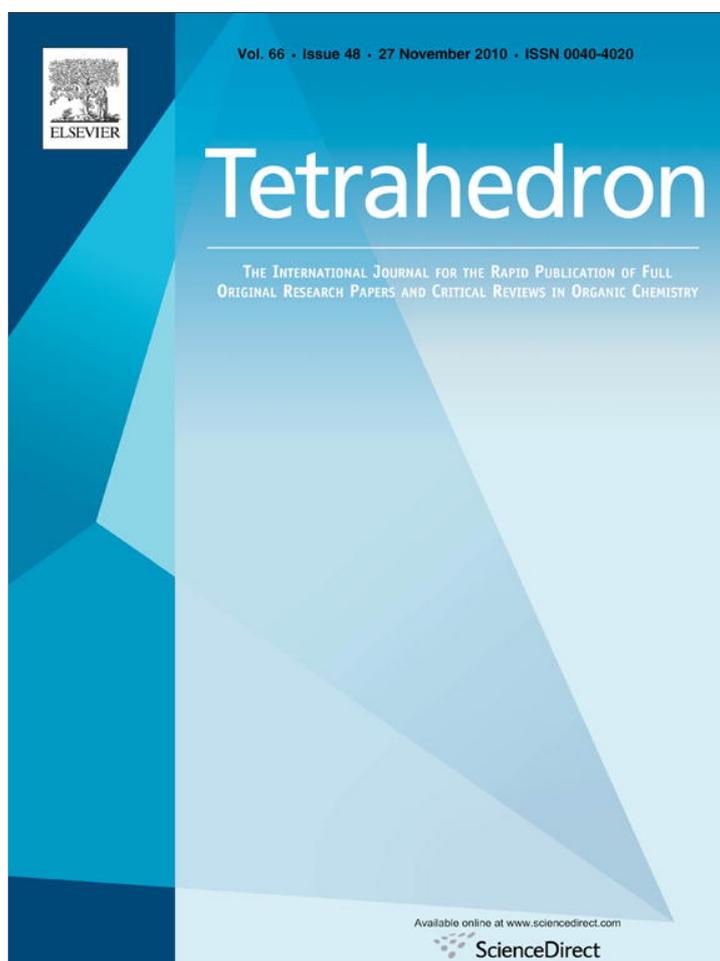


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Synthesis and phototransformations of novel styryl-substituted furo-benzobicyclo[3.2.1]octadiene derivatives

Ilijana Kikaš^a, Irena Škorić^a, Željko Marinić^b, Marija Šindler-Kulyk^{a,*}

^a Department of Organic Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10 000 Zagreb, Croatia

^b NMR Center, Rudjer Bošković Institute, Bijenička cesta 54, 10 000 Zagreb, Croatia

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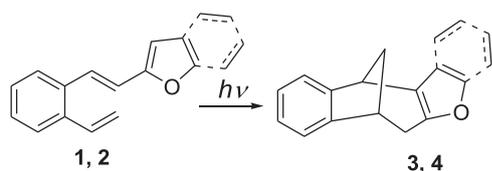
ABSTRACT

Novel *cis*- and *trans*-(*o*-H/Me/vinyl) substituted styryl furo-benzobicyclo[3.2.1]octadiene derivatives (**7a,b**, **8**) were prepared and transformed to the novel naphthofuran derivatives of benzobicyclo[3.2.1]octadiene (**6a,b**) and novel phenanthrene-benzobicyclo[3.2.1]octadiene derivative (**11**) by photochemical electrocyclic ring closure in the presence of iodine and by intramolecular photoinduced [4+2] cycloaddition, respectively. These novel annelated bicyclo[3.2.1]octadiene derivatives (**6a,b**, **11**) are especially interesting for their rigid methano-bridged junction of two aromatic units at defined geometrical arrangement and thereby as potentials for molecular clips.

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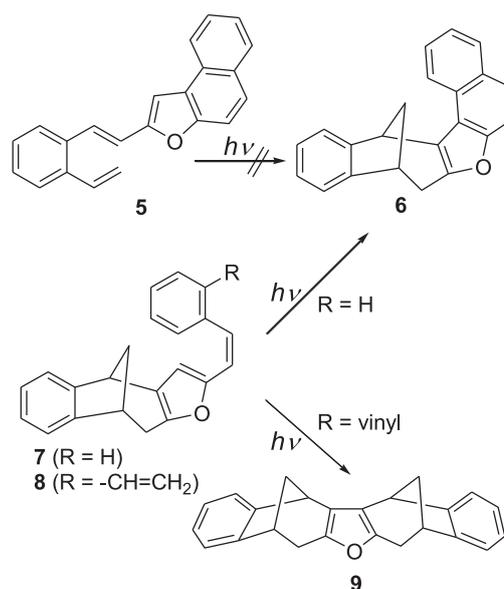
1. Introduction

Photochemical reactions are very important key steps in many syntheses of complex polycyclic compounds¹ and might in some cases shorten a total synthesis going from rather simple substrates. Thus, the *o*-vinyl substituted hetero-stilbene derivatives are convenient substrates for one-step photochemical ring closure to fused heteroaromatic benzobicyclo[3.2.1]octadienes.^{2–11} The photoreactions of furo-stilbenes have been particularly thoroughly investigated.^{2–10} Thus, irradiation of furan (**1**) and its annelated derivative, benzofuran (**2**), resulted in intramolecular cycloaddition and efficient formation of benzobicyclo[3.2.1]octadiene structures **3** and **4**, respectively, as the main photoproducts (Scheme 1).



Scheme 1.

With further annelation, naphthofuran derivative **5** gave no intramolecular cycloaddition product **6** (Scheme 2). The only products observed were traces of dimeric cyclobutane derivatives, although the irradiation has been performed under the same conditions, in diluted



Scheme 2.

* Corresponding author. Tel.: +385 1 4597242; fax: +385 1 4597250; e-mail address: marija.sindler@fkit.hr (M. Šindler-Kulyk).

solution.⁷ The intermolecular photocycloaddition was confirmed with the experiments performed in concentrated solutions.^{12,13}

Continuing our interest on the synthesis of rigid methano-bridged aromatics/heteroaromatics we turned our attention in this work to one other synthetic strategy: to synthesize the properly substituted novel styryl derivatives **7** and **8** (Scheme 2) from already available benzo-furo bicyclic structure **3** and submit them to additional photochemical transformations. Based on previous experiences with styryl furans^{2–10} and known photochemical reactions^{14–21} we visualized the synthesis of **6** by a 6π electrocyclic reaction of **7** and double bicyclic structure like **9** from the *o*-vinyl derivative **8** by intramolecular cycloaddition reaction. Both annelated bicyclo[3.2.1]octadiene derivatives, **6** and **9**, are especially interesting for their rigid methano-bridged junction of two aromatic units at defined geometrical arrangement (Figs. 1 and 2) and thereby have potential for the construction of molecular clips.²²

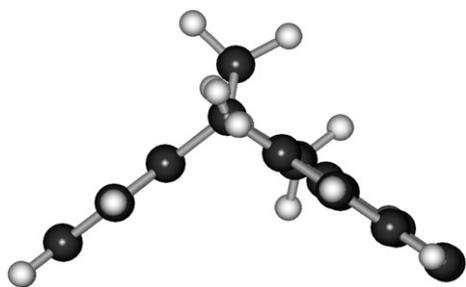


Fig. 1. Space filling model of the expected annelated photoproduct **6a**.

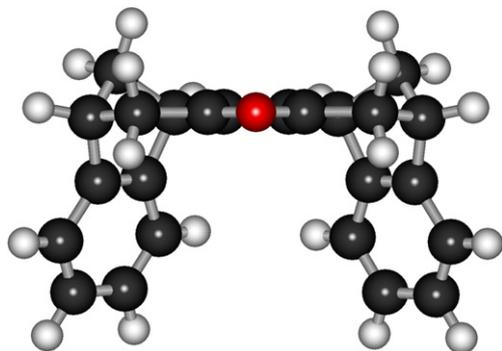


Fig. 2. Space filling model of the expected double bicyclic photoproduct **9** (one of two possible diastereoisomers).

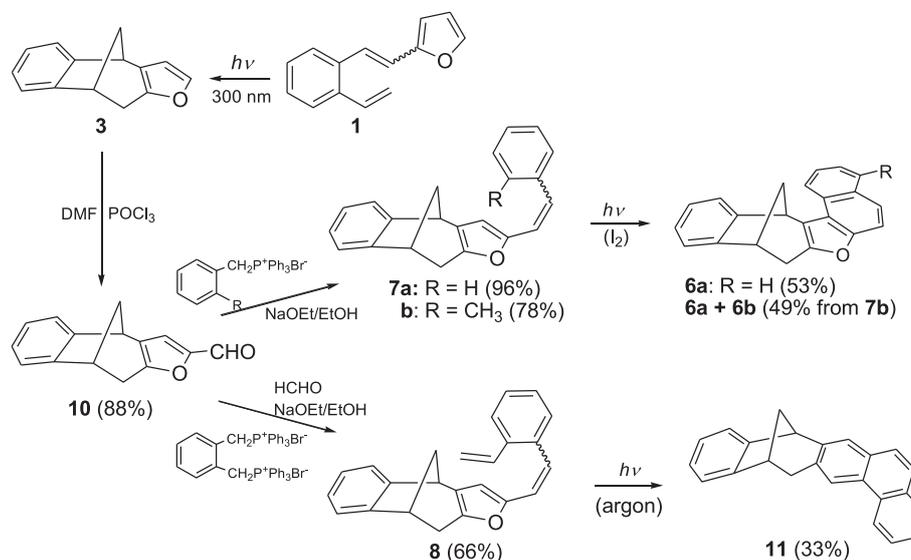
2. Results and discussion

Benzobicyclo[3.2.1]octadiene derivative **3** was obtained in one photochemical step according to the described method¹⁰ from the previously prepared β -furyl substituted *o*-divinylbenzene **1**. It is transformed via formyl derivative **10** followed by Wittig reaction with corresponding triphenylphosphonium salts to styryl derivatives **7a,b** and **8**, respectively (Scheme 3), the novel starting substrates for the further photochemical transformations.

The compounds **7a,b** and **8** were synthesized in very good yields (66–96%). All the new compounds **7a,b** and **8** were obtained as mixtures of *cis*-(12–20%) and *trans*-isomers (80–88%) that were separated by column chromatography and completely analysed and identified spectroscopically. The ratio of the isomers was determined from the NMR spectra. All the three *cis*-isomers show absorption maxima at 305–333 nm, while *trans*-isomers show bathochromic shift to the maxima at 331–338 nm. Irradiation experiments were performed with their *cis*–*trans* mixtures.

On irradiation of a 10^{-3} M benzene solution of *cis*- and *trans*-**7a**, in the presence of iodine at 300 nm, naphthofuran derivative of benzobicyclo[3.2.1]octadiene **6a** in 53% of isolated yield was obtained (Scheme 3). On irradiation of methyl derivative **7b** a mixture of two naphthofuran derivatives **6a** and **6b**, in 49% of isolated yield was found. According to ¹H NMR spectrum of the photomixture the ratio of the methyl derivative **6b** and demethylated **6a** was 3:1. The formation of both naphthofuran derivatives, **6a** and **6b**, can be explained by electrocyclic process from different conformations of *cis* configuration (*cis*-**7b**) followed by an aromatization step with concomitant loss of hydrogen and methane,^{19–22} respectively. The *o*-vinyl derivative **8**, irradiated under the anaerobic conditions at 300 nm, produced a large amount of tarry material and therefore the irradiations were performed at 350 nm. Contrary to our expectation, the irradiation of vinyl derivative **8** resulted in fused phenanthrene bicyclic derivative **11** in 33% isolated yield, besides high-molecular-weight products. A double bicyclic structure, such as **9** was not isolated. In the ¹H NMR spectrum of some enriched chromatographic fractions traces of the easily recognisable bicyclo[3.2.1]octadiene pattern has been seen but in to small quantities to be completely identified.

The photoproducts, **6a**, **6b** and **11** were isolated by column and thin-layer chromatography and characterized spectroscopically. The structure of these photoproducts was obvious from the presence of the characteristic aromatic protons of the naphthofuran and phenanthrene moieties. As it is seen in the ¹H NMR spectrum (Fig. 3b) two doublets for naphthofuran moiety of **6a** appeared between 7.9 and



Scheme 3.

8.7 ppm with characteristic aromatic coupling constants. The photoproduct **11** has in the region 8.2–8.7 ppm (Fig. 3c) singlet and doublet of H₁ and H₂, respectively, characteristic signals for inner phenanthrene protons. In the aliphatic region (Fig. 4b and c) the well resolved and recognisable six-proton-patterns of **6a** and **11**, respectively, between 2.0 and 4.8 ppm unmistakably pointed to the bicyclo[3.2.1]octadiene structure in both compounds as shown for comparison with the known bicyclic structure **3** (Fig. 4a). Moreover, proton A in **6a** (Fig. 4b) as expected is shifted to lower field in comparison with the proton A in **3** (Fig. 4a) and **11** (Fig. 4c) due to the anisotropic effect of the properly oriented naphthalene moiety.

Additionally, MS spectra were very informative. Molecular ions m/z 296 (**6a**) and m/z 310 (**6b**), two mass units lower than starting compounds **7a** and **7b**, respectively, indicated that an electrocyclization

process and loss of hydrogen molecule occurred. The byproduct in the reaction of **7b** had also molecular ion m/z 296 but as a consequence of electrocyclization process and loss of methane molecule. Molecular ion m/z 306 (**11**), 18 a mass lower than starting compound **8** together with ¹³C NMR spectrum of **11** clearly revealed that its structure does not incorporate the furan moiety.

The formation of the phenanthrene structure **11** instead of expected bicyclic **9** prompted us to synthesize the compounds **12** and **13** (Scheme 4) as model compounds of 4,5-dialkyl substituted styrylfurans that were not considered in our previous research. They resemble the compounds **7** and **8** where the methano-bridged junction on furan moiety has been replaced by two methyl substituents.

The starting compounds **12** and **13** were synthesized following the procedure described for styryl derivatives **7** and **8** (see Experimental)

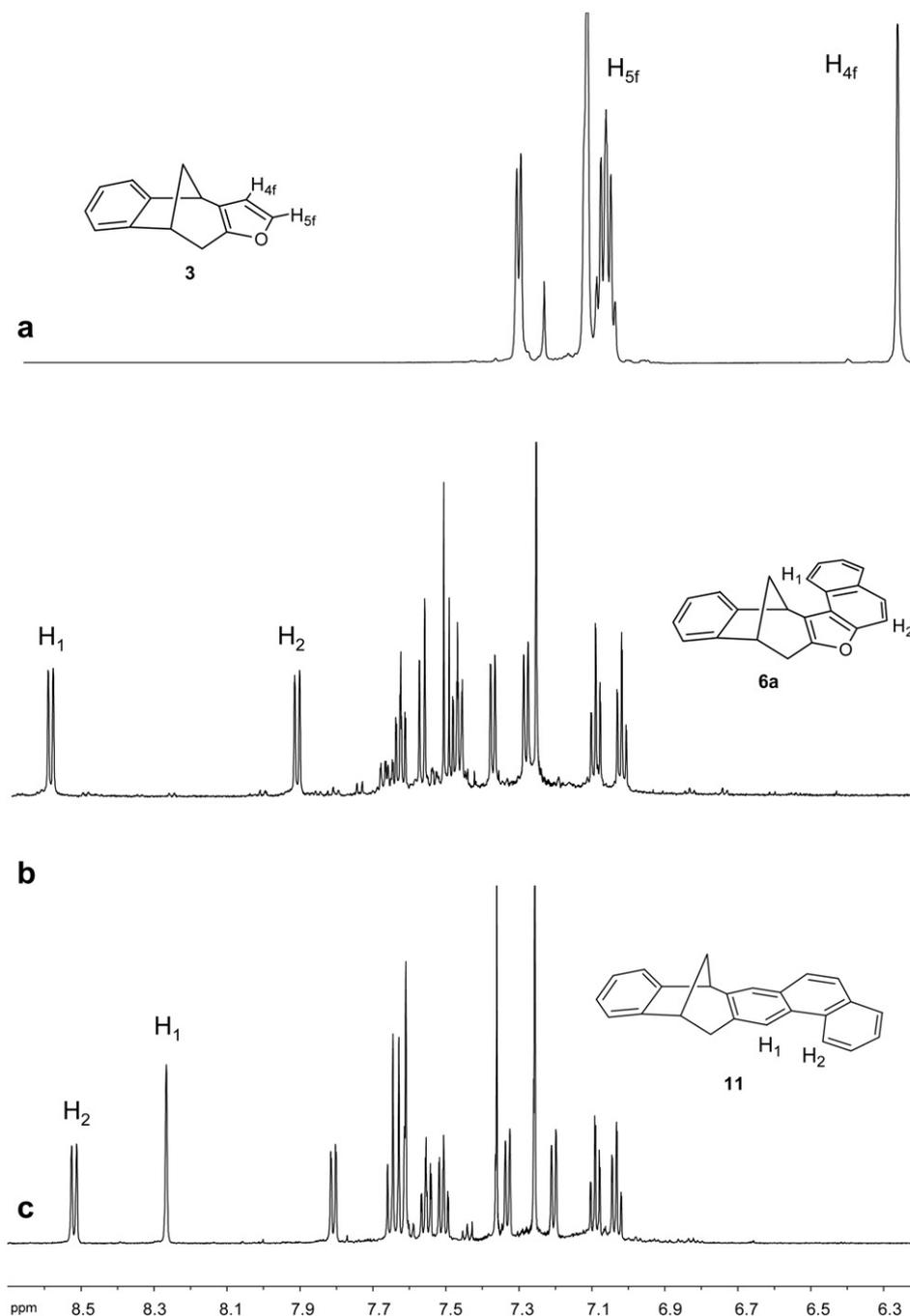


Fig. 3. Aromatic region of the ¹H NMR spectra: (a) bicyclic **3**; (b) bicyclic **6a**; (c) bicyclic **11** (CDCl₃, 300 MHz).

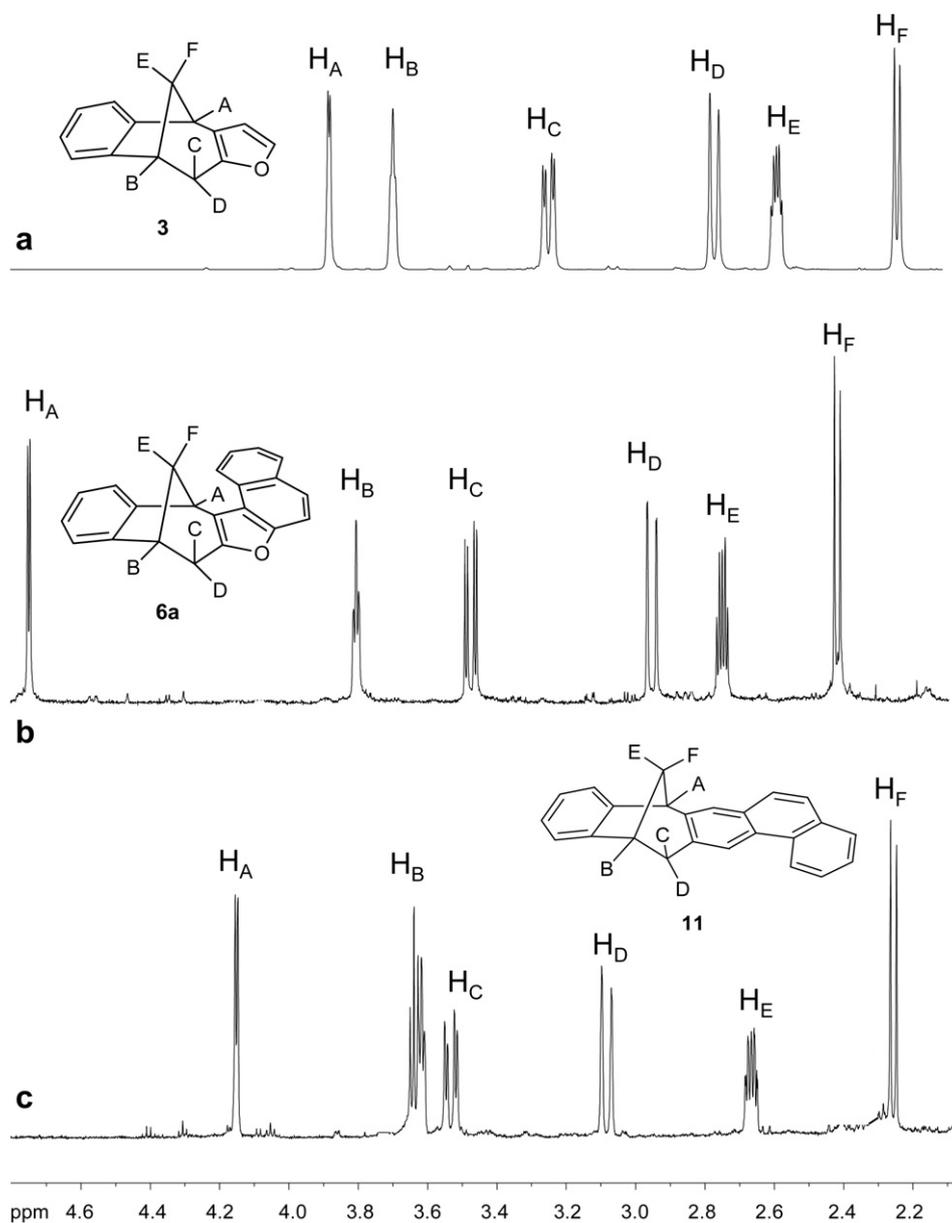
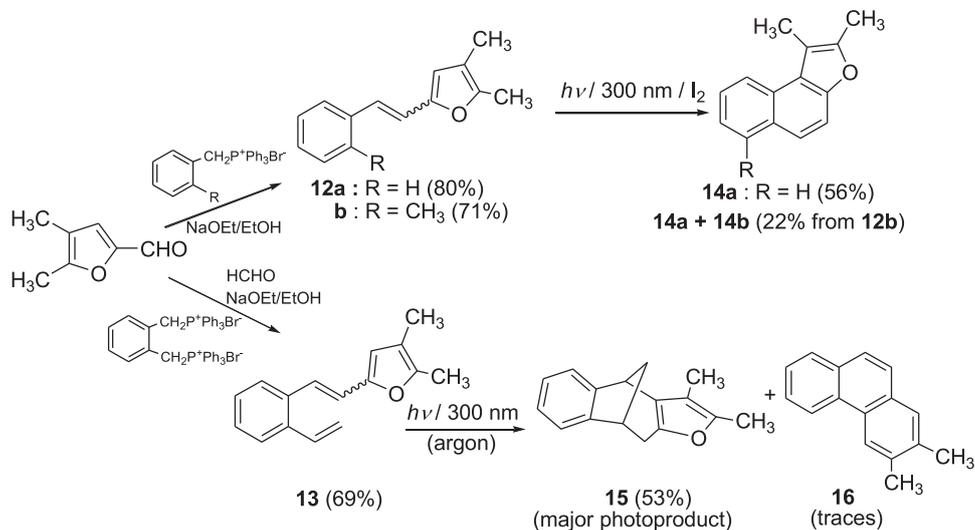


Fig. 4. Aliphatic region of the ^1H NMR spectra: (a) bicyclic **3**; (b) bicyclic **6a**; (c) bicyclic **11** (CDCl_3 , 300 MHz).



Scheme 4.

and submitted to irradiation under conditions for electrocyclic and intramolecular cycloaddition, respectively. On irradiation of 10^{-3} M benzene solution of *cis*- and *trans*-**12b**, in the presence of iodine at 300 nm, a mixture of two naphthofuran derivatives **14a** and **14b** was obtained in 22% isolated yield. Their ratio (1:2.5, respectively) was established from the ^1H NMR spectrum of the photomixture. The presence of demethylated photoproduct **14a** was confirmed on irradiation of **12a** and formation of **14a** in 56% of isolated yield. These experiments demonstrate that styryl derivatives of dimethylfurans **12** reacted in a same way as described for **7a** and **7b**. The irradiation of *o*-vinylstyryl furan derivative **13** under anaerobic conditions afforded benzobicyclo[3.2.1]octadiene derivative **15** in 33% of isolated yield, besides traces of phenanthrene derivative **16**. These results were consistent to photochemistry of our *o*-vinylstyryl furan system studied previously.^{2,6,7,9,10}

If we compare the normalized UV curves of styryl bicyclic furan derivative **8** and styryl furan derivative **13** (Fig. 5), we see the similarity in absorption maxima and habitual pattern for geometrical isomers with bathochromic shift of their absorption maxima for *trans*-isomers. Irradiation experiments of **8** and **13** isomers followed by UV spectroscopy showed that in both cases, depending on irradiation wavelength (300 or 350 nm), *cis*–*trans* or *trans*–*cis* isomerization competes with the intramolecular cycloaddition reactions. No exact conclusion could be made about various reactivity of these two compounds with the same chromophore, *o*-vinylstyryl-furan, responsible for photochemical reaction.

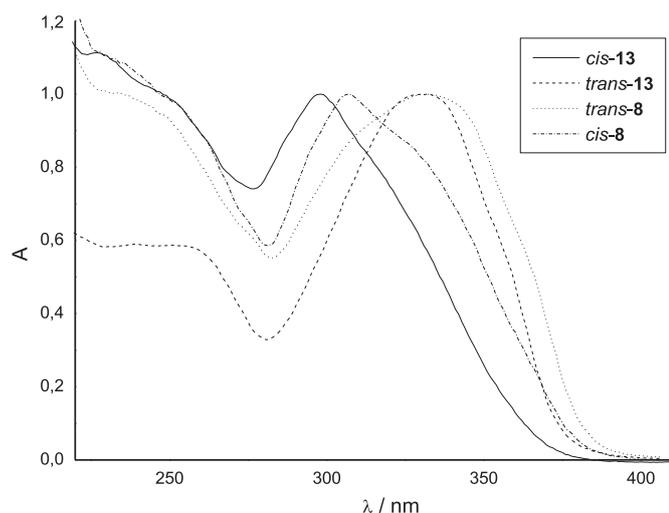
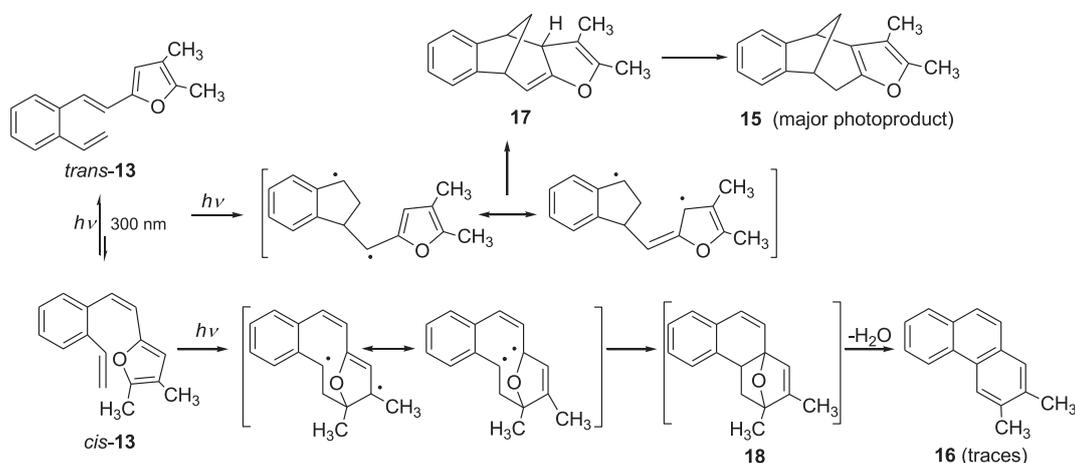


Fig. 5. Normalized UV curves of *cis*-**8**, *trans*-**8**, *cis*-**13** and *trans*-**13** in 96% EtOH.



Scheme 5.

The formation of main photoproduct benzobicyclo[3.2.1]octadiene **15** is explained (Scheme 5) from the singlet state of **13** via a 1,4-biradical followed by the preferred cyclohexene ring closure to **17** and photochemically allowed suprafacial 1,3-H shift. The byproduct 2,3-dimethylphenanthrene (**16**) can be explained by initial photoinduced [4+2] cycloaddition reaction of *cis*-**13** to the epoxy derivative **18**, which loses water during the work-up procedure and aromatizes to the final photoproduct **16**. It is not surprising that only traces of phenanthrene **16** have been found. The phenanthrene derivative **16** could be formed only from *cis* configuration of **13** in its particular conformation and this is the less favourable process.

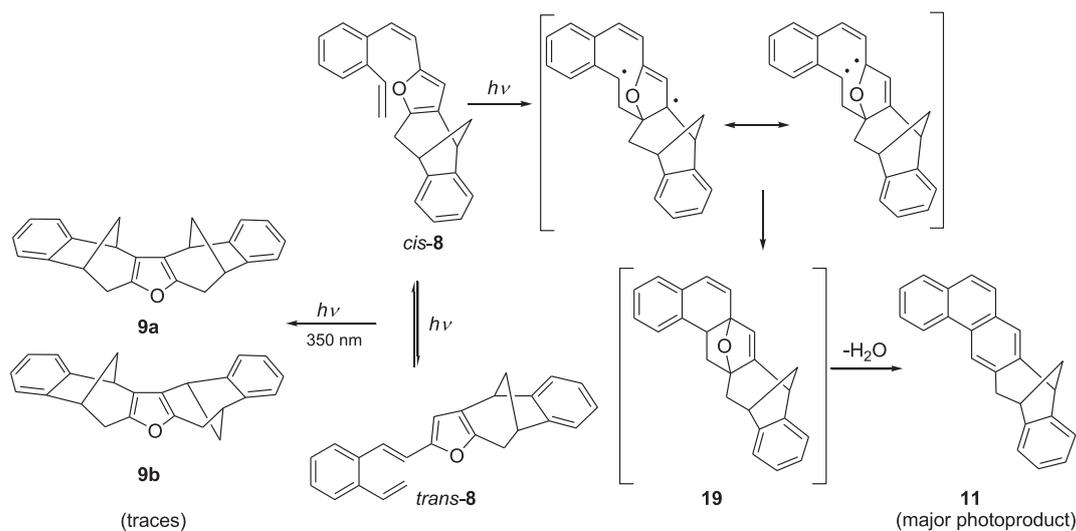
The formation of the main bicyclo-phenanthrene photoproduct **11** is explained (Scheme 6) by the same mechanism as described for phenanthrene **16**. After excitation and initial photoinduced 1,4-biradical formation the epoxy derivative **19** is formed, which loses water during the work-up procedure and aromatizes to the final photoproduct **11**. Formation of phenanthrene derivative **11** by thermal intramolecular Diels–Alder reaction of the vinyl group and the furan moiety of the *cis*-**8** is ruled out. Namely, no products were obtained in a tube that was kept in the dark during irradiation experiments.

The initial intramolecular [2+2]-photocycloaddition leading to double bicyclic structures **9** is apparently a less favourable process. The initial [4+2]-photocycloaddition leading to **11** is a dominant process. This unique behaviour of the *o*-vinylstyryl furan derivative in the last case is ascribed to conformational changes (Scheme 7). We assume that due to the π – π intramolecular interaction the *cis*-**8** is forced to reside in conformation **A** from which the fast ring closure to the epoxy derivative **19** is afforded. In case of dimethylfuran derivative **13** no additional intramolecular forces are operating and the ring closure from other most populated conformations of either *trans* or *cis* configuration is possible leading to bicyclic structure **15**.

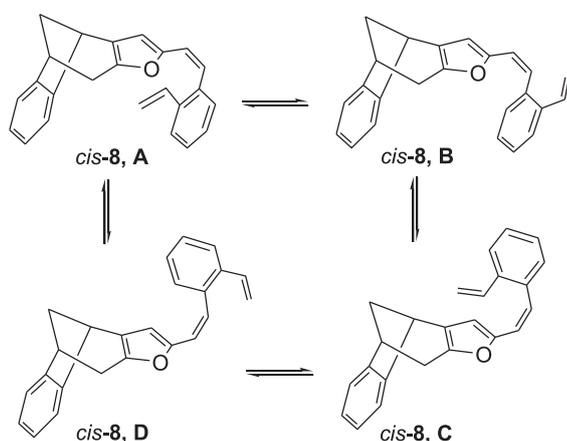
In an effort to prepare the double bicyclic photoproducts **9** we applied the new strategy: irradiation of 2,5-bis(*o*-vinylstyryl)furan **20** (Scheme 8). The starting compound **20** was prepared via formyl derivative **21** and subsequent Wittig reaction with diphosphonium salt and formaldehyde (see Experimental). Irradiation of the mixture of isomers afforded only photoisomerization to *trans,trans*-**20** and on continuing irradiation polymerization. No double bicyclic photoproducts **9** were formed.

3. Conclusion

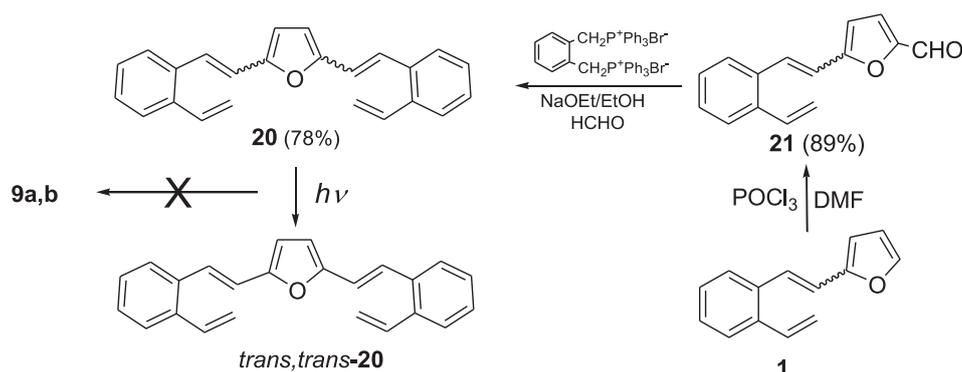
In summary, we have demonstrated that the naphthofuran-benzobicyclo derivative **6** can be efficiently synthesized by photoelectrocyclization of styryl benzobicyclo-furan derivative **7** and fused phenanthrene derivative **11** by photocycloaddition reaction of *o*-vinylstyryl derivative **8**. Both types of annelated bicyclo[3.2.1]



Scheme 6.



Scheme 7.



Scheme 8.

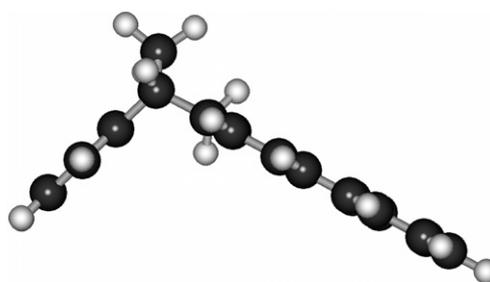


Fig. 6. Space filling model of benzobicyclo-phenanthrene 11.

reference. The assignment of the signals is based on 2D-CH correlation and 2D-H-H-COSY experiments. UV spectra were measured on a Varian Cary 50 UV/vis Spectrophotometer. Mass spectra were obtained on a Varian Saturn 2200 equipped with FactorFour Capillary Column VF-5ms. Melting points were obtained using an

octadiene derivatives, **6** (Fig. 1) and **11** (Fig. 6), are interesting for their rigid methano-bridged junction of two aromatic units.

4. Experimental

4.1. General

The 1H and ^{13}C NMR spectra were recorded on a Bruker AV-600 Spectrometer at 300 or 600 and at 75 or 150 MHz, respectively. All NMR spectra were measured in $CDCl_3$ using tetramethylsilane as

Original Kofler Mikroheitztisch apparatus (Reichert, Wien) and are uncorrected. All the novel compounds were identified and proved by GC-MS system. The GC-MS analysis was performed on a Varian CP-3800 Gas Chromatograph-Varian Saturn 2200 equipped with FactorFour Capillary Column VF-5ms, 30 m \times 0.25 mm ID; GC operating conditions for all experiments: column temperature programmed from 110 $^{\circ}C$ to 300 $^{\circ}C$ (6 min isothermal) at a rate of 33 $^{\circ}C$ min $^{-1}$; carrier gas: helium; flow rate: 1 mL min $^{-1}$; injector temperature: 300 $^{\circ}C$; volume injected: 5 μ L. IR spectra were recorded on Perkin-Elmer Spectrum One. Elemental analyses were

carried out on Perkin–Elmer, Series II, CHNS Analyzer 2400. High-resolution mass spectra (HRMS) were obtained on a matrix-assisted laser desorption/ionization–time-of-flight MALDI-TOF/TOF mass spectrometer (4800 Plus MALDI-TOF/TOF analyzer, Applied Biosystems Inc., Foster City, CA, USA) equipped with Nd:YAG laser operating at 355 nm with firing rate 200 Hz in the positive ion reflector mode. 1600 shots per spectrum was taken with mass range 100–1000 Da, focus mass 500 Da and delay time 100 ns. Nicotinamide and azithromycin were used for external mass calibration in positive ion mode. Each spectrum was internally calibrated, providing measured mass accuracy within 5 ppm of theoretical mass. All preparative irradiation experiments were carried out in 10^{-3} M solutions in a Quartz tube or in Pyrex vessels and in a Rayonet reactor equipped with RPR 3000 Å and RPR 3500 Å lamps. Silica gel (Merck 0.063–0.2 mm) and aluminium oxide 90 (Merck 0.063–0.2 mm) were used for chromatographic purifications. Thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60 F₂₅₄ and on Merck Al₂O₃ neutral 1.5 mm 60 F₂₅₄ plates. Solvents were purified by distillation.

Furan-2-carboxaldehyde was obtained from a commercial source (Aldrich). The corresponding aryltriphenylphosphonium salts (*o*-tolyl- and benzyltriphenylphosphonium bromides) and α,α' -*o*-xylyl(ditriphenylphosphonium)bromide were synthesized from the corresponding bromides and triphenylphosphine. Compounds **1** and **3** were prepared in our laboratory and published before.¹⁰

4.1.1. Preparation of 5-oxatetracyclo[6.6.1.0^{2,6}.0^{9,14}]pentadeca-2(6),3,9,11,13-pentaene-4-carbaldehyde (10). To the compound **3** (0.29 g, 1.5 mmol) in dry *N,N*-dimethylformamide (1 mL, 0.013 mol) at 12 °C phosphorus oxychloride (0.25 g, 1.6 mmol) was added and stirred for 15 min. The reaction mixture was allowed gradually to warm up to room temperature, stirred for 1 day, worked up with 10% NaOH (2 mL) solution and the product extracted with diethyl ether (60 mL). The diethyl ether extracts were washed with water and then dried with MgSO₄. After column chromatography on silica gel using petroleum ether/diethyl ether (0–5%) as eluent the product **10** was isolated in 88% (0.30 g) yield.

4.1.2. 5-Oxatetracyclo[6.6.1.0^{2,6}.0^{9,14}]pentadeca-2(6),3,9,11,13-pentaene-4-carbaldehyde (10). *R_f* 0.23 (petroleum ether/diethyl ether 20:1); yellow solid; mp 135 °C; UV (EtOH) λ_{\max} ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 308 (16,794) nm; IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1666 (C=O), 1504 (C=C); ¹H NMR (CDCl₃, 300 MHz) δ_{H} 9.41 (s, 1H, CHO), 7.32 (dd, *J*=7.2, *J*=1.4 Hz, 1H, H-ar), 7.16–7.08 (m, 4H, 3H-ar, H-f), 3.91 (d, *J*_{AE}=4.4 Hz, 1H, H-A), 3.66 (dt, *J*_{BC,BE}=4.9 Hz, *J*_{BD}=0.5 Hz, 1H, H-B), 3.20 (dd, *J*_{CD}=17.8 Hz, *J*_{BC}=4.9 Hz, 1H, H-C), 2.72 (dd, *J*_{CD}=17.8 Hz, *J*_{BD}=0.5 Hz, 1H, H-D), 2.48 (ddd, *J*_{EF}=10.7 Hz, *J*_{BE}=4.9 Hz, *J*_{AE}=4.4 Hz, 1H, H-E), 2.4 (d, *J*_{EF}=10.7 Hz, 1H, H-F); ¹³C NMR (CDCl₃, 75 Hz) δ_{C} 176.6 (d), 156.0 (s), 151.3 (s), 150.6 (s), 144.1 (s), 128.5 (s), 126.9 (d), 126.9 (d), 124.1 (d), 121.0 (2×d), 42.5 (t), 39.6 (d), 39.1 (d), 31.4 (t); MS *m/z* (EI) 224 (M⁺, 100%), 167 (23), 115 (10). Anal. Calcd for C₁₅H₁₂O₂: C, 80.34; H, 5.39. Found: C, 80.41; H, 5.42.

4.1.3. Preparation of 4-(2-phenylethenyl)-5-oxatetracyclo[6.6.1.0^{2,6}.0^{9,14}]pentadeca-2(6),3,9,11,13-pentaene (7a) and 4-[2-(2-methylphenyl)ethenyl]-5-oxatetracyclo[6.6.1.0^{2,6}.0^{9,14}]pentadeca-2(6),3,9,11,13-pentaene (7b). To the stirred solutions of the formyl derivative **10** (0.1 g, 0.4 mmol) and the corresponding aryltriphenylphosphonium salts (0.5 mmol) in abs ethanol (30 mL) a solution of sodium ethoxide (0.01 g, 0.5 mmol in 5 mL abs ethanol) was added dropwise. Stirring was continued for 2 h at rt. After removal of the solvent, water (15 mL) was added to the residue, extracted with benzene (45 mL) and the benzene extracts dried with MgSO₄. The crude reaction mixture was purified and the mixtures of *cis*- and *trans*-isomers of the products **7a** and **7b** were separated by column chromatography on silica gel using

petroleum ether and petroleum ether/diethyl ether (0–5%) mixtures as eluent. The product **7a** was isolated in 96% (0.11 g) yield (*cis/trans*=1:7, according to ¹H NMR), and the product **7b** in 78% (0.10 g) yield (*cis/trans*=1:4, according to ¹H NMR).

Compound *cis*-**7a**: *R_f* 0.71 (petroleum ether/diethyl ether 10:1); colourless oil; UV (EtOH) λ_{\max} ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 333 (9825) nm; IR (evaporated film from diethyl ether) $\nu_{\max}/\text{cm}^{-1}$: 2916, 2846, 1737, 1457, 1258, 949, 750; ¹H NMR (CDCl₃, 600 MHz) δ_{H} 7.44 (dd, *J*=7.8, 0.9 Hz, 2H, H-ar), 7.32–7.28 (m, 3H, H-ar), 7.25–7.22 (m, 1H, H-ar), 7.09–7.02 (m, 3H, H-ar), 6.27 (d, *J*=12.7 Hz, 1H, H-et), 6.20 (d, *J*=12.7 Hz, 1H, H-et), 6.14 (s, 1H, H-f), 3.72 (d, *J*_{AE}=4.3 Hz, 1H, H-A), 3.58 (dt, *J*_{BE,BC}=5.0, *J*_{BD}=1.3 Hz, 1H, H-B), 3.09 (dd, *J*_{CD}=16.7, *J*_{BC}=5.0 Hz, 1H, H-C), 2.58 (dd, *J*_{CD}=16.7, *J*_{BD}=1.3 Hz, 1H, H-D), 2.40 (ddd, *J*_{EF}=10.5, *J*_{BE}=5.0, *J*_{AE}=4.3 Hz, 1H, H-E), 2.02 (d, *J*_{EF}=10.5 Hz, 1H, H-F); ¹³C NMR (CDCl₃, 75 MHz) δ_{C} 129.1 (d), 128.8 (d), 128.6 (d), 128.3 (d), 128.0 (d), 126.5 (d), 126.2 (d), 125.6 (d), 123.8 (d), 120.6 (d), 118.2 (d), 108.6 (d), 42.8 (t), 40.2 (d), 39.2 (d), 30.9 (t), singlets are not seen due to small quantities; MS *m/z* (EI) 298 (M⁺, 100%).

Compound *trans*-**7a**: *R_f* 0.80 (petroleum ether/diethyl ether 10:1); colourless solid; mp 157 °C; UV (EtOH) λ_{\max} ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 337 (14,366), 350 (sh, 13,395) nm; IR (evaporated film from diethyl ether) $\nu_{\max}/\text{cm}^{-1}$: 2901, 2822, 1730, 1457, 1258, 948, 750; ¹H NMR (CDCl₃, 600 MHz) δ_{H} 7.38 (dd, *J*=7.6, 1.0 Hz, 2H, H-ar), 7.32 (d, *J*=7.4 Hz, 1H, H-ar), 7.29 (t, *J*=7.6 Hz, 2H, H-ar), 7.18 (dt, *J*=7.6, 1.0 Hz, 1H, H-ar), 7.13 (d, *J*=7.4 Hz, 1H, H-ar), 7.08 (dt, *J*=7.4, 1.3 Hz, 1H, H-ar), 7.06 (dt, *J*=7.4, 1.3 Hz, 1H, H-ar), 6.84 (d, *J*=16.2 Hz, 1H, H-et), 6.74 (d, *J*=16.2 Hz, 1H, H-et), 6.22 (s, 1H, H-f), 3.81 (d, *J*_{AE}=4.3 Hz, 1H, H-A), 3.63 (dt, *J*_{BE,BC}=5.1, *J*_{BD}=1.2 Hz, 1H, H-B), 3.19 (dd, *J*_{CD}=16.8, *J*_{BC}=5.1 Hz, 1H, H-C), 2.67 (dd, *J*_{CD}=16.8, *J*_{BD}=1.2 Hz, 1H, H-D), 2.44 (ddd, *J*_{EF}=10.4, *J*_{BE}=5.1, *J*_{AE}=4.3 Hz, 1H, H-E), 2.07 (d, *J*_{EF}=10.4 Hz, 1H, H-F); ¹³C NMR (CDCl₃, 75 MHz) δ_{C} 151.6 (s), 151.2 (s), 147.3 (s), 144.8 (s), 137.4 (s), 128.6 (2×d), 127.2 (d), 127.0 (s), 126.6 (d), 126.3 (d), 126.1 (2×d), 125.1 (d), 123.9 (d), 120.6 (d), 116.7 (d), 107.8 (d), 42.9 (t), 40.2 (d), 39.3 (d), 31.1 (t); MS *m/z* (EI) 298 (M⁺, 100%), 255 (10). Anal. Calcd (for the mixture of geometrical isomers of **7a**) for C₂₂H₁₈O: C, 88.56; H, 6.08. Found: C, 88.45; H 5.88.

Compound *cis*-**7b**: *R_f* 0.64 (petroleum ether/diethyl ether 10:0.5); colourless oil; UV (EtOH) λ_{\max} ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 305 (4534) nm; IR (evaporated film from diethyl ether) $\nu_{\max}/\text{cm}^{-1}$: 3013, 2924, 2852, 1598, 1460, 956, 749; ¹H NMR (CDCl₃, 300 MHz) δ_{H} 7.34 (d, *J*=6.9 Hz, 1H, H-ar), 7.30–7.01 (m, 7H, H-ar), 6.32 (d, *J*=12.5 Hz, 1H, H-et), 6.29 (d, 1H, *J*=12.5 Hz, H-et), 5.79 (s, 1H, H-f), 3.65 (d, 1H, *J*_{AE}=4.2 Hz, H-A), 3.56 (dt, 1H, *J*_{BE,BC}=5.0, *J*_{BD}=1.3 Hz, H-B), 3.06 (dd, 1H, *J*_{CD}=16.8, *J*_{BC}=5.0 Hz, H-C), 2.54 (dd, 1H, *J*_{CD}=16.8, *J*_{BD}=1.3 Hz, H-D), 2.32–2.40 (ddd, 1H, *J*_{EF}=10.4, *J*_{BE}=5.0 Hz, *J*_{AE}=4.2 Hz, H-E), 2.22 (s, 3H, CH₃), 1.98 (d, 1H, *J*_{EF}=10.4 Hz, H-F); ¹³C NMR (CDCl₃, 150 Hz) δ_{C} 151.1 (s), 144.3 (s), 129.4 (d), 128.2 (d), 126.7 (d), 126.0 (s), 125.9 (d), 125.6 (d), 125.0 (d), 124.6 (d), 123.6 (d), 120.1 (d), 118.7 (d), 107.1 (d), 42.3 (t), 39.7 (d), 38.7 (d), 30.4 (t), 19.3 (q), singlets are not seen due to small quantities; MS *m/z* (EI) 312 (M⁺, 100%), 269 (10), 115 (5).

Compound *trans*-**7b**: *R_f* 0.71 (petroleum ether/diethyl ether 10:0.5); colourless solid; mp 165 °C; UV (EtOH) λ_{\max} ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 338 (13,869) nm; IR (evaporated film from diethyl ether) $\nu_{\max}/\text{cm}^{-1}$: 3016, 2943, 1597, 1460, 954, 750; ¹H NMR (CDCl₃, 300 MHz) δ_{H} 7.46 (d, *J*=6.9 Hz, 1H, H-ar), 7.33 (dd, *J*=6.1, 2.0 Hz, 1H, H-ar), 7.20–7.01 (m, 7H, H-ar), 7.05 (d, *J*=16.0 Hz, 1H, H-et), 6.65 (d, *J*=16.0 Hz, 1H, H-et), 6.22 (s, 1H, H-f), 3.81 (d, *J*_{AE}=4.26 Hz, 1H, H-A), 3.64 (dt, *J*_{BE,BC}=5.0, *J*_{BD}=1.2 Hz, 1H, H-B), 3.20 (dd, *J*_{CD}=16.9, *J*_{BC}=5.0 Hz, 1H, H-C), 2.68 (dd, *J*_{CD}=16.9, *J*_{BD}=1.2 Hz, 1H, H-D), 2.40–2.48 (ddd, *J*_{EF}=10.4, *J*_{BE}=5.0, *J*_{AE}=4.26 Hz, 1H, H-E), 2.37 (s, 3H, CH₃), 2.08 (d, *J*_{FE}=10.4 Hz, 1H, H-F); ¹³C NMR (CDCl₃, 150 Hz) δ_{C} 151.1 (s), 151.0 (s), 146.7 (s), 144.3 (s), 135.8 (s), 135.1 (s), 129.9 (d), 126.6 (d), 126.4 (s), 126.0 (d), 125.8 (d), 125.6 (d), 124.2 (d), 123.4 (d), 122.3 (d), 120.1 (d), 117.3 (d), 107.2 (d), 42.3 (t), 39.7 (d), 38.8

(d), 30.6 (t), 19.5 (q); MS m/z (EI) 312 (M^+ , 100%), 269 (10), 115 (5). Anal. Calcd (for the mixture of geometrical isomers of **7b**) for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found: C, 88.59; H 6.29.

4.1.4. Irradiation experiments. Preparation of 13-oxahexacyclo[14.6.1.0^{2,14}.0^{3,12}.0^{4,9}.0^{17,22}]-tricoso-2(14),3(12),4,6,8,10,17,19,21-nonaene (6a) and 8-methyl-13-oxahexacyclo[14.6.1.0^{2,14}.0^{3,12}.0^{4,9}.0^{17,22}]-tricoso-2(14),3(12),4,6,8,10,17,19,21-nonaene (6b). To a mixture of *cis*- and *trans*-isomers of **7a** or **7b** in benzene (**7a**: 3.4×10^{-3} M; **7b**: 4.7×10^{-3} M) a small quantity (5 mg) of iodine was added. A solution was irradiated at 300 nm in a Rayonet reactor in a Quartz tube. Irradiation time varied depending on the starting compound (for compound **7a** it was 15 h and for **7b**, 10 h). After irradiation of compounds **7a** or **7b** the solvent was removed in vacuo and the oily residue chromatographed on silica gel column using petroleum ether as eluent. While the irradiation of **7a** resulted with only one photoproduct **6a** (in 53% yield, 0.01 g), the irradiation of derivative **7b** resulted in a formation of two photoproducts **6a** and **6b** in the ratio of 1:3 (0.01 g, 49% of isolated yield was found). In the last case, the main photoproduct **6b** was isolated from the photomixture by thin-layer chromatography using petroleum ether as eluent.

Compound **6a**: R_f 0.17 (petroleum ether/diethyl ether 10:1); colourless oil; UV (EtOH) λ_{max} ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 305 (5581), 316 (5606), 331 (5338) nm; IR (evaporated film from diethyl ether) ν_{max}/cm^{-1} : 3062, 2930, 1769, 1678, 1467, 1349, 1272, 1118, 798, 752; 1H NMR ($CDCl_3$, 600 MHz) δ_H 8.61 (d, $J=8.2$ Hz, 1H, H-ar), 7.92 (d, $J=8.2$ Hz, 1H, H-ar), 7.63 (dt, $J=7.5, 1.3$ Hz, 1H, H-ar), 7.57 (d, $J=8.9$ Hz, 1H, H-ar), 7.50 (d, $J=8.9$ Hz, 1H, H-ar), 7.48 (dt, $J=7.5, 1.3$ Hz, 1H, H-ar), 7.38 (d, $J=7.3$ Hz, 1H, H-ar), 7.29 (d, $J=7.3$ Hz, 1H, H-ar), 7.09 (dt, $J=7.5, 1.1$ Hz, 1H, H-ar), 7.02 (dt, $J=7.5, 1.1$ Hz, 1H, H-ar), 4.76 (d, $J_{AE}=4.5$ Hz, 1H, H-A), 3.76 (dt, $J_{BC, BE}=5.0, J_{BD}=1.3$ Hz, 1H, H-B), 3.41 (dd, $J_{CD}=16.7, J_{BC}=5.0$ Hz, 1H, H-C), 2.85 (dd, $J_{CD}=16.7, J_{BD}=1.3$ Hz, 1H, H-D), 2.65 (ddd, $J_{EF}=10.4, J_{BE}=5.0, J_{AE}=4.5$ Hz, 1H, H-E), 2.29 (d, $J_{EF}=10.4$ Hz, 1H, H-F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 151.5 (s), 151.3 (s), 149.4 (s), 144.6 (s), 130.6 (s), 129.0 (d), 128.2 (s), 126.6 (d), 126.4 (d), 125.9 (d), 124.0 (d), 123.9 (d), 123.6 (d), 123.1 (d), 122.0 (s), 120.8 (d), 120.4 (s), 112.4 (d), 42.9 (t), 39.8 (d), 39.6 (d), 31.5 (t); MS m/z (EI) 296 (M^+ , 100%). Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.45; H 5.29.

Compound **6b**: R_f 0.15 (petroleum ether); colourless oil; UV (EtOH) λ_{max} ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 307 (3058), 320 (3017), 334 (3153) nm; IR (evaporated film from diethyl ether) ν_{max}/cm^{-1} : 3062, 2930, 1769, 1678, 1467, 1349, 1272, 1118, 798, 752; 1H NMR ($CDCl_3$, 300 MHz) δ_H 8.53 (d, $J=8.2$ Hz, 1H, H-ar), 7.77 (d, $J=9.2$ Hz, 1H, H-ar), 7.59–7.52 (m, 2H, H-ar), 7.42–7.30 (m, 3H, H-ar), 7.11 (dt, $J=7.5, 1.2$ Hz, 1H, H-ar), 7.03 (dt, $J=7.5, 1.2$ Hz, 1H, H-ar) 4.79 (d, $J_{AE}=4.5$ Hz, 1H, H-A), 3.77 (dt, $J_{BC, BE}=5.0, J_{BD}=1.1$ Hz, 1H, H-B), 3.43 (dd, $J_{CD}=16.9, J_{BC}=5.0$ Hz, 1H, H-C), 2.87 (dd, $J_{CD}=16.9, J_{BD}=1.1$ Hz, 1H, H-D), 2.76 (s, 3H, CH₃), 2.66 (ddd, $J_{EF}=10.5, J_{BE}=5.0, J_{AE}=4.5$ Hz, 1H, H-E), 2.31 (d, $J_{EF}=10.5$ Hz, 1H, H-F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 126.6 (d), 126.4 (d), 125.6 (d), 125.0 (d), 124.0 (d), 121.5 (d), 120.8 (d), 119.6 (d), 111.9 (d), 42.9 (t), 39.8 (d), 39.6 (d), 31.5 (t), 20.2 (q), singlets are not seen due to small quantities; MS m/z (EI) 310 (M^+ , 100%). Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.85; H 5.58.

4.1.5. Preparation of *cis*- and *trans*-isomers of 4-[2-(2-vinylphenyl)ethenyl]-5-oxatetrayclo[6.6.1.0^{2,6}.0^{9,14}]pentadeca-2(6),3,9,11,13-pentaene (8) and 2,3-dimethyl-5-[2-(2-vinylphenyl)ethenyl]furan (13). To a stirred solution of α, α' -*o*-xylyl(ditriphenylphosphonium) bromide (3.94 g, 5.00 mmol), and the corresponding aldehydes (**10**: 5.50 mmol (1.20 g) and 4,5-dimethyl-furan-2-carbaldehyde: 5.50 mmol (0.68 g)) in abs ethanol (100 mL) a solution of sodium ethoxide (0.63 g, 2.75 mmol in 10 mL ethanol) was added dropwise. Under a stream of nitrogen gaseous formaldehyde (obtained by the decomposition of an excess of paraformaldehyde) was introduced and an additional quantity of sodium ethoxide (2.75 mmol) was added. After removal of the solvent, the residue was worked up

with water and benzene. The benzene extract was dried and concentrated. The crude reaction mixtures were purified and products were isolated in 66% (1.10 g) yield for compound **8** (*cis/trans*=1:5, according to 1H NMR) and 69% (0.77 g) yield for **13** (*cis/trans*=1:3, according to 1H NMR). The mixtures of *cis*- and *trans*-isomers were separated by TLC or column chromatography on aluminium oxide using petroleum ether as eluent.

Compound *cis*-**8**: R_f 0.66 (petroleum ether/diethyl ether 10:1); yellow oil; UV (EtOH) λ_{max} ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 307 (8916) nm; IR (evaporated film from diethyl ether) ν_{max}/cm^{-1} : 3020, 2950, 1593, 1468, 1003, 957, 752; 1H NMR ($CDCl_3$, 300 MHz) δ_H 7.57 (d, $J=7.7$ Hz, 1H, H-ar), 7.32 (dd, $J=7.7, 1.2$ Hz, 1H, H-ar), 7.28 (dt, $J=7.6, 1.2$ Hz, 1H, H-ar), 7.27 (d, $J=7.3$ Hz, 1H, H-ar), 7.22 (dt, $J=7.6, 1.2$ Hz, 1H, H-ar), 7.05 (dt, $J=4.7, 1.2$ Hz, 1H, H-ar), 7.07–7.00 (m, 2H, H-ar), 6.84 (dd, $J_{1,3}=17.5, J_{2,3}=11.0$ Hz, 1H, H-3), 6.35 (AB_q, 2H, H-et), 5.79 (s, 1H, H-f), 5.64 (dd, $J_{1,3}=17.5, J_{1,2}=1.0$ Hz, 1H, H-1), 5.18 (dd, $J_{2,3}=11.0, J_{1,2}=1.0$ Hz, 1H, H-2), 3.64 (d, $J_{AE}=4.3$ Hz, 1H, H-A), 3.55 (dt, $J_{BC, BE}=5.2, J_{BD}=1.2$ Hz, 1H, H-B), 3.05 (dd, $J_{CD}=16.8, J_{BC}=5.2$ Hz, 1H, H-C), 2.53 (d, $J_{CD}=16.8$ Hz, 1H, H-D), 2.53 (ddd, $J_{AE}=4.3, J_{BE}=5.2, J_{EF}=10.1$ Hz, 1H, H-E), 1.97 (d, $J_{EF}=10.3$ Hz, 1H, H-F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 151.9 (s), 150.4 (s), 146.7 (s), 145.1 (s), 136.9 (s), 136.2 (s), 135.3 (d), 129.7 (d), 128.9 (s), 127.8 (d), 127.8 (d), 126.8 (d), 126.5 (d), 125.6 (d), 124.8 (d), 124.1 (d), 121.0 (d), 120.2 (d), 115.4 (t), 108.5 (d), 43.2 (t), 40.5 (d), 39.5 (d), 31.1 (t); MS m/z (EI) 324 (M^+ , 100%), 209 (15), 115 (9).

Compound *trans*-**8**: R_f 0.74 (petroleum ether/diethyl ether 10:1); yellow oil; UV (EtOH) λ_{max} ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 332 (13,689) nm; IR (evaporated film from diethyl ether) ν_{max}/cm^{-1} : 3060, 2952, 1624, 1468, 1003, 957, 752; 1H NMR ($CDCl_3$, 300 MHz) δ_H 7.44–7.41 (m, 2H, H-ar), 7.32 (d, $J=7.3$ Hz, 1H, H-ar), 7.23–7.18 (m, 2H, H-ar), 7.12 (d, $J=16.0$ Hz, 1H, H-et), 7.12 (d, $J=7.3$ Hz, 1H, H-ar), 7.10–7.06 (m, 1H, H-ar), 7.05 (dd, $J_{1,3}=17.4, J_{2,3}=11.0$ Hz, 1H, H-3), 6.63 (d, $J=16.0$ Hz, 1H, H-et), 6.22 (s, 1H, H-f), 5.60 (dd, $J_{1,3}=17.4, J_{1,2}=1.3$ Hz, 1H, H-1), 5.31 (dd, $J_{2,3}=11.0, J_{1,2}=1.3$ Hz, 1H, H-2), 3.81 (d, $J_{AE}=4.3$ Hz, 1H, H-A), 3.63 (dt, $J_{BC, BE}=5.1, J_{BD}=1.3$ Hz, 1H, H-B), 3.19 (dd, $J_{CD}=16.9, J_{BC}=5.1$ Hz, 1H, H-C), 2.68 (d, $J_{CD}=16.9$ Hz, 1H, H-D), 2.43 (ddd, $J_{AE}=4.3, J_{BE}=5.1, J_{EF}=10.2$ Hz, 1H, H-E), 2.07 (d, $J_{EF}=10.2$ Hz, 1H, H-F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 151.9 (s), 151.7 (s), 147.7 (s), 145.1 (s), 136.6 (s), 135.9 (s), 135.4 (d), 128.1 (d), 127.6 (d), 127.3 (s), 126.9 (2 × d), 126.6 (d), 126.0 (d), 124.2 (d), 123.0 (d), 121.0 (d), 119.2 (d), 116.6 (t), 108.2 (d), 43.2 (t), 40.6 (d), 39.7 (d), 31.5 (t); MS m/z (EI) 324 (M^+ , 100%), 209 (15), 115 (9); HRMS (TOF ES⁺) m/z calculated (for the mixture of geometrical isomers of **8**) for $C_{24}H_{20}O$ 324.1519; found 324.1506.

Compound *cis*-**13**: R_f 0.38 (petroleum ether); colourless oil; UV (EtOH) λ_{max} ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 298 (11,584) nm; IR (evaporated film from diethyl ether) ν_{max}/cm^{-1} : 3066, 2920, 1759, 1616, 1365, 1126, 922, 760; 1H NMR ($CDCl_3$, 600 MHz) δ_H 7.57 (d, $J=7.6, 1.2$ Hz, 1H, H-ar), 7.34 (dd, $J=7.6, 1.2$ Hz, 1H, H-ar), 7.27 (dt, $J=7.6, 1.2$ Hz, 1H, H-ar), 7.22 (dt, $J=7.6, 1.2$ Hz, 1H, H-ar), 6.90 (dd, $J_{1,3}=17.5, J_{2,3}=11.1$ Hz, 1H, H-3), 6.40 (AB_q, $J=12.0$ Hz, 2H, H-et), 5.69 (s, 1H, H-f), 5.67 (dd, $J_{1,3}=17.5, J_{1,2}=1.2$ Hz, 1H, H-1), 5.22 (dd, $J_{2,3}=11.1, J_{1,2}=1.2$ Hz, 1H, H-2), 2.10 (s, 3H, CH₃), 1.79 (s, 3H, CH₃); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 149.4 (s), 147.1 (s), 136.8 (s), 136.0 (s), 135.2 (d), 129.4 (d), 127.6 (d), 127.5 (d), 125.3 (d), 124.8 (d), 120.0 (d), 116.0 (s), 115.1 (t), 113.0 (d), 11.4 (q), 9.9 (q); MS m/z (EI) 224 (M^+ , 100%), 181 (4).

Compound *trans*-**13**: R_f 0.32 (petroleum ether); yellow oil; UV (EtOH) λ_{max} ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 332 (19,301) nm; IR (evaporated film from diethyl ether) ν_{max}/cm^{-1} : 3066, 2973, 1759, 1616, 1365, 1126, 922, 760; 1H NMR ($CDCl_3$, 600 MHz) δ_H 7.49 (dd, $J=7.6, 1.2$ Hz, 1H, H-ar), 7.45 (dd, $J=7.6, 1.2$ Hz, 1H, H-ar), 7.19 (d, $J=16.0$ Hz, 1H, H-et), 7.27–7.19 (m, 2H, H-ar), 7.12 (dd, $J_{1,3}=17.4, J_{2,3}=11.0$ Hz, 1H, H-3), 6.67 (d, $J=16.0$ Hz, 1H, H-et), 6.14 (s, 1H, H-f), 5.63 (dd, $J_{1,3}=17.4, J_{1,2}=1.5$ Hz, 1H, H-1), 5.35 (dd, $J_{2,3}=11.0, J_{1,2}=1.5$ Hz, 1H, H-2), 2.26 (s, 3H, CH₃), 1.94 (s, 3H, CH₃); ^{13}C NMR 150.7 (s), 148.0 (s), 136.4 (s), 135.7 (s), 135.2 (d), 127.9 (d), 127.3 (d), 126.7 (d), 125.8 (d), 122.7 (d), 119.0 (d), 116.4 (s), 116.3 (t), 112.7 (d), 11.7 (q), 10.0 (q); MS m/z (EI)

224 (M⁺, 100%), 109 (8); HRMS (TOF ES⁺) *m/z* calculated (for the mixture of geometrical isomers of **13**) for C₁₆H₁₆O 224.1207; found 224.1199.

4.1.6. Irradiation experiment. Preparation of 13,14-dihydro-8H-8,13-methanobenzo[5,6]cyclohepta[1,2-b]phenanthrene (11). A mixture of cis- and trans-isomers of **8** in benzene (4.2 × 10⁻³ M) was purged with argon for 20 min and irradiated at 350 nm in a Rayonet reactor in a Quartz tube for 56 h. Solvent was removed in vacuum and the oily residue chromatographed on a silica gel column using petroleum ether/diethyl ether (9%). The isolated product was phenanthrene **11** in 33% (0.02 g) yield.

Compound **11**: *R_f* 0.20 (petroleum ether); colourless oil; UV (EtOH) λ_{max} (ε/dm³ mol⁻¹ cm⁻¹) 258 (14,702) nm; IR (evaporated film from diethyl ether) ν_{max}/cm⁻¹: 2918, 2849, 1734, 1460, 1377, 1014, 807, 751; ¹H NMR (CDCl₃, 600 MHz) δ_H 8.52 (d, *J*=8.2 Hz, 1H, H-ar), 8.27 (s, 1H, H-ar), 7.81 (dd, *J*=8.2, 1.4 Hz, 1H, H-ar) 7.65 (d, *J*=9.0 Hz, 1H, H-ar), 7.62 (d, *J*=9.0 Hz, 1H, H-ar), 7.61 (s, 1H, H-ar), 7.55 (dt, *J*=6.9, 1.4 Hz, 1H, H-ar), 7.50 (dt, *J*=6.9, 1.4 Hz, 1H, H-ar), 7.33 (d, *J*=7.3 Hz, 1H, H-ar), 7.21 (d, *J*=7.3 Hz, 1H, H-ar), 7.08 (dt, *J*=7.3, 1.1 Hz, 1H, H-ar) 7.04 (dt, *J*=7.3, 1.1 Hz, 1H, H-ar), 4.15 (d, *J*_{AE}=4.2 Hz, 1H, H-A), 3.62 (dt, *J*_{BE,BC}=5.1, *J*_{BD}=1.0 Hz, 1H, H-B), 3.54 (dd, *J*_{CD}=16.8, *J*_{BC}=5.1 Hz, 1H, H-C), 3.08 (dd, *J*_{DC}=16.8, *J*_{DB}=1.0 Hz, 1H, H-D), 2.67 (ddd, *J*_{EF}=10.5, *J*_{BE}=5.1, *J*_{AE}=4.2 Hz, 1H, H-E), 2.26 (d, *J*_{EF}=10.5 Hz, 1H, H-F); ¹³C NMR (CDCl₃, 150 MHz) δ_C 150.1 (s), 145.6 (s), 142.3 (s), 133.1 (s), 131.9 (s), 130.4 (s), 130.1 (s), 129.5 (s), 128.8 (d), 127.1 (d), 127.0 (d), 126.9 (d), 126.6 (d), 126.5 (d), 126.4 (d), 124.5 (2 × d), 123.6 (d), 122.6 (d), 122.1 (d), 47.4 (d), 41.5 (t), 40.8 (d), 35.2 (t); HRMS (TOF ES⁺) *m/z* calculated for C₂₄H₁₈ 306.1414; found 306.1401.

4.1.7. Irradiation experiment. Preparation of 2,3-dimethylfuro[3,2-b]-6,7-benzobicyclo[3.2.1]octa-2,6-diene (15). A mixture of cis- and trans-isomers of **13** in petroleum ether (2.6 × 10⁻³ M) was purged with argon for 20 min and irradiated at 300 nm in a Rayonet reactor in a Quartz tube for 16 h. Solvent was removed in vacuum and the oily residue chromatographed on a aluminium oxide column using petroleum ether/diethyl ether (5%). The isolated product was benzobicyclic derivative **15** in 53% (0.06 g) yield.

Compound **15**: *R_f* 0.20 (petroleum ether); colourless oil; UV (EtOH) λ_{max} (ε/dm³ mol⁻¹ cm⁻¹): 251 (4467), 268 (1585), 284 (1349) nm; IR (evaporated film from diethyl ether) ν_{max}/cm⁻¹: 3062, 2932, 2868, 1756, 1720, 1454, 1151, 1114, 757; ¹H NMR (CDCl₃, 600 MHz) δ_H 7.28 (d, *J*=6.4 Hz, 1H, H-ar), 7.09–7.01 (m, 3H, H-ar), 3.73 (d, *J*_{AE}=4.5, 1H, H-A), 3.56 (t, *J*_{BC,BE}=5.0 Hz, 1H, H-B), 3.07 (dd, *J*_{CD}=16.2 Hz; *J*_{BC}=5.0 Hz, 1H, H-C), 2.52 (d, *J*_{CD}=16.2 Hz, 1H, H-D), 2.40 (ddd, *J*_{EF}=10.2, *J*_{BE}=5.0, *J*_{AE}=4.5 Hz, 1H, H-E), 2.07 (d, *J*=0.6 Hz, 3H, CH₃), 2.01 (d, *J*_{EF}=10.2 Hz, 1H, H-F), 1.93 (d, *J*=0.6 Hz, 3H, CH₃); ¹³C NMR (CDCl₃, 150 MHz) δ_C 152.3 (s), 45.1 (s), 145.1 (s), 143.4 (s), 126.5 (d), 126.1 (d), 124.0 (d), 120.3 (d), 43.1 (t), 40.6 (d), 38.0 (d), 30.8 (t), 11.5 (q), 8.1 (q); MS *m/z* (EI) 224 (M⁺, 100%). Anal. Calcd for C₁₆H₁₆O: C, 85.68; H, 7.19. Found: C, 85.45; H 7.41.

4.1.8. Preparation of 2,3-dimethyl-5-(2-*o*-tolylvinyl)furan (12b) and 2,3-dimethyl-5-styryl furan (12a). To the stirred solutions of 4,5-dimethylfuran-2-carboxaldehyde (1 g, 8.05 mmol) and the corresponding aryltriphenylphosphonium salts (8.05 mmol) in abs ethanol (60 mL) a solution of sodium ethoxide (0.20 g, 8.84 mmol in 15 mL abs ethanol) was added dropwise. Stirring was continued for 24 h at rt. After removal of the solvent, water (20 mL) was added to the residue, extracted with benzene (60 mL) and the benzene extracts dried with MgSO₄. The crude reaction mixture of **12b** was purified by column chromatography on silica gel using petroleum ether as eluent and the mixture of cis- and trans-isomers were separated by TLC on aluminium oxide using petroleum ether as eluent. The mixture of cis- and trans-isomers of the product **12a** were separated by column chromatography on aluminium oxide

using petroleum ether as eluent. The product **12b** was isolated in 71% (1.20 g) yield (65% (0.78 g) trans and 35% (0.42 g) cis, according to ¹H NMR), and the product **12a** in 80% (1.28 g) yield (cis/trans=1:2, according to ¹H NMR).

Compound *cis*-**12b**: *R_f* 0.53 (petroleum ether); colourless oil; UV (EtOH) λ_{max} (ε/dm³ mol⁻¹ cm⁻¹): 306 (13,235) nm; IR (evaporated film from diethyl ether) ν_{max}/cm⁻¹: 2919, 2850, 1734, 1462, 1054; ¹H NMR (CDCl₃, 600 MHz) δ_H 7.35 (dd, *J*=8.2, 1.1 Hz, 1H, H-ar), 7.22–7.17 (m, 2H, H-ar), 7.15 (dt, *J*=7.4, 1.2 Hz, 1H, H-ar), 6.36 (AB_q, *J*=12.5 Hz, 2H, H-et), 5.69 (s, 1H, H-f), 2.25 (s, 3H, CH₃), 2.11 (s, 3H, CH₃), 1.80 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 150 MHz) δ_C 149.5 (s), 146.9 (s), 137.6 (s), 136.1 (s), 130.0 (d), 128.8 (d), 127.4 (d), 125.6 (d), 125.5 (d), 119.3 (d), 116.0 (s), 112.5 (d), 19.9 (q), 11.4 (q), 9.8 (q); MS *m/z* (EI) 212 (M⁺, 100%), 169 (15).

Compound *trans*-**12b**: *R_f* 0.32 (petroleum ether); yellow oil; UV (EtOH) λ_{max} (ε/dm³ mol⁻¹ cm⁻¹): 319 (19,832) nm; IR (evaporated film from diethyl ether) ν_{max}/cm⁻¹: 2940, 2900, 1750, 1462, 1098; ¹H NMR (CDCl₃, 600 MHz) δ_H 7.51 (d, *J*=7.6 Hz, 1H, H-ar), 7.13 (d, *J*=16.2 Hz, 1H, H-et), 7.19–7.12 (m, 3H, H-ar), 6.70 (d, *J*=16.2 Hz, 1H, H-et), 6.14 (s, 1H, H-f), 2.42 (s, 3H, CH₃), 2.26 (s, 3H, CH₃), 1.94 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 150 MHz) δ_C 150.8 (s), 147.8 (s), 136.5 (s), 135.8 (s), 130.5 (d), 127.2 (d), 126.2 (d), 124.8 (d), 122.8 (d), 117.9 (d), 116.4 (s), 112.6 (d), 20.1 (q), 11.7 (q), 10.0 (q); MS *m/z* (EI): 212 (M⁺, 100), 169 (15); HRMS (TOF ES⁺) *m/z* calculated (for the mixture of geometrical isomers of **12b**) for C₁₅H₁₆O 212.1207; found 212.1211.

Compound *cis*-**12a**: *R_f* 0.35 (petroleum ether); colourless oil; UV (EtOH) λ_{max} (ε/dm³ mol⁻¹ cm⁻¹): 228 (9191), 315 (12,885) nm; IR (evaporated film from diethyl ether) ν_{max}/cm⁻¹: 3027, 2925, 1679, 1610, 1450, 1364, 1248, 1120, 700; ¹H NMR (CDCl₃, 600 MHz) δ_H 7.48 (d, *J*=7.6 Hz, 2H, H-ar), 7.31 (t, *J*=7.6 Hz, 2H, H-ar), 7.23 (t, *J*=7.3 Hz, 1H, H-ar), 6.33 (d, *J*=12.6 Hz, 1H, H-et), 6.25 (d, *J*=12.6 Hz, 1H, H-et), 6.05 (s, 1H, H-f), 2.15 (s, 3H, CH₃), 1.86 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 150 MHz) δ_C 149.4 (s), 147.2 (s), 137.9 (s), 128.8 (2 × d), 128.1 (2 × d), 127.2 (d), 126.1 (d), 118.3 (d), 116.0 (s), 113.6 (d), 11.5 (q), 9.9 (q); MS *m/z* (EI) 196 (M⁺, 100%), 155 (17).

Compound *trans*-**12a**: *R_f* 0.30 (petroleum ether); white solid; mp 45 °C; UV (EtOH) λ_{max} (ε/dm³ mol⁻¹ cm⁻¹): 235 (8029), 331 (28,306), 344 (sh, 22,331) nm; IR (evaporated film from diethyl ether) ν_{max}/cm⁻¹: 3060, 2978, 1704, 1610, 1450, 1364, 1248, 1166, 758; ¹H NMR (CDCl₃, 600 MHz) δ_H 7.43 (d, *J*=7.6 Hz, 2H, H-ar), 7.31 (t, *J*=7.6 Hz, 2H, H-ar), 7.20 (t, *J*=7.5 Hz, 1H, H-ar), 6.91 (d, *J*=16.3 Hz, 1H, H-et), 6.78 (d, *J*=16.3 Hz, 1H, H-et), 6.14 (s, 1H, H-f), 2.25 (s, 3H, CH₃), 1.94 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 150 MHz) δ_C 150.6 (s), 147.9 (s), 137.6 (s), 128.8 (2 × d), 127.2 (d), 126.6 (2 × d), 125.2 (d), 116.9 (d), 116.4 (s), 112.6 (d), 11.7 (q), 10.0 (q); MS *m/z* (EI) 196 (M⁺, 100%), 155 (12); HRMS (TOF ES⁺) *m/z* calculated (for the mixture of geometrical isomers of **12a**) for C₁₄H₁₄O 198.1050; found 198.1045.

4.1.9. Irradiation experiments. Preparation of 1,2,6-trimethyl-naphtho[2,1-*b*]furan (14b) and 1,2-dimethyl-naphtho[2,1-*b*]furan (14a). To a mixture of cis- and trans-isomers of **12b** or **12a** in petroleum ether (**12b**: 5.2 × 10⁻³ M; **12a**: 5.3 × 10⁻³ M) a small quantity (5 mg) of iodine was added. A solution was irradiated at 300 nm in a Rayonet reactor in a Quartz tube. Irradiation time varied depending on the starting compound (for compound **12b** it was 35 h and for **12a** 16 h). After irradiation the solvent was removed in vacuo and the oily residue chromatographed on aluminium oxide column using petroleum ether as eluent. While the irradiation of **12a** resulted with only one photoproduct **14a** (in 56% (0.03 g) yield), the irradiation of derivative **14b** resulted in a formation of two photoproducts **14a** and **14b** in the ratio of 1:2.5 (22% (0.02 g) of isolated yield was found).

Compound **14b**: *R_f* 0.65 (petroleum ether); colourless oil; IR (evaporated film from diethyl ether) ν_{max}/cm⁻¹: 3055, 2920, 2849, 1650, 1598, 1397, 990, 800, 750; ¹H NMR (CDCl₃, 600 MHz) δ_H 8.28 (d, *J*=8.3 Hz, 1H, H-ar), 7.81 (d, *J*=9.2 Hz, 1H, H-ar), 7.59 (d, *J*=9.2 Hz, 1H, H-ar), 7.44 (dd, *J*=8.3; 7.0 Hz, 1H, H-ar), 7.30 (d, *J*=7.0 Hz, 1H, H-

ar), 2.74 (s, 3H, CH₃), 2.55 (s, 3H, CH₃), 2.47 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 150 MHz) δ_C 151.4 (s), 150.1 (s), 135.3 (s), 129.7 (s), 129.0 (s), 125.6 (d), 125.0 (d), 121.6 (d), 120.1 (d), 111.7 (d), 20.6 (q), 14.3 (q), 11.7 (q), one singlet is not seen; MS *m/z* (EI): 210 (M⁺, 100%).

Compound **14a**: *R*_f 0.30 (petroleum ether); colourless oil; UV (EtOH) λ_{max} (ε/dm³ mol⁻¹ cm⁻¹): 220 (27,691), 250 (19,555), 301 (6745), 515 (6042), 329 (5841) nm; IR (evaporated film from diethyl ether) ν_{max}/cm⁻¹: 3055, 2917, 2849, 1621, 1579, 1397, 1272, 993, 800, 743; ¹H NMR (CDCl₃, 600 MHz) δ_H 8.36 (d, *J*=8.4 Hz, 1H, H-ar), 7.91 (d, *J*=8.4 Hz, 1H, H-ar), 7.61 (d, *J*=8.7 Hz, 1H, H-ar), 7.54 (d, *J*=8.7 Hz, 1H, H-ar), 7.52 (dt, *J*=8.4, 1.2 Hz, 1H, H-ar), 7.42 (dt, *J*=8.4, 1.2 Hz, 1H, H-ar), 2.53 (s, 3H, CH₃), 2.45 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 150 MHz) δ_C 151.4 (s), 150.0 (s), 130.8 (s), 129.0 (d), 128.9 (s), 125.9 (d), 124.1 (d), 123.9 (d), 123.4 (s), 123.1 (d), 112.2 (d), 111.8 (s), 11.8 (q), 11.5 (q); MS *m/z* (EI): 196 (M⁺, 100%); HRMS (TOF ES⁺) *m/z* calculated for C₁₄H₁₂O 196.0894; found 196.0899.

4.1.10. Preparation of 5-[2-(2-vinylphenyl)ethenyl]-furan-2-carboxaldehyde (21). Compound **21** was prepared by Vilsmeier formylation. The reaction was carried out from mixture of *cis*- and *trans*-isomers of β-(2-furyl)-*o*-divinylbenzene (**1**) (1.37 g, 7.01 mmol) dissolved in dimethylformamide (5.4 mL, 0.07 mol). After being stirred at 10 °C for 10 h, phosphorus oxychloride (1.18 g, 7.71 mmol) was added and the reaction mixture was allowed gradually to warm up to room temperature and stirred for 28 h. The reaction mixture was decomposed by the continuous addition (with cooling) of 10% sodium hydroxide solution (9 mL) and the product was worked up with ether. The ether extracts were washed with water and then dried with MgSO₄. After column chromatography on silica gel using petroleum ether/diethyl ether (0–10%) as eluent the product **21** was isolated in 89% (1.4 g) yield.

Compound *cis*-**21**: *R*_f 0.23 (petroleum ether/diethyl ether 10:1); red oil; UV (EtOH) λ_{max} (ε/dm³ mol⁻¹ cm⁻¹): 326 (20,035) nm; IR (evaporated film from CHCl₃) ν_{max}/cm⁻¹: 1675 (C=O), 1501 (C=C); ¹H NMR (CDCl₃, 600 MHz) δ_H 9.50 (s, 1H, CHO), 7.62 (d, *J*=7.9 Hz, 1H, H-ar) 7.37–7.34 (m, 1H, H-ar), 7.30–7.27 (m, 1H, H-ar), 7.04 (d, *J*_{3f,4f}=3.8 Hz, 1H, H-4f), 6.93 (d, *J*=12.2 Hz, 1H, H-et) 6.85 (dd, *J*_{1,3}=17.5, *J*_{2,3}=11.0 Hz, 1H, H-3), 6.64 (d, *J*=12.2 Hz, 1H, H-et), 5.96 (d, *J*_{3f,4f}=3.8 Hz, 1H, H-3f), 5.71 (dd, *J*_{1,3}=17.5, *J*_{1,2}=1.0 Hz, 1H, H-1), 5.27 (dd, *J*_{2,3}=11.0, *J*_{1,2}=1.0 Hz, 1H, H-2); ¹³C NMR (CDCl₃, 75 MHz) δ_C 177.4 (d), 157.4 (s), 151.2 (s), 136.0 (s), 135.3 (s), 134.5 (d), 133.9 (d), 128.9 (d), 128.6 (2×d), 128.1 (d), 125.8 (d), 119.6 (d), 116.3 (t), 111.9 (d); MS *m/z* (EI): 224 (M⁺, 100%), 195 (35%), 166 (20%).

Compound *trans*-**21**: *R*_f 0.10 (petroleum ether/diethyl ether 10:1); red solid; mp 48–51 °C; UV (EtOH) λ_{max} (ε/dm³ mol⁻¹ cm⁻¹): 354 (13,800) nm; IR (evaporated film from CHCl₃) ν_{max}/cm⁻¹: 1671 (C=O), 1503 (C=C); ¹H NMR (CDCl₃, 600 MHz) δ_H 9.61 (s, 1H, CHO), 7.67 (d, *J*=16.0 Hz, 1H, H-et), 7.54 (dd, *J*=6.7, 2.1 Hz, 1H, H-ar), 7.49 (dd, *J*=6.7, 2.1 Hz, 1H, H-ar), 7.34–7.27 (m, 2H, H-ar), 7.26 (d, *J*_{3f,4f}=3.7 Hz, 1H, H-4f), 7.11 (dd, *J*_{1,3}=17.4, *J*_{2,3}=11.1 Hz, 1H, H-3), 6.84 (d, *J*=16.0 Hz, 1H, H-et), 6.55 (d, *J*_{3f,4f}=3.6 Hz, 1H, H-3f), 5.66 (dd, *J*_{1,3}=17.4, *J*_{1,2}=1.2 Hz, 1H, H-1), 5.42 (dd, *J*_{2,3}=11.1, *J*_{1,2}=1.2 Hz, 1H, H-2); ¹³C NMR (CDCl₃, 75 MHz) δ_C 177.4 (d), 159.0 (s), 152.2 (s), 137.6 (s), 134.9 (d), 134.2 (s), 131.2 (d), 129.2 (2×d), 128.3 (d), 127.3 (d), 126.4 (d), 117.9 (t), 117.5 (d), 111.1 (d); MS *m/z* (% fragment): 224 (M⁺, 100%), 195 (35%), 166 (20%); HRMS (TOF ES⁺) *m/z* calculated (for the mixture of geometrical isomers of **21**) for C₁₅H₁₂O₂ (MH⁺) 225.0910; found 225.0914.

4.1.11. Preparation of 2,5-bis-[2-(2-vinylphenyl)ethenyl]furan (20). To a stirred solution of 5-[2-(2-vinylphenyl)ethenyl]furan-2-carboxaldehyde (**21**) (0.08 g, 0.35 mmol) and the diposphonium salt (0.25 g, 0.32 mmol), in abs ethanol (50 mL) a solution of sodium ethoxide (0.01 g, 0.35 mmol in 10 mL ethanol) was added dropwise. Under a stream of nitrogen gaseous formaldehyde (obtained by the decomposition of an excess of paraformaldehyde) was

introduced and an additional quantity of sodium ethoxide (0.3518 mmol) was added. After removal of the solvent, the residue was worked up with water (10 mL) and benzene (35 mL). The benzene extract was dried and concentrated. The crude reaction mixture was purified and the mixture of two isomers of product was isolated by column chromatography on silica gel using petroleum ether as eluent. After the photochemical isomerization of the photomixtures of **20** the *trans,trans*-isomers of **20** was isolated as the main isomer. A mixture of isomers of **20** in benzene (3.4×10⁻³ M) was purged with argon for 20 min and irradiated at 350 nm in a Rayonet reactor in a Pyrex tube. After 20 min the reaction mixture of **20** contained pure *trans,trans*-**20**. The solvent was removed in vacuum and the oily residue chromatographed on silica gel using petroleum ether to isolate pure *trans,trans*-**20** in 78% (0.08 g) yield.

Compound *trans,trans*-**20**: *R*_f 0.67 (petroleum ether/diethyl ether 10:1); yellow solid; mp 79–81 °C; UV (EtOH) λ_{max} (ε/dm³ mol⁻¹ cm⁻¹) 385 (24,060) nm; IR (evaporated film from diethyl ether) ν_{max}/cm⁻¹: 3049, 2912, 2846, 1621, 1591, 1470, 955, 765; ¹H NMR (CDCl₃, 600 MHz) δ_H 7.56–7.53 (m, 4H, H-ar), 7.50–7.47 (m, 4H, H-ar), 7.41 (d, *J*=16.1 Hz, 2H, H-et), 7.15 (dd, *J*_{1,3}=17.4, *J*_{2,3}=11.0 Hz, 2H, H-3), 6.79 (d, *J*=16.1 Hz, 2H, H-et), 6.41 (s, 2H, H-f), 5.67 (dd, *J*_{1,3}=17.4, *J*_{1,2}=1.4 Hz, 2H, H-1), 5.40 (dd, *J*_{2,3}=11.0, *J*_{1,2}=1.4 Hz, 2H, H-2); ¹³C NMR (150 MHz, CDCl₃) δ_C 153.7 (2×s), 136.3 (2×s), 135.5 (2×s), 135.3 (2×d), 128.2 (2×d), 128.0 (2×d), 127.1 (2×d), 126.2 (2×d), 125.2 (2×d), 118.7 (2×d), 117.0 (2×t), 111.6 (2×d); MS *m/z* (% fragment): 324 (M⁺, 100%); HRMS (TOF ES⁺) *m/z* calculated for C₂₄H₂₀O 324.1406; found 324.1411.

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Supplementary data

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