SYNTHESIS AND PHOTOCHEMISTRY OF STYRYL SUBSTITUTED ANNELATED FURAN DERIVATIVES[#]

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Abstract - New β-substituted benzo- and naphthofuryl derivatives (**5**, **6** and **7**) of *o*-divinylbenzene, were synthesized and irradiated in order to form annelated bicyclo[3.2.1]octadienes. While 2-[2-(2-vinylphenyl)ethenyl]benzo[*b*]furan (**5**) upon irradiation gives the bicyclo[3.2.1]octadiene derivative (**12**) in 65% yield, 2-[2-(2-vinylphenyl)ethenyl]naphtho[2,1-*b*]furan (**6**) and 2-[2-(2-vinylphenyl)ethenyl]naphtho[1,2-*b*]furan (**7**), undergo *cis-trans*-isomerization but not form intramolecular photocycloaddition products. The mechanism of the intramolecular [2+2] photocycloaddition is explained *via* intermediate (**17**) which was proved by the formation of products (**18**) and (**19**), by irradiation in methanol and deuteromethanol.

INTRODUCTION

In one of our previous papers[1a] on the photochemistry of heteroaromatic stilbene like compounds[1] we demonstrated the first example of an intramolecular photocycloaddition in which a 2-furyl β-substituted compound (**1a**) gives the bicyclo[3.2.1]octadiene derivative (**2a**) in contrast to the earlier results with the β-aryl substituted compound (**1c**),[2] where the main products are bicyclo[2.1.1]hexene derivatives (**3**) or bicyclo[3.1.0]hexene derivatives (**4**). Further investigations of the 2-furyl derivatives, substituted at the position 5 of the furan ring,[1c] showed the substituent influence on the reaction course. Thus, when the β-

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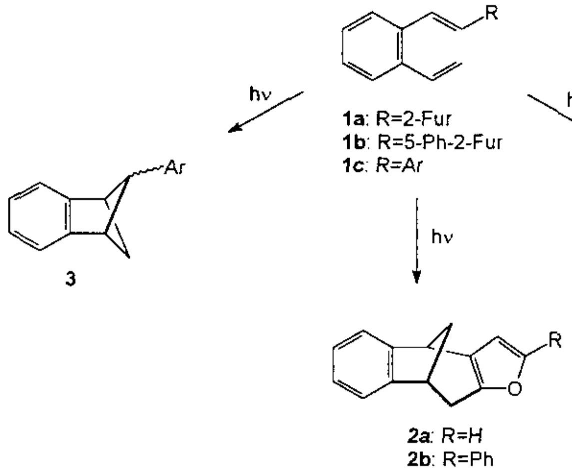
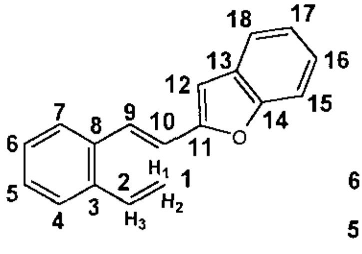
[#] This article is dedicated to D.C. Neckers, McMaster Distinguished Professor, in gratitude, on the occasion of his sixtieth birthday.

(5-phenyl-2-furyl)-*o*-divinylbenzene (**1b**) was irradiated, a system with extended π delocalization, besides *cis-trans* isomerization and high molecular weight products, just a trace of bicyclo[3.2.1]octadiene derivative (**2b**) was formed.

Scheme 1



In this paper we extend the chemistry to the condensed heteroaromatic analogues, styrylbenzofuran (5), styrylnaphtho[2,1-*b*]- (6) and styrylnaphtho[1,2-*b*]furans (7) in order to develop a synthetic pathway to annelated bicyclic structures as building blocks for polycyclic compounds.



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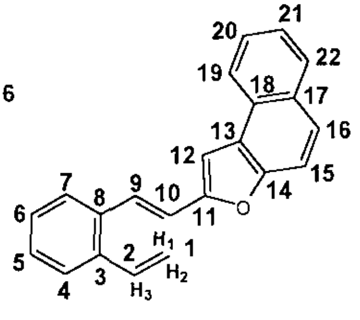

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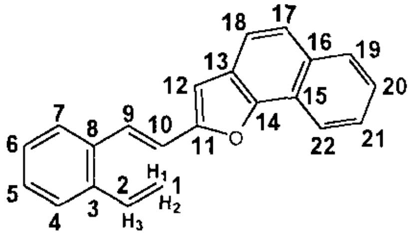

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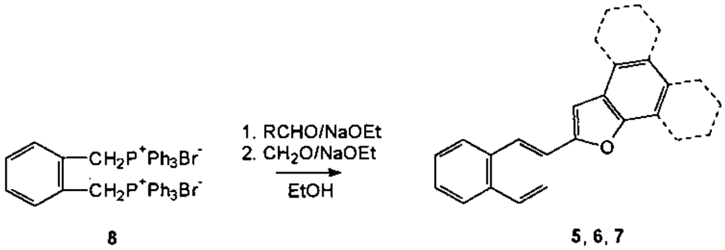
RESULTS AND DISCUSSION

The starting compounds, styrylbenzofuran (5) and styrylnaphtho[2,1-*b*]- (6) and styrylnaphtho[1,2-*b*]furans (7), were prepared by the Wittig reaction according to the described method,[9] from *α,α'*-xylyldi(triphe-nylphosphonium bromide) and the corresponding aldehydes (9-11) (Scheme 2). Each synthesis yielded a mixture of *trans*- and *cis*-isomers which were separated by column chromatography and identified spectroscopically.

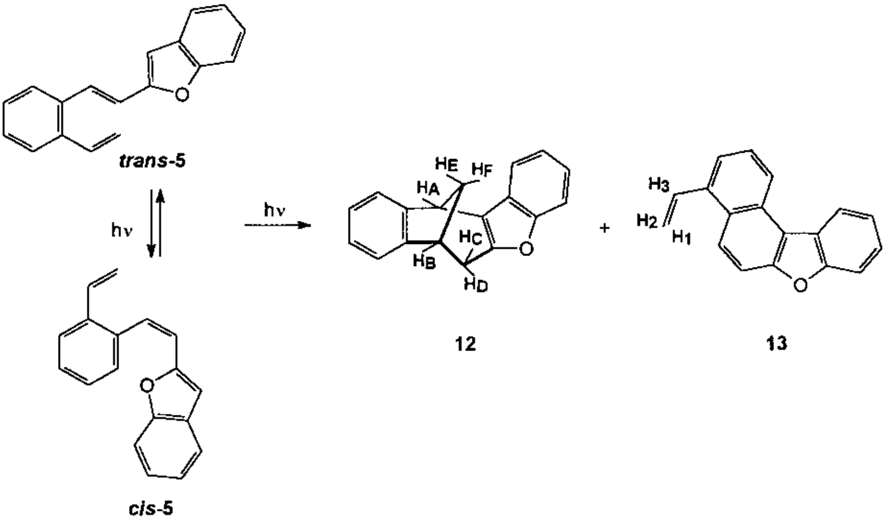
Scheme 2



9: R=2-benzofuryl
10: R=2-naphtho[2,1-*b*]furyl
11: R=2-naphtho[1,2-*b*]furyl

Irradiation experiments were carried out in diluted benzene or petroleum ether solutions (concentration 10^{-3}-10^{-4}M) and under anaerobic conditions. Thus, the irradiation of benzofuran derivative (5) in the Rayonet reactor at 300 nm gave exclusively, after a purification on silica gel column, a single crystalline bicyclic product (**12**) (Scheme 3) in 60-80% yield, as well as traces (~ 2%) of electrocyclization product, 4-vinylbenzo[*d*]naphtho[2,1-*b*]furan (**13**).

Scheme 3



The very good resolved six-proton-pattern in the ^{1}H NMR spectrum of **12** between 2 and 4.2 ppm unmistakably pointed to the bicyclic structure. From the ^{1}H and ^{13}C NMR spectra, using different techniques (COSY, NOESY and HETCOR) combined with the data for dihedral angles obtained from X-Ray crystallographic analysis (Figure 1) the structure of the bicyclo[3.2.1]octadiene derivative (**12**) is completely assigned. The compound (**12**) has two chiral carbon atoms C1 and C5. The crystal structure consists of (*R*,*R*) and (*S*,*S*) pairs of enantiomers. Details concerning the X-Ray analysis are recorded in the Experimental Section.

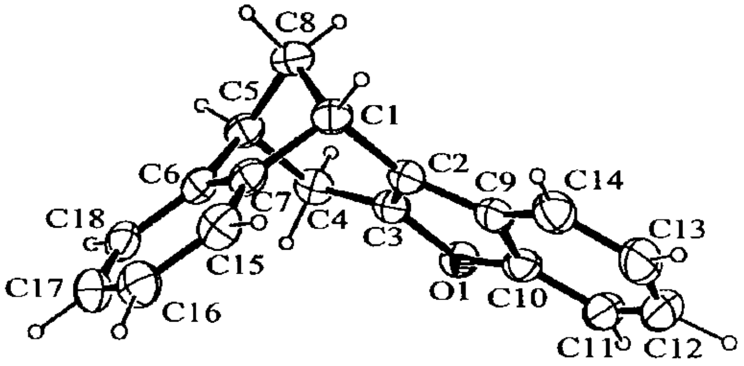
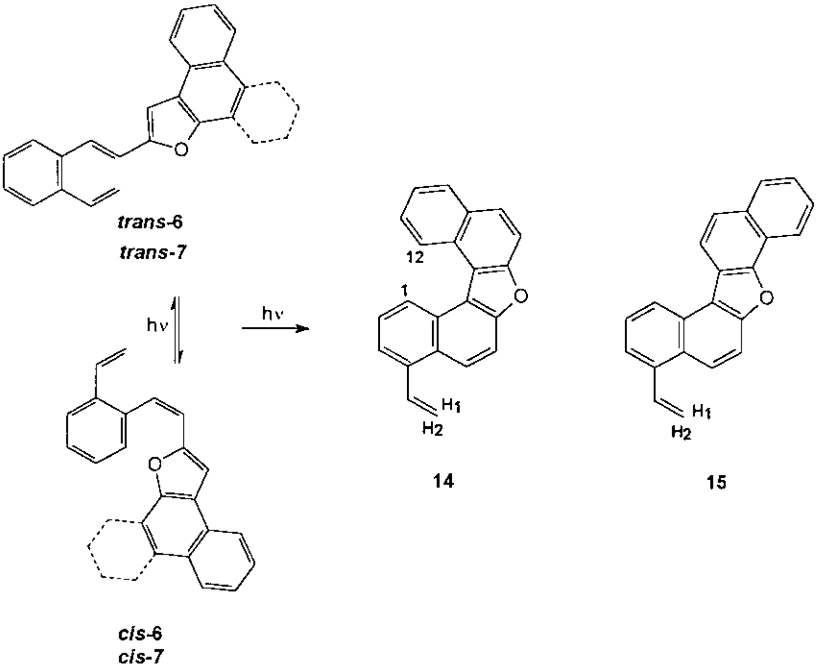


Figure 1. Perspective view of the X-Ray structure of **12**

Contrary to this result, the irradiation of naphtho[2,1-*b*]- (**6**) and naphtho[1,2-*b*]furan derivatives (**7**) gave (Scheme 4) primarily *cis-trans-* and *trans-cis*-isomerization, besides some electrocyclization product, 4-vinyldinaphtho[2,1-*b*: 1',2'-*d*]furan (**14**) and 4-vinyldinaphtho[2,1-*b*: 2',1'-*d*]furan (**15**), respectively.

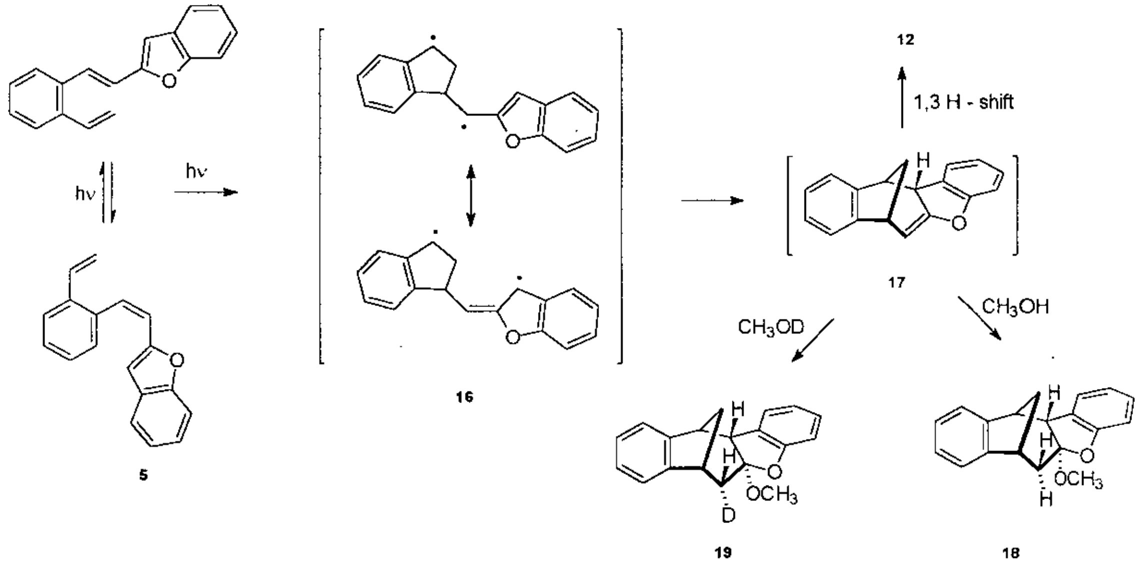
Scheme 4



No intramolecular addition products were detected. After prolonged irradiation time, along with decomposition material, minor amounts of dimeric products[3] were observed in the ^{1}H NMR spectra, even at the concentration of 10^{-4} M. An explanation for this lack of reactivity of naphthofuran derivatives (**6** and **7**) in sense of intramolecular cycloaddition, may be ascribed to the fast formation of the excited state complex. It has been found[4] that excimer formation is widespread among aromatic hydrocarbons and this tendency is increasing with their size.

The formation of the bicyclic product (**12**) can be explained as follows (Scheme 5): from the singlet state of **5** the 1,4-biradical (**16**) is formed followed by the preferred cyclohexene ring closure to **17**, which was not isolated but after 1,3-H shift transformed into **12**. To confirm the reaction mechanism and formation of the intermediate (**17**) irradiation of **5** was performed in methanol solution. The only adduct formed was **18** and it was formed almost quantitatively. This was clear from the presence of only one signal for the methoxy group in the ^{1}H NMR spectrum. The formation of **18** implicates the existence of the double bond in compound (**17**) as presented. The adduct (**18**) could have been obtained by the addition of methanol to the already produced photoproduct (**12**). Therefore irradiation of **12** was performed under the same conditions as irradiation of **5** in methanol. No reaction was observed in the ^{1}H NMR spectrum.

Scheme 5



This result confirms that the addition of methanol took place to intermediate (**17**), moreover regiospecific. To determine the relative stereochemistry of the aliphatic hydrogens and make complete assignment of carbons in compound (**18**) it was necessary to take the NMR spectra in deuterobenzene and in deuterochloroform to avoid the overlapping of the key signals (Figure 2).

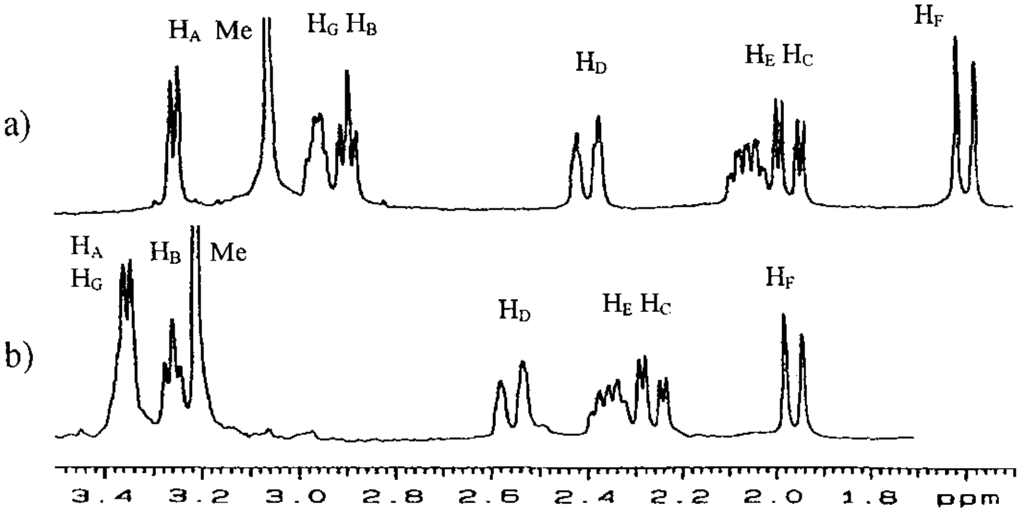
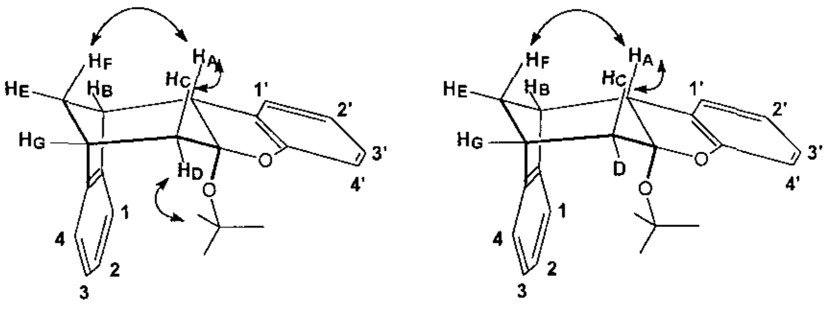


Figure 2. The aliphatic region of the ^1H NMR spectrum for **18** in a) C_6D_6 and b) $CDCl_3$.

The binding of the methoxy group to the furan carbon nearest to the oxygen in **18** is evident based on the existence of two pairs of geminal protons in ^1H NMR (C_6D_6). This is also observed in compound (**12**). Moreover, the ^{13}C NMR spectrum ($CDCl_3$), in addition to a new doublet at 51.94 ppm (C-H_A) shows a new singlet in much lower field at 109.62 ppm (C-c) which could be a result of the influence of two oxygens. The attack of methoxy group from the less hindered site of compound (**17**), that is opposite to the methano bridge, was confirmed by NOESY experiments. It can be seen the interaction between H_D- and methoxy-hydrogens, no interaction was observed between H_A- and methoxy-hydrogens. Based on the interaction of H_A- and H_F-hydrogens the stereochemistry of H_A was established.

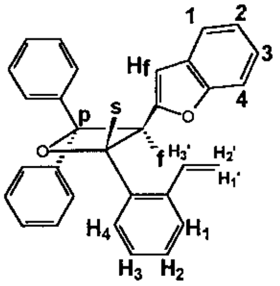


18 **19**

Figure 3. Important NOE interactions.

The other unequivocal evidence for the existence of **17** was the irradiation of **5** in deuterated methanol, CH_3OD. The only adduct formed **19** is the result of *syn*-addition of CH_3OD to the intermediate (**17**). It is evident from the ^1H NMR spectra that the only difference in signals of **19** compared with **18** is the disappearance of the H_D-signal and simplification of the H_C-signal, due to the building in of the deuteroatom. The regiospecific and stereospecific addition of the methanol to **17** can be explained by steric reason and by the formation of the more stable cyclohexane chair-conformation (Figure 3).

Irradiation of **5** in benzene in the presence of benzophenone as triplet sensitizer was performed under conditions to ensure the excitation of the sensitizer. Energy transfer does not occur but the n-π* triplet state of the carbonyl moiety of benzophenone adds to the double bond of **5** *via* the most stable 1,4-biradical and oxetane (**20**), *trans*-2-(2-vinylphenyl)-3-(2-benzofuryl)-4,4-diphenyl-1-oxetane, was isolated as the major product. The *trans*-2-(2-benzofuryl)-3-(2-vinylphenyl)- 4,4-diphenyl-1-oxetane (**21**) was formed in traces only as observed from the ^{1}H NMR spectrum.



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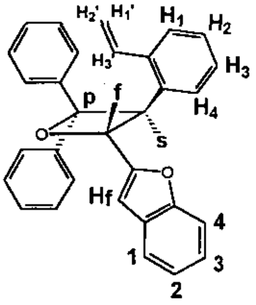

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The structure of **20** is based on the spectroscopic data. The orientation of addition of benzofuran derivative (**5**) to the carbonyl group of the benzophenone was determined from the MS spectrum. The signal at *m/z* 296, which is Ph_2C=CH-benzofuryl fragment, clearly showed this. (Scheme 3). The *trans*-configuration of the oxetane hydrogens **s** and **f** was unambiguously determined by NOESY experiment. The same coupling constant, *J*=8.4 Hz, found in the minor product, pointed to the only alternative *trans* structure of **20**, product (**21**).

We might conclude that the irradiation of furan and annelated, benzofuran derivatives, heterocyclic analogues of *o*-vinylstilbene, together with trapping of the intermediate, opens a simple synthetic pathway to polycyclic compounds with the exact stereochemistry.

EXPERIMENTAL SECTION

General. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian GEMINI 300 spectrometer at 300 and 75 MHz respectively in $CDCl_3$ and where necessary in C_6D_6 Me_4Si as an internal standard. The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY and NOESY experiments. UV spectra were measured on Perkin Elmer LAMBDA 20 Spectrophotometer. HRMS spectra were measured on an Auto Spec Q (VG Analytical Manchester, GB). Elemental analyses were carried out in the Microanalytical Laboratory at The Rugjer Boskovic Institute. Melting points were obtained on a capillary melting point apparatus and are uncorrected.

Benzofurancarboxaldehyde (9) was obtained from commercial source and used without further purification.

Preparation of 2-formylnaphtho[2,1-*b*]furan (10).[5] This compound was prepared from 2-hydroxynaphthocarboxaldehyde according to the described procedure.

Preparation of 2-formylnaphtho[1,2-*b*]furan (11):[6] **11** was prepared by Vilsmeyer formylation of naphtho[1,2-*b*]furan[7] obtained by photochemical ring closure of 3-styrylfuran.[8] 3-Styrylfuran was obtained by the Wittig reaction from benzyltriphenylphosphonium bromide and 3-furancarboxaldehyde as described for 2-furyl derivative. [9] The physical data, not found in the literature, for the prepared compounds are given bellow:

***cis*-3-Styrylfuran**: 14% yield; oil; UV (EtOH): λ_{max} (log ε) 225 (3.95), 265 (3.95); ^{1}H NMR (CDCl$_3$) δ 7.40-7.20 (m, 7H, 5H$_{ar}$,2H$_f$), 6.53 (d, 1H, *J* 12.0 Hz, H$_{et}$), 6.36 (d, 1H, *J* 12.0 Hz, H$_{et}$), 6.11 (d, 1H, *J* 1 Hz, H$_f$); ^{13}C NMR (CDCl$_3$) δ 142.37 (d), 141.92 (d), 137.79 (s), 129.30 (d), 128.53 (d), 128.09 (d), 126.99 (d), 122.16 (s), 119.96 (d), 110.08 (d);

***trans*-3-Styrylfuran**: 56% yield; mp 91-92 °C (MeOH); UV (EtOH): λ_{max} (log ε) 223 (4.12), 282 (4.34), 304 (4.10); ^{1}H NMR (CDCl$_3$) δ 7.60-7.20 (m, 7H, 5H$_{ar}$,2H$_f$), 6.97 (d, 1H, *J* 16.3 Hz, H$_{et}$), 6.81 (d, 1H, *J* 16.3 Hz, H$_{et}$); ^{13}C NMR (CDCl$_3$) δ 143.59 (d), 140.82 (d), 137.25 (s), 128.52 (d), 128.30 (d), 127.21 (d), 126.00 (d), 124.43 (s), 118.28 (d), 107.26 (d); MS *m/z* (relative intensity) 171 (MH$^+$, 100), 170 (M$^+$, 34), 141 (45), 115 (18); HRMS calcd for $C_{12}H_{10}O$ 170.072616, found 170.067567; Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.61; H, 6.09.

Naphtho[1,2-*b*]furan: 15% yield; oil; ^{1}H NMR (CDCl$_3$) δ 8.31 (d, 1H, *J* 8.2 Hz, H$_{10}$), 7.92 (d, 1H, *J* 8.2 Hz, H$_7$), 7.75 (d, 1H, *J* ~ 1 Hz, H$_1$), 7.65 (s, 2H, H$_4$,H$_5$), 7.58 (dd, 1H, *J* 8.2, 7.0 Hz), 7.47 (dd, 1H, *J* 8.2, 7.0 Hz), 6.88 (d, 1H, *J* ~ 1 Hz, H$_2$); ^{13}C NMR (CDCl$_3$) δ 150.59 (s, C$_{12}$), 144.10 (d, C$_1$), 131.40 (s, C$_6$), 128.29 (d), 126.28 (d), 125.05 (d), 123.38 (d), 122.90 (s), 121.47 (s), 119.97 (d), 119.70 (d), 107.53 (d, C$_2$).

Naphtho[1,2-*b*]furan-2-carboxaldehyde (11): 65% yield; mp 120-121 °C (MeOH); UV (EtOH): λ_{max} (log ε) 216 (4.25), 242 (4.19), 274 (4.25), 312 (4.12), 356 (3.66); IR(KBr): 1675 (C=O), 1630 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 9.91 (s, 1H, H$_{ald}$), 8.47 (dd, 1H, *J* 7.2, 1.4 Hz, H$_{10}$), 7.96 (dd, 1H, *J* 7.2, 1.4 Hz, H$_7$), 7.75-7.59 (m, 5H, H$_2$,H$_4$,H$_5$,H$_8$,H$_9$); ^{13}C NMR (CDCl$_3$) δ 179.14 (d), 153.42 (s), 152.59 (s), 133.80 (s, C$_6$), 128.54 (d, C$_7$), 127.54 (d), 127.17 (d), 125.36 (d, C$_5$), 122.77 (s), 121.37 (s), 121.23 (d, C$_{10}$), 120.08 (d, C$_4$), 118.48 (d, C$_2$); MS *m/z* (relative intensity) 196 (M$^+$, 100), 139 (27), 128 (22); HRMS calcd for $C_{13}H_8O_2$ 196.0518, found 196.0490. Anal. Calcd for $C_{13}H_8O_2$: C, 79.58; H, 4.11. Found: C, 79.72; H, 4.36.

Preparation of 2-[2-(2-vinylphenyl)ethenyl]benzo[*b*]furan (5), 2-[2-(2-vinylphenyl)ethenyl]naphtho-[2,1-*b*]furan (6) and 2-[2-(2-vinylphenyl)ethenyl]naphtho[1,2-*b*]furan (7) by the Wittig one-pot reaction[10] from diphosphonium salt (**8**), formaldehyde and corresponding aldehydes (**9**, **10**, **11**). To a stirred solution of *o*-xylylenebis(triphenylphosphonium bromide) (**8**) (4.73 g, 6 mmol) and the corresponding aldehyde (6 mmol of **9**, **10**, **11**, resp.) in 150 mL of absolute ethanol a solution of sodium ethoxide (150 mg, 6.6 mmol in 10 mL of abs. ethanol) was added dropwise. The stirring was continued at rt for 0.5 h. Under the stream of dry nitrogen gaseous formaldehyde (obtained by decomposition of paraformaldehyde taken in excess, 0.5 g) was introduced and the next quantity of sodium ethoxide (138 mg, 6 mmol in 10 mL of abs. ethanol) was added dropwise. The reaction mixture was left to stand overnight. After removal of the solvent the residue was worked up with water and benzene. The benzene extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude reaction mixture was chromatographed on silica gel column with dichloromethane to separate the product (**5**, **6**, and 7). The *cis*- and *trans*- isomers were separated and fully characterised by repeated column chromatography using petroleum ether/ether (9:1 to 9:3) mixture as an eluens.

2-[2-(2-Vinylphenyl)ethenyl]benzo[*b*]furan (5): 1.2 g, 81% yield; a mixture of 44% *cis*- and 56% *trans*-5. ***cis***- 5: colorless oil; UV (EtOH): λ_{max} (log ε) 308 (4.21), 300 (4.17, sh), 232 (4.25); ^{1}H NMR ($CDCl_3$) δ 7.66 (d, 1H, *J* 8.0 Hz, H_{ar}), 7.46-7.14 (m, 7H, H_{ar}), 6.96 (dd, 1H, *J* 17.5, 11.0 Hz, H_3), 6.85 (d, 1H, *J* 12.3 Hz, H_9), 6.68 (d, 1H, *J* 12.3 Hz, H_{10}), 6.32 (s, 1H, H_f), 5.75 (dd, 1H, *J* 17.5, 1.1 Hz, H_1), 5.30 (dd, 1H, *J* 11.0, 1.1 Hz, H_2); ^{13}C NMR ($CDCl_3$) δ 154.13 (s) and 153.80 (s, C_{11}/C_{14}), 135.95 (s) and 135.87 (s, C_3/C_8), 134.69 (d, C_2), 130.76 (d, C_9), 129.18 (d), 128.67 (s, C_{13}), 127.95 (d), 127.59 (d), 125.42 (d), 124.37 (d), 122.66 (d), 120.83 (d), 119.89 (d, C_{10}), 115.62 (t, C_1), 110.92 (d, C_{15}), 105.70 (d, C_{12});
trans-5: colorless oil; UV (EtOH): λ_{max} (log ε) 355 (4.07, sh), 332 (4.32), 262 (3.86, sh), 230 (4.06); ^{1}H NMR ($CDCl_3$) δ 7.61 (d, 1H, *J* 16.1 Hz, H_9), 7.58-7.45 (m, 4H, H_{ar}), 7.32-7.16 (m, 4H, H_{ar}), 7.16 (dd, 1H, *J* 17.3, 11.0 Hz, H_3), 6.88 (d, 1H, *J* 16.1 Hz, H_{10}), 6.65 (s, 1H, H_f), 5.67 (dd, 1H, *J* 17.3, 1.3 Hz, H_1), 5.40 (dd, 1H, *J* 11.0, 1.3 Hz, H_2); ^{13}C NMR ($CDCl_3$) δ 155.10 (s) and 154.90 (s, C_{11}/C_{14}), 136.75 (s) and 134.54 (s, C_3/C_8), 134.70 (d, C_2), 129.03 (s, C_{13}), 128.06 (d), 127.81 (d), 127.61 (d, C_9), 126.68 (d), 125.83 (d), 124.60 (d), 122.82 (d), 120.78 (d), 118.34 (d, C_{10}), 116.82 (t, C_1), 110.85 (d, C_{15}), 105.29 (d, C_{12}); MS *m/z* (relative intensity) 246 (M^+, 22), 146 (34), 131 (100); HRMS for $C_{18}H_{14}O$ 246.1044, found 246.1026. Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.78; H, 5.93.

2-[2-(2-Vinylphenyl)ethenyl]naphtho[2,1-*b*]furan (6): 0.94 g, 53% yield; an 1:1 mixture of *cis*- and *trans*-6. ***cis*-6**: mp 63-64 °C (MeOH); UV (EtOH): λ_{max} (log ε) 210 (4.59), 236 (4.44), 314 (4.12), 344 (4.35); ^{1}H NMR ($CDCl_3$) δ 7.90 (d, 1H_{19}, J ~ 7 Hz, H_{19}), 7.88 (d, 1H, J ~ 7 Hz, H_{22}), 7.68-7.62 (m, 2H), 7.54-7.26 (m, 6H), 6.95 (dd, 1H , J 17.4, 10.8 Hz, H_3), 6.81 (d, 1H, J 12.3 Hz, H_9), 6.77 (s, 1H, H_{12}), 6.72 (d, 1H, J 12.3 Hz, H_{10}), 5.72 (dd, 1H, J 17.40, 1.20 Hz, H_1), 5.26 (dd, 1H, J 10.80, 1.20 Hz, H_2); ^{13}C NMR ($CDCl_3$) δ 153.39 (s), 151.68 (s), 136.01 (s), 135.98 (s), 134.75 (d, C_2), 130.24 (s, C_{18}), 129.70 (d, C_9), 129.23 (d), 128.66 (d, C_{22}), 127.99 (d), 127.63 (d), 127.37 (s, C_{17}), 126.11 (d), 125.48 (d), 125.37 (d), 124.45 (d), 124.00 (s, C_{13}), 123.34 (d, C_{19}), 119.84 (d, C_{10}), 115.63 (t, C_1), 112.09 (d C_{15}), 104.81 (d, C_{12}); MS *m/z* (relative intensity) 296 (M^+, 100), 281 (16), 265 (17), 252 (17), 181 (80), 168 (17), 152 (18), 115 (18); HRMS calcd for $C_{22}H_{16}O$ 296.1195, found 296.1246.

***trans*-6**: mp 96-98 °C (MeOH); UV (EtOH): λ_{max} (log ε) 212 (4.66), 246 (4.34), 324 (4.28), 362 (4.61); ^{1}H NMR ($CDCl_3$) δ 8.11 (d, 1H, J 8.1 Hz, H_{19}), 7.93 (d, 1H, J 8.1 Hz, H_{22}), 7.75-7.44 (m, 7H), 7.29 (d, 1H, J 7.2 Hz), 7.26 (d, 1H, J 16.0 Hz, H_9), 7.23 (dd, 1H, J 17.4, 10.9 Hz, H_3), 7.17 (s, 1H, H_{12}), 7.00 (d, 1H, J 16.0 Hz, H_{10}), 5.70 (dd, 1H, J 17.4, 1.2 Hz, H_1), 5.45 (dd, 1H, J 10.9, 1.2 Hz, H_2); ^{13}C NMR ($CDCl_3$) δ 154.74 (s), 152.45 (s), 136.78 (s), 134.84 (d, C_2), 134.77 (s), 130.37 (s, C_{18}), 128.78 (d, C_{22}), 128.02 (d), 127.91 (d, C_9), 127.45 (s, C_{17}), 126.91 (d), 126.77 (d), 126.29 (d), 125.85 (d), 125.63 (d), 124.57 (d), 124.45 (s, C_{13}), 123.43 (d, C_{19}), 118.51 (d, C_{10}), 116.87 (t, C_1), 112.07 (d, C_{15}), 104.35 (d, C_{12}); Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.12; H, 5.68.

2-[2-(2-Vinylphenyl)ethenyl]naphtho[1,2-*b*]furan (7): 1.3 g, 74% yield; an 1:1 mixture of *cis*- and *trans*-7. ***cis*-7**: oil; UV (EtOH): λ_{max} (log ε) 240 (4.46), 322 (4.16), 352 (4.02); ^{1}H NMR ($CDCl_3$) δ 7.92 (d, 1H, J 8.0 Hz, H_{22}), 7.85 (d, 1H, J 8.0 Hz, H_{19}), 7.66 (d, 1H, J 7.8 Hz), 7.55 (d, 1H, J 8.7 Hz, H_{18}), 7.53-7.27 (m, 6H), 6.96 (dd, 1H, J 17.4, 11.1 Hz, H_3), 6.80 (d, 1H, J 12.3 Hz, H_9), 6.72 (d, 1H, J 12.3 Hz, H_{10}), 6.48 (s, 1H, H_{12}), 5.70 (dd, 1H, J 17.4, 1.2 Hz, H_1), 5.23 (dd, 1H, J 11.1, 1.2 Hz, H_2); ^{13}C NMR ($CDCl_3$) δ 153.44 (s), 149.84 (s), 136.29 (s), 135.95 (s), 134.84 (d, C_2), 131.49 (d, C_{16}), 129.37 (d), 129.26 (d, C_9), 128.22 (d, C_{19}), 127.83 (d), 127.51 (d), 126.22 (d), 125.31 (d), 125.06 (d), 124.09 (s, C_{15}), 123.39 (d, C_{18}), 121.07 (s, C_{13}), 120.00 (d, C_{22}), 119.76 (d, C_{10}), 119.39 (d), 115.42 (t, C_1), 107 09 (d, C_{12});

***trans*-7**: mp 110-111 °C (MeOH); UV (EtOH): λ_{max} (log ε) 244 (4.14), 286 (4.00), 356 (4.17); ^{1}H NMR ($CDCl_3$) δ 8.40 (d, 1H, J 8.1 Hz, H_{22}), 7.92 (d, 1H, J 8.1 Hz, H_{19}), 7.70 (d, 1H, J 16.1 Hz, H_9), 7.67-7.45 (m, 6H), 7.33-7.27 (m, 2H), 7.23 (dd, 1H, J 17.4, 10.8 Hz, H_3), 6.98 (d, 1H, J 16.1 Hz, H_{10}), 6.82 (s, 1H, H_{12}), 5.72 (dd, 1H, J 17.4, 1.4 Hz, H_1), 5.46 (dd, 1H, J 10.8, 1.4 Hz, H_2); ^{13}C NMR ($CDCl_3$) δ 154.73 (s), 150.44 (s), 136.75 (s), 134.87 (d, C_2), 131.71 (s), 128.42 (d, C_{19}), 127.98 (d), 127.91 (d), 126.91 (d,

C_9), 126.78 (d), 126.31 (d), 125.97 (d), 125.97 (s, C_{16}), 125.16 (d), 124.69 (s, C_{15}), 123.60 (d), 121.16 (s, C_{13}), 120.19 (d, C_{22}), 119.39 (d), 118.70 (d, C_{10}), 116.84 (t, C_1), 106.27 (d, C_{12}); MS *m/z* (relative intensity) 296 (M^+, 100), 281 (25), 265 (22), 252 (21), 181 (88), 168 (13), 152 (15), 115 (15); Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44.Found: C, 89.26; H, 5.65.

Irradiation experiments. A solution of light petroleum ether ($3x10^{-3}$ M) of **5**, **6** or **7** was irradiated under argon for 30 h in Rayonet (8 lamps) at 300 (**5**) and 350 nm (**6**,**7**) at rt, respectively, in a quartz tube. The solvent was removed in vacuum and the residue was chromatographed on the silica gel column using petroleum ether- ether (9:1 to 9:3) as the eluent.

Irradiation of 2-[2-(2-vinylphenyl)ethenyl]benzo[*b*]furan (**5**). **13** was isolated in the first fractions followed by **12**:

4-Vinylbenzo[*d*]naphtho[2,1-*b*]furan (13) (9.2 mg, 2.5 %): colorless crystals, mp 68-70 °C; UV (EtOH): λ_{max} (log ε) 219 (4.36), 235 (4.33), 242 (4.44, sh), 247 (4.48), 270 (3.63, sh), 317 (4.08), 328 (3.97, sh), 335 (3.93, sh), 342 (3.95); ^{1}H NMR ($CDCl_3$) δ 8.60 (dd, 1H, *J* 7.4, 1.7 Hz, H_{ar}), 8.40 (dd, 1H, *J* 6.6, 2.4 Hz, H_{ar}), 8.23 (d, 1H, *J* 9.2 Hz, H_{ar}), 7.79 (d, 1H, *J* 9.2 Hz, H_{ar}), 7.73-7.63 (m, 2H, H_{ar}), 7.56 (dd, 1H, *J* 17.3, 10.9 Hz, H_3), 7.53-7.43 (m, 3H, H_{ar}), 5.84 (dd, 1H, *J* 17.3, 1.5 Hz, H_1), 5.55 (dd, 1H, *J* 10.9, 1.5 Hz, H_2); ^{13}C NMR ($CDCl_3$) δ 155.81 (s), 154.06 (s), 152.03 (s), 136.96 (s), 134.88 (d), 129.29 (s), 127.88 (s), 126.92 (d), 125.85 (d), 124.83 (s), 124.27 (d), 123.25 (d), 123.03 (d), 122.46 (d), 121.90 (d), 117.72 (t), 112.47 (d), 111.79 (d); MS *m/z* (relative intensity) 244 (M^+, 100); HRMS calcd for $C_{18}H_{12}O$ 244.0882, found 244.0900.

11,12-Dihydro-6,11-methano-6*H*-benzo[4,5]cyclohepta[1,2-*b*]benzo[*d*]furan (12) (240 mg, 65%): colorless crystals, mp 85-87 °C (ptroleum ether); UV (EtOH): λ_{max} (log ε) 256 (3.86), 265 (3.74, sh), 273 (3.64, sh), 278 (3.48, sh), 286 (3.25); ^{1}H NMR ($CDCl_3$) δ 7.56 (dd, 1H, *J* 7.3, 1.3 Hz, H_{ar}), 7.36-7.00 (m, 7H, H_{ar}), 4.13 (d, 1H, J_{AE} 4.5 Hz, H_A), 3.72 (dt, 1H, $J_{BC,BE}$ 5.1 Hz; J_{BD} 1.5 Hz, H_B), 3.30 (dd, 1H, J_{CD} 17.0 Hz; J_{BC} 5.1 Hz, H_C), 2.75 (dd, 1H, J_{CD} 17.0 Hz; J_{BD} 1.5 Hz, H_D), 2.54 (ddd, 1H, J_{EF} 10.4 Hz; J_{BE} 5.1 Hz; J_{AE} 4.5 Hz, H_E), 2.15 (d, 1H, J_{EF} 10.4 Hz, H_F); ^{13}C NMR ($CDCl_3$) δ 154.47 (s), 151.62 (s), 150.36 (s), 144.93 (s), 126.96 (2s), 126.78 (d), 126.56 (d), 124.13 (d), 123.00 (d), 122.52 (d), 120.82 (d), 118.06 (d), 111.18 (d), 42.79 (t, $C_{E,F}$), 40.27 (d, C_B), 37.63 (d, C_A), 31.19 (t, $C_{C,D}$); MS (EI) *m/z* (relative intensity) 246 (M^+, 100), 231 (40), 218 (88); HRMS calcd for $C_{18}H_{14}O$ 246.1044, found 246.1021. Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.52; H, 6.00.

X-Ray Crystallographic Analysis of the Structure of 12.

Crystals suitable for X-Ray analysis were grown by slow evaporation at rt from petroleum ether solution. The crystal data for **12**: $C_{18}H_{14}O$, M_r = 246.3, orthorhombic, space group *Pccn* (No. 56), a = 19.288(5)

Å, b = 16.393(5) Å, c = 8.276(3) Å, V = 2617(1) Å^3, Z = 8, D_{calc} = 1.250 g cm^{-3}.

The intensities were collected at 293(2) K on a Philips PW1100 diffractometer updated by Stoe[11] using graphite-monochromated CuKα radiation (λ = 1.54186 Å). The structure was solved by a direct method (SHELXS86).[12] The non-hydrogen atoms were refined anisotropically (SHELXL93).[13] All hydrogen atoms were located from difference Fourier maps and included in the refinement with individual isotropic displacement. The final R- ,wR- and S factors after full-matrix least-squares refinements were 0.042, 0.124 and 1.06 for 1637 observed reflections with $I>2\sigma(I)$. Additional crystallographic data are available as supplementary materials.[14]

Irradiation of 2-[2-(2-vinylphenyl)ethenyl]naphtho[2,1-*b*]furan (6). From the irradiation mixture of **6** only one photoproduct was isolated: **4-vinyldinaphtho[2,1-*b*:1',2'-*d*]furan (14)** (7mg, 1.5 %): colorless crystals, mp 54-56 °C; UV (EtOH): $\lambda_{\max}$ (log ε) 212 (4.58), 223 (4.55), 239 (4.50), 250 (4.35, sh), 259 (4.31, sh), 303 (3.94), 330 (4.02), 344 (4.29), 360 (4.38); ^{1}H NMR (CDCl$_3$) δ 9.12 (m, 2H, H-1,H-12), 8.27 (dd, 1H, J 9.0, ~1 Hz), 8.07 (dd, 1H, J 8.1, ~1 Hz), 7.97 (dd, 1H, J 9.0, ~1 Hz), 7.89-7.82 (m, 2H), 7.78-7.70 (m, 3H), 7.65-7.54 (m, 2H), 5.86 (dd, 1H, J 17.4, 1.5 Hz, H$_1$), 5.57 (dd, 1H, J 10.8, 1.5 Hz, H$_2$); ^{13}C NMR (CDCl$_3$) δ 154.46 (s), 154.19 (s), 137.16 (s), 135.38 (d), 131.21 (s), 129.46 (d), 128.86 (s), 128.69 (s), 128.57 (s), 128.45 (d), 126.16 (d), 125.82 (d), 125.52 (d), 124.57 (d), 124.39 (d), 124.00 (d), 122.68 (d), 119.76 (s), 119.31 (s), 117.88 (t), 112.67 (d), 112.45 (d); MS *m/z* (relative intensity) 294 (M$^+$, 100); HRMS calcd for $C_{22}H_{14}O$ 294.1039, found 294.1088.

Irradiation of 2-[2-(2-vinylphenyl)ethenyl]naphtho[1,2-*b*]furan (7). In ^{1}H NMR spectrum of the irradiation mixture of 7 only one photoproduct was observed, **4-vinyldinaphtho[2,1-*b*:2',1'-*d*]furan** (15) (~1%): ^{1}H NMR (CDCl$_3$) δ 8.70 (dd, 1H, J 7.2, 2.7 Hz), 8.53 (d, 1H, J 8.1 Hz), 8.47 (d, 1H, J 9.0 Hz), 8.23 (d, 1H, J 9.0 Hz), 8.04 (d, 1H, J 8.1 Hz), 7.72-7.38 (m, 4H), 7.34-7.17 (m, 3H), 5.85 (dd, 1H, J 17.4, 1.4 Hz, H$_1$), 5.56 (dd, 1H, J 10.8, 1.4 Hz, H$_2$); MS *m/z* (relative intensity) 294 (M$^+$, 100).

Irradiation of 5 in methanol. A solution of 10 mg of **5** in 10 mL of methanol (4x10^{-3} M) was purged with argon and irradiated at 300 nm for 2 h at rt. The solvent was removed and the product **18** isolated (7.3 mg, 65%) on TLC plate eluting with petroleum ether/ether (9:1): mp 68-69 °C; UV (EtOH): $\lambda_{\max}$ (log ε) 215 (4.05, sh), 267 (3.44), 273 (3.51), 282 (3.44); ^{1}H NMR (CDCl$_3$) δ 7.29 (d, 1H, J 7.2 Hz, H$_1$'), 7.15 (d, 1H, J 7.2 Hz, H$_1$), 7.04 (t, 1H, J 7.2 Hz, H$_2$), 7.01 (dd, 1H, J 8.1, 7.2 Hz, H$_3$'), 6.91 (t, 1H, J 7.2 Hz, H$_2$'), 6.69 (t, 1H, J 7.2 Hz, H$_3$), 6.39 (d, 1H, J 8.1 Hz, H$_4$'), 6.14 (d, 1H, J 7.2 Hz, H$_4$), 3.35 (d, 2H, J_{AB} 4.5 Hz, H$_A$, H$_G$ under the signal of H$_A$), 3.26 (t, 1H, J_{AB} =J_{BE} 4.5 Hz, H$_B$), 3.21 (s, 3H, OCH$_3$), 2.56 (dd, 1H, J_{CD} 13.5 Hz, J_{DG} ~1.8 Hz, H$_D$), 2.36 (m, 1H, H$_E$), 2.27 (dd, 1H, J_{CD} 13.5 Hz, J_{CG} 4.5 Hz, H$_C$), 1.96 (d, 1H, J_{EF} 10.8 Hz, H_F); ^{1}H NMR (C_6D_6) δ 7.10-6.95 (m, 3H, H_1',H_1,H_2), 6.88 (dt, 1H, J 7.5, ~1 Hz, H_2'), 6.83 (t, 1H, J 7.0 Hz, H_3'), 6.69 (dt, 1H, J 7.0, ~1 Hz, H_3), 6.43 (d, 1H, J 7.8 Hz, H_4'), 6.26 (d, 1H, J 7.5 Hz, H_4), 3.26 (d, 1H, J_{AB} 4.5 Hz, H_A), 3.06 (s, 3H, OCH_3), 2.96 (ddd, 1H, J_{GE} ~5 Hz, J_{GC} 4.2 Hz, J_{GD}~2z, H_G), 2.89 (dd, 1H, J_{BE} 5.0 Hz, J_{BA} 4.5 Hz, H_B), 2.40 (dd, 1H, J_{CD} 13.5 Hz, J_{DG} ~2 Hz, H_D), 2.06 (dddd, 1H, J_{EF} 10.8 Hz, J_{EB} 5 Hz, J_{EG} ~5 Hz, J_{ED} ~2 Hz, H_E), 1.97 (dd, J_{CD} 13.5 Hz, J_{CG} 4.2 Hz, H_C), 1.60 (d, 1H, J_{EF} 10.8 Hz, H_F); ^{13}C NMR ($CDCl_3$) δ 157.77 (s, C-a), 146.16 (s), 142.66 (s), 130.61 (s, C-b), 127.91 (d, C-H_3'), 126.88 (d, C-H_2), 125.43 (d, C-H_3), 123.89 (d, C-H_4), 123.80 (d, C-H_1'), 121.96 (d, C-H_1), 120.79 (d, C-H_2'), 109.82 (s, C-c), 109.44 (d, C-H_4'), 51.94 (d, C-H_G), 48.36 (q, OCH_3), 45.36 (d, C-H_B), 40.18 (t, C-H_E,H_F), 38.95 (d, C-H_A), 37.69 (t, C-H_C,H_D); ^{13}C-NMR (C_6D_6) δ 159.11 (s, C-a), 146.90 (s), 143.50 (s), 131.80 (s, C-b), 128.08 (d, C-H_2'), 127.46 (d, C-H_2), 126.14 (d, C-H_3), 124.62 (d, C-H_4), 124.26 (d, C-H_1'), 122.82 (d, C-H_1), 121.13 (d, C-H_3'), 110.22 (d, C-H_4'), 110.22 (s, C-c), 52.66 (d, C-H_A), 48.48 (q, OCH_3), 45.96 (d, C-H_B), 40.86 (t, C-H_E,H_F), 39.73 (d, C-H_G), 38.55 (t, C-H_C,H_D); MS (EI) *m/z* (relative intensity) 278 (M^+, 100%), 246 (M^+-CH_3OH, 35), 163 (58), 149 (87), 131 (2-benzofurylmethyl, 99), 129 (indenylmethyl, 54), 115 (indenyl, 76).

Irradiation of 5 in deuteromethanol. A solution of 5 (16 mg, 0.065 mmol) in 13 mL of CH_3OD ($5x10^{-3}$ M) was irradiated at 300 nm for 2 h at rt. The solvent was removed and the product **19** isolated on TLC plate (13 mg, 72%) as colorless oil, eluting with petroleum/ether (9:1): ^{1}H NMR ($CDCl_3$) δ 7.29 (d, 1H, J 7.2 Hz, H_1'), 7.15 (d, 1H, J 7.2 Hz, H_1), 7.04 (dt, 1H, J 7.2, 1.2 Hz, H_2), 7.01 (ddd, 1H, J 7.8, 7.2, 1.2 Hz, H_3'), 6.91 (dt, 1H, J 7.2, 1.2 Hz, H_2'), 6.69 (dt, 1H, J 7.2, 1.2 Hz, H_3), 6.39 (d, 1H, J 7.8 Hz, H_4'), 6.14 (d, 1H, J 7.2 Hz, H_4), 3.35 (d, 2H, J_{AB} 4.5 Hz, H_A; H_G under the signal of H_A), 3.26 (dd, 1H, J_{AB} 4.5 Hz, J_{BE} 5.4 Hz, H_B), 3.21 (s, 3H, OCH_3), 2.36 (dt, 1H, J_{EF} 11.1 Hz, J_{EB} J_{EG} 5.4 Hz, H_E), 2.25 (d, 1H, J_{CG} 3.9 Hz, H_C), 1.96 (d, 1H, J_{EF} 11.1 Hz, H_F); ^{13}C-NMR ($CDCl_3$) δ 158.02 (s, C-a), 146.41 (s), 142.92 (s), 130.86 (s, C-b), 128.17 (d, C-H_3'), 127.13 (d, C-H_2), 125.68 (d, C-H_3), 124.14 (d, C-H_4), 124.07 (d, C-H_1'), 122.21 (d, C-H_1), 121.04 (d, C-H_2'), 109.84 (s, C-c), 109.70 (d, C-H_4'), 52.18 (d, C-H_A), 48.61 (q, OCH_3), 45.63 (d, C-H_B), 40.38 (t, C-H_E,H_F), 39.11 (d, C-H_G), 37.58 (C-H_CD); MS (EI) *m/z*: 279 (M^+, 100%), 247(M^+-CH_3OH, 22), 149 (25), 132 (2-benzofuryl-CHD, 27), 115 (indenyl, 14). HRMS calcd for $C_{19}DH_{17}O_2$ 279.136, found 279.126.

Irradiation of 12 in methanol. A solution of 10 mg of **12** ($4x10^{-3}$ M) was purged with argon and irradiated at 250 nm for 2 h at rt. The solvent was removed and in the residue some traces of **18** were observed in ^{1}H NMR spectrum. After prolonged irradiation the decomposition of **12** was observed.

Irradiation of 5 in the presence of benzophenone. To a solution of 80 mg (0.3 mmol) of 5 in 100 mL of benzene, 250 mg (1.4 mmol) of benzophenone was added, purged with argon and irradiated at 350 nm (8 lamps) for 20 h at rt. The solvent was removed in vacuum and the residue chromatographed on TLC silica gel plate with petroleum ether-CH_2Cl_2 (7:3) as eluens. The main product, ***trans*-2-(2-vinylphenyl)-3-(2-benzofuryl)-4,4-diphenyl-1-oxetane (20)**, was isolated in 24% yield (31 mg): colorless crystals, mp 51-52 °C; UV (EtOH): λ_{max} (log ε) 206 (4.82), 208 (4.81, sh), 248 (4.43), 278 (3.70), 286 (3.47); ^1H NMR ($CDCl_3$) δ 7.76 (dd, 1H, *J* 7.0, 2.1 Hz, H_{ar}), 7.66 (d, 2H, *J* 7.2 Hz, H_{ar}), 7.51-7.13 (m, 15H, H_{ar}), 6.80 (dd, 1H, *J* 17.4, 10.8 Hz, H_3'), 6.45 (d, 1H, *J* 8.4 Hz, H-s), 6.43 (s, 1H, H_f), 5.54 (dd, 1H, *J* 17.4, ~1 Hz, H_1'), 5.11 (dd, 1H, *J* 10.8, ~1 Hz, H_2'), 4.95 (d, 1H, *J* 8.4 Hz, H-f); ^{13}C NMR ($CDCl_3$) δ 154.99 (s), 153.55 (s), 147.04 (s), 142.18 (s), 138.48 (s), 135.78 (s), 133.92 (d, C-H_3'), 128.57 (2d), 128.36 (d), 128.30 (d), 128.10 (2d), 127.44 (d), 127.17 (d), 126.07 (d), 126.02 (d), 125.80 (2d), 125.11 (2d), 124.18 (d), 122.78 (d), 120.95 (d), 117.04 (t, C-H_1',H_2'), 111.12 (d, C-4), 105.86 (d, C-H_f), 88.64 (s, C_p), 77.92 (d, C-s), 53.71 (d, C-f); MS (FAB) *m/z* (relative intensity) 428 (M^+, <1), 296 (Ph_2C=CH-benzofuryl, 25), 246 (M^+-Ph_2CO, 90), 132 (*o*-vinylbenzaldehyde, 35), 131 (benzofurylmethyl, 70), 105 ($PhCO^+$, 47). Anal. Calcd for $C_{31}H_{24}O_2$: C, 86.89; H, 5.65. Found: C, 86.81; H, 5.62.

***trans*-2-(2-Benzofuryl)-3-(2-vinylphenyl)-4,4-diphenyl-1-oxetane (21)**, minor product (*ca.* 2%) seen only in ^1H NMR ($CDCl_3$) δ 7.80-6.80 (m, 19H, H_{ar}+H_3'), 6.80 (s, 1H, H_f), 6.01 (d, 1H, *J* 8.4 Hz, H-f), 5.60 (dd, 1H, *J* 16.8, ~1 Hz, H_1'), 5.55 (d, 1H, *J* 8.4 Hz, H-s), 5.26 (dd, 1H, *J* 8.4 Hz, H_2').

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14. Atomic coordinates and standard crystallographic results (bonding dimensions and Uij values) for the compound (**12**) have been deposited with the Cambridge Crystallographic Data Centre, Cambridge, U.K. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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