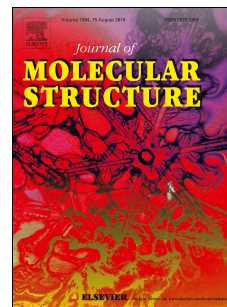


# Accepted Manuscript

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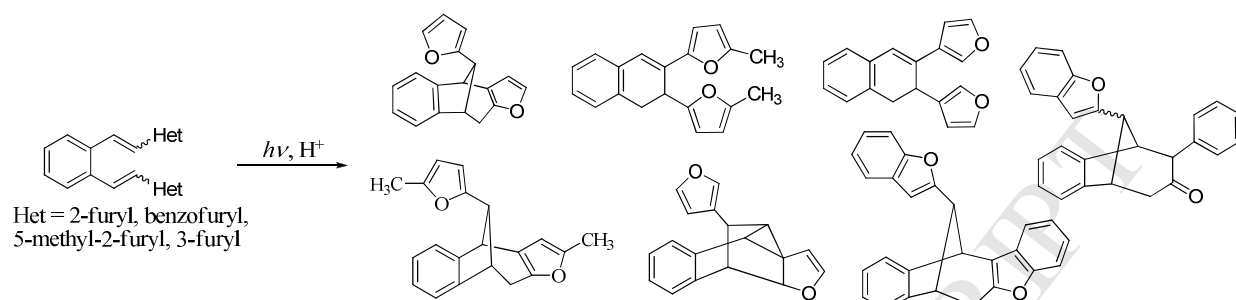
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## Graphical abstract

Synthesis of new furan polycycles *via* photochemical reaction in neutral and acidic medium



## Synthesis of new furan polycycles *via* photochemical reaction in neutral and acidic medium

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### Abstract

New furan derivatives of *o*-divinylbenzenes were synthesized and their photochemical reactivity has been investigated in neutral and acidic medium. Depending of the structure of the starting materials and pH value, the new cyclization (**11**, **16**, **20**), cycloaddition (**12**, **13**, *endo*-**17**, *exo*-**18**), electrocyclization (**21**, **22**) and dimeric (**15**, **19**) products were isolated. While photochemical investigation in neutral medium showed that the main intramolecular process is cycloaddition, in the case of acidic photochemistry, due to the protonation of the starting molecule, electrocyclization process comes to expression and formation of dihydronaphthalene products **21** and **22**.

Keywords: Furan, Photochemistry, Electrocyclization, Cycloaddition, Protonation

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## Introduction

The photochemistry of stilbene-like [1-3] compounds was the subject of intensive research over the past years [4-17] while it was considered as a convenient way for photochemical synthesis of complex polycyclic structures whose synthesis has been hampered by a classical procedure. Of particular interest in this field are annulated heterocyclic derivatives of *o*-divinylbenzenes [12-17] which could produce a number of new interesting compounds, depending on structure of starting material and experimental conditions. In few of our previous papers [12-15], photoreactivity of annulated difuran and dithiophene derivatives was thoroughly explored and mutually compared. While difuryl derivatives [14] upon irradiation mostly gave intramolecular products of cycloaddition reaction, in the case of dithienyl derivatives [12] the main photochemical process is electrocyclization process, depending on the position of the sulphur in the aromatic moiety.

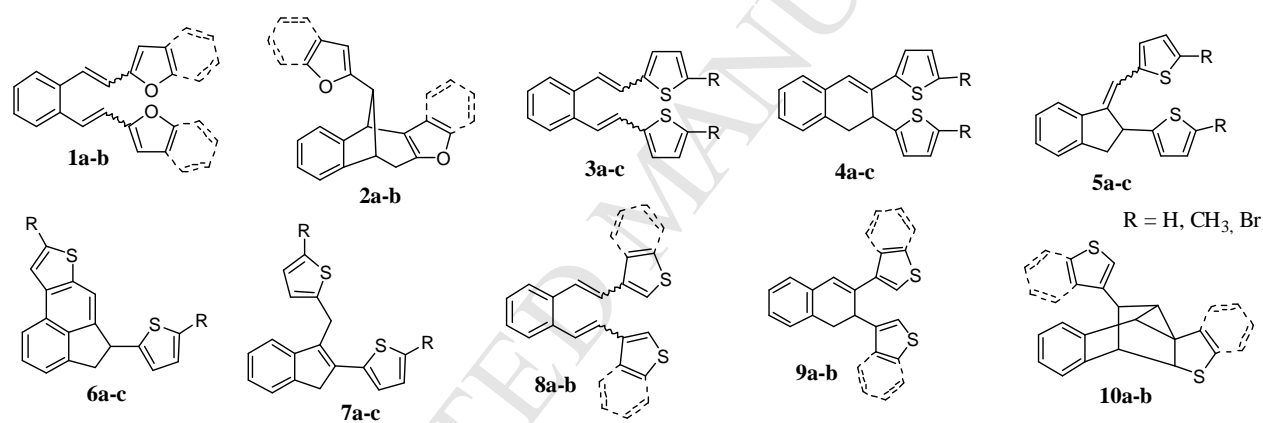


Figure 1.

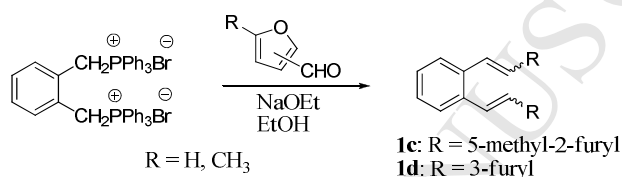
Further, in one of our previous paper, we studied the photochemical behavior of dithienyl derivatives in acidic medium and showed that the photoreactivity could be completely changed upon different pH value [13]. While the main isolated photoproduct in neutral medium was dihydronaphthalene derivative **3a-c**, photochemistry in acidic medium towards the reaction course to the other direction and formation of compounds **5a-c**, **6a-c** and **7a-c**. On the other side, except the pH value, we showed that the position of heteroatom in the aromatic moiety may also affect to the photochemical reactivity of starting material, whereby the new complex polycyclic systems **10a-b** were obtained.

As a continuation of the previous study, the aim of this work is to explore the influence of type of heteroatom in the aromatic moiety to the reaction mechanism, which could bring the useful information from the synthetic point of view. For this purpose the novel annulated furyl

derivatives with different position of oxygen in furan were prepared and their photoreactivity was investigated in neutral and acidic medium.

## Results and Discussion

The synthesis of 2-[(*E*)-2-{2-[(*E*)-2-(furan-2-yl)ethenyl]phenyl}ethenyl]furan (**1a**) and 2-[(*E*)-2-{2-[(*E*)-2-(1-benzofuran-2-yl)ethenyl]phenyl}ethenyl]-1-benzofuran (**1b**) have been previously reported [11]. The novel compounds **1c-d** were prepared by analogue procedure [14] from  $\beta,\beta$ -*o*-xylyl(ditriphenylphosphonium)dibromide and the corresponding aldehydes (Scheme 1). The products are obtained in very good yields (75-90 %) as mixtures of *cis,cis*-, *cis,trans*- and *trans,trans*-isomers.



Scheme 1.

After repeated column chromatography the isomers of 3-[2-{2-[2-(furan-3-yl)ethenyl]phenyl}ethenyl]furan (**1d**) were isolated and completely characterized, while in the case of 2-methyl-5-[2-{2-[2-(5-methylfuran-2-yl)ethenyl]phenyl}ethenyl]furan (**1c**), only *trans,trans*-isomer was isolated as it was obtained as the major product in the reaction mixture. Compared <sup>1</sup>H NMR spectra of *cis,cis*-, *cis,trans*- and *trans,trans*-isomers **1d** are shown on Figure 2. Ethylenic protons in all cases appear as doublets between 6.30 and 7.10 ppm, with shift to higher field of *trans*-ethylenic protons in accordance with its increased molecular planarity.

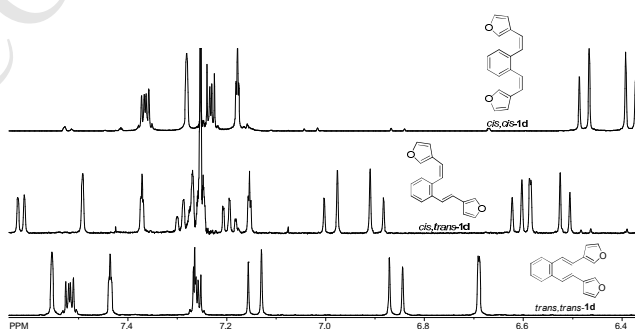


Figure 2.

UV spectra for isomers of compound **1d** (Figure 3) show expected red shift of *trans,trans-1d* with hyperchromic effect in regards to the *cis,cis*-isomer.

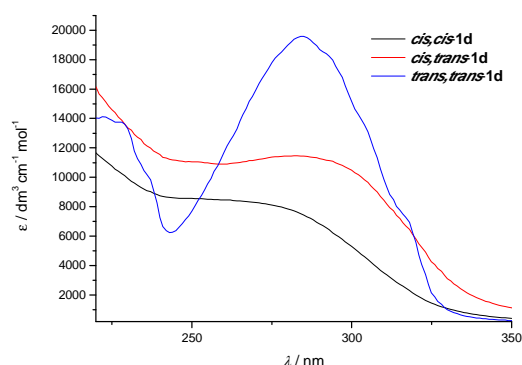
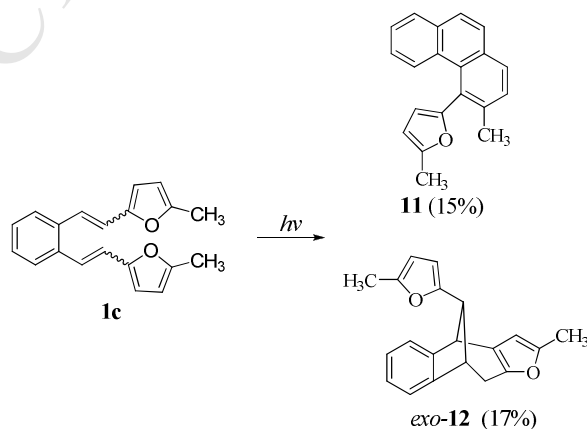


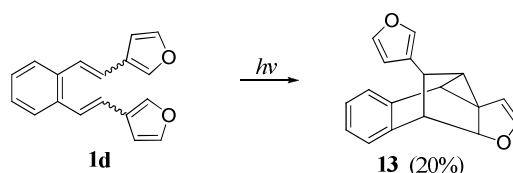
Figure 3.

#### Photochemistry in neutral media

Prepared compounds **1c-d** were subjected to irradiation in neutral medium, while the irradiation experiments in acidic medium were performed for all the compounds **1a-d**. Irradiation in neutral medium were performed by the previously described procedure for the compounds **1a-b** [14]. The mixture of isomers of starting compounds **1c-d** were irradiated in toluene under anaerobic conditions in Rayonet reactor at 350 nm during 16 h. After evaporation of the solvent the crude reaction mixture was chromatographed with petroleum ether as eluent. The mixture obtained from irradiation of dimethyl derivative **1c** gave two novel products, the phenanthrene derivative **11** and the furo-benzobicyclo[3.2.1]octadiene compound *exo-12* (Scheme 2). In the case of 3-furyl derivative **1d** the polycyclic compound **13** was the only isolated photoproduct (Scheme 3).

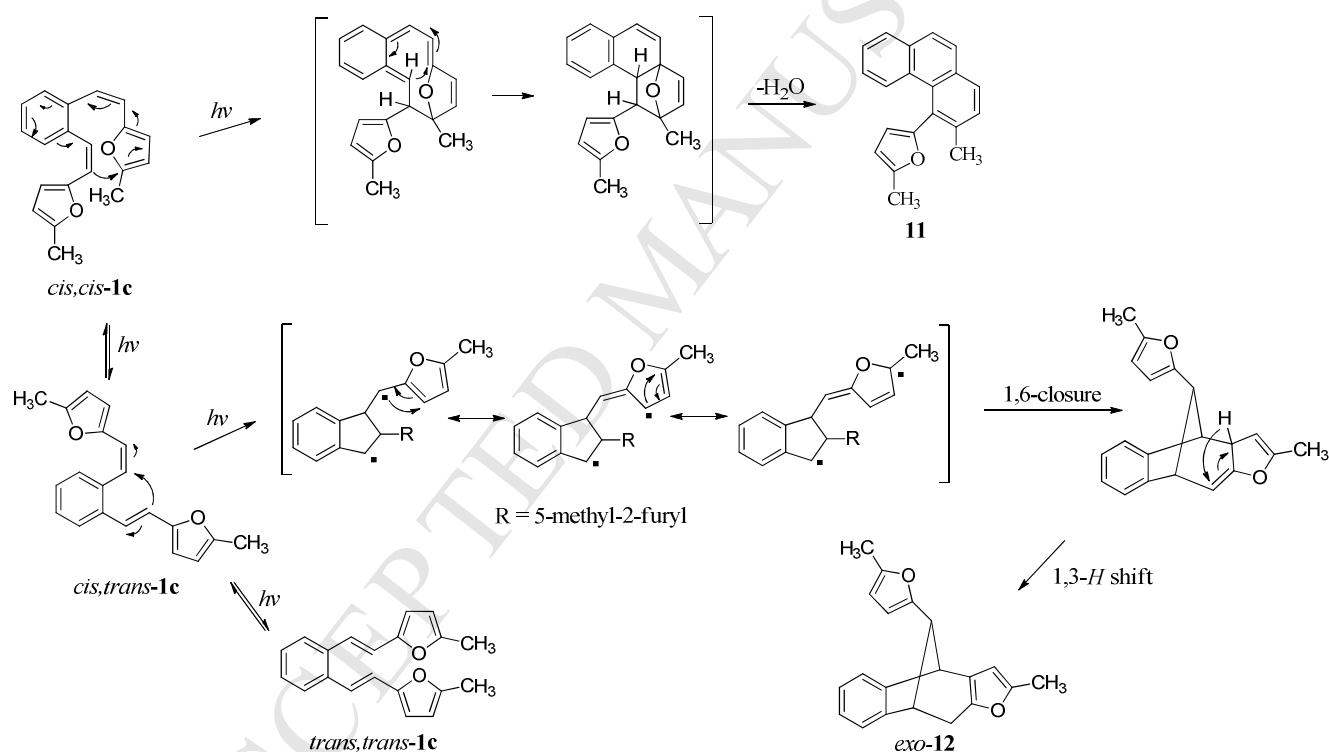


Scheme 2.



Scheme 3.

Scheme 4. shows assumed mechanism of formation of photoproducts **11** and *exo*-**12**. Cyclization derivative **11** formed by  $10\pi$  electrocyclic process and subsequent elimination of water, while the furo-benzobicyclo[3.2.1]octadiene compound **12** was generated *via* the well studied cycloaddition reaction of **1b** followed by 1,6-ring closure and hydrogen shift.



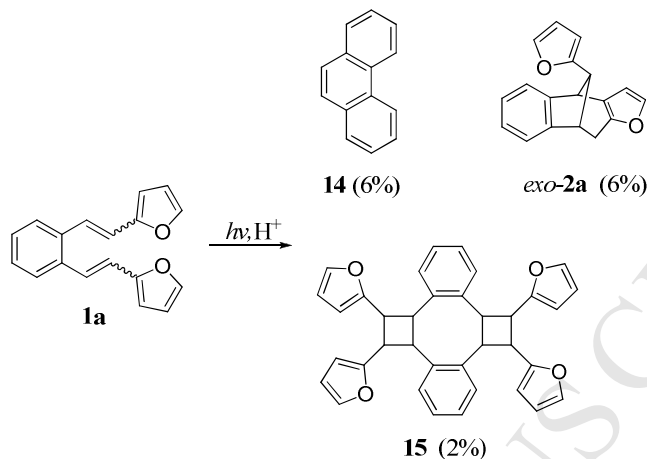
Scheme 4.

### Photochemistry in acidic media

Photochemical experiment in acidic media were performed by irradiation of starting compounds **1a-d** in acetonitrile solution in the presence of hydrochloric acid in anaerobic conditions for 2 h. After treatment, the reaction mixture was chromatographed by the column chromatography, by which all formed products were isolated, respectively.

Analysis of the photochemical results of the unsubstituted derivative **1a** gave three products: molecule of phenanthrene **14** (6 %), furo-benzobicyclo[3.2.1]octadiene derivative *exo*-**2a**

(6%) and dimeric product **15** (2%), which were also obtained by irradiation of the same compound in neutral medium [14]. The indane/indene derivatives which were formed by acidic irradiation of the analogue thiophene derivative [13] in this case were not found.

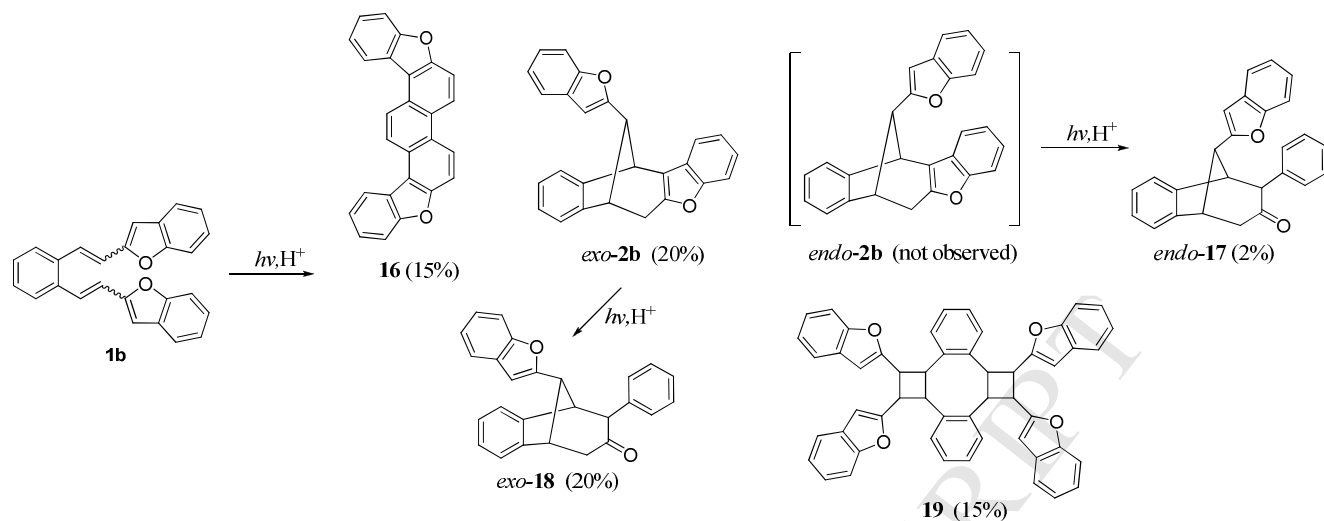


Scheme 5.

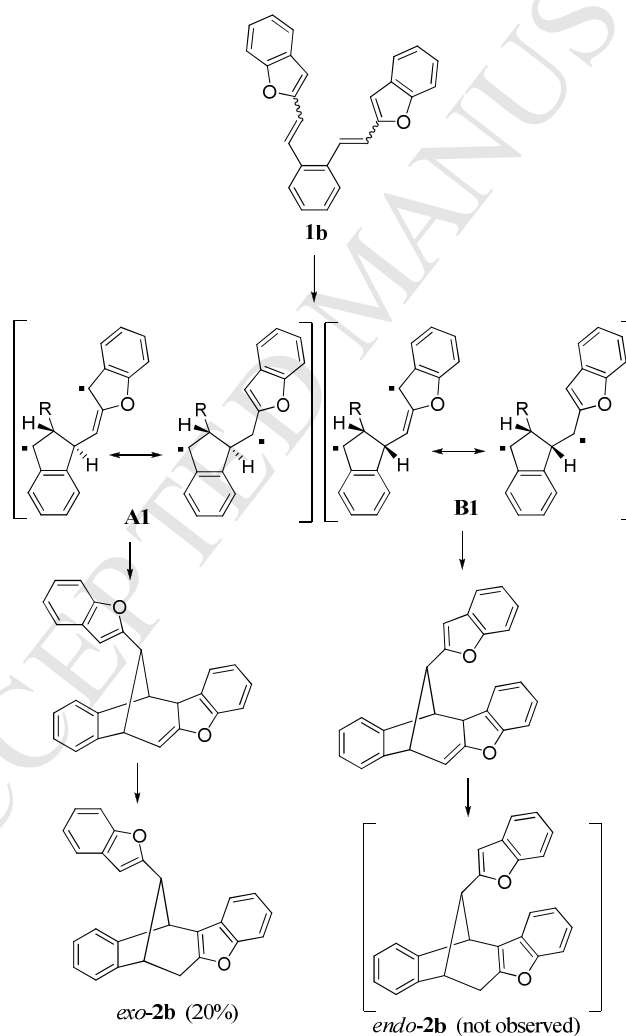
The irradiation of benzofuro-derivative **1b** led to similar results. In the first fraction the cyclisation compound **16** (15%) was isolated, followed by benzobicyclo[3.2.1]octadiene photoproducts *exo-2b* (20%), *endo-17* (2%), *exo-18* (20%) and dimeric product **19** (15%). While the bicyclo[3.2.1]octadiene *exo-2b* and dimer **19** were obtained in the neutral medium, the photoproducts **16-18** were the new compounds isolated only in the acidic medium.

Formation of bicyclic derivatives *endo-17* and *exo-18* may put in the correlation with the previous results obtained on photochemical investigation of difuran derivatives **1a** and **1b** in neutral medium. As a main intramolecular product bicyclo[3.2.1]octadiene compound of *exo* orientation was obtained, while the *endo* derivative found only in traces or was not observed, respectively. The similar proportion of isomers was noticed in the case of *endo-17* and *exo-18*. The product *exo-18* was isolated as the main photoproduct, while derivative *endo-17* was observed as a minor product. The assumption is that the products *endo-17* and *exo-18* were formed probably by opening of furan ring in acidic medium of bicyclic derivatives *exo-2b* and *endo-2b*, respectively. Larger ratio of *exo* compound was explained by formation of sterically more favorable intermediate **A1** due to preferred *trans* ring closure (Scheme 7).





Scheme 6.



Scheme 7.

Structures of the new compounds *endo-17* and *exo-18* are completely characterized and confirmed by spectroscopic techniques. Figure 4. shows the aliphatic region of  $^1\text{H}$  NMR spectra of new bicyclic derivatives *endo-17* and *exo-18*, compared with the known compound *exo-2b*. Six-proton pattern between 3.2 and 4.8 ppm in the case of *endo-17* and *exo-18* clearly indicates the opening of the furan ring. Proton A in both cases appears with similar shifts as triplet or doublet of doublets, due to the coupling with protons E and F. It is interesting that proton A couples with the both *endo* and *exo*-oriented proton E, respectively, unlike the bicyclic compound **2b**, where only the couple with *exo*-oriented proton was visible.

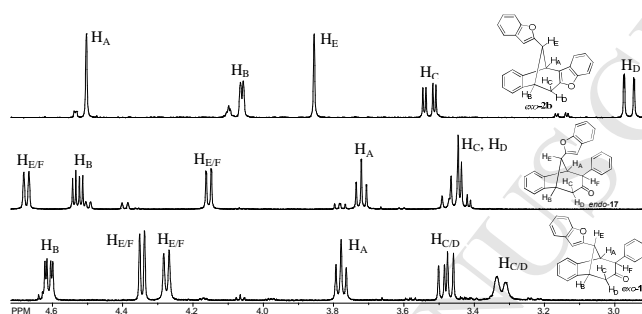
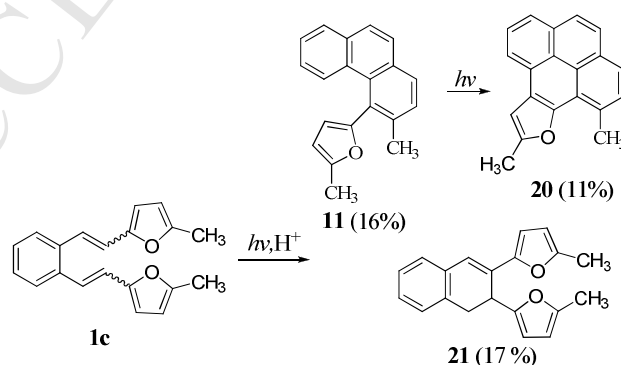


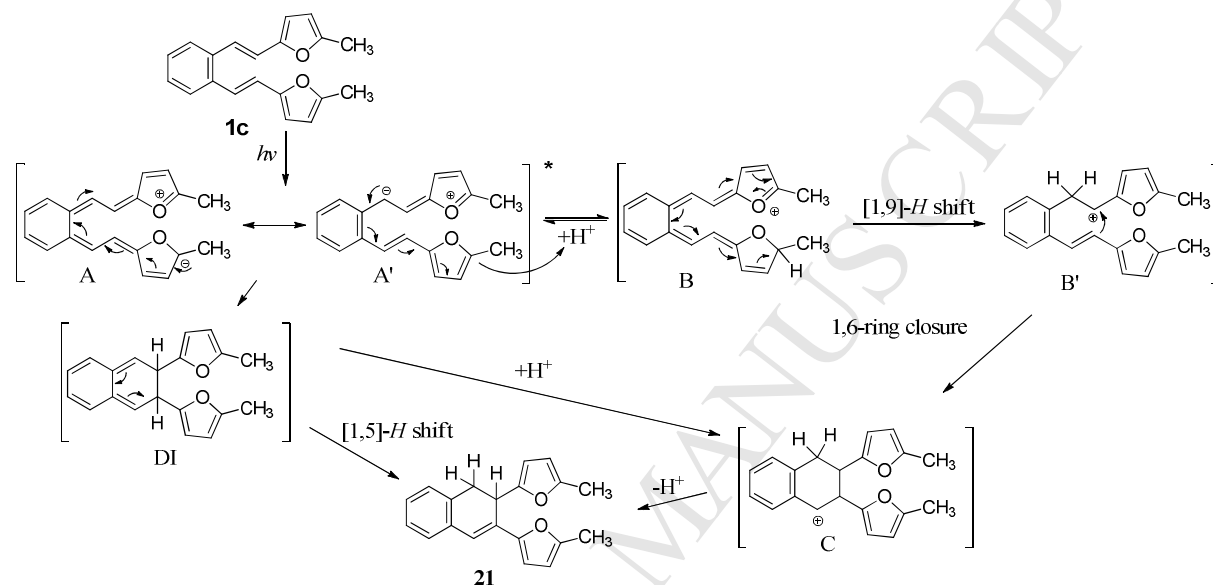
Figure 4.

Further, photochemical investigation in acidic medium has been expanded to the dimethyl derivative **1c** showing completely different photoreactivity (Scheme 8). Under  $6\pi$  electrocyclization process photoproduct **11** (16 %) was formed, which through additional cyclization reaction led to the photoproduct **20** (11%). Unlike previous cases, where cycloaddition reaction and formation of bicyclic skeleton preceded, in this case as a main photoproduct dihydronaphthalene derivative **21** (17%) was isolated.



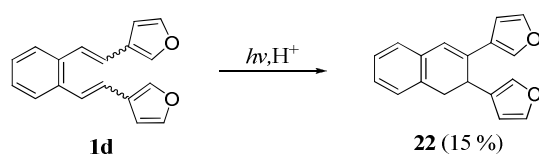
Scheme 8.

The assumed mechanism of formation of product **21** is shown on scheme 9. Polarization of the starting molecule (**A**, **A'**) in the excited state [18] enables an easier protonation which lead to intermediate **B**. Subsequently 1,9-*H* shift of intermediate **B** give carbocation **B'** which undergoes 1,6-ring closure to intermediate **C** and by deprotonation process gives the final photoproduct. The intermediate **C** could be formed also by protonation of the dihydronaphthalene intermediate **DI** and 1,5-*H* shift.



Scheme 9.

It is interesting that 3-furyl derivative **1d** in acidic medium behaves very similar, whereby the dihydronaphthalene compound **22** was isolated as the only photoproduct (Scheme 10). The aliphatic part of  $^1\text{H}$  NMR spectra of **21** and **22** present classical three-proton pattern of ABX systems, with a slight shift of signals to the lower field in the case of compound **22**.



Scheme 10.

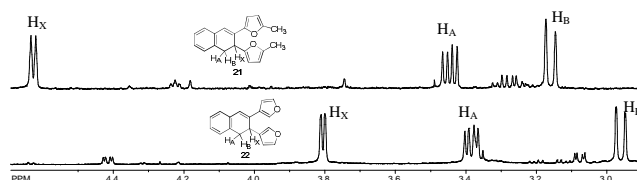


Figure 5.

Further, these results could be compared with analogue photochemical investigation on thiophene derivatives [13]. In the case of three substituted heteroaromatic moiety similar results were obtained regardless of the type of heteroatom. In both cases the polycyclic product (in neutral) and dihydronaphthalene derivative (in acidic) were isolated, respectively. On the other hand, the position 2 of heteroatom in aromatic moiety leads us in the opposite direction. Due to the greater influence of heteroatom on electronic properties of starting molecule, completely different type of products were obtained with the change of heteroatom in the molecule. Thus, as the 2-substituted thiophene derivatives of *o*-divinylbenzene prefers electrocyclization process in neutral and acidic medium, the presence of furyl moiety leads to cycloaddition products, with some cyclization and dimeric derivatives, whereby the type and share of photoproducts depends of annelation of the starting material and pH value. The cyclization reaction in the presence of iodine has also been carried out on all starting compounds **1a-d**, whereby similar cyclization products were not observed.

## Conclusion

Through this paper we showed how slightly change of structure can have a significant impact on the reaction mechanism and distribution of products. By changing the type of heteroatom, its position in the heteroaromatic ring and experimental conditions (time of reaction, concentration and pH value) it could be obtained a set of completely different compounds. While in neutral medium the cycloaddition reaction is the predominant intramolecular process, in acidic medium, due to the protonation of the starting material other processes appears and towards the reaction course in a different direction. In this way, by choosing the photochemical conditions it is possible to obtain by simple synthetic procedure the complex polycyclic structures, whose skeleton is often found in numerous natural biologically active molecules [19-22]. Since their isolation from the plants, as well as their synthesis, often could be found with some difficulties, there is an increasing need for such simple and environmental friendly controlled synthesis.

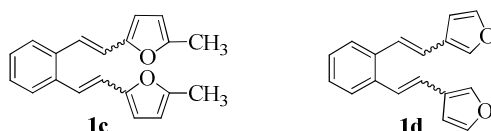
## 4. Experimental section

#### 4.1. General experimental information

The  $^1\text{H}$  spectra were recorded on a spectrometer at 300 and 600 MHz. The  $^{13}\text{C}$  NMR spectra were registered at 150 MHz. All NMR spectra were measured in  $\text{CDCl}_3$  using tetramethylsilane as reference. The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY experiments. UV spectra were measured on an UV/VIS Cary 50 spectrophotometer. IR spectra were recorded on an FTIR-ATR (film). Mass spectra were obtained on a GC-MS system. Irradiation experiments were performed in a quartz vessel in toluene solution in a photochemical reactor equipped with 3500 Å lamps. All irradiation experiments were carried out in deaerated solutions by bubbling a stream of argon prior to irradiation. Melting points were obtained using microscope equipped apparatus and are uncorrected. HRMS analysis were carried out on a mass spectrometer (MALDI TOF/TOF analyser), equipped with Nd:YAG laser operating at 355 nm with firing rate 200 Hz in the positive ( $\text{H}^+$ ) or negative ( $\text{H}^-$ ) ion reflector mode. Silica gel (0.063e0.2 mm) was used for chromatographic purifications. Thin-layer chromatography (TLC) was performed silica gel 60 F254 plates. Solvents were purified by distillation.

#### 4.2. General method for the synthesis of starting compounds 1a-d

To a stirred solution of the triphenylphosphonium salt (0.005 mol) and the corresponding aldehyde (0.011 mol) in absolute ethanol (100 mL) the solution of sodium ethoxide (0.253 g, 0.011 mol in 15 mL of absolute ethanol) was added dropwise. The reaction was complete within 3 - 4 h (usually was left to stand overnight). After removal of the solvent, the residue was worked up with water and benzene. The benzene extracts were dried (anhydrous  $\text{MgSO}_4$ ) and concentrated. The crude reaction mixture was purified and the isomers of products and were separated by repeated column chromatography on silica gel using petroleum ether as the eluent. The first fractions yielded *cis,cis*-, *cis,trans*- and the last fractions *trans,trans*-isomers. All isomers of 3-[(*E*)-2-{2-[(*E*)-2-(furan-3-yl)ethenyl]phenyl}ethenyl]furan (**1d**) are separated and described by spectroscopic methods whereas in the case of **1c** only *trans,trans*-isomer is isolated. Compounds **1a-b** are described previously [14].



**2-methyl-5-[(*E*)-2-{2-[(*E*)-2-(5-methylfuran-2-yl)ethenyl]phenyl}ethenyl]furan (**1c**).** Yield 95%; according to  $^1\text{H}$  NMR spectra a mixture of 10% *cis,cis*-**1c**, 50% *cis,trans*-**1c** and 40%

*trans,trans*-**1c**. Compound *trans,trans*-**1c**:  $R_f$  0.42 (petroleum ether / dichloromethane = 9:1); yellow crystals; mp 60 - 65 °C; UV (EtOH)  $\lambda_{\max}$  ( $\epsilon$ ) 298 (9069);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.48 – 7.52 (m, 2H, H-ar), 7.32 (d,  $J$  = 16.1 Hz, 2H, H-et), 7.19 - 7.23 (m, 2H, H-ar), 6.73 (d,  $J$  = 16.1 Hz, 2H, H-et), 6.25 (d,  $J$  = 3.3 Hz, 2H, H-4f), 6.02 (d,  $J$  = 3.3 Hz, 2H, H-3f), 2.37 (s, 3H, H- $\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  151.9 (s), 151.5 (s), 150.8 (s), 150.2 (s), 135.3 (s), 126.8 (d), 125.6 (d), 122.7 (d), 118.4 (d), 109.5 (d), 107.3 (d), 13.3 (q); IR 2160, 1977, 1719, 763  $\text{cm}^{-1}$ ; HRMS:  $M^+_{\text{calcd}}$  291.1385;  $M^+_{\text{found}}$  291.1393.

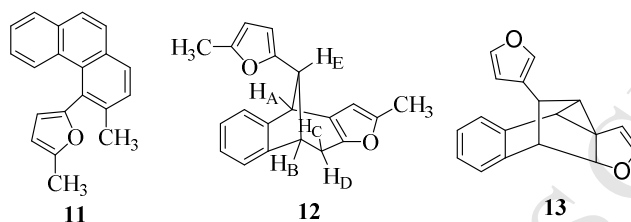
**3-[(*E*)-2-{2-[(*E*)-2-(furan-3-yl)ethenyl]phenyl}ethenyl]furan (**1d**)**. Yield (75%); according to  $^1\text{H}$  NMR spectra a mixture of 15% *cis,cis*-**1d**, 15% *cis,trans*-**1d** and 45% *trans,trans*-**1d**. Compound *cis,cis*-**1d**:  $R_f$  0.85 (petroleum ether / dichloromethane = 9:1); colourless oil; UV (EtOH)  $\lambda_{\max}$  ( $\epsilon$ ) 274 (8253);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.36 (dd,  $J$  = 8.8 Hz, 1H, H-ar), 7.28 (s,  $J$  = 5.7 Hz, 1H, H-f), 7.23 (dd,  $J$  = 8.8 Hz, 1H, H-ar), 7.18 (t,  $J$  = 1.8 Hz, 1H, H-f), 6.48 (d,  $J$  = 12.3 Hz, 1H, H-et), 6.38 (d,  $J$  = 12.3 Hz, 1H, H-et), 5.95 (d,  $J$  = 1.77 Hz, 1H, H-f);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  142.0 (d), 141.6 (d), 140.8 (s), 136.5 (s), 128.8 (d), 128.6 (d), 126.7 (d), 119.9 (d), 109.6 (d).

Compound *cis,trans*-**1d**:  $R_f$  0.81 (petroleum ether / dichloromethane = 9:1); colourless oil; UV (EtOH)  $\lambda_{\max}$  ( $\epsilon$ ) 286 (11337);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.62 (d,  $J$  = 7.8 Hz, 1H, H-ar), 7.49 (s, 1H, H-f), 7.37 (t,  $J$  = 1.5 Hz, 1H, H-f), 7.24-7.30 (m, 3H, H-ar, H-f), 7.19 (td,  $J$  = 7.5; 1.5 Hz, 1H, H-ar), 7.15 (t,  $J$  = 1.5 Hz, 1H, H-f), 6.98 (d,  $J$  = 16.2 Hz, 1H, H-et), 6.89 (d,  $J$  = 16.2 Hz, 1H, H-et), 6.61 (d,  $J$  = 11.8 Hz, 1H, H-et), 6.58 (d,  $J$  = 1.7 Hz, 1H, H-f), 6.52 (d,  $J$  = 11.8 Hz, 1H, H-et), 5.92 (d,  $J$  = 1.7 Hz, 1H, H-f);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  143.1 (d), 142.0 (d), 141.7 (d), 140.4 (d), 136.2 (s), 135.1 (s), 129.2 (d), 127.4 (d), 127.1 (d), 126.6 (d), 125.9 (d), 124.5 (d), 124.3 (s), 122.0 (s), 120.8 (d), 119.1 (d), 109.6 (d), 107.0 (d).

Compound *trans,trans*-**1d**: due to the similar chromatographic properties with another two isomers it was not possible to obtain a sufficient amount of pure *trans,trans*-**1d** for  $^{13}\text{C}$  NMR;  $R_f$  0.76 (petroleum ether / dichloromethane = 9:1); colourless oil; UV (EtOH)  $\lambda_{\max}$  ( $\epsilon$ ) 243 (6239), 285 (19376);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.55 (s, 1H, H-f), 7.52 (d,  $J$  = 7.5 Hz, 1H, H-ar), 7.44 (t,  $J$  = 1.3 Hz, 1H, H-f), 7.24-7.27 (m, 1H, H-ar), 7.14 (d,  $J$  = 16.1 Hz, 1H, H-et), 6.86 (d,  $J$  = 16.1 Hz, 1H, H-et), 6.69 (d,  $J$  = 1.3 Hz, 1H, H-f); IR 2160, 1752, 1655  $\text{cm}^{-1}$ ; HRMS:  $M^+_{\text{calcd}}$  263.1072;  $M^+_{\text{found}}$  263.1082.

#### 4.3. Irradiation experiments of **1c-d** in neutral medium

A mixture of *cis,cis*-, *cis,trans*- and *trans,trans*-isomers of **1c-d** in toluene ( $3.4 \times 10^{-4}$  M) was purged with argon for 30 min and irradiated at 350 nm in a Rayonet reactor (16 lamps) in a quartz vessel for 21 h. After irradiation the solvent was removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The photoproduct **11** was isolated from the enriched first chromatographic fractions followed by compound **12**. In the case of **1d** the product **13** was the only isolated product. High-molecular-weight products remained on the column.



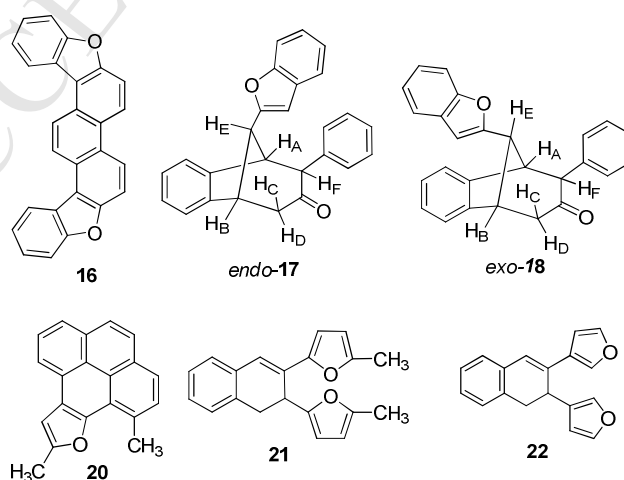
**2-methyl-5-(3-methylphenanthren-4-yl)furan (11):**  $R_f$  0.45 (petroleum ether / dichloromethane = 9:1); colourless crystals; mp 55 - 60 °C; UV (EtOH)  $\lambda_{max}$  ( $\epsilon$ ) 354 (1406), 337 (1640), 299 (8531), 287 (9181), 268 (14892, sh), 251 (26129);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.83 (d,  $J_{A,B} = 8.0$  Hz, 1H, H-B), 7.80 (d,  $J_{D,E} = 7.8$  Hz, 1H, H-E), 7.67 (dd,  $J_{D,E} = 7.8$ ;  $J_{C,D} = 13.3$  Hz, 2H, H-D, H-C), 7.5 (d,  $J_{A,B} = 8.0$  Hz, 1H, H-A), 7.44-7.48 (m, 1H, H-F), 7.25-7.29 (m, 1H, H-G), 7.24 (1H, H-H), 2.44 (s, 3H,  $-\text{CH}_3$ ), 2.39 (s, 3H,  $-\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  138.3 (s); 133.1 (s); 131.2 (s); 130.3 (s); 129.9 (s); 129.3 (d); 128.9 (s), 128.1 (d); 127.8 (d); 127.1 (s); 126.5 (d); 126.4 (d); 126.2 (d); 125.5 (d); 125.0 (d); 113.5 (s); 109.4 (d); 106.9 (d), 18.7 (q), 13.6 (q). IR 2160, 1831, 1685, 1449, 744  $\text{cm}^{-1}$ ; HRMS:  $M^+_{\text{calcd}}$  273.1279;  $M^+_{\text{found}}$  273.1282.

**4-methyl-15-(5-methylfuran-2-yl)-5-oxatetracyclo[6.6.1.0<sup>2,6</sup>.0<sup>9,14</sup>]pentadeca-2(6),3,9,11,13-pentaene (12):**  $R_f$  0.12 (petroleum ether / dichloromethane = 9:1); colourless oil; UV (EtOH)  $\lambda_{max}$  ( $\epsilon$ ) 278 (1588), 270 (1701), 229 (17183, sh);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.28 (d,  $J = 7.08$  Hz, 1H, H-ar), 7.01-7.08 (m, 3H, H-ar), 5.85 (d,  $J = 0.7$  Hz, 1H), 5.67 (dd,  $J = 1.3$  Hz, 1H), 5.49 (d,  $J = 3.0$  Hz, 1H), 3.92 (s, 1H, H-A), 3.71-3.75 (m, 1H, H-B), 3.52 (s, 1H, H-E), 3.22 (dd,  $J = 4.97$ ; 16.0 Hz, 1H, H-C), 2.68 (d,  $J_{C,D} = 16.0$  Hz, 1H, H-D), 2.19 (s, 3H,  $-\text{CH}_3$ ), 2.17 (s, 3H,  $-\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  154.9 (s), 150.1 (s), 149.8 (s), 149.7 (s), 144.1 (s), 142.5 (s), 126.2 (d), 125.8 (d), 124.9 (s), 124.0 (d), 120.6 (d), 105.3 (q), 105.1 (q), 103.8 (d), 52.3 (d), 44.8 (d), 43.6 (d), 31.0 (t), 13.1 (q), 13.0 (q). IR 2160, 1977, 1735, 763  $\text{cm}^{-1}$ ; HRMS:  $M^+_{\text{calcd}}$  291.1385;  $M^+_{\text{found}}$  291.1373.

**15-(furan-3-yl)-11-oxapentacyclo[7.5.1.0<sup>2,14</sup>.0<sup>3,8</sup>.0<sup>10,14</sup>]pentadeca-3,5,7,12-tetraene (13):**  $R_f$  0.62 (petroleum ether / dichloromethane = 9:1); colourless oil; UV (EtOH)  $\lambda_{max}$  ( $\epsilon$ ) 229 (5922), 214 (10905);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ; 600 MHz)  $\delta$  7.25 (d,  $J = 7.5$  Hz, 1H, H-ar), 7.17 (td,  $J = 7.5$  Hz, 1H, H-ar), 7.07 (t,  $J = 1.5$  Hz, 1H, H-f), 7.04 (td,  $J = 7.5$  Hz, 1H, H-ar), 6.88 (d,  $J = 7.5$  Hz, 1H, H-ar), 6.76 (d,  $J = 0.7$  Hz, 1H, H-f), 6.59 (d,  $J = 2.85$  Hz, 1H, H-f), 5.61 (d,  $J = 0.7$  Hz, 1H, H-f), 5.32 (d,  $J = 2.85$  Hz, 1H, H-f), 4.18 (s, 1H, H-B), 3.92 (dd,  $J = 7.1$ ; 3.2 Hz, 1H, H-A), 3.59 (d,  $J = 4.1$  Hz, 1H, H-C), 2.9 (d,  $J = 7.2$  Hz, 1H, H-D), 1.61 (dd,  $J = 7.2$ ; 3.2 Hz, 1H, H-E);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  149.3 (d), 135.0 (s), 134.8 (s), 134.7 (s), 126.7 (d), 126.3 (d), 125.4 (d), 125.0 (d), 122.9 (s), 109.9 (d), 103.5 (d), 92.3 (d), 48.0 (d), 33.4 (d), 31.1 (d), 29.2 (d), 29.1 (d), 26.7 (d). IR 2160, 1701, 1685  $\text{cm}^{-1}$ ; HRMS:  $M^+_{\text{calcd}}$  263.1072;  $M^+_{\text{found}}$  263.1071.

#### 4.4. Irradiation experiments of 1a-d in acidic medium

A mixture of *cis,cis*-, *cis,trans*- and *trans,trans*-isomers of **1a-d** in acetonitrile ( $4 \times 10^{-3}$  M), with addition of hydrochloric acid (36 %, 0.5 ml, 17 eq), was purged with argon for 30 min and irradiated at 350 nm in a Rayonet reactor (16 lamps) in a quartz vessel for 2 h. After irradiation the reaction mixture was neutralized with solution of sodium hydroxide (10 %) and extracted with ethylacetate ( $4 \times 5$  ml). After drying over magnesium sulphate the solvents were removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The obtained mixtures of the products were rechromatographed and after the repeated column chromatography different new photoproducts were isolated from **1a-d**. High-molecular-weight products remained on the column. The data for the synthesized and isolated compounds are given below.





**11-*exo*-2-furyl-9,10-dihydro-4,9-methano-4*H*-benzo[4,5]cyclohepta[1,2-*b*]furan (*exo*-2a)** [14]: Yield 6.0 %, colourless crystals, m.p. 104-105 °C;  $R_f = 0.42$  (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> 4:1); UV (EtOH):  $\lambda_{\max} (\epsilon)$  267 (4365), 222 nm (10965); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (d,  $J = 6.9$  Hz, 1H; H(ar)), 7.24 (d,  $J = 1.8$  Hz, 1H; H-5), 7.16 (d,  $J \sim 1$  Hz, 1H; H-5'), 7.11-7.03 (m, 3H; H(ar)), 6.29 (d,  $J = 1.8$  Hz, 1H; H-4), 6.12 (dd,  $J = \sim 1, 3.3$  Hz, 1H; H-4'), 5.65 (d,  $J = 3.3$  Hz, 1H; H-3'), 4.04 (s, 1H; H-A), 3.81 (d,  $J = 4.8$  Hz, 1H; H-B), 3.59 (s, 1H; H-E), 3.26 (dd,  $J = 4.8, 16.2$  Hz, 1H; H-C), 2.74 (d,  $J = 16.2$  Hz, 1H; H-D); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  156.8 (s), 150.1 (s), 146.6 (s), 142.5 (s), 140.8, 140.6 (2d), 126.7 (d), 126.4 (d), 124.4 (s), 121.2 (d), 109.9 (d), 108.1 (d), 104.9 (d), 52.6 (d; C-B), 45.0 (d; C-C), 44.0 (d; C-A), 31.4 (t; C-DE), 1 signal is covered; MS (EI):  $m/z$  (%): 262 (100) [M<sup>+</sup>], 233 (5), 181 (25); elemental analysis calcd (%) for C<sub>18</sub>H<sub>14</sub>O (262.3): C 82.42, H 5.38; found: C 82.56, H 5.29.

**13-*exo*-(2-benzo[*b*]furyl)-11,12-dihydro-6,11-methano-6*H*-benzo[4,5]cyclohepta[1,2-*b*]benzo[*d*]furan (*exo*-2b)** [14]: Yield 20.0%; colourless crystals, m.p. 158-159 °C;  $R_f = 0.31$  (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> 7:3); UV (EtOH)  $\lambda_{\max} (\epsilon)$  304 (37153), 254 (2754), 217 nm (14791); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (d,  $J = 7.2$  Hz, 1H), 7.32-7.43 (m, 3H, H-2; H-2'), 7.00-7.27 (m, 8H), 6.15 (s, 1H; H-6'), 4.49 (s, 1H; H-A), 4.04 (d,  $J = 4.8$  Hz, 1H; H-B), 3.83 (s, 1H; H-E), 3.50 (dd,  $J = 4.8, 17.1$  Hz, 1H; H-C), 2.94 (d,  $J = 17.1$  Hz, 1H; H-D); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  159.5 (s), 154.5 (s), 154.4 (s), 150.15 (s), 149.4 (s), 142.2 (s), 128.5 (s), 127.1 (d), 126.8 (d), 126.3 (s), 124.6 (d), 123.4 (d), 123.1 (d), 122.5 (d), 122.5 (d), 121.7 (s), 121.4 (d), 120.6 (d), 117.9 (d), 111.1 (d), 110.7 (d), 102.5 (d), 52.7 (d; C-B), 44.8 (d; C-C), 42.0 (d; C-A), 31.8 (t; C-DE); MS (ESI):  $m/z$  (%): 362.5 (30) [M<sup>+</sup>], 145.2 (80), 83.3 (100); elemental analysis calcd (%) for C<sub>26</sub>H<sub>18</sub>O<sub>2</sub> (362.4): C 86.16, H 5.01; found: C 86.03, H 5.13.

**6,25-dioxaheptacyclo[15.11.0.0<sup>2</sup>,<sup>14</sup>.0<sup>5</sup>,<sup>13</sup>.0<sup>7</sup>,<sup>12</sup>.0<sup>18</sup>,<sup>26</sup>.0<sup>19</sup>,<sup>24</sup>]octacosane-1(17),2(14),3,5(13),7,9,11,15,18(26),19(24),20,22,27-tridecaene (16)**: Yield 15 %;  $R_f = 0.36$  (petroleum ether / dichloromethane = 4:1); colourless crystals; mp 145 - 148 °C; UV (EtOH)  $\lambda_{\max} (\epsilon)$  374 (945), 355 (1714), 346 (4709), 330 (5307), 315 (3940), 300 (4161), 275 (6992), 253 (7860), 239 (10208); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.90 (d,  $J = 9.2$  Hz, 1H, H-ar), 8.89 (s, 1H, H-ar), 8.52 (dd,  $J = 7.7; 1.3$  Hz, 1H, H-ar), 7.97 (d,  $J = 9.2$  Hz, 1H, H-ar), 7.74 (dd,  $J = 7.7; 1.3$  Hz, 1H, H-ar), 7.56 (dd,  $J = 7.7; 1.3$  Hz, 1H, H-ar), 7.53 (dd,  $J = 7.7; 1.3$  Hz, 1H, H-ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$  135.0 (s), 132.5 (s), 132.4 (s), 128.6 (s), 128.5 (s), 127.7 (d), 126.9 (s), 126.3 (s), 126.1 (d), 124.3 (d), 122.7 (d), 122.4 (d), 121.8 (d), 120.4 (q), 118.6 (d), 110.6 (d); IR 2346, 2160, 1774, 1655 cm<sup>-1</sup>; HRMS: M<sup>+</sup><sub>calcd</sub> 359.1072; M<sup>+</sup><sub>found</sub> 359.1070.

***endo*-12-(1-benzofuran-2-yl)-9-phenyltricyclo[6.3.1.0<sup>2,7</sup>]dodeca-2(7),3,5-trien-10-one**

**(endo-17):** Yield 2 %;  $R_f = 0.28$  (petroleum ether / dichloromethane = 4:1); colourless crystals; mp 190 - 193 °C; UV (EtOH)  $\lambda_{max}$  ( $\epsilon$ ) 284 (1757), 277 (1891), 252 (5648);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 7.4$  Hz, 1H, H-ar), 7.35 (dd,  $J = 7.4$ ; 0.8 Hz, 1H, H-ar), 7.10-7.28 (m, 7H, H-ar), 7.05 (d,  $J = 7.4$  Hz, 1H, H-ar), 6.90 (d,  $J = 7.4$  Hz, 1H, H-ar), 6.79 (d,  $J = 7.4$  Hz, 1H, H-ar), 6.66 (dt,  $J = 7.4$ ; 0.8 Hz, 1H, H-ar), 6.34 (s, 1H, H-f), 4.67 (d,  $J = 8.8$  Hz, H-E/F), 4.53 (dd,  $J = 11.8$ ; 5.7 Hz, H-B), 4.16 (d,  $J = 8.8$  Hz, H-E/F), 3.72 (t,  $J = 8.8$  Hz, H-A), 3.40-3.50 (m, 2H, H-C, H-D).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  180.0 (s), 159.8 (s), 155.6 (s), 154.4 (s), 136.0 (s), 133.9 (s), 128.4 (2d), 128.2 (d), 127.8 (s), 127.3 (d), 127.0 (2d), 126.8 (d), 126.2 (d), 123.2 (d), 122.0 (d), 120.6 (d), 120.1 (d), 110.3 (d), 109.8 (d), 57.7 (d), 50.0 (d), 46.2 (d), 42.7 (d), 37.3 (t); IR 1977, 1655, 1459, 745  $\text{cm}^{-1}$ .

***exo*-12-(1-benzofuran-2-yl)-9-phenyltricyclo[6.3.1.0<sup>2,7</sup>]dodeca-2(7),3,5-trien-10-one** (*exo-*

**18):** Yield 20 %;  $R_f = 0.11$  (petroleum ether / dichloromethane = 4:1); colourless crystals; mp 196 - 198 °C; UV (EtOH)  $\lambda_{max}$  ( $\epsilon$ ) 284 (2723), 277 (2722), 250 (5809);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 7.4$  Hz, 1H, H-ar), 7.39 (dd,  $J = 7.4$ ; 0.8 Hz, 1H, H-ar), 7.10-7.28 (m, 7H, H-ar), 7.03 (d,  $J = 7.4$  Hz, 1H, H-ar), 6.90 (d,  $J = 7.4$  Hz, 1H, H-ar), 6.74 (d,  $J = 7.4$  Hz, 1H, H-ar), 6.68 (dt,  $J = 7.4$ ; 0.8 Hz, 1H, H-ar), 6.42 (s, 1H, H-f), 4.61 (dd,  $J = 10.0$ ; 3.5 Hz, 1H, H-B), 4.34 (d,  $J = 8.3$  Hz, 1H, H-E/F), 4.27 (d,  $J = 9.3$  Hz, 1H, H-E/F), 3.77 (dd,  $J = 9.3$ ; 8.3 Hz, 1H, H-A), 3.48 (dd,  $J = 15.4$ ; 10.0 Hz, 1H, H-C/D), 3.32 (d,  $J = 15.4$  Hz, 1H, H-C/D).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  180.0 (s), 159.6 (s), 155.9 (s), 154.5 (s), 135.5 (s), 128.6 (d), 127.8 (s), 127.2 (d), 126.6 (d), 126.3 (2d), 126.1 (d), 125.9 (s), 123.3 (d), 122.1 (d), 120.7 (2d), 120.2 (d), 110.4 (d), 110.3 (d), 103.5 (d), 57.1 (d), 48.1 (d), 48.8 (d), 42.0 (d), 35.8 (t); IR 2160, 1735, 1671  $\text{cm}^{-1}$ ; HRMS:  $M^+_{calcd}$  365.1542;  $M^+_{found}$  365.1536.

**8,10-dimethylpyreno[4,5-b]furan (20):** due to instability of the compound, it was not possible to analyze it completely; Yield 11 %;  $R_f = 0.55$  (petroleum ether / dichloromethane = 9:1); colourless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ; 600 MHz)  $\delta$  8.31 (dd,  $J_{F,G} = 7.8$  Hz, 1H, H-G), 8.09 (dd,  $J_{E,F} = 7.5$  Hz, 1H, H-E), 8.02 (d,  $J_{A,B} = 7.7$  Hz, 1H, H-B), 8.0 (dd,  $J = 14.8$ ; 8.7 Hz, 2H, H-C, H-D), 7.99 (t,  $J_{F,G} = 7.8$  Hz;  $J_{F,E} = 7.5$  Hz, 1H, H-F), 7.85 (dd,  $J_{A,B} = 7.7$ ;  $J = 1.0$  Hz, 1H, H-A), 7.07 (s, 1H, H-f), 3.28 (s, 3H,  $-\text{CH}_3$ ), 2.69 (s, 3H,  $-\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  131.8 (s), 129.6 (s), 129.5 (s), 128.6 (d), 127.2 (d), 126.4 (s), 126.2 (d), 125.2 (d), 123.6 (d), 123.2 (d), 122.4 (s), 122.3 (s), 120.1 (s), 119.6 (d), 117.2 (s), 113.5 (s), 101.8 (d), 13.6 (q); IR 2160, 1718, 1685, 1458  $\text{cm}^{-1}$ .

**2-methyl-5-[3-(5-methylfuran-2-yl)-3,4-dihydronaphthalen-2-yl]furan (21):** Yield 17 %;  $R_f = 0.39$  (petroleum ether / dichloromethane = 9:1); colourless oil; UV (EtOH)  $\lambda_{\max}$  ( $\epsilon$ ) 349 (10668), 334 (13416), 319 (10668, sh), 295 (7058, sh), 252 (5450, sh), 228 (10946);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ; 600 MHz)  $\delta$  7.53 (d,  $J = 7.34$  Hz, 1H), 7.16-7.25 (m, 3H, H-ar), 6.85 (d,  $J = 1.6$  Hz, 1H), 6.11 (d,  $J = 3.0$  Hz, 1H), 5.90 (d,  $J = 2.7$  Hz, 1H), 5.72 (s, 2H), 4.63 (d,  $J_{\text{B,X}} = 8.4$ , 1H, H-X), 3.44 (dd,  $J_{\text{A,X}} = 8.4$ ;  $J_{\text{A,B}} = 16.7$  Hz, 1H, H-A), 3.16 (d,  $J_{\text{A,B}} = 16.8$  Hz, 1H, H-B), 2.27 (s, 3H,  $-\text{CH}_3$ ), 2.24 (s, 3H,  $-\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  155.3 (s), 151.7 (s), 151.4 (s), 146.0 (s), 143.9 (s), 143.9 (s), 141.6 (s), 140.4 (s), 126.2 (d), 125.8 (d), 124.0 (d), 120.6 (d), 106.3 (d), 105.3 (d), 105.1 (d), 104.4 (d), 103.8 (d), 52.3 (d), 41.4 (d), 38.0 (s); IR 2160, 1794, 1522, 1459  $\text{cm}^{-1}$ ; HRMS:  $M^+_{\text{calcd}}$  291.1385;  $M^+_{\text{found}}$  191.1372.

**3-[3-(furan-3-yl)-3,4-dihydronaphthalen-2-yl]furan (22):** Yield 15 %;  $R_f = 0.60$  (petroleum ether / dichloromethane = 9:1); colourless oil; UV (EtOH)  $\lambda_{\max}$  ( $\epsilon$ ) 311 (1642), 238 (2562, sh);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ; 600 MHz)  $\delta$  7.52 (s, H-f), 7.42 (t,  $J = 1.8$  Hz, 1H, H-f), 7.07-7.16 (m, 6H, 5H-ar, H-f), 6.80 (s, H-f), 6.68 (d,  $J = 1.8$  Hz, 1H, H-f), 6.11 (d,  $J = 1.8$  Hz, 1H, H-f), 3.81 (d,  $J = 6.7$  Hz, 1H, H-X), 3.38 (dd,  $J = 15.6$ ; 6.7 Hz, 1H, H-A), 2.96 (dd,  $J = 15.6$ ; 1.5 Hz, 1H, H-B),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  136.6 (s), 133.5 (s), 132.4 (s), 132.3 (s), 131.9 (s), 128.5 (d), 128.1 (d), 127.5 (d), 127.0 (d), 126.7 (d), 126.2 (d), 125.6 (d), 125.3 (d), 121.8 (d), 109.6 (d), 107.2 (d), 38.4 (d), 37.2 (d), 35.0 (t), 32.6 (d), 29.2(d); IR 2160, 1655, 1542  $\text{cm}^{-1}$ ; HRMS:  $M^+_{\text{calcd}}$  263.1072;  $M^+_{\text{found}}$  263.1072.

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ACCEPTED MANUSCRIPT

**Synthesis of new furan polycycles *via* photochemical reaction in neutral and acidic medium****Highlights**

- Photoreactivity of the starting material changes upon different pH value
- The change of the heteroatom affects the course of the photochemical reaction
- Novel polycyclic photoproducts were synthesized and characterized