Synthesis and photochemistry of *β*-(3-substituted-2-furyl)-*o*-divinylbenzenes; [2+2] and [4+2] intramolecular cycloadditions

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Dedicated to Professor Branko Stanovnik on his 65th birthday

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Abstract

Irradiation of 3-X-2-[2-(2-vinylphenyl)ethenyl]furans (**6a**, X=CH_3; **6b**, X=Br; **6c**, X= vinyl) gave 2-(3-X-2-furyl)-2,3-dihydro-1,3-methano-1*H*-indenes (**14a-c**) and 1-X-phenanthrenes (**15a-c**). The formation of benzobicyclo[2.1.1]hexene structures (**14a-c**) is explained by intramolecular [2+2] photocycloaddition and the formation of phenanthrenes (**15a-c**) by photoinduced intramolecular [4+2] cycloaddition followed by dehydration.

Keywords: Furan, bicyclo[2.1.1]hexene, photochemical cycloaddition

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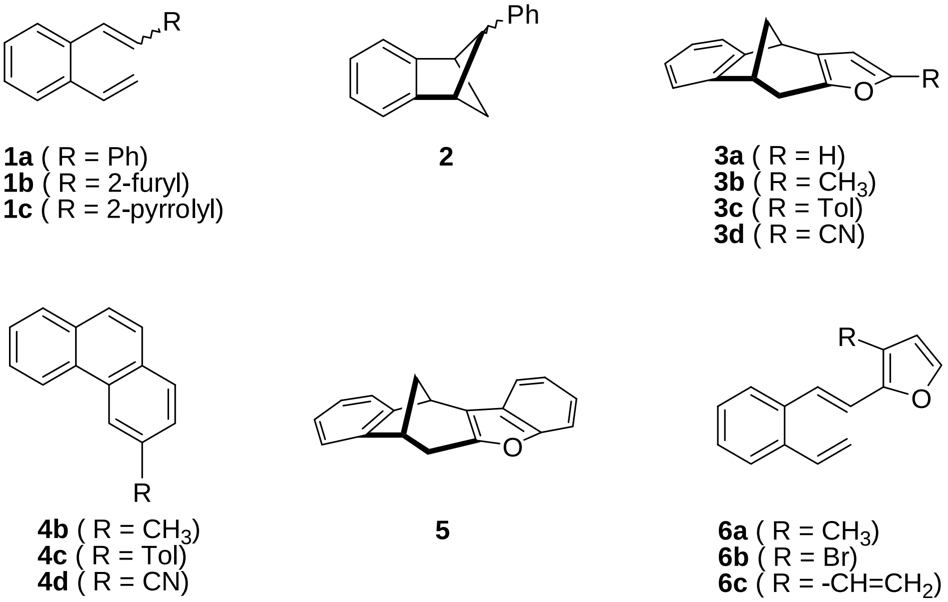
Introduction

Intramolecular photochemical cycloadditions of aryl *o*-divinylbenzenes (**1a**) (Figure 1) have been the subject of intensive investigations.[1-10] This work has been extended to furan (**1b**)[11-16] and pyrrole (**1c**)[17-21] analogues. It has been found that contrary to *o*-vinylstilbene (**1a**), which undergoes an intramolecular [2+2] photocycloaddition that generates benzobicyclo[2.1.1]hexene structure (**2**), the furano analogue (**1b**) gives benzobicyclo[3.2.1]octadiene structure (**3a**) while the pyrrolo analogue (**1c**) reacts completely different and is transformed into an intermolecular adduct. A study of furan derivatives with different functionalities at the 5 position of the furan ring showed a profound effect on the intramolecular cycloaddition.[12] While the unsubstituted (**3a**) and methyl substituted (**3b**) benzobicyclo[3.2.1]octadiene derivatives were formed in very good yields, **3c** and **3d** were found only in traces. Unexpected 3-substituted phenanthrenes (**4b-4d**) were also isolated. The use of benzofuran derivatives provided a route to the fused benzobicyclo[3.2.1]octadiene structure **5**, without the formation of phenanthrene derivatives.

Herein we report the substituent effect on the intramolecular cycloaddition process and the formation of photoproducts by irradiation of 3-substituted furan derivatives (**6a**-**6c**).



1a (R = Ph)
1b (R = 2-furyl)
1c (R = 2-pyrrolyl)

2

3a (R = H)
3b (R = CH_3)
3c (R = Tol)
3d (R = CN)

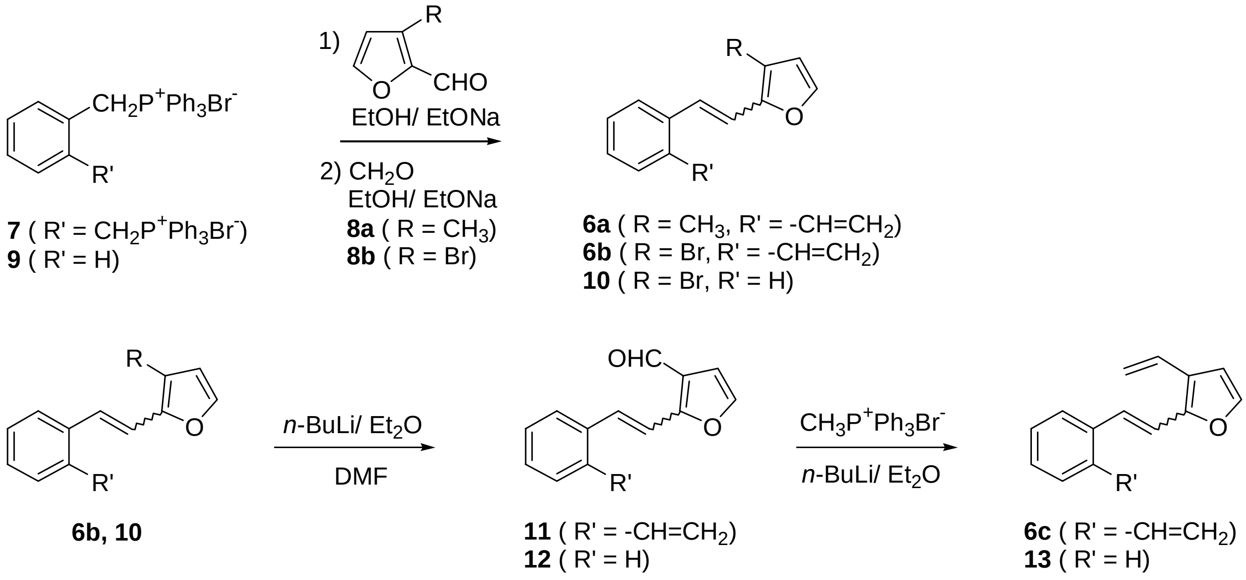
4b (R = CH_3)
4c (R = Tol)
4d (R = CN)

5

6a (R = CH_3)
6b (R = Br)
6c (R = $-CH=CH_2$)

Figure 1

Results and Discussion



7 (R' = $CH_2P^+Ph_3Br^-$)
9 (R' = H)

8a (R = CH_3)
8b (R = Br)

6a (R = CH_3, R' = $-CH=CH_2$)
6b (R = Br, R' = $-CH=CH_2$)
10 (R = Br, R' = H)

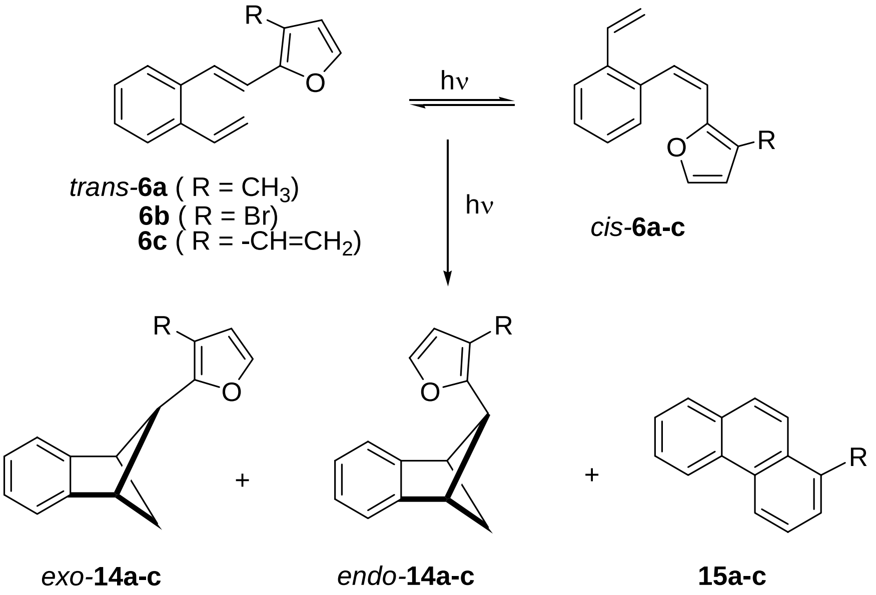
6b, 10

11 (R' = $-CH=CH_2$)
12 (R' = H)

6c (R' = $-CH=CH_2$)
13 (R' = H)

Scheme 1

The starting compounds for the irradiation experiments, **6a**-**6c** and **13**, were prepared using the Wittig reaction, from corresponding phosphonium salts and aldehydes (Scheme 1). They were obtained in moderate to good yields (40-80%) as mixtures of *cis*- and *trans*-isomers. The isomers were separated by column chromatography on silica gel and identified spectroscopically.



Scheme 2

Irradiation of 10^{-3} molar solutions of **6** in petroleum ether under anaerobic conditions at 300 nm, followed by evaporation of the solvent and chromatographic separation of the dark residue, gave a mixture from which *exo*-benzobicyclo[2.1.1]hexenes (10-30%) and *endo*-benzobicyclo[2.1.1]hexenes (**14a**-**c**, 5-10%) were isolated as main photoproducts in addition to 1-substituted phenanthrenes (**15a**-**c**, 2-10%) (Scheme 2).

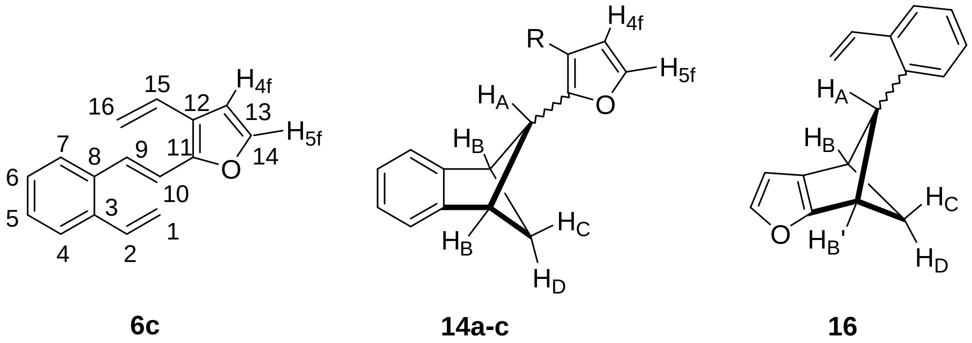
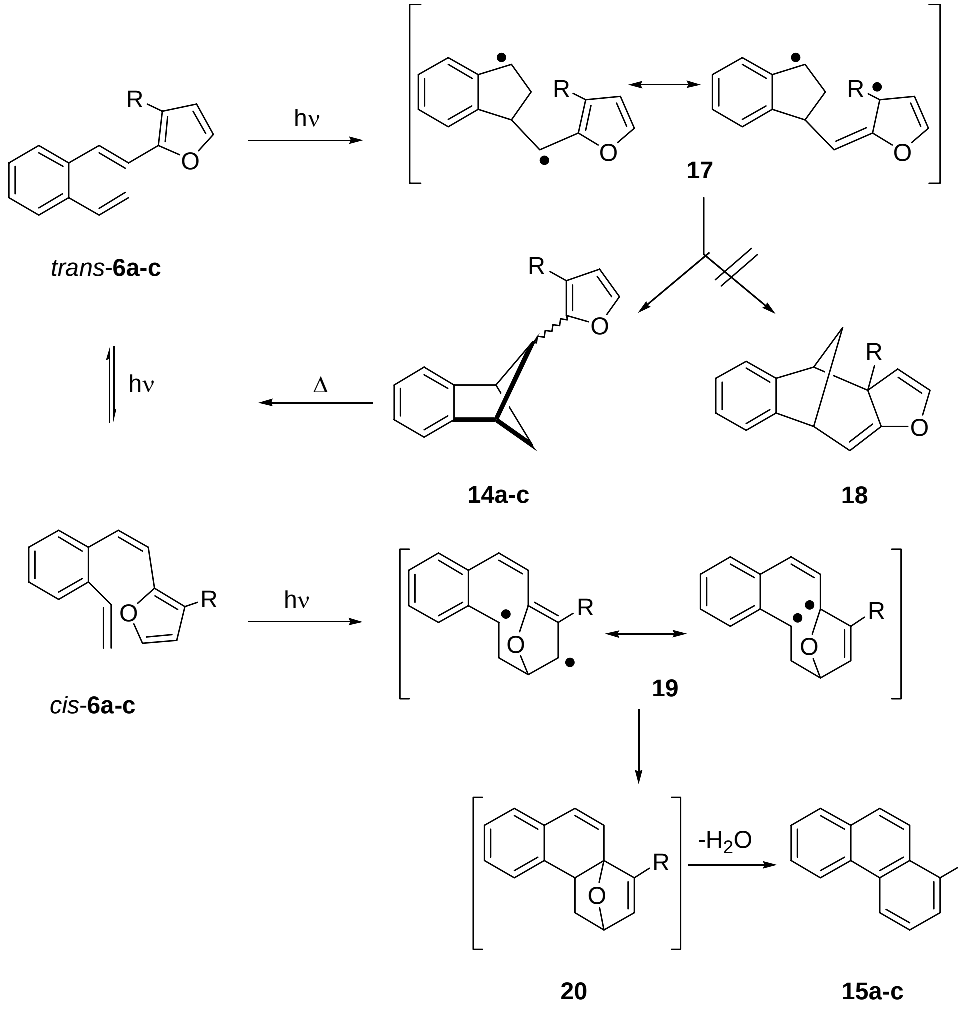


Figure 2

The structures of the photoproducts were determined spectroscopically and were based on their ^{1}H NMR spectra. The pattern of four signals for five protons of **14a-c** (Figure 2., H_A, $2H_B$, H_C and H_D) appeared in the ^{1}H NMR spectrum between 2 and 4 ppm and is characteristic for 5-substituted-benzobicyclo[2.1.1]hexenes. The *exo*-isomer could be detected from the appearance of H_A as a doublet ($J_{AD} = 7.5$ Hz) and the *endo*-isomer from H_A as a triplet with small coupling constants ($J_{AB} = 2$ Hz). The starting compound **6c** with two vinyl groups could react and form the product **16**, instead of **14c**. This could show a similar pattern in the ^{1}H NMR spectrum. The non-participation of the vinyl group of the furan ring in the reaction and formation of **14c** was confirmed on irradiation of **13**. Under the same conditions the 2-styryl-3-vinylfuran (**13**) gave only high-molecular weight material, besides small quantities of unidentified products.

The structures of phenanthrenes **15a-c** with the substituent at position 1 were confirmed by comparison with the ^{1}H NMR spectra of authentic samples.



Scheme 3

On irradiation of 3-substituted-furyl-*o*-divinylbenzenes (**6a**-**c**) no formation of benzobicyclo[3.2.1]octadiene structures **18** was observed (Scheme 3). The preferred photoreaction of **6a**-**c** was the [2+2] cycloaddition and formation of the benzobicyclo[2.1.1]hexene (**14a**-**c**) *via* a 1,4-biradical intermediate (**17**)[2,10] that in this case, for steric reasons, does not give the ring closure to cyclohexene, and formation of **18**. A competing process was the [4+2] photoinduced cycloaddition and formation of phenanthrenes **15a**-**c** *via* the biradicals **19** and epoxide derivatives **20**. This process is seen more often with starting compounds such as **6**, 3-substituted furan derivatives, than as it was seen in 5-substituted derivatives,[12] possibly because of steric effects. Thus, due to the substituent in position 3 the *cis*-configuration of **6** is forced preferred, as illustrated in Scheme 3. This arrangement allows better overlap of the vinyl and the furan moieties. The formation of phenanthrenes as the sole products in the case of prolonged irradiation, besides a lot of tarry material, was explained by the thermal instability of **14**. Benzobicyclo[2.1.1]hexenes give, after ring opening, the starting compounds **6**, that might again react by [2+2] or [4+2] cycloaddition. The thermal ring opening to starting compounds, a mixture of *cis*- and *trans*-isomers, was confirmed by warming the pure isolated **14**. Formation of phenanthrenes **15** by thermal intramolecular reaction of the vinyl group and the furan moiety of **6**, in the *cis*-configuration, was ruled out by carrying out dark reactions.

Experimental Section

General Procedures. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 at 300 and 75 MHz, respectively. All NMR spectra were measured in $CDCl_3$ and when necessary in C_6D_6 solutions using tetramethylsilane reference. The assignment of the signals was based on 2D-CH correlation and 2D-HH-COSY, LRCOSY and NOESY experiments. IR spectra were recorded on a Perkin Elmer M-297 Spectrometer. UV spectra were measured on Perkin-Elmer LAMBDA 20 Spectrophotometer. HRMS spectra were measured on an Extrel FT MS 2001 DD. Melting points were obtained on an Original Kofler Mikroheitztisch apparatus (Reichert, Wien) and are uncorrected. Silica gel (Merck 0.05-0.2 mm) was used for chromatographic purifications. Solvents were purified by distillation.

3-Substituted-2-furancarbaldehydes

3-Methyl-2-furancarbaldehyde (**8a**)[22] was prepared by oxidation of 3-methyl-2-furfurylalcohol[23] that was obtained from 3-methyl-2-furoate[24] with $LiAlH_4$. 3-Bromo-2-furancarbaldehyde (**8b**) was prepared from 2-furancarboxylic acid according to the known procedure.[25]

Synthesis of 6a, 6b and 10

Starting compounds **6a** and **6b** were prepared by the method described[26] from the α,α'-*o*-xylyl(ditriphenylphosphonium)bromide (**7**, 0.01 mol) and the corresponding aldehydes (**8a**: 0.01 mol, **8b**: 0.01 mol) in absolute ethanol (200 mL) and sodium ethoxide (0.01 mol) as the base.

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 (0.011 mol) was added. The reaction mixture was purified and the isomers were separated by repeated column chromatography on silica gel using petroleum ether as eluent. The first fractions yielded the *trans*- and the last fractions the *cis*-isomer.

Starting compound **10** was obtained similarly[27] starting from benzyltriphenylphosphonium bromide (**9**) and 3-bromo-2-furancarbaldehyde (**8b**).

3-Methyl-2-[2-(2-vinylphenyl)ethenyl]furan (6a). Yield 81%; according to ^{1}H NMR a mixture of 56% *trans*- and 44% *cis*-isomer.

trans-**6a**. oil. UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 323 (4.42), 257 (4.12). IR ν_{max}/cm^{-1} (neat): 3070, 3040, 2910, 2850, 1620, 1080, 950. ^{1}H NMR (CDCl$_3$) δ/ppm: 7.17-7.61 (m, 6H), 7.12 (dd, 1H, J = 17.40; 10.84 Hz), 6.77 (d, 1H, J_{et} = 16.11 Hz), 6.27 (d, 1H, J = 1.76 Hz), 5.63 (dd, 1H, J = 17.40; 1.50 Hz), 5.34 (dd, 1H, J = 10.84; 1.50 Hz), 2.11 (s, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$) δ/ppm: 149.26 (s), 141.63 (d), 136.56 (s), 135.82 (s), 135.20 (d), 128.03 (d), 127.55 (d), 126.79 (d), 125.82 (d), 123.24 (d), 119.05 (s), 117.02 (d), 116.57 (t), 114.38 (d), 9.83 (q).

cis-**6a**. oil. UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 301 (4.11), 255 (4.10). IR ν_{max}/cm^{-1} (neat): 3070, 3040, 3000, 2910, 2850, 1620, 1080, 845. ^{1}H NMR (CDCl$_3$) δ/ppm: 7.11-7.60 (m, 5H), 6.92 (dd, 1H, J = 17.29; 10.84 Hz), 6.50; 6.39 (AB$_q$, 2H, J_{et} = 12.59 Hz), 6.13 (d, 1H, J = 1.76 Hz), 5.63 (dd, 1H, J = 17.29; 1.47 Hz), 5.23 (dd, 1H, J = 10.84; 1.47 Hz), 1.90 (s, 3H, C**H$_3$**). ^{13}C NMR (CDCl$_3$) δ/ppm: 148.20 (s), 141.63 (d), 136.69 (s), 136.35 (s), 135.47 (d), 129.97 (d), 127.40 (d), 127.15 (d), 125.44 (d), 120.26 (s), 117.10 (d), 115.41 (t), 113.59 (d), 10.29 (q). MS: *m/z* 210 (M$^+$, 11%), 196 (16), 167 (10), 166 (11), 165 (31), 152 (13), 115 (15), 95 (100). Exact mass Calcd.: 210.103916. Found: 210.103583.

Anal. Calcd. for $C_{15}H_{14}O$ (210.27): C, 85.68; H, 6.71%. Found: C, 85.80; H, 6.58%.

3-Bromo-2-[2-(2-vinylphenyl)ethenyl]furan (6b). Yield 53%; according to ^{1}H NMR a mixture of 60% *trans*- and 40% *cis*-isomer.

trans-**6b**. oil. UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 328 (4.39), 318 (4.39), 255 (4.11). ^{1}H NMR (CDCl$_3$) δ/ppm: 7.21-7.61 (m, 4H), 7.42; 6.84 (AB$_q$, 2H, J = 16.14 Hz), 7.35 (d, 1H, J = 1.96 Hz), 7.09 (dd, 1H, J = 17.34; 10.99 Hz), 6.48 (d, 1H, J = 1.96 Hz), 5.65 (dd, 1H, J = 17.34; 1.34 Hz), 5.40 (dd, 1H, J = 10.99; 1.34 Hz). ^{13}C NMR (CDCl$_3$): 149.89 (s), 141.71 (d), 136.46; 134.48 (2s), 134.60 (d), 127.71 (d), 127.60 (d), 126.47 (d), 126.36 (d), 125.62 (d), 116.48 (t), 115.79 (d), 114.84 (d), 98.93 (s).

cis-**6b**. oil. UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 298 (4.24), 255 (4.18). ^{1}H NMR (CDCl$_3$) δ/ppm: 7.14-7.60 (m, 4H), 7.11 (d, 1H, J = 1.98 Hz), 6.89 (dd, 1H, J = 17.45; 10.99 Hz), 6.67; 6.48 (AB$_q$, 2H, J = 12.36 Hz), 6.38 (d, 1H, J = 1.98 Hz), 5.65 (dd, 1H, J = 17.45; 1.25 Hz), 5.26 (dd, 1H, J = 10.99; 1.25 Hz). ^{13}C NMR (CDCl$_3$): 148.87 (s), 142.10 (d), 136.01; 135.50 (2s), 134.82 (d), 129.40 (d), 128.11 (d), 127.43 (d), 126.81 (d), 125.11 (d), 115.35 (t), 115.35 (d), 114.11 (d), 100.91 (s). MS: *m/z* 276, 274 (M$^+$, 14%), 195 (23), 167 (31), 165 (100), 139 (12), 128 (13), 115 (15), 102 (7), 89 (15), 51 (8). Exact mass Calcd.: 273.998777. Found: 274.002048.

Anal. Calcd. for $C_{14}H_{11}BrO$ (275.15): C, 61.11; H, 4.03%. Found: C, 61.22; H 3.93%.

3-Bromo-2-(2-phenylethenyl)furan (10). Yield 82%; according to ^{1}H NMR a mixture of 66% *trans*- and 37% *cis*-isomer.
trans-**10**. colourless crystals; mp 48-49 °C. UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 338 (4.39), 323 (4.54), 312 (3.45). ^{1}H NMR (CDCl$_3$) δ/ppm: 7.18-7.50 (m, 6H), 7.09; 6.92 (2d, 2H, J = 16.35 Hz), 6.43 (d, 1H, J = 1.95 Hz). ^{13}C-NMR (CDCl$_3$) δ/ppm: 149.90 (s), 142.00 (d), 136.60 (s), 128.80 (d), 127.90 (d), 128.70; 126.50 (4d), 115.00 (d), 113.50 (d), 99.00 (s).
cis-**10**. oil. UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 334 (3.92, sh), 317 (4.22, sh), 308 (4.26). ^{1}H NMR (CDCl$_3$) δ/ppm: 7.22-7.40 (m, 5H), 7.16 (d, 1H, J = 1.98 Hz), 6.55 (d, 1H, J = 12.63 Hz), 6.40 (d, 1H, J = 1.98 Hz), 6.33 (d, 1H, J = 12.63 Hz); ^{13}C NMR (CDCl$_3$) δ/ppm: 149.07 (s), 141.84 (d), 136.76 (s), 129.83 (d), 128.96 (d), 127.84 (d), 127.53 (d), 114.52 (d), 113.98 (d), 101.24 (s). MS: *m/z* 250, 248 (M$^+$, 27 %), 169 (48), 141, 139 (100), 115 (68). Exact mass Calcd.: 247.983127. Found: 247.982529.
Anal. Calcd. for $C_{12}H_9OBr$ (248.22): C, 57.86; H, 3.64%. Found: C, 57.79; H, 3.68%.

Synthesis of 11 and 12

To a stirred solution of 3.0 mmol **6b** (a mixture of *trans*- and/or *cis*-isomers) or **10** (a mixture of *trans*- and/or *cis*-isomers), respectively, in 40 mL of anhydrous ether cooled to –70 ºC, 3.3 mmol butyl lithium (1,6 M hexane solution) was added under a stream of nitrogen during 30 min. After additional stirring for 30 min, 6.6 mmol of anhydrous *N,N*-dimethylformamide was added. After 1 h on that temperature, the mixture was allowed gradually to warm up to 0 ºC, during 3 h. Dilute hydrochloric acid was added, 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/ ether (0-10%) as eluent.
2-(2-Phenylethenyl)furan-3-carbaldehyde (12). Yield 59%; *trans*-**12**: yellow crystals; mp 63-64 °C. UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 345 (4.44), 263 (3.93), 235 (4.16). IR ν_{max}/cm^{-1} (neat): 1673 (C=O), 1626 (C=C). ^{1}H NMR (CDCl$_3$) δ/ppm: 10.10 (s, CHO), 7.54 (d, 2H, J = 7.20 Hz), 7.44-7.24 (m, 6H), 6.78 (d, 1H, J = 1.39 Hz). ^{13}C NMR (CDCl$_3$) δ/ppm: 183.89 (CHO), 158.34 (s), 142.22 (d), 135.30 (s), 133.76 (d), 128.66 (d), 128.41 (2d), 126.71 (2d), 122.06 (s), 112.83 (d), 109.27 (d); MS: *m/z* 198 (M$^+$, 68 %), 169 (27), 141 (100), 115 (74).
cis-**12**. oil. IR ν_{max}/cm^{-1} (neat): 1673 (C=O), 1633 (C=C). ^{1}H NMR (CDCl$_3$) δ/ppm: 9.99 (s, 1H, CHO), 7.17-7.61 (m, 6H), 6.89 (d, 1H, J = 12.36 Hz), 6.76 (d, 1H, J = 1.80 Hz), 6.75 (d, 1H, J = 12.36 Hz). ^{13}C NMR (CDCl$_3$) δ/ppm: 184.29 (CHO), 158.13 (s), 142.45 (d), 135.58 (s), 134.11 (d), 129.04 (d), 128.79 (2d), 128.27 (2d), 123.70 (s), 113.15 (d), 109.62 (d). MS *m/z*: 198 (M$^+$, 78 %), 169 (27), 141 (100), 115 (76).
Anal. Calcd. for $C_{13}H_{10}O_2$ (198.22): C, 78.77; H, 5.09%. Found C, 78.80; H, 5.20%.
2-[2-(2-Vinylphenyl)ethenyl]furan-3-carbaldehyde (11). Yield 47%; *trans*-**11**: oil; UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 348 (4.12), 337 (4.09, sh). IR ν_{max}/cm^{-1} (neat): 1670 (C=O), 1635 (C=C). ^{1}H NMR (CDCl$_3$) δ/ppm: 10.11 (s, 1H, CHO), 7.75; 7.23 (AB$_q$, 2H, J = 15.90 Hz), 7.40 (d, 1H, J = 1.95 Hz), 7.11 (dd, 1H, J = 17.10; 11.25 Hz), 6.81 (d, 1H, J = 1.95 Hz), 5.67 (dd, 1H, J = 17.10; 1.20 Hz), 5.44 (dd, 1H, J = 11.25; 1.20 Hz). ^{13}C NMR (CDCl$_3$) δ/ppm:

184.46 (d, CHO), 158.95 (s), 142.79 (d), 137.41 (s), 133.76 (s), 134.44 (d), 131.77 (d), 129.05 (d), 128.00 (d), 127.01 (d), 126.14 (d), 122.62 (s), 117.64 (t), 115.07 (d), 109.66 (d).
cis-**11**. oil. UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 331 (3.92). IR ν_{max}/cm^{-1} (neat): 1670 (C=O). ^{1}H NMR (CDCl$_3$) δ/ppm: 9.96 (s, 1H, CHO), 6.80-7.65 (m, 6H), 7.00 (d, 1H, J = 12.36 Hz), 6.89 (d, 1H, J = 12.36 Hz), 6.69 (d, 1H, J = 1.11 Hz), 5.66 (d, 1H, J = 17.70 Hz), 5.28 (d, 1H, J = 11.50 Hz). MS: *m/z* 224 (M$^+$, 25%), 206 (53), 115 (100). Exact mass Calcd.: 224.083181. Found: 224.085716.
Anal. Calcd. for $C_{15}H_{12}O_2$ (224.25): C, 80.34; H 5.39%. Found: C, 80.20; H, 5.52%.

Synthesis of 6c and 13

To a stirred solution of **11** (2.0 mmol) or **12** (2.0 mmol), respectively, and methyltriphenylphosphonium bromide (2.2 mmol) in 40 mL anhydrous ether, 2.2 mmol butyl lithium (1.6 M hexane solution) was added under a stream of nitrogen. The mixture was stirred overnight, water added (40 mL) and the product extracted with ether (60 mL). After extraction the combined organic phases were dried over anhydrous $MgSO_4$. The reaction mixture was purified and separated by column chromatography on silica gel using petroleum ether/ ether (0-15%) as eluent. The first fractions yielded the vinyl derivatives (first *trans*- and than *cis*-isomer) and in the last fractions the unreacted formyl derivatives were recovered.
3-Vinyl-2-[2-(2-vinylphenyl)ethenyl]furan (6c) (for notations see Figure 2). Yield 37%;
trans-**6c**. oil. UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 358 (4.30), 345 (4.45), 332 (4.43), 260 (4.07), 232 (4.29). ^{1}H NMR (CDCl$_3$) δ/ppm: 7.35; 6.88 (2d, 2H, J = 15.90 Hz, H$_{et}$), 7.30 (d, 1H, J = 1.65 Hz, H$_{5f}$), 7.10 (dd, 1H, J = 17.40; 11.10 Hz, H$_3$(C$_2$)), 6.71 (dd, 1H, J = 17.10; 10.80 Hz, H$_3$(C$_{15}$)), 6.65 (d, 1H, J = 1.65 Hz, H$_{4f}$), 5.63 (dd, 1H, J = 17.40; 1.35 Hz, H$_1$(C$_1$)), 5.47 (dd, 1H, J = 17.10; 1.20 Hz, H$_1$(C$_{16}$)), 5.35 (dd, 1H, J = 11.10; 1.35 Hz, H$_2$(C$_1$)), 5.20 (dd, 1H, J = 10.80; 1.20 Hz, H$_2$(C$_{16}$)). ^{13}C NMR (CDCl$_3$) δ/ppm: 149.74 (s, C$_{11}$), 142.27 (d, C$_{14}$), 136.52, 135.09 (2s, C$_{3/8}$), 134.81 (d, C$_2$), 127.79, 127.66, 126.64, 125.66 (4d, C$_{4\text{-}7}$).
cis-**6c**. oil. UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 320 (3.88), 235 (3.67). ^{1}H NMR (CDCl$_3$) δ/ppm: 7.51 (d, 1H, J = 7.90 Hz), 7.15-7.30 (m, 3H), 7.09 (d, 1H, J = 1.62 Hz, H$_{5f}$), 6.91 (dd, 1H, J = 17.40; 11.01 Hz, H$_3$(C$_2$)), 6.62 (dd, 1H, J = 17.30; 10.83 Hz, H$_3$(C$_{15}$)), 6.61 (d, 1H, J = 12.80 Hz, H$_{et}$), 6.51 (d, 1H, J = 12.80 Hz, H$_{et}$), 6.48 (d, 1H, J = 1.62 Hz, H$_{4f}$), 5.65 (dd, 1H, J = 17.40; 1.30 Hz, H$_1$(C$_1$)), 5.45 (dd, 1H, J = 17.30; 1.26 Hz, H$_1$(C$_{16}$)), 5.24 (dd, 1H, J = 11.00; 1.30 Hz, H$_2$(C$_1$)), 5.17 (dd, 1H, J = 10.83; 1.26 Hz, H$_2$(C$_{16}$)). ^{13}C NMR (CDCl$_3$) δ/ppm: 148.64 (s, C$_{11}$), 142.31 (d, C$_{14}$), 136.19, 136.12 (2d, C$_{3/8}$), 135.15 (d, C$_2$), 129.72 (d, C$_9$), 127.40 (d), 127.03 (d), 126.93 (d), 126.36 (d), 125.20 (d, C$_{15}$), 116.39 (d, C$_{12}$), 115.99, 115.40 (2d, C$_{1/16}$), 114.00 (d, C$_{10}$), 107.95 (d, C$_{13}$). MS: *m/z* 222 (M$^+$, 90%), 207 (74), 179 (79), 165 (44), 115 (65). Exact mass Calcd.: 222.103916. Found: 222.102833.
Anal. Calcd. for $C_{16}H_{14}O$ (222.28): C, 86.45; H, 6.35%. Found: C, 86.31; H, 6.48%.
3-Vinyl-2-(2-phenylethenyl)furan (13).[28a,b] Yield 32%;
trans-**13**. colourless crystals; mp 58 °C. UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 353 (4.40), 335 (4.57), 320 (4.47, sh), 245 (4.22). ^{1}H NMR (CDCl$_3$) δ/ppm: 7.20-7.56 (m, 6H), 7.05; 7.03

(2H, AB$_q$, *J* = 16.10 Hz), 6.76 (dd, 1H, *J* = 17.20; 10.90 Hz), 6.59 (d, 1H, *J* ≈ 2 Hz), 5.50 (dd, 1H, *J* = 17.20; ≈ 1 Hz), 5.23 (dd, 1H, *J* = 10.90; ≈ 1 Hz). ^{13}C NMR (C_6D_6) δ/ppm: 150.61 (s), 142.84 (d), 137.86 (s), 129.29 (2d), 128.51 (d), 128.26 (d), 127.21 (2d), 127.11 (d), 123.02 (s), 114.70 (d), 114.15 (t), 109.41 (d). MS: *m/z* 196 (M$^+$, 100), 167 (52), 115 (17), 91 (20).
cis-**13**. oil. UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 320 (3.92), 245 (3.71, sh). ^{1}H NMR ($CDCl_3$) δ/ppm: 7.18-7.51 (m, 6H), 6.62 (dd, 1H, *J* = 17.40; 10.80 Hz), 6.55 (d, 1H, *J* = 1.95 Hz), 6.51; 6.42 (2H, AB$_q$, *J* = 12.40 Hz), 5.47 (dd, 1H, *J* = 17.40; 1.20 Hz), 5.18 (dd, 1H, *J* = 10.80; 1.20 Hz). MS: *m/z* 196 (M$^+$, 100), 167 (69), 115 (25), 91 (40).
Anal. Calcd. for $C_{14}H_{12}O$ (196.24): C, 85.68; H, 6.16%. Found: C, 85.24; H, 6.08%.

Irradiation experiments

Furan derivatives **6a-c** (10^{-3} M) were dissolved in distilled petroleum ether (bp 40-60 °C), flushed with nitrogen or argon for 30 min, and irradiated in a Quartz tube using a Rayonet Reactor with 300 nm lamps. Irradiation time varied depending on the starting compound (**6a** and **6b** 40-60 h and **6c** 2-4 h, respectively). The solvent was evaporated and the residue separated by column chromatography on silica gel using petroleum ether as eluent. The first fractions yielded 1-substituted-phenanthrenes (**15a-c**) followed by *exo*- and *endo*-isomers (**14a-c**). High-molecular weight products remained on the column.

Irradiation products of 6a

2-(3-Methyl-2-furyl)-2,3-dihydro-1,3-methano-1*H*-indene (14a). *exo*-**14a**. 31%; oil. ^{1}H NMR ($CDCl_3$) δ/ppm: 7.23-7.32 (m, 3H), 6.97-7.03 (m, 2H), 6.22 (d, 1H, *J* = 1.60 Hz, H_{4f}), 3.76 (d, 1H, J_{AD} = 7.60 Hz, H_A), 3.47 (d, 2H, J_{BC} = 2.50 Hz, H_B), 3.33 (dt, 1H, J_{CD} = 6.20 Hz; J_{BC} = 2.50 Hz, H_C), 2.40 (dd, 1H, J_{AD} = 7.60 Hz; J_{CD} = 6.20 Hz, H_D), 2.03 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$) δ/ppm: 152.46 (s), 149.34 (s), 139.82 (d), 124.21 (d), 118.81 (d), 115.76 (s), 113.30 (d), 70.66 (d), 60.82 (t), 48.99 (d), 10.12 (q).
endo-**14a**. 7%; oil. ^{1}H NMR ($CDCl_3$) δ/ppm: 6.82-7.20 (m, 5H), 5.87 (d, 1H, *J* = 1.80 Hz, H_{4f}), 4.19 (m, 1H, J_{AB} = 2.50 Hz; J_{AMe} = 0.80 Hz, H_A), 3.52 (t, 2H, J_{BC} = 2.50 Hz, H_B), 2.79 (dt, 1H, J_{CD} = 5.90 Hz; J_{BC} = 2.50 Hz, H_C), 2.39 (d, 1H, J_{CD} = 5.90 Hz, H_D), 1.81 (d, 3H, J_{AMe} = 0.80 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 150.13 (s), 149.94 (s), 140.13 (d), 124.42 (d), 119.98 (d), 115.22 (s), 112.76 (d), 69.01 (d), 61.16 (t), 48.84 (d), 9.77 (q). Exact mass Calcd.: 210.103916. Found: 210.102710.
Anal. Calcd. for $C_{15}H_{14}O$ (210.27): C, 85.68; H 6.71%. Found: C, 85.53; H, 6.87%.
1-Methylphenanthrene (15a). 10%; ^{1}H NMR spectrum identical to the spectrum of an authentic sample.[29]

Irradiation products of 6b

2-(3-Bromo-2-furyl)-2,3-dihydro-1,3-methano-1*H*-indene (14b). *exo*-**14b**. 7%; oil. ^{1}H NMR ($CDCl_3$) δ/ppm: 7.33 (d, 1H, *J* = 1.90 Hz, H_{5f}), 7.20-7.30 (m, 2H), 6.99-7.01 (m, 2H), 6.42 (d, 1H, *J*= 1.90 Hz, H_{4f}), 3.74 (d, 1H, *J* = 7.50 Hz, H_A), 3.60 (d, 2H, *J* = 2.40 Hz, H_B), 3.24 (dt, 1H,

J = 7.50; 2.40 Hz, H_C), 2.42 (t, 1H, J = 7.50 Hz, H_D). ^{13}C NMR ($CDCl_3$) δ/ppm: 152.05 (s), 150.78 (s), 141.22 (d), 124.39 (d), 118.98 (d), 114.20 (d), 97.31 (s), 69.63 (d), 60.71 (t), 48.59 (d). MS *m/z*: 276,274 (M^+, 80%), 195 (100). Exact mass Calcd.: 273.99877. Found: 274.034001.

endo-**14b**. 9%; oil. ^{1}H NMR ($CDCl_3$) δ/ppm: 7.15-7.21 (m, 2H), 6.98 (d, 1H, J = 1.90 Hz, H_{5f}), 6.86-6.92 (m, 2H), 6.09 (d, 1H, J = 1.90 Hz, H_{4f}), 4.15 (t, 1H, J = 2.60 Hz, H_A), 3.63 (t, 2H, J = 2.60 Hz, H_B), 2.80 (dt, 1H, J = 6.00; 2.60 Hz, H_C), 2.40 (d, 1H, J = 6.00 Hz, H_D). ^{13}C NMR ($CDCl_3$) δ/ppm: 149.53 (s), 149.53 (s), 141.19 (d), 124.30 (d), 120.00 (d), 113.32 (d), 96.55 (s), 67.96 (d), 60.50 (t), 48.51 (d). MS *m/z*: 276,274 (M^+, 20%), 195 (55) 165 (100). Exact mass Calcd.: 273.99877. Found: 274.000346.

Anal. Calcd. for $C_{14}H_{11}BrO$ (275.15): C, 61.11%; H, 4.03%. Found: C, 61.23%; H, 3.91%.

1-Bromophenanthrene (15b).[30] 3%; colourless crystals; mp 110-112 °C (lit.[31] mp = 112 °C). ^{1}H NMR ($CDCl_3$) δ/ppm: 8.69 (d, 2H, J = 8.20 Hz), 8.21 (d, 1H, J = 9.00 Hz), 7.80-7.95 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ/ppm: 132.02 (s), 131.90 (s), 130.71 (d), 130.55 (s), 129.92 (s), 128.66 (d), 128.48 (d), 127.20 (d), 127.08 (d), 126.85 (d), 125.26 (d), 123.69 (s), 122.86 (d), 122.31 (d). MS: *m/z* 258,256 (M^+, 60%), 176 (100), 150 (35). Exact mass Calcd.: 255.988212. Found: 255.998328.

Irradiation products of 6c

2-(3-Vinyl-2-furyl)-2,3-dihydro-1,3-methano-1*H*-indene (14c). *exo*-**14c**. 11%; oil. ^{1}H NMR ($CDCl_3$) δ/ppm: 7.34 (d, 1H, J = 1.80 Hz, H_{5f}), 7.27-7.29 (m, 2H), 7.02-7.04 (m, 2H), 6.62 (dd, 1H, J = 17.40; 11.10 Hz, H_3), 6.57 (d, 1H, J = 1.80 Hz, H_{4f}), 5.42 (dd, 1H, J = 17.40; 1.20 Hz, H_1), 5.14 (dd, 1H, J = 11.10; 1.20 Hz, H_2), 3.87 (d, 1H, J_{AD} = 7.50 Hz, H_A), 3.53 (d, 2H, J_{BC} = 2.40 Hz, H_B), 3.34 (dt, 1H, J_{CD} = 6.60 Hz; J_{CB} = 2.40 Hz, H_C), 2.43 (dd, 1H, J_{AD} = 7.50 Hz; J_{DC} = 6.60 Hz, H_D). ^{13}C NMR (C_6D_6) δ/ppm: 151.71 (s), 149.29 (s), 134.43 (d), 124.57 (d), 118.87 (d), 116.16 (t), 115.55 (d), 114.93 (s), 114.52 (d), 68.29 (d), 60.30 (t), 48.50 (d).

endo-**14c**. 5%; oil. ^{1}H NMR ($CDCl_3$) δ/ppm: 7.56-6.98 (m, 5H), 6.65 (d, 1H, J = 1.80 Hz, H_{4f}), 5.49 (dd, 1H, J = 17.40; 1.80 Hz, H_1), 5.18 (dd, 1H, J = 11.40; 1.80 Hz, H_2), 4.26 (m, 1H, H_A), 3.58 (t, 2H, J_{BC} = 2.40 Hz, H_B), 2.82 (dt, 1H, J_{CD} = 11.40 Hz; J_{BC} = 2.40 Hz, H_C), 2.56 (d, 1H, J_{CD} = 11.40 Hz, H_D). MS: *m/z* 222 (M^+, 83%), 207 (69), 165 (48), 115 (66).

Anal. Calcd. for $C_{16}H_{14}O$ (222.28): C, 86.45; H, 6.35%. Found: C, 86.51; H, 6.24%.

1-Vinylphenanthrene (15c). traces seen in ^{1}H NMR spectrum, identical to the spectrum of an authentic sample.[2]

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