126.03 (2d), 125.38 (d), 118.60 (s), 114.57 (d), 114.08 (d), 10.00 (q); MS (EI) m/z (%) 184 (M$^+$, 100), 141 (10), 115 (5); HRMS (EI) Calcd for $C_{13}H_{12}O$: 184.088266. Found: 184.093546.

cis-**16a**: R_f 0.55 (petroleum ether); colorless oil; UV (EtOH) λ_{max} (log ε) 325 (3.83, sh), 317 (4.16), 311 (4.18) nm; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H 7.43 (d, J=7.5 Hz, 1H), 7.23–7.35 (m, 4H-ar), 7.21 (d, J=1.8 Hz, 1H, H-5f), 6.44 (d, J=12.3 Hz, 1H, H-et), 6.28 (d, J=12.3 Hz, 1H, H-et), 6.20 (d, J=1.8 Hz, 1H, H-4f), 1.98 ppm (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ_C 147.76 (s), 140.88 (d), 137.31 (s), 128.81 (2d), 127.68 (2d), 126.91 (2d), 120.08 (s), 115.36 (d), 113.45 (d), 10.37 (q); MS (EI) m/z (%) 184 (M$^+$, 100), 141 (25), 115 (10); Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.68; H, 6.67.

4.2.2. 3-Bromo-2-(2-furylethenyl)furan (16c).

Yield 47.0%; according to ^{1}H NMR spectroscopy, a mixture of 34% *cis* and 66% *trans* isomers was obtained.

trans-**16c**: R_f 0.61 (petroleum ether); colorless crystals; mp 45–46 °C; UV (EtOH) λ_{max} (log ε) 337 (4.27), 319 (4.46), 312 (4.40, sh) nm; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H 7.46 (m, 1H, H-1), 7.35 (d, J=1.8 Hz, 1H, H-5), 6.89 (AB$_q$, J=16.1 Hz, 2H, H-et), 6.49 (d, J=1.8 Hz, 1H, H-4), 6.45 (m, 1H, H-2), 6.40 (d, J=3.2 Hz, 1H, H-3); ^{13}C NMR (CDCl$_3$) δ_C 152.71 (s), 149.81 (s), 142.56 (d), 142.02 (d), 116.36 (d), 115.20 (d), 111.98 (d), 111.87 (d), 109.71 (d), 99.14 (s); MS (EI) m/z (%) 238/240 (M$^+$, 100), 159 (10), 131 (70).

cis-**16c**: R_f 0.52 (petroleum ether); colorless oil; UV (EtOH) λ_{max} (log ε) 321 (3.80, sh), 315 (4.09), 311 (4.14) nm; ^{1}H NMR (600 MHz, CDCl$_3$) δ_H 7.46 (d, J=1.9 Hz, 1H, H-5), 7.43 (m, 1H, H-1), 7.10 (d, J=3.4 Hz, 1H, H-3), 6.52 (d, J=1.9 Hz, 1H, H-4), 6.46 (m, 1H, H-2), 6.37 (d, J=13.4 Hz, 1H, H-et), 6.19 (d, J=13.4 Hz, 1H, H-et); ^{13}C NMR (CDCl$_3$) δ_C 151.58 (s), 148.77 (s), 141.94 (d), 141.51 (d), 115.75 (d), 114.44 (d), 111.43 (d), 110.74 (d), 109.52 (d), 100.92 (s); MS (EI) m/z (%) 238/240 (M$^+$, 75), 159 (10), 131 (100); Anal. Calcd for $C_{10}H_7BrO_2$: C, 82.42; H, 5.38. Found: C, 82.20; H, 5.45.

4.3. Preparation of 17b

To a stirred solution of *trans*-**16c** (3.0 mmol) in anhydrous diethyl ether (40 mL) cooled to −70 °C, *n*-butyl lithium (3.3 mmol, 1.6 M hexane solution) was added under a stream of nitrogen over 30 min. After additional stirring for 30 min, anhydrous *N*,*N*-dimethylformamide (6.6 mmol, 0.48 mL) was added. After 1 h at that temperature, the mixture was allowed gradually to warm up to 0 °C, over 3 h. Dilute hydrochloric acid (1.5 mL, 7 mol/L) was added and the layers were separated. After extraction, the combined organic phase was dried over MgSO$_4$. The reaction mixture was purified and separated by column chromatography on silica gel using petroleum ether/diethyl ether (0–10%) as the eluent. After the separation of the starting compound from the first fractions, the last fractions yielded 2-*trans*-(2-furylethenyl)-furan-3-carbaldehyde (**17b**) in 52% yield. Compound **17b** was confirmed by GC–MS measurements before the next reaction step, the preparation of **9d**.

4.4. Preparation of 9a–d

Starting compounds **9a**–**c** were prepared by Wittig reaction from the 2-*trans*-(2-phenylethenyl)furan-3-carbaldehyde (*trans*-**17a**) and corresponding triphenylphosphonium salts, benzyltriphenylphosphonium bromide, *p*-methylbenzyltriphenylphosphonium bromide, and 2-furylmethyltriphenylphosphonium bromide, respectively. To a stirred solution of the corresponding triphenylphosphonium salts (1.9 mmol) and the 2-*trans*-(2-phenylethenyl)furan-3-carbaldehyde (*trans*-**17a**) (0.350 g, 1.8 mmol) in absolute ethanol (50 mL), a solution of sodium ethoxide (0.067 g, 2.9 mmol in 10 mL ethanol) was added dropwise. Stirring was continued under a stream of nitrogen for 1 day at room temperature. After removal of the solvent, water was added to the residue and extracted with benzene. The benzene extracts were dried and concentrated. The crude reaction mixture was purified and the isomers of products **9a**–**c** were separated by repeated column chromatography on silica gel using petroleum ether and petroleum ether/diethyl ether (0–5%) mixture as eluent. Starting compound **9d** was prepared similarly by Wittig reaction from the 2-*trans*-[2-(2-furyl)ethenyl]furan-3-carbaldehyde (*trans*-**17b**) and *p*-tolyltriphenylphosphonium bromide. The first fractions yielded *cis*,*trans*-isomer and the last fractions yielded *trans*,*trans* isomers. Characterization data of the new compounds **9a**–**d** are given below.

4.4.1. 2-(2-Phenylethenyl)-3-(2-phenylethenyl)furan (9a).

Yield 83.2%; according to ^{1}H NMR spectroscopy, a mixture of 29% *cis*,*trans*- and 71% *trans*,*trans* isomers was obtained.

cis,*trans*-**9a**: R_f 0.40 (petroleum ether); yellow-green crystals; mp 85–86 °C; UV (EtOH) λ_{max} (log ε) 346 (4.46), 279 (4.02), 235 (4.02) nm; ^{1}H NMR (600 MHz, CDCl$_3$) δ_H 7.44 (d, J=7.2 Hz, 2H, H-ar), 7.28–7.36 (m, 6H), 7.21–7.26 (m, 2H), 7.20 (d, J=1.8 Hz, 1H, H-5f), 7.05 (d, J=16.2 Hz, 1H, H(et)-2β), 6.97 (d, J=16.2 Hz, 1H, H(et)-2α), 6.62 (d, J=12.0 Hz, 1H, H(et)-3β), 6.53 (d, J=12.0 Hz, 1H, H(et)-3α), 6.11 (d, J=1.8 Hz, 1H, H-4f); ^{13}C NMR (CDCl$_3$) δ_C 150.65 (s, C-2), 141.37 (d, C-5$_f$), 137.40 (s), 136.99 (s), 130.08 (d, C-3β), 128.77 (2d), 128.56 (2d), 128.07 (2d), 127.54 (d), 127.43 (d), 127.13 (d), 126.32 (2d), 119.99 (s, C-3), 119.46 (d, C-3α), 114.37 (d, C-2α), 111.60 (d, C-4f); IR (evaporated film from CHCl$_3$) 2985, 2908, 2853, 1580, 1500, 965, 750 cm^{-1}; MS (EI) m/z (%) 272 (M$^+$, 100), 243 (7), 115 (6).

trans,*trans*-**9a**: R_f 0.38 (petroleum ether); yellow crystals; mp 165–166 °C; UV (EtOH) λ_{max} (log ε) 376 (4.36, sh), 359 (4.51), 343 (4.41, sh), 279 (4.29), 236 (3.91) nm; ^{1}H NMR (600 MHz, CDCl$_3$) δ_H 7.50–7.53 (m, 4H), 7.35–7.39 (m, 5H), 7.24–7.28 (m, 2H), 7.13 (d, J=16.2 Hz, 1H, H(et)-3α), 7.12 (d, J=16.2 Hz, 1H, H(et)-2α), 7.09 (d, J=16.2 Hz, 1H, H(et)-2β), 6.84 (d, J=16.2 Hz, 1H, H(et)-3β), 6.68 (d, J=1.8 Hz, 1H, H-4f); ^{13}C NMR (CDCl$_3$) δ_C 150.00 (s, C-2), 142.40 (d, C-5f), 137.27 (s), 136.96 (s), 128.80 (d, C-3β), 128.60 (2d), 128.57 (2d), 128.35 (d), 128.21 (d), 127.59 (d), 127.40 (d), 127.36 (d), 126.33 (2d), 126.12 (2d), 121.99 (s, C-3), 117.78 (d, C-3α), 113.69 (d, C-2α), 108.69 (d, C-4f); IR (evaporated film from $CHCl_3$) 2973, 2915, 2849, 1583, 1500, 1433, 950, 750, 683 cm^{-1}; MS (EI) *m*/*z* (%) 272 (M$^+$, 100), 243 (8), 115 (5); Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.53; H, 5.65.

4.4.2. 2-(2-Phenylethenyl)-3-[2-(4-methylphenyl)ethenyl]furan (9b).

Yield 95.1%; according to ^{1}H NMR spectroscopy, a mixture of 35% *cis*,*trans*- and 65% *trans*,*trans*-isomers was obtained.

cis,*trans*-**9b**: R_f 0.43 (petroleum ether); yellow-green crystals; mp 124 °C; UV (EtOH) λ_{max} (log ε) 346 (4.48), 284 (4.04), 235 (4.04) nm; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.49 (d, J=7.8 Hz, 2H), 7.30–7.36 (m, 5H), 7.14 (d, J=12.6 Hz, 1H), 7.13 (d, J=7.8 Hz, 2H), 7.08 (d, J=16.2 Hz, 1H), 6.89 (d, J=12.6 Hz, 1H), 6.73 (d, J=16.2 Hz, 1H), 6.37 (s, 1H, H-4f), 2.32 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ_C 152.31 (s), 141.23 (d), 137.65 (s), 136.34 (s), 133.29 (s), 129.02 (2d), 128.39 (d), 128.26 (2d), 128.06 (d), 127.45 (d), 126.08 (2d), 126.00 (2d), 123.10 (s, C-3), 113.90 (d), 112.89 (d), 112.58 (d), 20.80 (q); IR (evaporated film from $CHCl_3$) 3000, 2915, 2849, 1583, 1500, 950, 750 cm^{-1}; MS (EI) *m*/*z* (%) 286 (M$^+$, 100).

trans,*trans*-**9b**: R_f 0.39 (petroleum ether); yellow crystals; mp 134 °C; UV (EtOH) λ_{max} (log ε) 378 (4.38, sh), 360 (4.51), 344 (4.41, sh), 284 (4.36), 278 (4.34, sh), 235 (3.99) nm; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.53 (d, J=7.8 Hz, 2H), 7.41 (d, J=7.8 Hz, 2H), 7.37 (m, 4H), 7.18 (d, J=7.8 Hz, 2H), 7.13 (d, J=16.0 Hz, 1H), 7.10 (d, J=16.0 Hz, 1H), 7.09 (d, J=16.0 Hz, 1H), 6.83 (d, J=16.0 Hz, 1H), 6.69 (d, J=1.6 Hz, 1H, H-4f), 2.37 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ_C 149.41 (s), 141.98 (d), 136.91 (s), 136.69 (s), 134.16 (s), 128.92 (2d), 128.47 (d), 128.22 (2d), 127.15 (d), 126.84 (d), 125.94 (2d), 125.67 (2d), 122.00 (s), 116.45 (d), 113.45 (d), 108.35 (d), 20.74 (q); IR (evaporated film from $CHCl_3$) 3000, 2907, 2849, 1583, 1500, 1432, 965, 750 cm^{-1}; MS (EI) *m*/*z* (%) 286 (M$^+$, 100); Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.35; H, 6.19.

4.5. Photochemical isomerization of the mixture of isomers of 9c,d into *trans*,*trans*-9c,d

A mixture of *cis*,*trans*- and *trans*,*trans*-isomers of **9c**,**d** (~1:1) in benzene (7.7 mM) was purged with argon for 15 min and irradiated at 350 nm in a Rayonet reactor in a Pyrex tube for 30 min. The photochemical isomerization from *cis*,*trans*-isomers of **9c**,**d** to *trans*,*trans*-isomers of **9c**,**d** was followed by GC–MS measurements with time. After 15 min, the reaction mixture contained 91% of the *trans*,*trans*-isomers of **9c**,**d**. The solvent was removed in vacuum and the oily residue chromatographed on silica gel column using petroleum ether to get pure *trans*,*trans*-**9c**,**d** in the last fractions.

4.5.1. 2-(2-Phenylethenyl)-3-(2-furylethenyl)furan (9c).

Yield 75.3%; according to ^{1}H NMR spectroscopy, a mixture of 27% *cis*,*trans*- and 73% *trans*,*trans*-isomers was obtained.

trans,*trans*-**9c**: R_f 0.43 (petroleum ether); yellow crystals; mp 110 °C; UV (EtOH) λ_{max} (log ε) 383 (4.38, sh), 364 (4.49), 346 (4.40, sh), 292 (4.34), 280 (4.30, sh) nm; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.53 (d, J=7.6 Hz, 2H), 7.41 (d, J~1 Hz, 1H), 7.36 (m, 2H), 7.26 (t, J=7.6 Hz, 2H), 7.11 (d, J=16.1 Hz, 1H), 7.07 (d, J=16.1 Hz, 1H), 7.05 (d, J=15.9 Hz, 1H), 6.62 (d, J=15.9 Hz, 1H), 6.61 (d, J~1 Hz, 1H), 6.43 (m, 1H), 6.32 (d, J=3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ_C 152.83 (s), 149.76 (s), 142.06 (d), 141.53 (d), 136.62 (s), 128.22 (2d), 127.20 (d), 127.04 (d), 125.96 (2d), 121.41 (s), 116.19 (d), 116.03 (d), 113.33 (d), 111.20 (d), 108.03 (d), 107.68 (d); IR (evaporated film from $CHCl_3$) 2915, 2824, 1608, 1500, 1440, 965, 750 cm^{-1}; MS (EI) *m*/*z* (%) 262 (M$^+$, 100), 233 (10), 115 (7); Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.73; H, 5.09.

4.5.2. 2-(2-Furylethenyl)-3-[2-(4-methylphenyl)ethenyl]furan (9d).

Yield 64.8%.

trans,*trans*-**9d**: R_f 0.40 (petroleum ether); yellow crystals; mp 117 °C; UV (EtOH) λ_{max} (log ε) 385 (4.41), 366 (4.50), 347 (4.36, sh), 289 (4.32), 280 (4.28, sh), 249 (4.03), 241 (4.06) nm; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.41 (d, J=7.9 Hz, 2H), 7.39 (d, J~1 Hz, 2H), 7.34 (d, J=1.3 Hz, 1H), 7.16 (d, J=7.9 Hz, 2H), 7.07 (d, J=16.1 Hz, 1H), 7.03 (d, J=15.8 Hz, 1H), 6.84 (d, J=15.8 Hz, 1H), 6.80 (d, J=16.1 Hz, 1H), 6.66 (d, J=1.3 Hz, 1H), 6.43 (m, 1H), 6.35 (d, J=3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ_C 152.72 (s), 149.23 (s), 141.96 (d), 141.73 (d), 136.86 (s), 134.17 (s), 128.90 (2d), 128.36 (d), 125.68 (2d), 121.96 (s), 116.44 (d), 114.32 (d), 111.81 (d), 111.40 (d), 108.68 (d), 108.36 (d), 20.73 (q); IR (evaporated film from $CHCl_3$) 3049, 2923, 2851, 1596, 1495, 1446, 961, 741 cm^{-1}; MS (EI) *m*/*z* (%) 276 (M$^+$, 100), 219 (2), 115 (2); Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.28; H, 5.49.

4.6. Preparation of 9e and 9f

To a solution of *trans*-3-methyl-2-(2-phenylethenyl)furan (*trans*-**16a**) (0.197 g, 1.0 mmol) in CCl_4 (20 mL) were added freshly crystallized *N*-bromosuccinimide (NBS) (0.430 g, 2.2 mmol) and a few mg (5–6 mg) of AIBN. The mixture was heated under reflux until the NBS was consumed (usually 6–7 h). The reaction mixture was cooled to room temperature and filtered to remove the succinimide and concentrated under reduced pressure to give a brown oil of the corresponding *trans*-dibromide. The oil was dissolved in benzene (10 mL) and triphenylphosphine (0.317 g, 1.1 mmol) was added and the solution was stirred overnight. The precipitated phosphonium salt was filtered and subjected to a Wittig reaction with the corresponding aldehydes, *p*-tolylaldehyde (0.144 g, 1.0 mmol) and furan-2-carbaldehyde (0.096 g, 1.0 mmol) in a similar manner as described above for **9a–d**. After column chromatography on silica gel with petroleum ether/diethyl ether (0–3%) mixture as eluent, a 57.8% yield of **9e** and 39% yield of **9f** were obtained for three reaction steps. In the first fractions *cis*,*trans*-isomers **9e**,**f** were isolated and in the last fractions *trans*,*trans*-isomers **9e**,**f** were isolated.

4.6.1. 5-Bromo-2-(2-phenylethenyl)-3-[2-(4-methylphenyl)ethenyl]furan (9e).

Yield 57.8%; according to ^{1}H NMR spectroscopy, a mixture of 38% *cis*,*trans*-isomers and 62% *trans*,*trans*-isomers were obtained.

cis,*trans*-**9e**: Too small a quantity to be analyzed completely; R_f 0.62 (petroleum ether/diethyl ether 19:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ_H 7.38 (d, J=7.9 Hz, 2H), 7.27–7.36 (m, 3H), 7.17 (d, J=7.9 Hz, 2H), 7.08 (d, J=7.9 Hz, 2H), 6.98 (d, J=15.9 Hz, 1H, H-et), 6.82 (d, J=15.9 Hz, 1H, H-et), 6.56 (d, J=12.0 Hz, 1H, H-et), 6.34 (d, J=12.0 Hz, 1H, H-et), 6.04 (s, 1H), 2.30 (s, 3H, CH$_3$); MS (EI) *m/z* (%) 364/366 (M$^+$, 100), 285 (20), 257 (30), 115 (20).

trans,*trans*-**9e**: R_f 0.57 (petroleum ether/diethyl ether 19:1); yellow-green crystals; mp 98–100 °C; UV (EtOH) λ_{max} (log ε) 380 (4.19, sh), 364 (4.33), 347 (4.24, sh), 286 (4.23), 237 (3.85) nm; ^{1}H NMR (600 MHz, CDCl$_3$) δ_H 7.47 (d, J=7.9 Hz, 2H), 7.33 (m, 4H), 7.22 (t, J=7.9 Hz, 1H), 7.13 (d, J=7.9 Hz, 2H), 7.02 (d, J=16.0 Hz, 1H, H-et), 6.96 (d, J=16.0 Hz, 1H, H-et), 6.94 (d, J=16.0 Hz, 1H, H-et), 6.72 (d, J=16.0 Hz, 1H, H-et), 6.56 (s, 1H), 2.32 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ_C 151.61 (s), 137.81 (s), 136.85 (s), 134.21 (s), 129.86 (d), 129.49 (2d), 128.78 (2d), 127.90 (d), 127.71 (d), 126.51 (2d), 126.29 (2d), 124.37 (s), 123.38 (s), 115.77 (d), 112.81 (d), 110.54 (d), 21.31 (q); IR (evaporated film from CHCl$_3$) 2932, 2873, 1600, 1500, 1456, 956, 940, 750 cm^{-1}; MS (EI) *m/z* (%) 364/366 (M$^+$, 100), 285 (15), 257 (30), 115 (15); Anal. Calcd for C$_{21}$H$_{17}$BrO: C, 69.05; H, 4.69. Found: C, 69.43; H, 4.33.

4.7. Photochemical isomerization of the mixture of isomers of 9f into *trans*,*trans*-9f

A mixture of *cis*,*trans*- and *trans*,*trans*-isomers of **9f** (~2:3) in benzene (9.5 mM) was purged with argon for 15 min and irradiated at 350 nm in a Rayonet reactor in a Pyrex tube. The photochemical isomerization from *cis*,*trans*-isomers of **9c**,**d** to *trans*,*trans*-isomers of **9f** was followed by GC–MS measurements with time. After 15 min, the reaction mixture contained 95% of the *trans*,*trans*-isomers of **9f**. The solvent was removed in vacuum and the oily residue was chromatographed on silica gel column using petroleum ether to get pure *trans*,*trans*-**9f** from the last fractions.

4.7.1. 5-Bromo-2-(2-phenylethenyl)-3-[2-(2-furyl)ethenyl]furan (*trans*,*trans*-9f).

R_f 0.59 (petroleum ether/diethyl ether 19:1); yellow crystals; mp 95 °C; UV (EtOH) λ_{max} (log ε) 385 (4.38), 367 (4.47), 351 (4.36, sh), 298 (4.38), 288 (4.36), 239 (3.80) nm; ^{1}H NMR (600 MHz, CDCl$_3$) δ_H 7.50 (dd, J=7.5, 1.6 Hz, 2H), 7.41 (d, J=1.5 Hz, 1H), 7.35 (dt, J=7.5, 1.6 Hz, 2H), 7.25 (m, 1H), 7.07 (d, J=16.0 Hz, 1H), 6.98 (d, J=16.0 Hz, 1H), 6.96 (d, J=16.2 Hz, 1H), 6.56 (d, J=16.2 Hz, 1H), 6.53 (s, 1H), 6.43 (dd, J=3.3, 1.5 Hz, 1H), 6.33 (d, J=3.3 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ_C 148.15 (s), 147.18 (s), 137.57 (d), 132.03 (s), 124.02 (2d), 123.18 (d), 123.14 (d), 121.79 (2d), 119.19 (s), 118.77 (s), 112.66 (d), 110.51 (d), 107.94 (d), 107.07 (d), 105.46 (d), 104.14 (d); IR (evaporated film from CHCl$_3$) 3044, 2922, 2840, 1595, 1508, 1494, 949, 928, 771 cm^{-1}; MS (EI) *m/z* (%) 340/342 (M$^+$, 100), 261 (5), 233 (5); Anal. Calcd for C$_{18}$H$_{13}$BrO$_2$: C, 63.36; H, 3.84. Found: C, 63.73; H, 3.53.

4.8. Preparation of 9b,c from 9e,f

To a stirred solution of *trans*,*trans*-**9e** or *trans*,*trans*-**9f** (0.9 mmol), respectively, in anhydrous diethyl ether (40 mL) cooled to −70 °C, *n*-butyl lithium (1.0 mmol, 1.6 M hexane solution) was added under a stream of nitrogen over 30 min. After additional stirring for 30 min, the mixture was allowed to gradually warm up to room temperature, over 4 h. To a stirred reaction mixture, water (1.0 mmol, 0.02 mL) was added and the solution was stirred overnight. Dilute hydrochloric acid (0.3 mL, 7 mol/L) was added and the layers were separated. After extraction, the combined organic phases were dried over MgSO$_4$. The reaction mixture was purified and separated by column chromatography on silica gel using petroleum ether/diethyl ether (0–2%) as eluent. After the separation of the starting compound from the first fractions, the last fractions yielded 2-(2-phenylethenyl)-3-[2-(4-methylphenyl)ethenyl]furan (*trans*,*trans*-**9b**) in a 71.3% yield or 2-(2-phenylethenyl)-3-[2-(2-furyl)ethenyl)ethenyl]-furan (*trans*,*trans*-**9c**) in a 65.5% yield.

4.9. Preparation of 18a–c

Starting compounds **18a–c** were prepared in three steps by a Wittig reaction and Vilsmeier formylation. In the first step, 2-styrylfuran was prepared by Wittig reaction from benzyltriphenylphosphonium bromide and freshly distilled furan-2-carbaldehyde. To a stirred solution of benzyltriphenylphosphonium bromide (8.29 g, 20.0 mmol) and furan-2-carbaldehyde (1.70 g, 18.0 mmol) in absolute ethanol (100 mL), a solution of sodium ethoxide (0.615 g, 27.0 mmol in 10 mL ethanol) was added dropwise. Stirring was continued under a stream of nitrogen for 1 day at room temperature. After removal of the solvent, the residue was worked up with water and benzene. The benzene extracts were dried and concentrated. The crude reaction mixture was purified and the pure mixture of isomers of 2-styrylfuran (81.8%) was separated by column chromatography on silica gel using petroleum ether as eluent. Vilsmeier formylation was carried out from 2-styrylfuran (1.26 g, 7.4 mmol) dissolved in dimethylformamide (1.71 mL, 22.0 mmol). After being stirred at ~12 °C for 15 min, phosphorus oxychloride (1.14 g, 7.4 mmol) was added and the reaction mixture was allowed gradually to warm up to room temperature and stirred for 4 days. The reaction mixture was decomposed by the continuous addition (with cooling) of 15% sodium hydroxide solution and the product was worked up with diethyl ether. The diethyl ether extracts were washed with water. After removal of the solvent, the crude reaction mixture of 2-formyl-5-styrylfuran (as a mixture of *cis*- and *trans*-isomer) was used in a Wittig reaction to prepare 2,5-distyrylfuran derivatives **18a–c**. To a stirred solution of formyl derivative (0.285 g, 1.4 mmol) and the phosphonium salts (1.6 mmol), benzyltriphenylphosphonium bromide, *p*-methylbenzyltriphenylphosphonium bromide, or 2-furylmethyltriphenylphosphonium bromide, respectively, in absolute ethanol (100 mL) a solution of sodium ethoxide (0.05 g, 2.2 mmol in 10 mL ethanol) was added dropwise. Stirring was continued under a stream of nitrogen for 1 day at room temperature. After removal of the solvent, the residue was worked up with water and benzene. The benzene extracts were dried and concentrated. The crude reaction mixture was purified and the mixture of four isomers of products **18a–c** were isolated by column chromatography on silica gel using petroleum ether/diethyl ether (0–3%) mixture as eluent. After the photochemical isomerization of the mixture of four isomers of **18a–c** (see the procedure for isolating *trans*,*trans*-**9f**) into *trans*,*trans*-isomers of **18a–c**. The solvent was removed in vacuum and the oily residue was chromatographed on silica gel column using petroleum ether to isolate pure *trans*,*trans*-**18a–c**. Characterization data of the new compounds *trans*,*trans*-**18b** and *trans*,*trans*-**18c** are given below.[55]

4.9.1. 2-(2-Phenylethenyl)-5-[2-(4-methylphenyl)ethenyl]furan (*trans*,*trans*-18b).

Yield 58.7%; R_f 0.63 (petroleum ether/CH$_2$Cl$_2$ 9:1); yellow-green crystals; mp 91–92 °C; UV (EtOH) λ_{max} (log ε) 386 (4.50), 281 (4.33), 276 (4.34) nm; ^{1}H NMR (600 MHz, CDCl$_3$) δ_H 7.49 (d, J=7.6 Hz, 2H), 7.39 (d, J=8.0 Hz, 2H), 7.34 (t, J=7.6 Hz, 2H), 7.24 (t, J=7.6 Hz, 2H), 7.16 (d, J=8.0 Hz, 1H), 7.11 (d, J=16.2 Hz, 1H), 7.10 (d, J=16.1 Hz, 1H), 6.87 (d, J=16.2 Hz, 1H), 6.83 (d, J=16.1 Hz, 1H), 6.37 (d, J=3.4 Hz, 1H), 6.34 (d, J=3.4 Hz, 1H), 2.35 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ_C 152.75 (s), 152.37 (s), 137.10 (s), 136.67 (s), 133.84 (s), 128.98 (2d), 128.24 (2d), 127.07 (d), 126.89 (d), 126.64 (d), 125.88 (2d), 125.84 (2d), 115.80 (d), 114.88 (d), 110.79 (d), 110.33 (d), 20.80 (q); IR (evaporated film from CHCl$_3$) 2981, 2925, 1592, 1507, 1442, 1017, 956, 782, 750 cm^{-1}; MS (EI) *m/z* (%) 286 (M$^+$, 100); Anal. Calcd for C$_{21}$H$_{18}$O: C, 88.08; H, 6.34. Found: C, 88.27; H, 6.18.

4.9.2. 2-(2-Furylethenyl)-5-(2-phenylethenyl)furan (*trans*,*trans*-18c).

Yield 64.2%; R_f 0.61 (petroleum ether/CH$_2$Cl$_2$ 9:1); yellow crystals; mp 87 °C; UV (EtOH) λ_{max} (log ε) 383 (4.52), 283 (4.35), 274 (4.34) nm; ^{1}H NMR (600 MHz, CDCl$_3$) δ_H 7.44 (d, J=7.6 Hz, 2H), 7.35 (d, J=1.4 Hz, 1H), 7.31 (t, J=7.6 Hz, 2H), 7.21 (m, 1H), 7.06 (d, J=16.1 Hz, 1H), 6.88 (d, J=16.1 Hz, 1H), 6.82 (d, J=16.1 Hz, 1H), 6.75 (d, J=16.1 Hz, 1H), 6.39 (m, 1H), 6.33 (d, J=3.4 Hz, 2H), 6.31 (d, J=3.4 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ_C 152.65 (s), 152.49 (s), 152.26 (s), 141.75 (d), 136.60 (s), 128.22 (d), 127.10 (2d), 126.78 (d), 125.89 (d), 125.86 (d), 115.69 (d), 114.53 (d), 114.08 (d), 111.36 (d), 110.97 (d), 110.90 (d), 108.49 (d); IR (evaporated film from CHCl$_3$) 2932, 2874, 1508, 956, 815, 782 cm^{-1}; MS (EI) *m/z* (%) 262 (M$^+$, 100); Anal. Calcd for C$_{18}$H$_{14}$O$_2$: C, 82.42; H, 5.38. Found: C, 82.29; H, 5.53.

4.10. Irradiation experiments

A mixture of *cis*,*trans*- and *trans*,*trans*-isomers of **9a–d** in benzene (3.3 mM) was purged with argon for 30 min and irradiated at 350 nm in a Rayonet reactor in a Pyrex tube. The reaction course was followed by GC–MS. The GC–MS analysis of the photomixtures was performed on a Varian CP-3800 Gas Chromatograph–Varian Saturn 2200 equipped with FactorFour Capillary Column VF-5ms, 30 m×0.25 mm ID; GC operating conditions for all experiments: column temperature programed from 110 to 300 °C (3 min isothermal) at a rate of 33 °C/min; carrier gas: helium; flow rate: 1 mL/min; injector temperature: 300 °C; volume injected: 5 μL.

According to chromatograms, the following data for irradiation of 2,3-divinylfuran derivatives **9a–d** were obtained [irrad. time/h, t_R./min, M$^+$, %, compd; 2-[2-(2-furyl)ethenyl]furan (M$^+$ 160), 2-styrylfuran (M$^+$ 170), stilbene (M$^+$ 180), 2-[2-(4-methylphenyl)ethenyl]furan (M$^+$ 184), 4-methylstilbene (M$^+$ 194), 4,4′-dimethylstilbene (M$^+$ 208)]:

Compound **9a**: 0 h: 7.53′, M$^+$ 272, 23%, *cis*,*trans*-**9a**; 8.38′, M$^+$ 272, 77%, *trans*,*trans*-**9a**; after 1 h: 7.02′, M$^+$ 272, 5%, **III/IV**; 7.97′, M$^+$ 272, 4%, **III/IV**; 8.12′, M$^+$ 272, 4%, **III/IV**; 8.38′, M$^+$ 272, 80%, *trans*,*trans*-**9a**; 8.88′, M$^+$ 272, 7%, *trans*,*trans*-**18a**; after 2 h: 4.69′, M$^+$ 180, 2%; 5.39′, M$^+$ 180, 1%; 7.02′, M$^+$ 272, 4%, **III/IV**; 7.97′, M$^+$ 272, 4%, **III/IV**; 8.12′, M$^+$ 272, 4%, **III/IV**; 8.38′, M$^+$ 272, 77%, *trans*,*trans*-**9a**; 8.88′, M$^+$ 272, 8%, *trans*,*trans*-**18a**; after 4 h: 4.69′, M$^+$ 180, 21%; 5.39′, M$^+$ 180, 6%; 7.02′, M$^+$ 272, 3%, **III/IV**; 7.97′, M$^+$ 272, 3%, **III/IV**; 8.12′, M$^+$ 272, 4%, **III/IV**; 8.38′, M$^+$ 272, 58%, *trans*,*trans*-**9a**; 8.88′, M$^+$ 272, 5%, *trans*,*trans*-**18a**; after 8 h: 4.69′, M$^+$ 180, 44%; 4.75′, M$^+$ 178, 5%, **25**; 5.39′, M$^+$ 180, 27%; 7.02′, M$^+$ 272, 1%, **III/IV**; 7.97′, M$^+$ 272, 1%, **III/IV**; 8.12′, M$^+$ 272, 1%, **III/IV**; 8.38′, M$^+$ 272, 19%, *trans*,*trans*-**9a**; 8.88′, M$^+$ 272, 2%, *trans*,*trans*-**18a**.

Compound **9b**: 0 h: 7.86′, M$^+$ 286, 33%, *cis*,*trans*-**9b**; 8.95′, M$^+$ 286, 67%, *trans*,*trans*-**9b**; after 1 h: 7.38′, M$^+$ 286, 4%, **III/IV**; 7.84′, M$^+$ 286, 5%, **III/IV**; 8.74′, M$^+$ 286, 4%, **III/IV**; 8.95′, M$^+$ 286, 80%, *trans*,*trans*-**9b**; 9.27′, M$^+$ 286, 7%, *trans*,*trans*-**18b**; after 2 h: 4.55′, M$^+$ 208, 2%; 4.69′, M$^+$ 180, 3%; 5.39′, M$^+$ 180, 1%; 7.38′, M$^+$ 286, 3%, **III/IV**; 7.84′, M$^+$ 286, 4%, **III/IV**; 8.74′, M$^+$ 286, 6%, **III/IV**; 8.95′, M$^+$ 286, 75%, *trans*,*trans*-**9b**; 9.27′, M$^+$ 286, 6%, *trans*,*trans*-**18b**; after 4 h: 4.55′, M$^+$ 208, 8%; 4.69′, M$^+$ 180, 13%; 5.11′, M$^+$ 194, 10%; 5.38′, M$^+$ 194, 1%; 5.39′, M$^+$ 180, 3%; 7.38′, M$^+$ 286, 2%, **III/IV**; 7.84′, M$^+$ 286, 3%, **III/IV**; 8.74′, M$^+$ 286, 3%, **III/IV**; 8.95′, M$^+$ 286, 53%, *trans*,*trans*-**9b**; 9.27′, M$^+$ 286, 4%, *trans*,*trans*-**18b**; after 8 h: 4.55′, M$^+$ 208, 17%; 4.69′, M$^+$ 180, 31%; 5.11′, M$^+$ 194, 12%; 5.31′, M$^+$ 192, 3%, **22**; 5.38′, M$^+$ 194, 3%; 5.39′, M$^+$ 180, 7%; 7.84′, M$^+$ 286, 1%, **III/IV**; 8.74′, M$^+$ 286, 1%, **III/IV**; 8.95′, M$^+$ 286, 23%, *trans*,*trans*-**9b**; 9.27′, M$^+$ 286, 2%, *trans*,*trans*-**18b**.

Compound **9c**: 0 h: 6.56′, M$^+$ 262, 41%, *cis*,*trans*-**9c**; 7.45′, M$^+$ 262, 59%, *trans*,*trans*-**9c**; after 1 h: 6.33′, M$^+$ 262, 4%, **III/IV**; 6.92′, M$^+$ 262, 4%, **III/IV**; 7.17′, M$^+$ 262, 3%, **III/IV**; 7.45′, M$^+$ 262, 82%, *trans*,*trans*-**9c**; 8.03′, M$^+$ 262, 7%, *trans*,*trans*-**18c**; after 2 h: 3.65′, M$^+$ 160, 1%; 4.08′, M$^+$ 170, 3%; 4.60′, M$^+$ 170, 1%; 4.69′, M$^+$ 180, 2%; 6.33′, M$^+$ 262, 4%, **III/IV**; 6.92′, M$^+$ 262, 3%, **III/IV**; 7.17′, M$^+$ 262, 2%, **III/IV**; 7.45′, M$^+$ 262, 78%, *trans*,*trans*-**9c**; 8.03′, M$^+$ 262, 6%, *trans*,*trans*-**18c**; after 4 h: 3.65′, M$^+$ 160, 6%; 4.08′, M$^+$ 170, 17%; 4.60′, M$^+$ 170, 6%; 4.69′, M$^+$ 180, 4%; 6.33′, M$^+$ 262, 2%, **III/IV**; 6.92′, M$^+$ 262, 3%, **III/IV**; 7.17′, M$^+$ 262, 1%, **III/IV**; 7.45′, M$^+$ 262, 57%, *trans*,*trans*-**9c**; 8.03′, M$^+$ 262, 4%, *trans*,*trans*-**18c**; after 8 h: 3.65′, M$^+$ 160, 13%; 4.08′, M$^+$ 170, 31%; 4.60′, M$^+$ 170, 19%; 4.69′, M$^+$ 180, 11%; 4.75′, M$^+$ 178, 2%, **25**; 6.33′, M$^+$ 262, 1%, **III/IV**; 6.92′, M$^+$ 262, 1%, **III/IV**; 7.45′, M$^+$ 262, 21%, *trans*,*trans*-**9c**; 8.03′, M$^+$ 262, 1%, *trans*,*trans*-**18c**.

Compound **9d**: 0 h: 7.10′, M$^+$ 276, 17%, *cis*,*trans*-**9d**; 7.88′, M$^+$ 276, 83%, *trans*,*trans*-**9d**; after 1 h: 6.85′, M$^+$ 276, 5%, **II/III/IV**; 7.29′, M$^+$ 276, 3%, **II/III/IV**; 7.48′, M$^+$ 276, 5%, **II/III/IV**; 7.88′, M$^+$ 276, 81%, *trans*,*trans*-**9d**; 8.41′, M$^+$ 276, 6%, **II/III/IV**; after 2 h: 3.65′, M$^+$ 160, 1%; 4.33′, M$^+$ 184, 2%; 4.55′, M$^+$ 208, 4%; 6.85′, M$^+$ 276, 5%, **II/III/IV**; 7.29′, M$^+$ 276, 4%, **II/III/IV**; 7.48′, M$^+$ 276, 5%, **II/III/IV**; 7.88′, M$^+$ 276, 75%, *trans*,*trans*-**9d**; 8.41′, M$^+$ 276, 4%, **II/III/IV**; after 4 h: 3.65′, M$^+$ 160, 2%; 4.33′, M$^+$ 184, 6%; 4.55′, M$^+$ 208, 24%; 6.85′, M$^+$ 276, 3%, **II/III/IV**; 7.29′, M$^+$ 276, 3%,

II/III/IV; 7.48′, M^+ 276, 3%, **II/III/IV**; 7.88′, M^+ 276, 55%, *trans*,*trans*-**9d**; 8.41′, M^+ 276, 4%, **II/III/IV**; after 8 h: 3.65′, M^+ 160, 8%; 4.33′, M^+ 184, 17%; 4.50′, M^+ 206, 4%, **26**; 4.55′, M^+ 208, 40%; 6.85′, M^+ 276, 1%, **II/III/IV**; 7.29′, M^+ 276, 1%, **II/III/IV**; 7.88′, M^+ 276, 27%, *trans*,*trans*-**9d**; 8.41′, M^+ 276, 2%, **II/III/IV**.

After complete conversion (8–10 h) of the starting material (**9a–d**) the solvent was removed in vacuum and the oily residue was chromatographed on a silica gel column using petroleum ether/diethyl ether (2–50%). The only obtained products (besides high amount of tarry material) were small quantities of stilbene derivatives (**20**, **21**) and their oxidation products phenanthrenes (**22**, **25**, and **26**), whose ratio varied depending on experimental efficiency of accomplishing anaerobic reaction conditions. In the representative example after complete conversion of the starting compound, from irradiation of 50 mg of **9a**, 20 mg of **20/25** was isolated.

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