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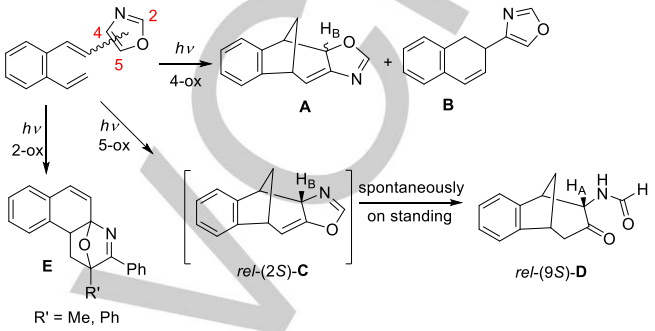
Versatile photochemical reactivity of diverse substituted 2-, 4- and 5-(*o*-vinylstyryl)oxazoles

Ivana Šagud,*[a] Marija Šindler-Kulyk,[a] Dragana Vojnović-Jandrić,[a] and Željko Marinić[b]

Abstract: To study the effects of the position of the hexatrienyl moiety on the oxazole ring, novel substituted *cis/trans*-2/4/5-(2-vinylstyryl)oxazoles have been synthesized. These novel compounds were prepared by Wittig reaction from diphosphonium salt of α,α'-*o*-xylenedibromide, formaldehyde and the corresponding 2-methyl-4-, 4-methyl-2-, 2-pheny-5- and 4-methyl-5-oxazolecarbaldehyde, respectively. Aldehydes were synthesized by several synthetic approaches. By intramolecular photocycloaddition 2-methyl-4-(2-vinylstyryl)oxazole afforded, as major product, fused oxazoline-benzobicyclo[3.2.1]octene with small quantities of 4-(1,2-dihydronaphthalen-2-yl)-2-methyloxazole, as electrocyclization product. Upon irradiation of 4-methyl-5-(2-vinylstyryl)oxazole *endo*- and *exo*-benzobicyclo[2.1.1]hexene products were formed by [2+2] cycloaddition and this was the first instance of the 1,4-closure to the bicyclo[2.1.1]hexene skeleton in the 2-, 4-, and 5-oxazole-stilbene derivatives studied so far. Derivatives, 2-phenyl-5- and 4-methyl-2-(2-vinylstyryl)oxazole do not react and give only high weight molecular products but are crucial as a comparison in the overall mechanistic study. We have found that depending on the position of the hexatrienyl moiety in the oxazole ring, as well as the position of the methyl/phenyl substituents these new vinylstyryl-2/4/5-oxazole derivatives show diverse photochemical behavior.

Introduction

In our previous paper we have described the synthesis of 2-(2-vinylstyryl)oxazoles[1] which upon irradiation gave quinolines via oxo-bridged derivatives. The study of the 5-tolyl-, 4,5-diphenyl- and 4-phenyl-5-methyl-2-(2-vinylstyryl)oxazole showed that the phenyl substituent on the position 4 in the oxazole ring has a high impact on the overall electron density distribution in the molecule and the photocyclization process (scheme 1).[1]



Scheme 1. Photoproducts of 2-, 4- and 5-(2-vinylstyryl)oxazoles. [1,2]

Only those derivatives that have a phenyl substituent in the position 4 on the ring react by 10π followed by 6π ring closure to products **E**. These experimental findings were confirmed by TD-DFT calculations. The oxo-bridged photoproducts **E** could further be easily converted to benzo[*f*]qouinolines (scheme 1). We have also described unsubstituted 4- and 5-(2-vinylstyryl)oxazoles which by intramolecular photocycloaddition gave fused tetracyclic oxazoline compounds (**A**, **C**, scheme 1).[2] New routes to oxazoline derivatives are more than welcome due to the presence of the oxazoline ring in ligand scaffolds, natural products[3,4] and potential pharmaceuticals.[5,6] In our case the obtained tetracyclic oxazoline compounds further hydrolyzed, either spontaneously, or during work up, and gave functionalized benzobicyclo[3.2.1]octenone derivatives. On the other side, this ring opening gave a new route for the synthesis of functionalized benzobicyclo[3.2.1]octenes which are useful reactive intermediates found in stereoselective transformations[7] as the bicyclo[3.2.1]octane skeleton appears in numerous biologically active natural compounds and their metabolites.[8] There are various methodologies and synthetic approaches for the synthesis of the oxazole ring incorporated into diverse skeletons[9] as the oxazole structure is commonly found in a vast number of natural products and pharmaceuticals.[10-13]

The examples of photochemical intermolecular cycloadditions that include oxazoles are numerous[14-20] but as for the intramolecular photocycloaddition, to the best of our knowledge, the only examples are the ones published by us for various substituted 2-(2-vinylstyryl)oxazoles[1] and the unsubstituted 4- and 5-(2-vinylstyryl)oxazoles.[2]

In this work, in order to study further the photochemical reactivity of oxazole derivatives, the hexatrienyl and alkyl or aryl substituents were placed in various positions on the oxazole ring. We synthesized new 4-methyl-2-(2-vinylstyryl)oxazole (**1**), 4-methyl-5-(2-vinylstyryl)oxazole (**2**), 2-methyl-4-(2-vinylstyryl)oxazole (**3**) and 2-phenyl-5-(2-vinylstyryl)oxazole (**4**).

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Excited state behavior of all of the new derivatives was investigated.

Results and Discussion

For the synthesis of *cis*/*trans*-isomers of 4-methyl-2-(2-vinylstyryl)oxazole (**1**), 4-methyl-5-(2-vinylstyryl)oxazole (**2**), 2-methyl-4-(2-vinylstyryl)oxazole (**3)** and 2-phenyl-5-(2-vinylstyryl)oxazole (**4**) Wittig reaction was utilized. The starting compounds were synthesized from the diphosphonium salt of α,α'-*o*-xylenedibromide, formaldehyde and the corresponding substituted oxazole-2/4/5-carbaldehydes (**5-8)** with the reaction taking place in absolute ethanol and sodium ethoxide as base (scheme 2).

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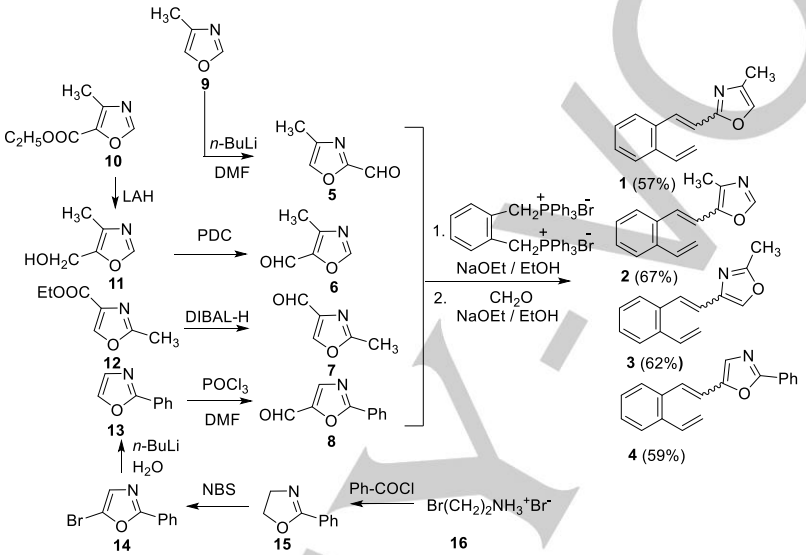


Scheme 2. Synthesis of substituted 2-, 4- and 5-(2-vinylstyryl)oxazoles (**1-4**).

In order to maximize the yields the described procedure for the multi-component Wittig reaction[21] was modified. The yield of the Wittig reaction for all of the three derivatives **1**-**4** was moderately good, ranging from 57 - 67%. Both *cis*- and *trans*-isomers of all of the new compounds **1-4**, were isolated by column chromatography on silica gel and characterized by spectroscopic methods (see Supporting information file). The synthesis of the required oxazole-2/4/5-carbaldehydes (**5-8**), needed for the Wittig reactions, proved to be challenging. The 4-methyl-oxazole-2-carbaldehyde[22] (**5**) was synthesized by *n*-BuLi/DMF formylation from the corresponding oxazole **9**[23]. To synthesize 4-methyl-oxazole-5-carbaldehyde[22] (**6**), from the parent oxazole, Villsmeyer formylation reaction was utilized. This reaction gave a mixture of oxazole-2- and oxazole-5-carbaldehyde,[22] where the 5-carbaldehyde **6** was the major product, but was impossible to purify due to its extreme volatility. The approach was changed and compound **6** was synthesized by a two-step reaction pathway from the corresponding ester **10**[23], via alcohol **11**,[24] (scheme 2) in a good overall yield of 60%. Compound 2-methyl-oxazole-4-carbaldehyde[25] (**7**) was prepared from the commercially available ester **12** by DIBAL-H reduction following the described procedure for the oxazole-4-carbaldehyde.[26] 2-phenyl-oxazole-4-carbaldehyde[27] (**8**) was prepared from 5-bromo-2-phenyloxazole[27] (**14**) in two steps. Derivative **14** was synthesized in a multiple step synthesis by a series of well-known reactions[28, 29] that included ring closure of 2-bromoethan-1-aminium bromide (**16**) with benzoyl chloride to 2-phenyloxazoline **15** followed by a reaction with NBS to form **14**. Preliminary irradiations of **1**-**4** were conducted in UV tubes, in ethanol ($c \approx 3 \times 10^{-5}$ mol/L) at 300 nm, and the process was followed by UV spectrophotometry. At the beginning of irradiation in the UV tubes the *trans*-*cis* isomerization is recorded and is shifted towards the *cis*-isomer. There is also a drop of the absorption maxima, indicating that the species that are formed have less, or no chromophores. One of the examined compounds, *cis*-2-methyl-4-(2-vinylstyryl)oxazole (**3)** was additionally irradiated in a sealed NMR tube in degassed deuterated benzene solution and the progress was followed by ^{1}H NMR measurements. By this combination of methods a more detailed analysis of the irradiation progress was obtained (figure 1).

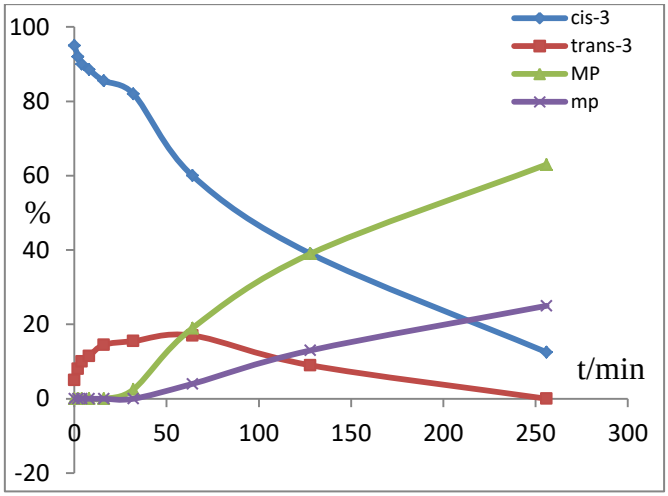
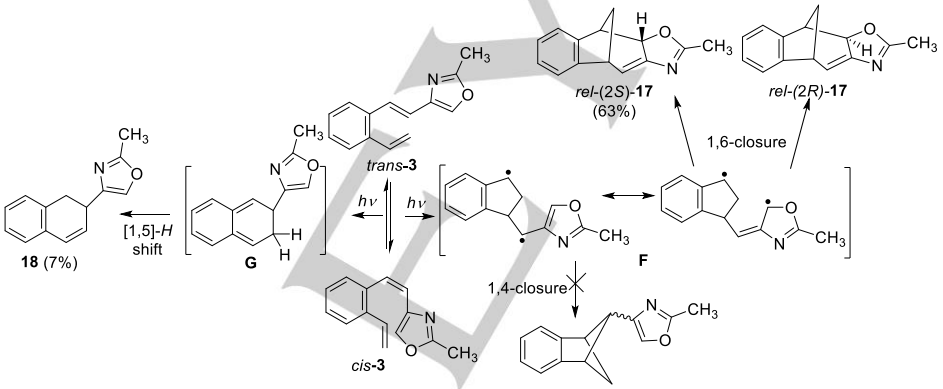


Figure 1. Graphical interpretation of irradiation of *cis*-2-methyl-4-(2-vinylstyryl)oxazole (**3**).

The *trans-cis* isomerization was confirmed. After 32 minutes of irradiation one major product (**MP**), later identified as *rel*-(2*S*)-**17** is detected and on continuing irradiation one other product (**mp**, *rel*-(2*R*)-**17**) is seen. At the end of irradiation almost all of the isomers are consumed and two new products are present in 5:2 ratio.

The preparative irradiation experiments were conducted in a Rayonet reactor equipped with 300 nm lamps, in petroleumether and benzene, respectively. All of the irradiation mixtures were purged with argon for 20 minutes. The four newly synthesized, substituted 2-, 4- and 5-(*o*-vinylstyryl)oxazoles reacted differently upon irradiation. The ^{1}H NMR spectra of the crude photo-mixtures of compounds 2-methyl-4-(2-vinylstyryl)oxazole (**3**) and 4-methyl-5-(2-vinylstyryl)oxazole (**2**) showed complete conversion after 5 and 15 hours of irradiation, respectively. Compound 4-methyl-2-(2-vinylstyryl)oxazole (**1**) and 2-phenyl-5-(2-vinylstyryl)oxazole (**4**) gave no product, only starting material was present after 5 and 10 h of irradiation and high molecular weight products after 24 h of irradiation.

In the case of 2-methyl-4-(2-vinylstyryl)oxazole (**3**) the crude reaction mixture consisted of *rel*-(2*S*)- and *rel*-(2*R*)-4-methyl-3-oxa-5-azatetracyclo[6.6.1.0^{2,6}.0^{9,14}]pentadeca-4,6,11,13-pentaene (**17**) as well as 5-(1,2-dihydronaphtalene-2-yl)-2-methyloxazole (**18**) (scheme 3).



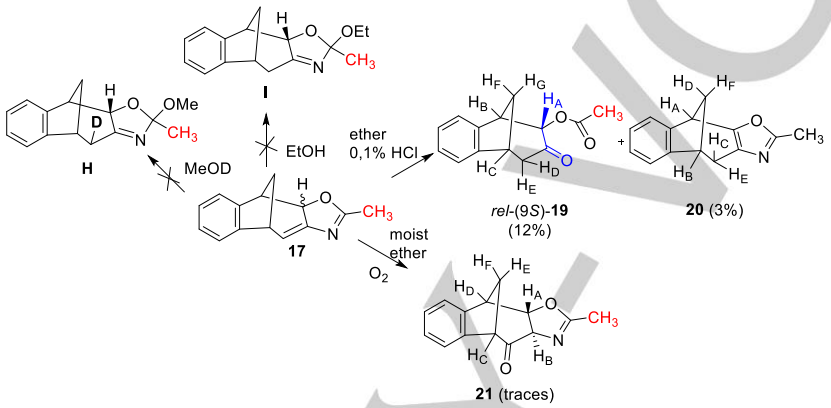
Scheme 3. Irradiation of 2-methyl-4(2-vinylstyryl)oxazole (**3**).

The methyl substituent at the position 2 of the oxazole moiety does not influence the excited state reaction course and the products are analogue to the ones that were obtained upon irradiation of the unsubstituted derivative.[2] Compounds *rel*-(2*S*)-**17** (63%) and cyclization product **18** (7%) were isolated and their structures were determined using COSY, NOESY and HSQC techniques (See Supporting Information).

The formation of the photoproduct **17** is explained by intramolecular cycloaddition and formation of the resonance stabilized biradical **F** followed by the 1,6-ring closure (scheme 3). An [1,3]-*H* shift that would result in aromatization of the oxazoline ring, that happens in furan and thiophene derivatives by default,[30] does not take place in the structure **17**. In the furan chemistry[31] the presence of the nonaromatic intermediate was only seen in ^{1}H NMR spectra, in the case of irradiation of 2-(2-(vinylstyryl)furan/benzofuran derivatives in NMR tubes. The 1,6-ring closure of the biradical **F** stereoselectively gives the major product *rel*-(2*S*)-**17** in which the hydrogen on C-2 is oriented toward the methano-bridge. The formation of the dihydronaphthalene derivative **18**, is explained by 6π electrocyclization of the benzo-divinyl moiety to intermediate **G.** The second step is the [1,5]-*H* shift and rearomatization of the benzene ring. Analogue electrocyclization was not detected in the, so far studied, phenyl- or furyl-substituted *o*-divinylbenzenes. In the case of the phenyl- or furyl-substituted *o*-divinylbenzenes, stilbene-like, 6π electrocyclization and formation of 1-

vinylphenanthrene[32] or 6-vinylnaphtho[2,1-*b*]thiophene[30] was seen, respectively.

Formerly described unsubstituted photoproduct, oxazoline-benzobicyclo[3.2.1]octene **A**[2] (scheme 1), was not stabile enough to be completely characterized and it underwent spontaneous ring-opening to a polycyclic ester derivative during the solvent evaporation from the crude irradiation mixture. The 2-methyl-oxazoline-benzobicyclo[3.2.1]octene product **17** does not undergo a spontaneous ring-opening, neither during the work up stage, nor during purification (scheme 4). It can be presumed that the methyl group at the position 2 on the oxazoline moiety significantly increases the stability of the oxazoline-benzobicyclo[3.2.1]octene product. As the polycyclic oxazoline derivatives[33-35] are of significant synthetic interest this modification of stability is more than welcome. To test the stability of the oxazoline ring incorporated into the polycyclic skeleton, in the product **17**, several different experiments were carried out. Again, as opposed to the unsubstituted product **A**[2] (scheme 1), product **17** did not react with ethanol to give **I**, nor with deuterated methanol to give **H** (scheme 4).



Scheme 4. Reactions of photochemical oxazoline product **17**.

The reaction of the oxazoline product **17** in moist, mildly acidic, ether gave the open ester derivative *rel*-(9*S*)-**19**. The stereochemistry of the product *rel*-(9*S*)-**19,** where H_A proton is facing the methano-bridge, was determined by NOE interaction between protons H_A and H_G. The *rel*-(9*R*)-**19** product was not detected, despite the fact that the starting photochemistry mixture had both oxazoline diastereomers present. This can be explained by the presence of keto-enol tautomerism in the segment of the molecule highlighted in blue (scheme 4). Upon formation of the ring opening product **19** only the thermodynamically more stable form (*rel*-(9*S*)-**19**) is detected as the end product. In figure 2 ^{1}H NMR spectrum of *rel*-(9*S*)-**19** is presented in which the specific signals H_A-H_G of the bicyclic skeleton are seen (figure 2).

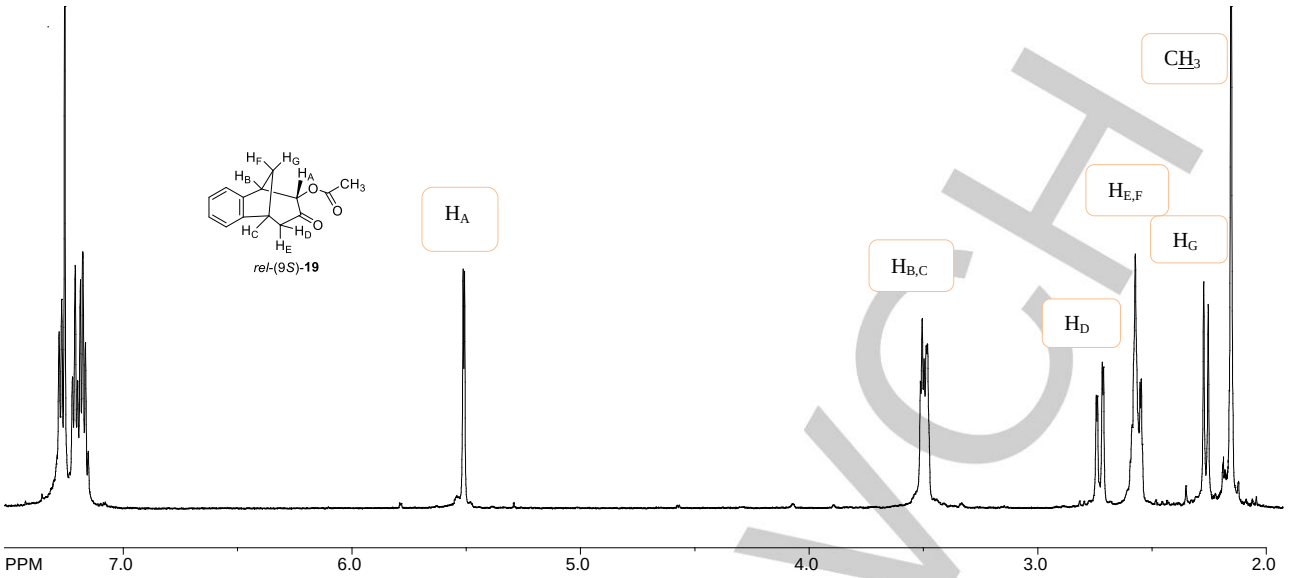
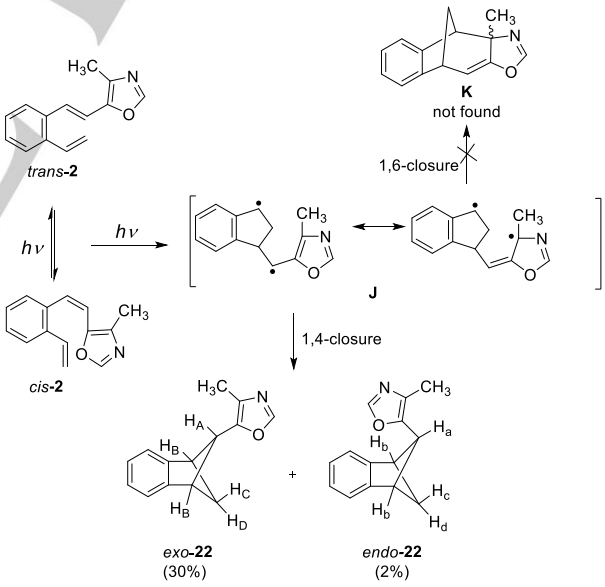


Figure 2. ^{1}H NMR spectra in $CDCl_3$ of *rel*-(9*S*)-**19.**

Using COSY and NOESY techniques all corresponding interactions were found. The signals of two carbonyl groups, with the bands at 1746 and 1720 cm^{-1}, in the IR spectrum, were confirmed with the presence of the chemical shifts in ^{13}C NMR spectrum at 201.6 (C=O) and 169.6 ppm (O-COCH3). Additional HRMS confirmed that the compound has no nitrogen present in the structure. After the reaction in mildly acidic ether product **20** (3%) (scheme 4) was also isolated, formed by rearomatization of the oxazoline ring.

If the photochemical product **17** is kept in moist ether and additionally aerated through a period of 6 h product **21,** that has a carbonyl group, is detected in traces (scheme 4) and the structure of this product was determined spectroscopically. Compound **21** has one signal for the carbon atom with two protons (H_E and H_F) in ^{13}C NMR spectrum (34.7 ppm). Furthermore, the compound **21** has a very strong band for the carbonyl group in the IR spectrum (1747 cm^{-1}) and a specific pattern for the protons of the bicyclic skeleton in the ^{1}H NMR spectrum (H_A – H_F) (See Supporting Information). It can be concluded that the 2-methyl-oxazoline-benzobicyclo[3.2.1]octene product **17** is stabile enough and can be used as a precursor in further synthesis, but it can too, in more rigorous conditions, be modified via oxazoline ring opening. As was described, 2-methyl-4-(2-vinylstyryl)oxazole (**3**) (scheme 3) reacts by the same path as the unsubstituted 4- and 5-(2-vinylstyryl)oxazoles giving the oxazoline-benzobicyclo[3.2.1]octene product **17**. Substituted 2-phenyl-5-(2-vinylstyryl)oxazole (**4**) and 4-methyl-5-(2-vinylstyryl)oxazole (**2**) reacted altogether differently than the unsubstituted 5-(2-vinylstyryl)oxazole.[2] 2-phenyl-5-(2-vinylstyryl)oxazole (**4**) was extremely unreactive. There was no reaction detected neither at 300, nor at 350 nm lamps, in any of the solvents that were tested (petroleumether, acetone, benzene, methanol, acetonitrile). At longer periods of irradiation (24 h) only high molecular weight products were detected. The methyl group at the position 4, on the oxazole ring, in the compound 4-methyl-5-(2-vinylstyryl)oxazole (**2**) directs the photoreaction towards formation of benzobicyclo[2.1.1]hexene product (scheme 5).

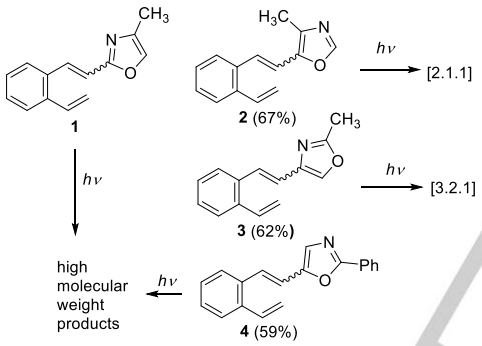


Scheme 5. Irradiation of 4-methyl-5-(2-vinylstyryl)oxazole (**2**).

Exo-**22** is the major product of the intramolecular photochemical cycloaddition reaction and is formed in 30% yield, while *endo*-**22** is formed in traces (2%). The formation of the benzobicyclo[2.1.1]hexene skeleton can be explained as a result of the competition between the electronic and steric effects in the intermediate **J** (scheme 5). In this case the steric effects of the CH_3 group were predominant and 1,4-ring closure was

favored. Both of the benzobicyclo[2.1.1]hexene isomers were completely characterized (See Supporting Information). Benzobicyclo[2.1.1]hexene product, *exo*-**22**, has a specific pattern in the ^{1}H NMR spectrum where the H_A - H_D protons fall in the region from 3.76 to 2.43 ppm. It is also important to note that this structure has a plane of symmetry and this makes the H_B protons chemically equivalent, having the same shift at 3.47 ppm. Reacting in this way the 4-methyl-5-(2-vinylstyryl)oxazole (**2**) gave a new venue, where polycyclic skeleton with the oxazole ring that is not incorporated into it can be easily obtained. The oxazole ring that is unsubstituted at the position 2 is prone to a broad spectrum of further functionalizations with the polycyclic skeleton preserved.

We have shown that the placement of the hexatrienyl moiety at the 2-, 4- or 5- position, respectively, on the oxazole ring, together with the influence of the methyl/phenyl substituents, plays a significant role in the photoreaction pathways due to the electronic and steric effects that are brought into the system. The diverse photoreactivity of the investigated oxazole derivatives (**1**-**4**) is summarized in the scheme 6.



Scheme 6. Schematical presentation of the photoreactivity of **1**-**4**.

Conclusions

In summary, as a continuation of a previous work that was done on 2-, 4- and 5-(2-vinylstyryl)oxazoles,[1,2] new methyl- and phenyl-substituted derivatives were synthesized and their photochemical behavior was studied. They gave diverse fused oxazoline and oxazole containing polycyclic products. Namely, 2-methyl-4-(2-vinylstyryl)oxazole (**3)** afforded by photochemical intramolecular cycloaddition reaction fused oxazoline-benzobicyclo[3.2.1]octene product **17** as a diasteromeric mixture. Product **17** was much more stabile than the analogue unsubstituted oxazoline product described earlier but in more rigorous conditions it did react further. In mildly acidic ether stereospecific product, *rel*-(9*S*)-**19,** was formed by hydrolysis. In the same reaction conditions aromatization of the oxazoline ring took place and benzobicyclo[3.2.1]octene product **20** was formed. As for the effect of substitution on the 5-(2-vinylstyryl)oxazoles, 2-phenyl derivative **4** was completely unreactive, while the 4-methyl derivative **2** gave by photochemical intramolecular cycloaddition reaction new benzobicyclo[2.1.1] hexene product **22**, with the predominant *exo*-form. This is the first instance of the 1,4-closure to the bicyclo[2.1.1]hexene skeleton in the 2-, 4-, and 5-oxazole-stilbene derivatives studied so far.[1,2] When the hexatrienyl moiety is not at the position 5, but 2 of the oxazole ring, as in the 4-methyl-2-(2-vinylstyryl)oxazole (**1**), the electronic effects are different and there is no reaction.

Herein we have reported a simple method for the synthesis of functionalized benzo-bicyclo[3.2.1]octene, as well as benzobicyclo[2.1.1]hexene oxazole containing derivatives, utilizing light as a clean reagent. New insights into the excited state reactivity of the 2-, 4- and 5-hexatrienyl substituted oxazole ring were also gathered.

Experimental data

General procedures

Reactions which required the use of anhydrous, inert atmosphere techniques were carried out under an atmosphere of nitrogen. Petroleum ether, bp 40-60 ºC, was used. Solvents were purified by distillation. Column chromatography was carried out on columns with silica gel (Fluka 0.063-0.2 nm and Fluka 60 Å, tehnical grade). TLC was carried out using plates coated with silica gel (0.2 mm and 0.5 mm, Kiselgel 60 F_{254}). Organic layers were routinely dried with anhydrous $MgSO_4$ and evaporated using a rotary evaporator. ^{1}H and ^{13}C NMR spectra were recorded on a spectrometer at 300 and 600 MHz. All NMR spectra were measured in $CDCl_3$ using tetramethylsilane as reference and some in C_6D_6. The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY experiments. The following abbreviations are used: s, singlet; d, dublet; t, triplet; q, quartet, dd, doublet of doublets; m, multiplet, br, broad, PE, petroleumether, E, ether. UV spectra were measured on a UV/VIS spectrophotometer. IR spectra were recorded on a FTIR spectrometer. Mass spectra were obtained on a GC-MS system. Melting points were obtained using a microscope equipped apparatus and are uncorrected. HRMS analysis were carried out on a mass spectrometer (MALDI TOF/TOF analyzer), equipped with Nd:YAG laser operating at 355 nm with firing rate 200 Hz in the positive (H+) or negative (-H) ion reflector mode. Irradiation experiments were performed in a quartz vessel in benzene solution in a photochemical reactor equipped with 300 nm lamps.

Synthesis of 4-methyl-2-[2-(2-vinylphenyl)ethenyl]oxazole (1)

4-methyl-oxazole-2-carbaldehyde[22,26] (**5**): In 20 mL of ether 30 mmol of oxazole 4-methyloxazole is dissolved. The mixture is cooled down to (-70) °C (dry ice/acetone) and then 30 mL of *n*-BuLi is added drop wise. The reaction mixture is kept under flow of nitrogen. 2.20 mL of *N*,*N*-dimethylformamide dissolved in 10 mL of dry ether is added drop wise next and the reaction mixture is left to stir for 30 minutes at (-70) °C and then additional 90 minutes at rt. The work up is done by acidification with 2M HCl (pH = 5-6) followed by extraction with dichloromethane, drying over magnesium sulphate and evaporation of the solvent under reduced pressure. Crude reaction mixture was purified by column chromatography on silica gel with petroleum ether/ether (0-10%) as eluent and gave 1.32 g (40%, lit.[26] 48%, bp 60-70 °C/20 mm Hg) as yellow oil; IR ν_{max}/cm^{-1} (KBr): 1700, 1580, 1520; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 9.73 (d, 1H, $J_{CHO,5}$ = 0.60 Hz, C<u>H</u>O), 7.62 (dd, 1H, $J_{5,CH3}$ = 1.08 Hz, $J_{5,CHO}$ = 0.60 Hz, H-5), 2.31 (d, 3H, $J_{CH3,5}$ = 1.08 Hz, C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$): δ/ppm 177.2 (d), 157.54 (s), 139.7 (s), 138.21 (d), 11.0 (q); MS, *m/z* (M^+, %): 111 (87), 55 (100), 54 (49).

4-methyl-2-[2-(2-vinylphenyl)ethenyl]oxazole (**1**)

Compound **1** was synthesized by Wittig reaction from diphosphonium salt of α,α'-*o*-xylenedibromide (10 mmol) and 4-methyloxazole-2-

carbaldehyde (**5**) (10 mmol). Mixture of isomers was purified by column chromatography on silica gel using PE/E (9.05:0.5) as eluent to give 0.361 g (57%) of mixture of *cis*/*trans* = 1:4 isomers of compound **1**. The isomers were separated by repeated column chromatography on silica gel.

Cis-4-methyl-2-[2-(2-vinylphenyl)ethenyl]oxazole (*cis*-**1**); oil: UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 247 (12178), 294 (11000); IR ν_{max}/cm^{-1} (NaCl): 3080, 3050, 2920, 1640, 1625, 1595, 1380, 1100, 985, 915, 770; ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 7.03-7.56 (m, 5H, H-ar), 7.28 (m, 1H, H-5), 6.97 (d, 1H, J_{et} = 12.4 Hz, H-et), 6.86 (dd, 1H, $J_{a,c}$ = 17,3 Hz, $J_{b,c}$ = 10.9 Hz, H-c), 6.52 (d, 2H, J_{et} = 12.4 Hz, H-et), 5.65 (dd, 1H, $J_{a,c}$ = 17.3 Hz, $J_{a,b}$ = 1.1 Hz, H-a), 5.27 (dd, 1H, $J_{b,c}$ = 10.9 Hz, $J_{a,b}$ = 1.1 Hz, H-b), 2.14 (d, 3H, $J_{CH3,5}$ = 1.2 Hz, H-CH$_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 159.7 (s), 136.9 (s), 136.0 (s), 134.6 (d), 134.5 (d), 134.2 (s), 133.8 (d), 129.2 (d), 127.9 (d), 126.8 (d), 125.2 (d), 116.6 (d), 115.8 (t), 11.1 (q); MS *m/z* (%, fragment) (EI): 211 (100%, M$^+$); HRMS (MALDI-TOF/TOF) for $C_{14}H_{13}NO$ (M-H)$^-$ calcd 210.091340, found 210.086531.

Trans-4-methyl-2-[2-(2-vinylphenyl)ethenyl]oxazole (*trans*-**1**), yellow powder: mp 32-33 °C; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}) : 250 nm (12869), 310 nm (19467); IR ν_{max}/cm^{-1} (KBr): 3080, 3060, 2920, 1640, 1625, 1595, 1380, 1100, 965; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.79 (d, 1H, J_{et} = 16.3 Hz, H-et), 7.55-7.54 (m, 1H, H-ar), 7.48-7.47 (m, 1H, H-ar), 7.34 (m, 1H, H-5) 7.30-7.28 (m, 2H, H-ar), 7.11 (dd, 1H, $J_{a,c}$= 17.3 Hz, $J_{b,c}$ = 11.0Hz, H-c), 6.81 (d, 1H, J_{et} = 16.2 Hz, H–et), 5.65 (dd, 1H, $J_{a,c}$ = 17.3, $J_{a,b}$ = 1.2 Hz, H-a), 5.40 (dd, 1H, $J_{b,c}$ = 11.0, $J_{a,b}$ = 1.2 Hz, H-b), 2.21 (d, 3H, $J_{CH3,5}$ = 1,2 Hz, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 160.7 (s), 137.4 (s), 136.8 (s), 134.1 (d, C-c), 134.5 (d, C-5), 133.2 (s), 132.8 (d, C-et), 128.4 (d, C-ar), 128.4 (d, C-5), 127.5 (d, C-ar), 126.4 (d, C-ar), 125.9 (d, C-ar), 117.0 (t, C-a,b), 115.6 (d, C-et), 11.2 (q, $\underline{C}H_3$).

Synthesis of 4-methyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (2)

(4-methyloxazol-5-yl)methanol[24] (**11**). In a suspension made of 3 g (78 mmol) lithium-aluminum-hydride and 50 mL anhydrous tetrahydrofuran 12.2 g (78 mmol) of ethyl-4-methyl-oxazole-5-carboxylate (**10**) in 40 mL anhydrous tetrahydrofuran is added dropwise at temperature of 6-10 ºC. Reaction mixture is left to stir overnight in an ice bath after which 15 g of ice is added and the mixture is filtered (sediment is washed with hot tetrahydrofuran). Filtrate is dried over anhydrous $MgSO_4$. Evaporation of solvent under reduced pressure afforded the crude product which is purified by vacuum distillation to give 3.24 g (36.8 %, lit[24] 62%) of 4-methyloxazol-5-yl)methanol (**11**) as white crystals: m_p 52 - 54 ºC (lit.[24] m_p 55 - 56 °C); IR (KBr, cm^{-1}): 3100, 1640, 1510, 1140, 1015, 925, 760, 655, 630; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.78 (s, 1H, H-2), 4.65 (s, 2H, C$\underline{H}_2$), 3.45 (brs, 1H, O$\underline{H}$), 2.18 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$): δ 150.0 (d, C-2), 146.2 (s), 132.6 (s), 53.4 (t, $\underline{C}H_2$), 10.1 (q, $\underline{C}H_3$).

4-methyl-oxazole-5-carbaldehyde (**6**)[22] In a solution of 1.1 g (11 mmol) of (4-methyloxazol-5-yl)methanol (11) in 4 mL of dichloromethane 1.5 g (4 mmol) of pyridinium dichromate is added. Reaction mixture is left to stir overnight at room temperature. Evaporation of the solvent under reduced pressure afforded the crude product which was further purified by column chromatography on silica gel using PE/E (variable ratio) as eluent and gave 4-methyl-oxazole-5-carbaldehyde (6) (0.66 g 57%) as white crystals: m_p 36-38 ºC; IR (KBr, cm^{-1}): 3120, 1685, 1595; ^{1}H NMR (90 MHz, $CDCl_3$): δ/ppm 9.90 (s, 1H, C$\underline{H}$O), 8.02 (s, 1H, H-2), 2.55 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$): δ 176.9 (d, $\underline{C}$HO), 152.9 (d, C-2), 147.1 (s), 144.9 (s), 12.2 (q, $\underline{C}H_3$); MS, m/z (M$^+$,%): 111 (100), 84 (33), 82 (53), 54 (68).

4-methyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (**2**). To a stirred solution of 7.88 g (10 mmol) triphenylphosphonium salt in absolute dry ethanol (3Å sieves) 1.11 g (10 mmol) of 4-methyl-oxazole-5-carbaldehyde (**6**) was added and a solution of sodium ethoxide (11 mmol, 0.253 g sodium in 14.5 mL absolute ethanol) was added drop wise in strictly anhydrous conditions under nitrogen. Reaction mixture was left to stir for 1 h. Under the stream of dry nitrogen, gaseous formaldehyde (obtained by decomposition of paraformaldehyde taken in excess, 1.5 g) was introduced together with the second quantity of sodium. Reaction mixture was left to stir overnight. After removal of the solvent the residue was worked up with ice-water, and extracted with benzene. Benzene extracts were dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure and gave the crude product which was further purified by column chromatography on silica gel using PE/E (10:1) as eluent to give **2** (1.410 g, 67%) as a mixture of *cis*- and *trans*-isomers. Isomers were separated by repeated column chromatography on silica gel using PE/E (variable ratio) to give *cis*-4-methyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (*cis*-**2**) as colorless oil: R_f (PE/E = 5:1) = 0.35; UV ((EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1})): 232 (14635), 255 (15396), 288 (13183); IR (NaCl, cm^{-1}): 2910, 1640, 1620, 1575, 1495, 1470, 1440, 1380, 1275, 1120, 1070, 770; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.57 (s, 1H, H-2), 7.52 (d, 1H, J_{ar} = 7.7 Hz, H-ar), 7.15-7.32 (m, 3H, H-ar), 6.87 (dd, 1H, $J_{c,a}$ = 17.3 Hz, $J_{c,b}$ = 11.0 Hz, H-c), 6.68 (d, 1H, J_{et} = 12.3 Hz, H-et), 6.42 (d, 1H, J_{et} = 12.3 Hz, H-et), 5.65 (dd, 1H, $J_{a,c}$ = 17.3 Hz, $J_{a,b}$ = 1.1 Hz, H-a), 5.25 (dd, 1H, $J_{b,c}$ = 11.0 Hz, $J_{b,a}$ = 1.1 Hz, H-b), 2.03 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 149.5 (d), 144.2 (s), 136.2 (s), 135. 6 (s), 134.9 (d), 134.8 (s), 129.4 (d), 128.6 (d), 127.7 (d), 127.2 (d), 125.4 (d), 115.7 (t, C-a,b), 115.2 (d), 11.7 (q, $\underline{C}H_3$); MS, m/z (M$^+$, %): 211 (15), 115 (47), 96 (100); HRMS (*m/z*): [M+H] calcd for $C_{14}H_{13}NO$ 211.099165, found 211.096086. *Trans*-4-methyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (*trans*-**2**) as colorless oil R_f (PE/E = 5:1) = 0.30; UV ((EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1})): 256 (14157), 309 (18919); IR (NaCl, cm^{-1}): 3050, 2920, 1640, 1620, 1585, 1495, 1470, 1445, 1385, 1250, 1225, 1115, 950; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.72 (s, 1H, H-2), 7.42-7.56 (m, 2H, H-ar), 7.20-7.36 (m, 3H, H-ar), 7.06 (dd, 1H, $J_{c,a}$ = 17.4 Hz, $J_{c,b}$ = 11.0 Hz, H-c), 6.73 (d, 1H, J_{et} = 15.9 Hz, H-et), 5.63 (dd, 1H, $J_{a,c}$ = 17.4 Hz, $J_{a,b}$ = 1.1 Hz, H-a), 5.36 (dd, 1H, $J_{b,c}$ = 11.0 Hz, $J_{b,a}$ = 1.1 Hz, H-b), 2.25 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 148.7 (d), 144.6 (s), 135.5 (s), 133.5 (d), 133.3 (s), 131.5 (s), 126.9 (d), 126.7 (d), 125.5 (d), 125.2 (d), 124.5 (d), 115.5 (t, C-a,b), 112.9 (d), 9.7 (q, $\underline{C}H_3$).

Synthesis of 2-methyl-4-[2-(2-vinylphenyl)ethenyl]oxazole (3)

2-methyl-oxazole-4-carbaldehyde[25] (**7**) was synthesized according to literature for oxazole-4-carbaldehyde[26] from methyl-2-methyloxazole-4-carboxylate (**12**). Reaction gave 0.66 g (84%, lit.[25] 65%)of 3 as colorless powder: ^{1}H NMR ($CDCl_3$; 600 MHz) *δ*/ppm: 9.90 (s, 1H, C$\underline{H}$O), 8.16 (brs, 1H, H-2), 2.53 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$; 600 MHz) *δ*/ppm: 183.8 (d, C$\underline{H}$O), 163.0 (s), 144.4 (d, C-5), 141.0 (s), 13.8 (q, C$\underline{H}_3$).

2-methyl-4-[2-(2-vinylphenyl)ethenyl]oxazole (**3**). Solution of diphosphonium salt of α,α'-*o*-xylenedibromide 4.6 g (6 mmol) in absolute ethanol (100 mL, kept on 3Å sieves) was stirred and then a solution of 2-methyl-oxazole-4-carbaldehyde (**7**) (6 mmol) in 4 mL of ethanol was added dropwise together with half of a solution of sodium ethoxide (0.31 g Na, 13.20 mmol) in strictly anhydrous conditions under nitrogen. After 1 h, under the stream of dry nitrogen, gaseous formaldehyde (gained by decomposition of paraformaldehyde, 1.0 g) was introduced and the second quantity of sodium ethoxide was added dropwise. Reaction mixture was left to stir for 24 h. After removal of the solvent on the rotatory evaporator the residue was worked up with ice-water, and extracted with toluene (4 × 20 mL). Toluene extracts were dried over anhydrous $MgSO_4$. Evaporation of the solvent afforded 0.786 g (62 %) of crude product as a mixture of *cis*- and *trans*-isomer (*cis* : *trans* = 1:4). Column chromatography on silica gel with PE/E as eluent gave *cis*-2-methyl-4-[2-(2-vinylphenyl)ethenyl]oxazole (*cis*-**3**) as oil: R_f (PE/E=7:1) = 0.30; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 244 (11968), 287 (Sh 4814); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*/ppm: 7.60 (brd, 1H, J_{ar} = 7.8 Hz, H-ar),7.31-7.29 (m, 1H, H-ar), 7.25-7.21 (m, 2H, H-ar), 6.86 (dd, $J_{a,c}$ = 17.5 Hz, $J_{b,c}$ = 11.0 Hz, 1H, H-c), 6.72 (d, J_{et} = 11.9 Hz, ,1H H-et), 6.70 (s, 1H, H-5), 6.51 (d, J_{et} = 11.9 Hz, 1H H-et), 5.68 (dd, $J_{a,b}$ = 1.0 Hz, $J_{a,c}$ = 17.54 Hz, 1H,H-a), 5.22 (dd, $J_{a,b}$ = 1.0 Hz, $J_{b,c}$ = 11.0 Hz, 1H,H-b), 2.37 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*/ppm: 159.7 (s), 136.4 (s), 135.2 (s), 135.2 (d, C-5), 135.0 (s), 134.0 (d, C-c), 129.7 (d, C-et), 128.1 (d, C-ar), 127.5 (d, C-ar), 127.4 (d, C-ar), 124.9 (d, C-ar), 122.0 (d, C-et), 114.8 (t, C-a,b), 13.1 (q, $\underline{C}H_3$); HRMS (MALDI-TOF/TOF) for $C_{14}H_{13}NO$: (M+H)$^+$ calcd 212.1070, found 212.1072.

Trans-2-methyl-4-[2-(2-vinylphenyl)ethenyl]oxazole (*trans*-**3**) as oil: R_f (PE/E=7:1) = 0.40; IR ν_{max}/cm^{-1}: 3058, 1592, 1438, 1102, 916; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 249 (16155), 288 (18316); ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 7.56 (d, 1H, J_{et} = 15.9 Hz, H-et), 7.53 (s, 1H, H-5), 7.51-7.50 (m, 1H, H-ar), 7.48-7.47 (m, 1H, H-ar), 7.26-7.24 (m, 2H, H-ar), 7.14 (dd, 1H, $J_{a,c}$ = 17.5 Hz, $J_{b,c}$ = 11.0 Hz, H-c), 6.76 (d, 1H, J_{et} = 15.9 Hz, H-et), 5.64 (dd, 1H, $J_{a,b}$ = 1.1 Hz, $J_{a,c}$ = 17.5 Hz, H-a), 5.34 (dd, 1H, $J_{a,b}$ = 1.1 Hz, $J_{b,c}$ = 11.0 Hz, H-b), 2.50 (s, 3H, $\underline{C}H_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 161.3 (s), 138.8 (s), 136.1 (s), 134.8 (s), 134.7 (d, C-5), 134.5 (d, C-c), 127.3 (d, C-et), 127.2 (d, C-ar), 127.2 (d, C-ar), 126.0 (d, C-ar), 125.6 (d, C-ar), 118.5 (d, C-et), 115.9 (t, c-a,b), 13.4 (q, $\underline{C}H_3$); MS *m/z* (%, fragment): 212 (100%, $(M+H)^+$.

Synthesis of 2-phenyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (4)

Synthesis of 2-phenyl-oxazole-5-carbaldehyde (**8**)

2-Bromoethylammonium bromide[28] (**16**). Prepared according to lit.[28] gave 269.9 g (80%; lit[28] 83%).of 16 as white crystals.

2-Phenyloxazoline[29] (**15**). Prepared according to lit.[29] gave 6.6 g (60%; lit.[29] 67%, bp 100-110 ºC/ 5mm Hg).

5-Bromo-2-phenyloxazole[29] (**14**). Prepared according to lit.[29] gave 3.05 g (34.6%, mp 64-66 °C).

2-Phenyloxazole[29] (**13**). In a solution of 4.31 g (20 mmol) of 5-Bromo-2-phenyloxazole (**14**) in 40 mL THF, *n*-BuLi was added drop wise at (-70) ºC. The reaction was conducted under a stream of nitrogen. After the addition of *n*-BuLi reaction mixture was left to stir for 30 min and after that 1.8 g of distilled water was added and left to stir overnight. Work up of the mixture was done by neutralization with HCl (HCl:water = 1:3). Water solution was extracted with ether (4 x 30mL), dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure on the rotator evaporator. Crude product was purified by column chromatography on silica gel with PE/E (9.05:0.5) as eluent and gave 1.74 g (60.7%) of 2-phenyloxazole (13) as oil (lit.[29] 88%, bp. 65-75 °C/5 mm Hg).

2-Phenyl-oxazole-5-carbaldehyde[29] (**8**)

Formylation mixture was made by adding of 0.41 g (6 mmol) of DMF to 0.86 g (0.006 mol) of phosphoryl chloride and the mixture was cooled in an ice bath. Into the mixture 0.81 g (0.006 mol) of 2-phenyloxazole (**13**) in 1 mL of DMF was added drop wise and the mixture was left to stir overnight. Next day the mixture was heated to 90 °C for 4 hours. The work up included addition of 12 g of ice and neutralization with 15% solution of NaOH. Water solution was extracted with dichloromethane (4 x 30mL), dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure on the rotatory evaporator. Crude product was purified by column chromatography on silica gel with PE/E (8:2) and gave 0.26 g (28%) of product (**8**) as white crystals: mp 74-76 °C (lit.[29] mp 72-74°C).); IR (KBr): ν 1680, 1665, 1605, 1560, 1530 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 9.82 (s, 1H), 8.10-8.27 (m, 2H), 7.95 (s, 1H), 7.44-7.59 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 175.9 (d), 165.1 (s), 149.3 (s), 138.8 (d), 131.9 (d), 128.7 (d), 127.4 (d), 125.6 (s).

2-phenyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (**4**). Compound **4** was synthesized by Wittig reaction from diphosphonium salt of α,α'-*o*-xylenedibromide (10 mmol) and 2-phenyloxazole-5-carbaldehyde (**8**) (10 mmol). Mixture of isomers was purified by column chromatography on silica gel using PE/E (9.05:0.5) as eluent to give *Cis*-2-phenyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (*cis*-**4**) as yellow oil: IR (evaporated film from $CHCl_3$): 3045, 1585, 1550, 1475, 1445, 1130, 980, 910 cm^{-1}; UV ((EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1})): 240 (15472), 312 (15538); ^{1}H NMR ($CDCl_3$): δ 7.70-7.80 (m, 2H), 7.59 (m, 1H), 7.21-7.40 (m, 6H), 6.87 (dd, 1H, $J_{a,c}$=17.5 Hz, $J_{b,c}$ = 11.0 Hz), 6.81 (s, 1H), 6.71 (d, 1H, J_{et}=12.3 Hz), 6.52 (d, 1H, J_{et} =12.3 Hz), 5.66 (dd, 1H, $J_{a,c}$ =17.5, $J_{a,b}$ = 1.3 Hz), 5.21 (dd, 1H, $J_{b,c}$ =11.0, $J_{a,b}$ = 1.3 Hz); ^{13}C NMR ($CDCl_3$): δ 160.7 (s), 149.1 (s), 135.9 (s), 135.8 (s), 134.6 (d), 130.2 (d), 129.3 (d), 128.9 (d), 128.6 (d), 127.9 (d), 127.9 (d), 127.5 (d), 127.2 (s), 126.2 (d), 125.4 (d), 116.5 (d), 115.6 (t).

Trans-2-phenyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (*trans*-**4**) as yellow powder: mp 75-76 °C; IR (evaporated film from $CHCl_3$): 3045, 1625, 1585, 1555, 1480, 1450, 1130, 985 cm^{-1}; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1})): 265 (15490), 338 (28879); ^{1}H NMR ($CDCl_3$): δ 8.08-8.12 (m, 2H), 7.42-7.55 (m, 6H), 7.27-7.30 (m, 2H), 7.16 (s, 1H), 7.13 (dd, 1H, $J_{a,c}$ =17.3 Hz, $J_{b,c}$ = 11.0 Hz), 6.82 (d, 1H, J_{et} = 16.2 Hz), 5.68 (dd, 1H, $J_{a,c}$ =17.3, $J_{a,b}$ = 1.3 Hz), 5.43 (dd, 1H, $J_{b,c}$ = 11.0 Hz, $J_{a,b}$ = 1.3 Hz); ^{13}C NMR ($CDCl_3$): δ 161.0 (s), 150.3 (s), 136.6 (s), 134.6 (d), 134.4 (s), 130.3 (d), 128.7 (d), 128.1 (d), 127.8 (d), 127.2 (s), 126.9 (d), 126.7 (d), 126.5 (d), 126.3 (d), 125.8 (d), 116.9 (t), 115.1 (d); MS, m/z (M^+, %): 273 (100), 168 (32), 158 (98), 142 (40), 105 (59); HRMS (*m/z*): $[M+H]^+$ calcd for $C_{19}H_{15}NO$ 273.1154, found 273.1153.

Photochemistry of 4-methyl-2-[2-(2-vinylphenyl)ethenyl]oxazole (1)

a) Preliminary irraddiation of (**1**)

Mixture of isomers of 2-phenyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (**1**) (2.66 x 10^{-3} mol/L) dissolved in 17 mL of petroleumether, acetone, benzene, methanol, acetonitrile (purged with argon for 20 minutes) was irradiated at 300 and 350 nm, respectively, in a photoreactor equipped with 16 UV lamps for 30 minutes, 2, 5, 10 and 24 h. Evaporation of solvent under reduced pressure afforded at shorter times only starting material and at longer irradiation times only high molecular weight products.

b) Preparative irraddiation of (**1**)

Mixture of isomers of 2-phenyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (**1**) (4.5 x 10^{-5} mol/L; 9 x 10^{-5}; 2.25 x 10^{-4}; 2.70 x 10^{-4}; 3 x 10^{-4}; 9 x 10^{-4}) dissolved in benzene (purged with argon for 30 minutes) was irradiated at 300 nm, respectively, in a photoreactor equipped with 16 UV lamps for 2-64h. Evaporation of solvent under reduced pressure afforded at shorter times shows only starting material and at longer irradiation times only high molecular weight products.

Photochemistry of 4-methyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (2)

0.257 g (1.9 x 10^{-3} mol/L) of 4-methyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (**2**) in 690 mL of petroleum ether (purged with argon for 30 minutes) was irradiated at 300 nm in a photo reactor equipped with 16 UV lamps for 15 h. Evaporation of solvent under reduced pressure afforded the crude product which was further purified by thin layer chromatography on silica gel using PE/E (variable ratio) as eluent afforded to afford *exo*-5-(4-methyl-5-oxazolyl)benzobycyclo[2.1.1]heks-2en (*exo*-**22**) (0.08 g, 30%) as colorless oil: R_f 0.28 (20% ether:petroleumether); ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.77 (s, 1H, H-2), 7.25-7.30 (m, 2H, H-ar), 7.01-7.04 (m, 2H, H-ar), 3.76 (d, $J_{a,d}$ = 7.30 Hz, 1H, H-A), 3.47 (d, $J_{b,c}$ = 2.60 Hz 2H, H-B), 3.25 (dt, $J_{b,c}$ = 2,60 Hz, $J_{c,d}$ = 6.40 Hz 1H, H-C), 2.43 (dd, $J_{c,d}$ = 6.4, $J_{a,d}$ = 7.30 Hz 1H, H-D), 2.22 (br s, 3H, $J_{CH3,a}$ < 0,8 Hz, H-C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 151.8 (d), 148.8 (s), 145.8 (s), 131.4 (s), 124.5 (d), 119.0 (d), 68.3 (d), 60.6 (t), 48.8 (d), 11.7 (q).

Endo-5-(4-methyl-5-oxazolyl)benzobycyclo[2.1.1]heks-2en (*endo*-**22**) (0.005 g, 2%) as colorless oil: R_f (PE/E = 5:1) = 0.25; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.42 (s,1H, H-2), 7.13-7.16 (m, 2H, H-ar), 6.86-6.90 (m, 2H, H-ar) 4.19 (br s, 1H, H-A), 3.53 (t, $J_{b,c}$ = $J_{b,a}$ = 2.50 Hz, 2H, H-B), 2.83 (dt, 1H, $J_{b,c}$ = 2.50, $J_{c,d}$ = 6.10 Hz, H-C), 2.44 (d, H, $J_{c,d}$ = 6.10 Hz, H-D), 1.94 (d, $J_{CH3,a}$ =1.10 Hz, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$): δ 149.2 (s), 148.7 (d), 145.9 (s), 131.2 (s), 124.5 (d), 112.0 (d), 66.7 (d), 61.3 (t, C-C,D), 48.6 (d), 11.4 (q, $\underline{C}H_3$); MS, m/z (M^+, %): 211 (43), 141 (30), 128 (27), 115 (35), 96 (100), 87 (44), 73 (60), 60 (97); HRMS (*m/z*): [M+H] calcd for $C_{14}H_{13}NO$ 211.099165, found 211.098184.

Photochemistry of 2-methyl-4-[2-(2-vinylphenyl)ethenyl]oxazole (3)

a) Preliminary irradiations of **3** in UV cuvettes

0.001 g of *cis*/*trans*-**3** is dissolved in 100 mL of 96% ethanol and irradiated in 2 mL UV cuvettes in the photo reactor equipped with 4 lamps of 300 nm. Photochemical changes are monitored by UV spectroscopy in timed intervals.

b) Preliminary irradiations of **3** in sealed NMR tubes

0.010 g of *cis*-**3** is dissolved in 4 mL of deuterated benzene in NMR tube degassed and the tube is sealed. The sample is irradiated in the photo reactor equipped with 4 lamps of 300 nm. Photochemical changes are monitored by NMR spectroscopy in timed intervals.

c) Preparative irradiations of **3**

0.024 g of mixture of *cis*-**3** and *trans*-**3** in 50 mL of benzene (c = 3 × 10^{-3} mol/L) (flushed with argon for 20 minutes) was irradiated at 300 nm (16 UV lamps) for 5h. After the removal of the solvent the crude product, by ^{1}H NMR, is a mixture of three products *rel*-(2*S*)-**17** : *rel*-(2*R*)-**17** : **18** = 70% : 23% : 7%. Multiple column and thin layer chromatographies on silica gel gave 0.015g (63%) of *rel*-(2*S*)-**17** and 0.002 g (7%) of **18**.

Product *rel*-(2*S*)-4-methyl-3-oxa-5-azatetracyclo[6.6.1.$0^{2,6}$.$0^{9,14}$]pentadeca-4,6,11,13-pentaene (*rel*-(2*S*)-**17**) was gained as colorless oil: R_f (PE/E=1:2) = 0.30; IR ν_{max}/cm^{-1}:2952, 1606, 1382, 1232; ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*/ppm: 7.22–7.20 (m, 1H, H-ar), 7.17–7.16 (m, 1H, H-ar), 7.10–7.09 (m, 2H, H-ar), 5.73 (dd, J_{AB} = 3.6 Hz, J_{AD} = 4.7 Hz, J_{AE} = 1.3 Hz, 1H, H–A), 5.23 (dd, J_{AB} = 3.6 Hz, J_{BC} = 4.2 Hz, 1H, H–B), 4.00 (t, J_{BC} = J_{CE} = 4.2 Hz, 1H, H–C), 3.41 (t, J_{AD} = J_{DE} = 4.7 Hz, 1H, H–D), 2.47–2.44 (m, 1H, H–E), 2.32 (d, J_{EF} = 11.3, 1H, H–F), 1.92 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*/ppm: 169.6 (s), 153.6 (s), 146.0 (s), 138.4 (s), 127.0 (d, C-ar), 126.6 (d, C-ar), 126.2 (d, C-ar), 120.8 (d, C-ar), 117.1 (d, C-A), 81.3 (d, C-B), 44.4 (d, C-C), 43.7 (t, C-E,F), 40.8 (d, C-D), 14.8 (q, $\underline{C}H_3$); HRMS (*m*/*z*): [M-e]$^-$ calcd for $C_{14}H_{13}NO$ 211,0992, found 211,0992.

Rel-(2*R*)-4-methyl-3-oxa-5-azatetracyclo[6.6.1.$0^{2,6}$.$0^{9,14}$]pentadeca-4,6,11,13-pentaene (*rel*-(2*R*)-**17**): (^{1}H i ^{13}C NMR spectra from mixture): R_f (PE/E=1:2) = 0.35; ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*/ppm: 7.14-7.09 (m, 4H, H-ar), 6.10 (dd, J_{ab} = 3.1 Hz, J_{ac} = 7.6 Hz, 1H, H-a), 4.46 (dd, J_{ab} = 3.1 Hz, J_{bd} = 0.8 Hz, 1H, H-b), 3.70 (dd, J_{ac} = 7.6 Hz, J_{ce} = 4.3 Hz, 1H, H-c), 3.66 (debeli d J_{bd} = 0.8 Hz, J_{de} = 3.5 Hz, 1H, H-d), 2.30-2.29 (m, 1H, H-e), 1.67 (d, J_{ef} = 10.3 Hz, 1H, H-f), 2.10 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*/ppm: 167.9 (s), 148.0 (s), 147.5 (s), 143.6 (s), 127.2 (d, C-ar), 126.7 (d, C-ar), 123.5 (d, C-ar), 122.9 (d, C-ar), 118.6 (d, C-ar), 81.5 (d, C-b), 41.4 (t, C-e,f), 41.3 (d, C-c), 40.8 (d, C-d), 15.1 (q, $\underline{C}H_3$).

5-(1,2-dihydronaphtalene-2-yl)-2-methyloxazole (**18**) as oil: R_f (PE/E=1:2) = 0.70; IR ν_{max}/cm^{-1}: 2945, 2923, 1577, 1226; ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*/ppm: 7.35 (d, J_{ar} = 7.5 Hz, 1H, H-ar), 7.33 (d, J_{ar} = 7.5 Hz, 1H, H-ar), 7.27-7.24 (m, 1H, H-ar), 7.21-7.16 (m, 1H, H-ar), 7.18 (s, 1H, H-5), 6.81 (dd, $J_{C,D}$ = 5.5 Hz, $J_{C,X}$ = 1.5 Hz, 1H, H-C), 6.51 (dd, $J_{C,D}$ = 5.5 Hz, $J_{D,X}$ = 1.8 Hz, 1H, H-D), 3.82 (dddd, $J_{A,X}$ = 6.3 Hz, $J_{B,X}$ = 9.0 Hz, $J_{C,X}$ = 1.5 Hz, $J_{D,X}$ = 1.8 Hz, 1H, H-X), 2.99 (dd, $J_{A,B}$ = 14.6 Hz, $J_{A/B,X}$ = 6.3 Hz, 1H, H-A/B), 2.61 (dd, $J_{A,B}$ = 14.6 Hz, $J_{A/B,X}$ = 9.0 Hz, 1H, H-A/B), 2.46 (s, 3H, C$\underline{H}_3$); ^{1}H NMR (C_6D_6, 600 MHz) *δ*/ppm: 7.24 – 7.15 (m, 4H, H-ar, 5), 7.10-7.07 (m, 1H, H-ar), 6.66 (dd, $J_{C,D}$ = 5.5 Hz, $J_{C,X}$ = 1.7 Hz, 1H, H-C), 6.49 (dd, $J_{C,D}$ = 5.5 Hz, $J_{D,X}$ = 1.8 Hz, 1H, H-D), 3.89 (dddd, $J_{A,X}$ = 6.3 Hz, $J_{B,X}$ = 8.7 Hz, $J_{C,X}$ = 1.7 Hz, $J_{D,X}$ = 1.8 Hz, 1H, H-X), 2.87 (dd, $J_{A,B}$ = 14.4 Hz, $J_{A/B,X}$ = 6.3 Hz, 1H, H-A/B), 2.51 (dd, $J_{A,B}$ = 14.4 Hz, $J_{A/B,X}$ = 8.7 Hz, 1H, H-A/B), 2.00 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*/ppm: 138.4 (d, C-D), 133.8 (d, C-5), 130.7 (d, C-C), 126.3 (d, C-ar), 124.3 (d, C-ar), 122.5 (d, C-ar), 120.6 (d, C-ar), 48.6 (d, C-X), 27.8 (t, C-A,B), 13.5 (q, $\underline{C}H_3$); HRMS (*m*/*z*): [M+H]$^+$ calcd for $C_{14}H_{13}NO$ 212.1070, found 212.1065.

Further reactions of oxazoline derivative (17)

In ethanol and deuterated methanol

0.030 g of crude photochemistry mixture was dissolved in 30 mL of ethanol (3Å) / 2 mL of deuterated methanol and left standing for 20 days. After the removal of the solvent ^{1}H NMR spectra showed that no reaction occurred.

In moist ether with aeration

Raw mixture from photochemistry was dissolved in 30 mL of ether and aerated with air for 11h. After removal of the solvent, crude residue was purified with column chromatography on silica gel with PE/E (3:1) as eluent. With a large quantities of unidentified products and tarry material traces of oxidation product (2*S*,6*R*)-**21** was isolated together with *rel*-(2*R*)-**17**. *rel*-(2*S*,6*R*)-4-methyl-3-oxa-5-azatetracyclo[6.6.1.$0^{2,6}$.$0^{9,14}$]pentadeca-4,9,11,13-tetraen-7-one ((2*S*,6*R*)-**20**) as oil: R_f (PE/E=1:2) = 0.35; IR ν_{max}/cm^{-1}: 2945, 1747 (C=O), 1604, 1470; ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*/ppm: 7.28–7.27 (m, 1H, H-ar), 7.25–7.24 (m, 1H, H-ar), 7.20 – 7.19 (m, 2H, H-ar), 5,79 (d, $J_{A,D}$ = 3.7 Hz, H–A), 4,46 (dd, $J_{B,C}$ = 4.0 Hz, $J_{B,F}$ = 1.0 Hz, 1H, H–B), 3.50 (t, $J_{B,C}$ = $J_{C,F}$ = 4.0 Hz, 1H, H–C), 3.44 (t, $J_{A,D}$ = $J_{D,F}$ = 3.7 Hz, 1H, H–D), 2.81 (d, $J_{E,F}$ = 12.0 Hz, 1H, H–E), 2.43 – 2.39 (m, 1H, H–F), 2.15 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): *δ*/ppm 201.5 (s, C=O), 169.0 (s), 142.2 (s, C-ar), 140.0 (s, C-ar), 127.0 (d, C-ar), 126.8 (d, C-ar), 124.5 (d, C-ar), 123.4 (d, C-ar), 76.6 (d, C-A), 76.1 (d, C-B), 46.0 (d, C-C), 44.4 (d, C-D), 34.7 (t, C-E,F), 19.7 (q, $\underline{C}H_3$); HRMS (*m*/*z*): [M+H]$^+$ calcd for $C_{14}H_{14}O_3$ 231.1016, found 231.1020.

In moist, mildly acidic ether

0.050 g of raw photochemistry mixture dissolved in 30 mL of ether with addition of 1 mL of HCl p.a. was stirred for 3h. After removal of the solvent the crude residue was dissolved in water, neutralized with NaOH and extracted with ether. Ether solution was dried over $MgSO_4$ and solvent was removed under reduced pressure. The crude product was purified by thin layer chromatography on silica gel with PE/E (1:1) as eluent. And two products were identified. 0.006 g (12%) of (9*S*)-10-oxotricyclo[6.3.1.$0^{2,7}$]dodeca-2,4,6-trien-9-yl acetate (*rel*-(9S)-**19**) as colorless oil: R_f (PE/E=1:1) = 0.5; IR ν_{max}/cm^{-1}: 2952, 1746 (C=O), 1720 (C=O), 1471, 1236, 1078; ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*/ppm: 7.27 (d, J_{ar} = 7.1 Hz, 1H, H-ar), 7.21 (t, J_{ar} = 7.1 Hz, 1H, H-ar), 7.18 – 7.15 (m, 2H, H-ar), 5,50 (dd, $J_{A,B}$ = 3.8 Hz, $J_{A,CH3}$ = 0.6 Hz H–A), 3.51 (t, $J_{A,B}$ = $J_{B,F}$ = 3.8 Hz, 1H, H–B), 3.49 (dd, $J_{C,D}$ = 3.5 Hz, $J_{C,F}$ = 7.6 Hz, 1H, H–C), 2.73 (dd, $J_{D,E}$ = 15.5 Hz, $J_{C,D}$ = 3.5 Hz, 1H, H–D), 2.57-2.54 (m, 2H, H-E, F), 2.26 (d, $J_{E,F}$ = 11.8 Hz, 1H, H–G), 2.15 (d, $J_{A,CH3}$ = 0.6 Hz, 1H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): *δ*/ppm 201.6 (s, C=O), 169.6 (s, C=O), 144.9 (s, C-ar), 141.0 (s, C-ar), 127.6 (d, C-ar), 126.8 (d, C-ar), 124.8 (d, C-ar), 122.6 (d, C-ar), 78.9 (d, C-C), 47.3 (t, C-D, E), 45.4 (d, C-A), 41.7 (t, C-F, G), 40.5 (d, C-B), 20.2 (q, $\underline{C}H_3$).

4-methyl-3-oxa-5-azatetracyclo[6.6.1.$0^{2,6}$.$0^{9,14}$]pentadeca-2(6),4,9,11,13-pentaene (**20**) (0.002 g, 3.33 %) as oil: R_f (PE/E=1:1) = 0.3; IR ν_{max}/cm^{-1}: 2917, 2851, 1566, 1462, 1374; ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*/ppm: 7.32 (d, J_{ar} = 7.5 Hz, 1H, H-ar), 7.16 (d, J_{ar} = 7.4 Hz, 1H, H-ar), 7.11 (dd, J_{ar} = 7.4 Hz, J_{ar} = 7.5 Hz, 1H, H-ar), 7.10 (dd, J_{ar} = 7.4 Hz, J_{ar} = 7.5 Hz, 1H, H-ar), 3.95 (d, $J_{A,D}$ = 4.6 Hz, 1H, H-A), 3.59 (t, $J_{B,D}$ = $J_{B,C}$ = 4.8 Hz, $J_{B,E}$ = 1.3 Hz, 1H, H-B), 3.05 (ddd, $J_{B,C}$ = 4.8 Hz, $J_{C,E}$ = 16.0 Hz, 1H, H-C), 2.51 (ddd, $J_{B,D}$ = 4.8 Hz, $J_{A,D}$ = 4.6 Hz, $J_{D,F}$ = 10.3 Hz, 1H, H-D), 2.46 (dd, $J_{C,E}$ = 16.0 Hz, $J_{B,E}$ = 1.3 Hz, 1H, H-E), 2.17 (d, $J_{D,F}$ = 10.3 Hz, 1H, H-F). ^{13}C NMR ($CDCl_3$, 150 MHz): *δ*/ppm 178.4 (s), 149.1 (s), 144.5 (s), 138.4 (s), 126.3 (d, C-ar), 125.8 (d, C-ar), 123.6 (d, C-ar), 120.1 (d, C-ar), 42.3 (t, C-D, F), 40.0 (d, C-B), 38.8 (d, C-A), 29.7 (t, C-C, E), 13.5 (q, CH_3).

Photochemistry of 2-phenyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (4)

Irraddiation of (**4**)

0.010 g (1.9 x 10^{-3} mol/L) of 2-phenyl-5-[2-(2-vinylphenyl)ethenyl]oxazole (**4**) in 17 mL of petroleumether, acetone, benzene, methanol, acetonitrile (purged with argon for 20 minutes) was irradiated at 300 and 350 nm, respectively, in a photoreactor equipped with 16 UV lamps for 5, 10 and 24 h. Evaporation of solvent under reduced pressure afforded at shorter times only starting material and at longer irradiation times only high molecular weight products.

Keywords: benzobicyclo[3.2.1]octene • intramolecular photocycloaddition • oxazoline • vinylstyryl

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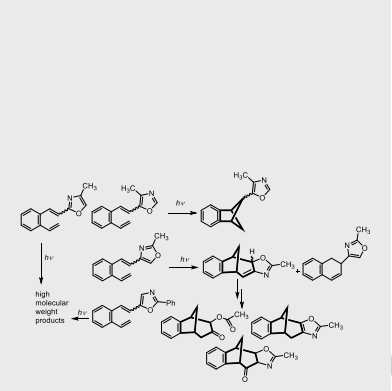
FULL PAPER

To study the effects of the position of the hexatrienyl moiety on the oxazole ring, targeted novel substituted *cis/trans*-2/4/5-(2-vinylstyryl)oxazoles have been synthesized and irradiated. Depending on the position of the hexatrienyl moiety in the oxazole ring, as well as the position of the methyl/phenyl substituents these new vinylstyryl-2/4/5-oxazole derivatives showed diverse photochemical behavior and gave new functionalized oxazole and oxazoline polycyclic products.



Oxazole Photochemistry*

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Versatile photochemical reactivity of diverse substituted 2-, 4- and 5-(*o*-vinylstyryl)oxazoles