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Photoinduced intramolecular formal [4+2] cycloaddition of aryl substituted *o*-vinylstyryl-2-oxazoles to form benzo[*f*]quinoline derivatives: experimental results and theoretical interpretation

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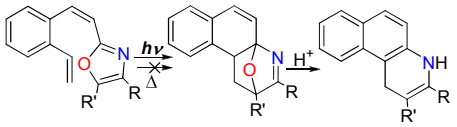
Graphical abstract

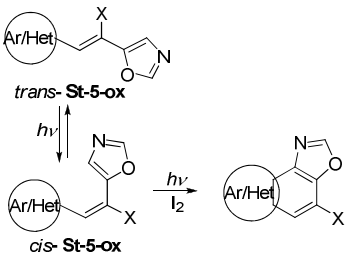


Abstract

A new approach to benzo[*f*]quinoline derivatives has been found by effective formal [4+2] photocycloaddition process from novel aryl substituted *o*-vinylstyryl-2-oxazoles. All of the *o*-vinylstyryl-2-oxazoles were synthesized by multicomponent Wittig reaction from diphosphonium salt of α,α'-*o*-xylenedibromide, formaldehyde and 5-tolyl-, 4-phenyl-5-methyl- and 4,5-diphenyloxazole-2-carbaldehydes. TD-DFT calculations revealed that the intramolecular photocyclization in 2-(2-vinylstyryl)oxazoles to form benzo[*f*]quinoline derivatives proceeds on the S_1 PES via stepwise pathway, namely by 10π followed by 6π ring closure. On that path the existence of a S_0/S_1 conical intersection was indicated. The reactivity of the photocyclization steps depends on the substitution pattern at the positions 4 and 5 of the oxazole ring where the aryl group in position 5 deactivates the reaction.

Introduction

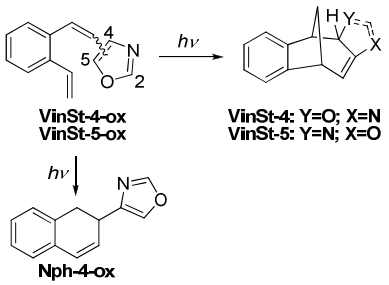
Benzo[*f*]quinolines (naphtho[2,1-*b*]pyridines) are the structural isomers of azaphenanthrenes.[1] A number of synthetic pathways to obtain these derivatives has been reported.[2-5] One of the very efficient and simple methods is the oxidative photocyclization of 2-styrylpyridine derivatives[6-8]. Photocyclization reactions of 2-styrylpyridine isomers[9-11] and their annelated derivatives[12,13] as well as Shiff's bases[14,15] provide a method to benzo[*h*]-, benzo[*f*]-, benzo[*f*](iso)-quinolines and azahelicenes, respectively. Benzoquinoline derivatives are very useful compounds with significant biological and pharmacological properties.[16-21] The use of heteroarylphenylethenes in photochemical synthesis[22] of potentially biologically active heteroaromatic compounds is expanding. Continuing our interest for conjugated heteroaromatic systems with furans,[23,24] thiophenes,[24,25] pyroles,[26] and sydnones,[27] as well as their photochemical reactions to heteropolycyclic compounds we extended research to oxazole derivatives.[28-30] We have recently described novel oxidative photocyclization of styryl/heteroarylethenyl-5-oxazoles (**St-5-ox**) to naphthooxazoles (Scheme 1).[28]



Scheme 1. Photochemical electrocyclization of styryl/heteroarylethenyl-5-oxazoles (**St-5-ox**)

Moreover, styryl-4- and 5-oxazoles (**VinSt-4/5-ox**), bearing a vinyl substituent in the ortho position, gave in the absence of oxygen diverse fused tetracyclic oxazoline compounds (Scheme 2) which further spontaneously hydrolyze to benzobicyclo[3.2.1]octenone derivatives.[29] The formation of the fused oxazoline products is explained by initial formal [2+2]cycloaddition followed by 1,6-ring closure of resonance stabilized intermediate. In addition, 4-(2-vinylstyryl)oxazole (**VinSt-4-ox**) gave a minor product 4-(1,2-

dihydronaphthalen-2-yl)oxazole (**Nph-4-ox**), formed in an electrocyclization process of the hexatriene system of the divinylbenzene moiety (Scheme 2).

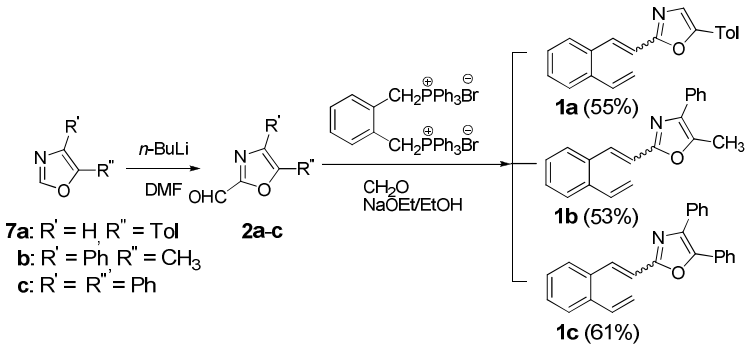


Scheme 2. Photochemical reactions of *o*-vinylstyryl-4/5-oxazoles (**VinSt-4/5-ox**)

In this work we describe the photochemical transformation of aryloxazole derivatives substituted with *o*-vinylstyryl group in the position 2 (**1a-c**). Irradiation of aryl substituted 2-(2-vinylstyryl)oxazole derivatives resulted in a completely unexpected photochemical process, formal intramolecular [4+2] cycloaddition. The influence of the aryl substituents at the oxazole ring to the transformation of these oxazoles to benzo[*f*]quinoline derivatives was observed and explained by molecular modeling. The described photochemical reaction represents a new synthetic approach for the synthesis of benzo[*f*]quinoline derivatives.

Results and Discussion

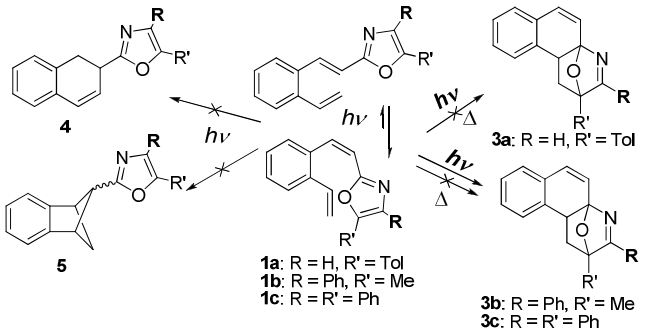
C*is/trans* isomers of 2-(*o*-vinylstyryl)oxazole derivatives (**1a-c**) were synthesized by Wittig reactions from the diphosphonium salt of α,α'-*o*-xylenedibromide, formaldehyde and appropriate oxazole-2-carbaldehydes (**2a-c**) following our established procedure for the synthesis of β-heteroaryl derivatives of *o*-divinylbenzene (Scheme 3).[29]



Scheme 3. Synthesis of 2-(2-vinylstyryl)oxazoles (**1a-c**)

All new compounds were obtained in moderate yields (53-61%) as mixtures of *cis*/*trans* isomers in a ratio 1:4. The isomers were isolated by column chromatography on silica gel and characterized by spectroscopic methods (see SI 1). The examination of UV spectra shows a bathochromic shift of absorption maxima of **1a** and **1c** [at 344 (*trans*-**1a**), 325 (*cis*-**1a**) and 345 (*trans*-**1c**), 330 (*cis*-**1c**) nm] compared to the absorption maximum of **1b** [at 328 (*trans*-**1b**), 308 (*cis*-**1b**) nm] due to prolonged conjugation by aryl substituent in the position 5 of the oxazole ring. The excitation gives rise to S_1 states that probably do not undergo efficient intersystem crossing to populate T_1 states, based on the styryl-5-oxazole.[30] However, compounds are weakly fluorescent or non-fluorescent because of efficient deactivation of S_1 by photochemical *trans-cis* isomerization, as reported for similar compounds.[30] Preliminary irradiation experiments in UV cuvettes indicated *trans-cis* isomerization (see SI 1). Longer irradiations resulted in a decrease of absorption which suggested formation of products with reduced conjugation. The ^{1}H NMR spectra of the crude reaction mixtures after the irradiation performed in a Rayonet reactor at λ_{max} 350 nm in petroleum ether, acetonitrile or benzene showed the highest conversion in benzene which was used as solvent in further preparative experiments. The irradiation in acetone gave only high-molecular weight materials, suggesting that the observed products in benzene do not arise via triplet excited state. A series of experiments were conducted with 5-tolyl-2-(2-vinylstyryl)oxazole (**1a**) by varying

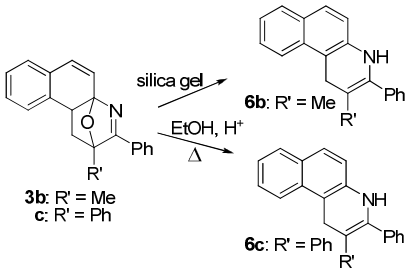
concentration of the compound, irradiation time, but none of them resulted in the formation of product **3a**. ^{1}H NMR spectra of the photo-mixtures after shorter irradiations (2h) indicated the *cis-trans* and *trans-cis* isomerization, whereas at longer times (6h) decomposition took place. On the contrary, the derivatives with the phenyl substituent in the position 4 on the oxazole, **1b** and **1c**, gave selectively new oxa-bridged derivatives **3b** and **3c**, respectively in very good (>72%) to good yields (38%) (Scheme 4).



Scheme 4. Photochemical reaction of 2-(2-vinylstyryl)oxazoles **1a-c**.

The observed photochemical reactivity of **1b** and **1c** is significantly different compared to our previous reports.[29] The possible photoproduct **4**, which would be an analogue to **Nph-4-ox** (Scheme 2) as a result of 6π electrocyclization process of the *o*-divinylbenzene moiety, was not detected. Furthermore, anticipated benzobicyclo[2.1.1]hexene photoproduct **5**, as a result of [2+2] cycloaddition which was the main process in 3-furan substituted 2-vinylstyrylfurans[31] was also not detected.

Photochemical product **3b** could not be isolated. During chromatography on silica gel it was spontaneously transformed to **6b**, isolated in 72% yield (Scheme 5). Photoproduct **3c** is stable, so it was isolated in 38% yield. Cleavage of the oxa-bridge and transformation to benzo[*f*]quinoline **6c** was performed by refluxing **3c** in slightly acidified ethanol (Scheme 5).



Scheme 5. Splitting of oxa-bridged **3b** and **3c**.

The structures of photochemical products **3b**,**c** and benzo[*f*]quinoline derivatives **6b**,**c** were determined by UV, IR, and ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry methods. In ^{1}H NMR spectra, compounds **3b** and **3c** have a characteristic ABX pattern where the geminal signals of protons H_A and H_B are at 2.40 and 2.02 ppm for **3b** and 2.76 and 2.54 ppm for **3c.** The signals of the protons in **3c** are shifted to low field compared to the signals of **3b**, probably due to a desheilding effect of the benzene ring. The signal of proton H_X is located at 3.24 and 3.37 ppm, respectively. Dihydroquinoline derivatives **6b** and **6c** have AB pattern of the geminal protons signals in the expected range of 3.24 to 3.76 ppm and a new signal of the N<u>H</u> proton at 2.35 and 2.67 ppm, respectively (See SI 1).

When the irradiation of **1b** and **1c** was performed under the same conditions, the conversion of diphenyl derivative **1c** to oxa-bridged quinoline **3c** (38%) was lower than the conversion of methylphenyl derivative **1b** to **3b** (>72%). This can be explained by an influence of the aryl substituent in the position 5 on the oxazole ring in **1c** which evidently reduces the efficiency of the cyloaddition process.

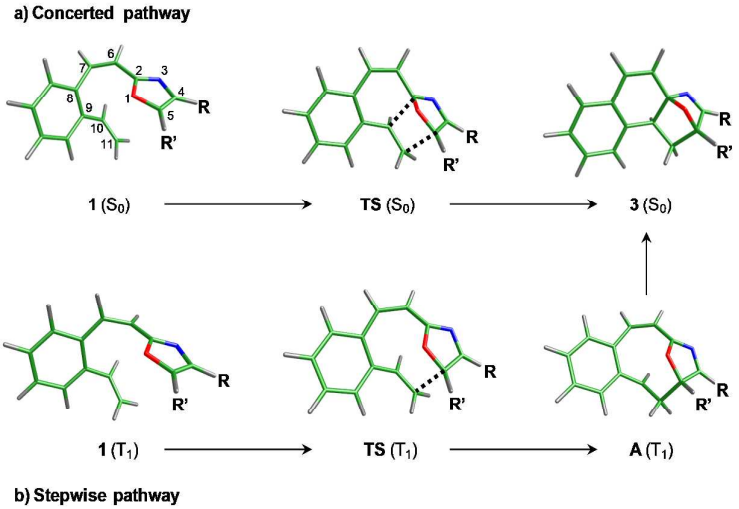
The evidence that the formation of products **3b** and **3c** proceeds photochemically and not as a result of intramolecular Diels-Alder thermal [4+2] cycloaddition was obtained by refluxing the starting compounds (*cis*-**1a**,**b**,**c**) in benzene, toluene and xylene. In all experiments no thermal reaction was observed and only starting material was isolated.

Irradiation of **1b** and **1c** in acetone or benzene solutions in aerobic conditions gave only high molecular weight products, suggesting that photochemical transformations take place from

singlet excited state. Furthermore, irradiation of similar annelated furan derivatives[32] in the presence of benzophenone as triplet sensitizer, performed under conditions to ensure the excitation of the sensitizer, gave no experimental evidence to the mechanism via the triplet state. It is presumed that the formation of these oxa-bridged derivatives (**3b**, **3c**) could proceed via 10π followed by 6π ring closure on singlet excited state surface. Since fluorescence measurements could not give insight into the singlet excited state reactivity of **1a**-**1c** due to competitive *cis*-*trans* isomerization, we resorted to theoretical calculations instead. To shed light into the mechanism of this reaction the topology of the ground state S_0, the first triplet T_1 and the first excited singlet state S_1 potential energy surface (PES) was probed by DFT calculations. The TD-DFT molecular modeling became a valuable tool in interpretation of UV-VIS spectroscopic data and understanding of photochemical processes.[33, 34] However, special attention to selection of proper density functional must be payed. In the present work TD-M06-2X/6-311++G(2d,p)//(U)M06/6-31+G(d) model was used. The selection of a hybrid meta-exchange-correlation M06-2X[35] density functional for calculating energies was motivated by its good performance in modeling of the Diels-Alder reaction of 1,3-butadiene and ethylene in the ground state[36] as well as its good description of the excited states.[35]

The comparison of calculated vertical excitation energies of *cis*-2-(2-vinylstyryl)oxazoles **1a**-**1c** with an available experimental values for λ_{max} of the first absorption band (see SI 2, Table SI5) showed the excellent agreement. Moreover, one can find that the excitation energies of substituted derivatives in Franck-Condon (FC) point were red-shifted compared to unsubstituted **1d**. In accordance to the experimental observation, the decrease of vertical excitation energy was the most pronounced for derivative **1c**. Just mentioned facts were taken as an additional confirmation of good quality of selected theoretical model for description of the S_1 PES in the present study.

The concerted synchronous closure of C11-C5 and C10-C2 bonds (Scheme 6a) and biradical stepwise pathway where one C-C bond forms before the other one (Scheme 6b) were found as more favorable pathways in the S_0 and T_1 states, respectively. A detailed analysis of the theoretical results and Cartesian coordinates of all stationary points were given in the Supporting information 2 (SI 2).



Scheme 6. Concerted (a) vs. stepwise (b) pathway for **1** to **3** transformation.

It should be emphasized that energy barriers higher than 25 kcal mol^{-1} for the Diels-Alder cycloaddition in the ground state hampered the thermal reaction (see SI 2: Figure SI1 and Table SI1) as was, indeed, found in experiment. The transformation of 2-(2-vinylstyryl)oxazoles (**1**) to epoxy-bridged derivatives on the T_1 PES was energetically more favorable than corresponding transformation on the S_0 PES. However, possibility that the photo induced cyclization proceeds on the triplet PES could be discarded due to still high calculated barriers for production of intermediate A. The barriers are in the range between 12.6 and 19.9 kcal mol^{-1} (see SI 2: Table SI4). Also, there is a disagreement between the experimental results and calculations. Namely, the lowest energy barrier was calculated for the derivative **a** where photo reaction was not observed at all. The energy barrier for transformation of derivative **b**, where the reaction proceeded with 70% yield, was 6.6 kcal

mol^{-1} higher than in the case **a**. It is also interesting to note that the stability of biradical intermediate **A** in the T_1 state depends on the substitution pattern. Phenyl substitution in the position 4 of oxazole ring stabilizes and tolyl substitution in the position 5 destabilizes the intermediate **A**.

From the discussion above it comes out that the photochemical reactivity mainly depends on the evolution of the system away from Franck-Condon (FC) point on the S_1 PES. Therefore, the topology of the S_1 PES was probed along both concerted and stepwise pathways by single point TD-DFT calculations in all stationary points found in the S_0 and T_1 states. Also, new stationary points on the S_1 PES were found and fully optimized for derivatives with substitution pattern **a** and **c**. Stepwise reaction path on the S_1 PES is more favorable: the S_1 energy is the lowest for **A**(T_1) geometries where C11-C5 bond is formed. The calculations also indicate the existence of S_0/S_1 conical intersection (CI) on the path for **1** to **3** transformation in a vicinity of **A**(T_1) minimum where efficient relaxation to the ground state is expected. It should be emphasized that direct downhill approach to the PES part with the structures with small S_1/S_0 gaps was found for **1b** (see Figure 1b) and **1d** (see SI 2, Figure SI5d) derivatives.

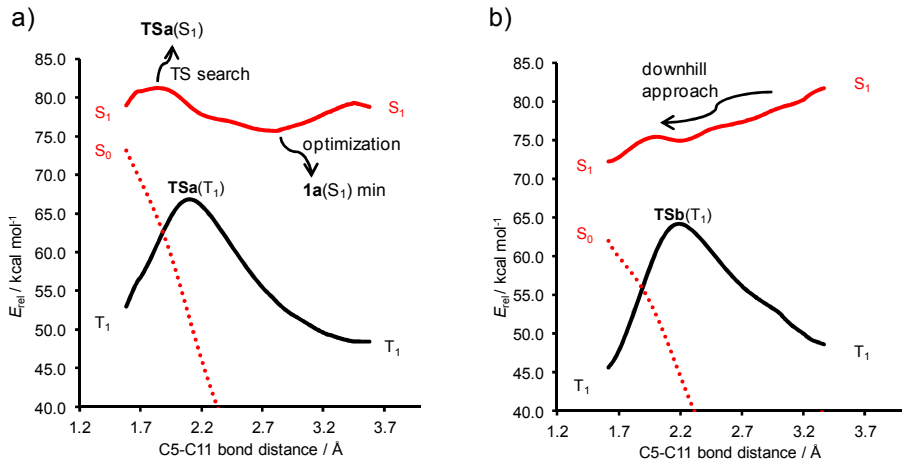


Figure 1. Comparison of IRC paths on the T_1 PES starting from (a) **TSa**(T_1) and (b) **TSb**(T_1) structures. The energies (kcal mol^{-1}) were calculated at the M06-2X/6-311++G(2d,p)//M06/6-

31+G(d) level of theory with respect to the ground state 2-(2-vinylstyryl)oxazole minimum **1**(S_0). Relative energies of the ground and the S_1 state along the paths were given as well.

Due to small S_1/S_0 gap, which is also an indication that conical intersection exists nearby, the molecules could switch to the ground state PES where further relaxation could bifurcate in different directions: toward products and reactants. On the other hand, the reaction is prevented by trapping the excited molecules in the S_1 minimum (see Figure 1a, fully optimized structure is given in SI 2, Figure SI5) in the case of derivative with substitution pattern **a**. Additionally a relaxed scan for a decrease of the C2-C10 distance on the S_1 PES was conducted. The **TSa**(S_1) transition structure (see SI 2, Figure SI5) was found and confirmed by vibrational analysis. The energy barrier of 5.7 kcal mol^{-1} using M06-2X/6-311++G(2d,p) method for the path in the S_1 excited state of **1a** is a consequence of aryl substitution in position 5 which, similar to what was found in the T_1 state, destabilizes structures with closed C11-C5 bond in the S_1 state. Although the molecule **1c** has similar shape of S_1 excited state PES (See SI 2, Figure SI4) as found in **1a**, it undergoes photochemical transformation due to lower energy barrier (3.4 kcal mol^{-1}). However, it is less reactive than **1b** (30% vs. 70% yield) since part of population doesn't have enough energy to surmount the barrier. From TD-DFT calculations can be concluded that substitution pattern on the oxazole ring can tune the reactivity of photocyclization in *o*-vinylstyryl-2-oxazoles by changing the shape of PES between Franck-Condon point and indicated S_1/S_0 CI where C5-C11 bond is already formed. A final evidence for the existence of the CI indicated by TD-DFT is provided by CASSCF(8,8)/6-31+G(d) conical intersection search[37] using the smallest model system with no substituents attached on oxazole ring, **1d** (optimized **CId**(S_1/S_0) structure is shown in SI 2, Figure SI6).

Conclusion

In conclusion, we have shown that 2-(2-vinylstyryl)oxazoles (**1b**, **1c**) afford oxa-bridged quinoline derivatives **3b**, **3c** as the major products by formal intramolecular photochemical [4+2] cycloaddition. The molecular modeling showed that the photocyclization involves formation of one C-C bond between C5 on oxazole ring and C11 from vinyl group on the S_1 PES followed by decay to the ground state via S_1/S_0 conical intersection and subsequent formation of second C-C bond between C2 and C11 in the ground state. Both experimental and theoretical results revealed the high impact of the phenyl substituent at the oxazole ring on the photocyclization process. The oxa-bridged derivatives **3b** and **3c** can easily be transformed to quinoline derivatives. Therefore, photochemistry of transformation of 2-(2-vinylstyryl)oxazoles provides a new synthetic approach for the synthesis of benzo[*f*]quinoline derivatives.

Experimental section

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, technical grade). TLC was carried out using plates coated with silica gel (0.2 mm, 0.5 mm, 1.0 mm, Kiselgel 60 F_{254}). Organic layers were routinely dried with anhydrous $MgSO_4$ and evaporated using a rotary evaporator. ^1H 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, doublet; t, triplet; q, quartet, dd, doublet of doublets; m, multiplet and br, broad. UV spectra were measured on a UV/VIS spectrophotometer. IR spectra were recorded on a FTIR-ATR and FTIR. 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 and on a EXTREL FTMS 2001 DD. Irradiation experiments of compound solutions were performed in a tightly closed vessel in a photochemical reactor equipped with the UVA lamps (316-400 nm). The solvent was removed on the rotatory evaporator under reduced pressure in a ventilated hood.

Oxazole ring formation

Compounds 5-(4-methylphenyl)oxazole **(7a)**,[38,39] 4-phenyl-5-methyloxazole **(7b),**[40] and 4,5-diphenyloxazole[40,41] **(7c)** were prepared according to procedures in the literature.[38-41]

5-(4-methylphenyl)oxazole (7a): 0.27 g (43%) as white crystals: mp = 63.6-63.8 ºC; R_f (PE/E = 10:2) = 0.35; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.89 (s, 1H, H-2), 7.55 (d, $J_{5a,5b}$ = 8.07 Hz, 2H, H-5a), 7.30 (s, 1H, H-4), 7.24 (d, $J_{5a,5b}$ = 8.07 Hz, 2H, H-5b); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 150.1 (d, H-2), 138.7 (s), 129.6 (d), 125.1 (s), 124.4 (d), 120.9 (d), 21.3 (q); MS *m/z* (%, fragment) (EI): 159 (100%, M^+), 130 (31%), 117 (5%), 90 (2%).

4-phenyl-5-methyloxazole (7b): 1.07 g (42%) as oil: R_f (PE/E = 10:1) = 0.30; ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 7.80 (s, 1H, H-2), 7.69 -7.66 (m, 2H, H-4a), 7.46-7.41 (m**,** 2H, H-4b), 7.33-7.30 (m, 1H, H-4c), 2.55 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 149.0 (d, C-2), 144.1 (s), 134.1 (s), 131.9 (s), 128.6 (d), 127.3 (d), 126.6 (d), 11.7 (q).

4,5-diphenyloxazole (7c): 1.92 g (35%) as colorless powder: ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.95 (s, 1H, H-2), 7.67-7.66 (m, 2H, H-ar), 7.61-7.60 (m, 2H, H-ar), 7.39-7.33 (m, 6H, H-ar).

*Synthesis of carbaldehydes (**2a-c**)*

In 20 mL of ether 30 mmol of oxazole (**7a-c**) is dissolved. The mixture is cooled down to -70 °C (dry ice in acetone) and then 30 mL of *n*-BuLi is added drop wise. The reaction mixture is

kept under flow of nitrogen over the whole period of the reaction. 2.20 mL of *N*,*N*-dimethylformamide dissolved in 10 mL of dry ether is added drop wise and the reaction mixture is stired for 30 minutes on low temperature and then additional 90 minutes at room temperature. The reaction is neutralized with 2M HCl (pH = 5-6) and the product extracted with dichloromethane, dryed over magnesium sulphate and the solvent evaporated under reduced pressure. Crude reaction mixture was purified by column chromatography on silica gel with petroleum ether/ether (0-10%) as eluent to give carbaldehydes **2a-c**.

5-(4-methylphenyl)oxazole-2-carbaldehyde (2a)

3.09 g (55%), oil: R_f (PE/E=10:2) = 0.35; IR ν_{max}/cm^{-1}: 3028, 1697 (C=O), 1483, 1609, 1485, 1276, 942; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 9.75 (s, 1H, C<u>H</u>O), 7.69 (d, 2H, $J_{5a/5b}$ = 8.01 Hz. H-5a), 7.58 (s, 1H, H-4), 7.29 (d, 2H, $J_{5a/5b}$ = 8,01 Hz, H-5b), 2.41 (s, 3H, C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 176.5 (d, <u>C</u>HO), 157.4 (s), 140,88 (s), 138.7 (s), 129.9 (d), 125.5 (d), 123.5 (s), 120.8 (d), 21.5 (q); MS *m/z* (EI) (%, fragment): 187 (100%, M^+), 159 (7,5%), 91 (5%) HRMS (MALDI-TOF/TOF) for $C_{11}H_9NO_2$ $(M+H)^+$ calcd 188.0706, found 188.0707

5-methyl-4-phenyloxazole-2-carbaldehyde (2b)

2.80 g (50%), oil: R_f (PE:E=10:2) = 0.30; IR ν_{max}/cm^{-1}: 3058, 2925, 2854, 1702 (CHO), 1530, 1492, 1337, 1016, 788; ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm 9.74 (s, 1H, C<u>H</u>O), 7.71-7.00 (m, 2H, H-4a), 7.49-7,46 (m, 2H, H- 4b), 7.41-7,38 (m, 1H, H-4c), 2.67 (s, 3H , C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 177.2 (d, <u>C</u>HO), 156.3 (s), 148.8 (s), 138.5 (s), 130.8 (s), 128.9 (d, C-Ar), 128.4 (d, C-Ar), 127.0 (d, C-Ar), 12.3 (q, <u>C</u>H$_3$); HRMS (MALDI-TOF/TOF) for $C_{11}H_9NO_2$ $(M+H)^+$ calcd 188.0706, found 188.0709.

4,5-diphenyloxazole-2-carbaldehyde[42] (2c)

6.88 g (92%), oil: IR ν_{max}/cm^{-1}: 2820, 1688, 1600, 1578, 1520, 1470, 1440, 1370, 1330; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 9.82 (s, 1H, C<u>H</u>O), 7.72-7.67 (m, 4H, H-ar), 7.44-7.38 (m, 6H, H-ar); MS *m/z* (%, fragment) (EI): 249 (100%, M^+), 221 (50%), 193 (75%) 165 (36%).

*Synthesis of 2-(2-vinylstyryl)oxazole (**1a-c**)*

To a stirred solution of diphosphonium salt of α,α'-*o*-xylenedibromide (3 mmol) in absolute ethanol (100 ml, kept on 3 Å sieves) simultaneously and dropwise was added a solution of oxazole-2-carbaldehyde (**2a-c**) (3 mmol) in 4 mL of ethanol and half of a solution of sodium ethoxide (6,6 mmol, 2.2 equiv in 30 mL of ethanol) in strictly anhydrous conditions under nitrogen. Reaction mixture was left to stir for 1h. Under the stream of dry nitrogen, gaseous formaldehyde (obtained by decomposition of paraformaldehyde taken in excess, 1.0 g) was introduced together with the second quantity of sodium ethoxide that was added dropwise. Reaction mixture was stirred overnight. After removal of the solvent the residue was worked up with ice-water, and extracted with benzene (4 × 20 mL). Benzene extracts were dried over anhydrous $MgSO_4$. Evaporation of solvent under reduced pressure afforded the crude product.

5-(4-methylphenyl)-[2-(2-vinylphenyl)ethenyl]oxazole (1a). By column chromatography on silica gel using petroleum ether/ether (variable ratio) as eluent afforded 0.47 g (55%) of mixture of *cis*/*trans*= 1:4 isomers of compound **1a** contaminated with small amounts of *cis*- and *trans*-5-(4-methylphenyl)-[2-(2-methylphenyl)ethenyl]oxazole (impurity). The isomers were purified and separated by repeated column chromatography on silica gel. *Cis*-isomer was impossible to purify completely.

<u>*Cis*-5-(4-methylphenyl)-[2-(2-vinylphenyl)ethenyl]oxazole (***cis*-1a** with 14% impurity);</u> oil: R_f (PE/E=10:3) = 0.30; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 243 (14076), 325 (12191); ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.59 (d, J_{ar} = 7.8 Hz, H-ar), 7.40-7.35 (m, 2H, H-ar), 7.28 (t, J_{ar} = 7.3 Hz, H-ar), 7.24 (s, 1H, H-4), 7.13-7.08 (m, 4H, H-ar), 7.05 (d, J_{et} = 12.2 Hz, 1H, H-et), 6.60 (d, J_{et} = 12.2 Hz, 1H, H-et), 5.65 (d, $J_{a,c}$ = 17.3 Hz, $J_{a,b}$ = 1.1 Hz 1H, H-a), 5.24 (d,

$J_{b,c}$ = 11.0 Hz, $J_{b,a}$ = 1.1 Hz 1H, H-b), 2.32 (s, 3H, C$\underline{H}_3$) 10; ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 137.9 (s), 135.6 (s), 134.4 (d), 132.7 (d), 129.1 (d), 128.9 (d), 127.6 (d), 126.8 (d), 125.9 (d), 124.9 (d), 123.8 (d), 123.5 (d), 117.1 (t), 116.8 (d), 115.5 (d), 115.4 (s), 20.9 (q, $\underline{C}H_3$).

Trans-5-(4-methylphenyl)-[2-(2-vinylphenyl)ethenyl]oxazole (***trans*-1a**); colorless powder: mp 85-87 °C; R_f (PE /E = 10:3) = 0.28; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 344 (23876), 266 (16718); IR ν_{max}/cm^{-1}: 2920, 2850, 2160, 1625, 1499, 1120, 966, 750, 505; ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 7.87 (d, 1H, J_{et} = 16.2 Hz, H-et), 7.61-7.58 (m, 2H, H-5a), 7.52-7.49 (m, 1H, H-Ar), 7.36 (s, 1H, H-4), 7.34-7.31 (m, 2H, H-Ar), 7.26-7.24 (m, 2H, H-5b), 7.15 (dd, 1H, $J_{a,c}$ = 17.4 Hz, $J_{b,c}$ = 10.9 Hz, H-c), 7.10-7.09 (m, 1H, H-Ar), 6.89 (d, 1H, J_{et} = 16.2 Hz, H-et), 5.68 (dd, 1H, $J_{a,c}$ = 17.4 Hz, $J_{a,b}$ = 1.3 Hz, H-a), 5.45 (dd, 1H, $J_{b,c}$ = 10.9 Hz, $J_{a,b}$ = 1.3 Hz, H-b), 2.40 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$; 150 MHz) δ/ppm: 160.3 (s), 150.7 (s), 138.1 (s), 136.8 (s), 134.1 (d), 133.2 (s), 132.7 (d), 129.1 (d), 128.5 (d), 127.5 (d), 126.5 (d), 125.9 (d), 124.7 (s), 123.7 (d), 123.7 (d), 122.6 (d), 117.1 (t), 115.5 (d), 20.9 (q); HRMS (MALDI-TOF/TOF) for $C_{20}H_{17}NO$ $(M+H)^+$ calcd 288.1383, found 288.1383.

5-methyl-4-phenyl-[2-(2-vinylphenyl)ethenyl]oxazole (1b). Column chromatography on silica gel using petroleum ether/ether (variable ratio) as eluent afforded 0.456 g (53%) of mixture of *cis*/*trans*= 1:4 isomers of compound **1b** contaminated with small amounts of *cis*- and *trans*-5-methyl-4-phenyl-[2-(2-methylphenyl)ethenyl]oxazole (impurity). The isomers were purified and separated by repeated column chromatography on silica gel. *Cis*- and *trans*-isomers were impossible to purify completely.

cis-4-phenyl-5-methyl-[2-(2-vinylphenyl)ethenyl]oxazole (***cis*-1b** with 12.5% *trans*-**1b**), oil: R_f (PE/E = 5:1) = 0.40; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 251 (15984), 308 (9631); ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.60 (m, 2H, H-Ar), 7.54 (brd, J_{Ar} = 7.5 Hz, 1H, H-Ar), 7.44 (brd, J_{Ar} = 7.5 Hz, 1H, H-Ar), 7.39 (t, J_{Ar} = 7.5 Hz, 1H, H-Ar), 7.33 – 7.23 (m, 3H, H-Ar),

6.99 (brd, J_{et} = 12.5 Hz, 1H, H-et), 6.90 (dd, $J_{a,c}$ = 17.6 Hz, $J_{b,c}$ = 11.2 Hz, 1H, H-c), 6.56 (d, J_{et} = 12.5 Hz, 1H, H-et), 5.66 (dd, $J_{a,c}$ = 17.6 Hz, $J_{a,b}$ = 1.1 Hz, 1H, H-a), 5.27 (dd, $J_{b,c}$ = 11.2 Hz, $J_{a,b}$ = 1.1 Hz, H-b) 2.33 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 157.5 (s), 143.2 (s), 135.8 (s), 135.0 (s), 134.5 (d, C-c), 134.3 (s), 133.9 (d, C-et), 131.7 (s), 129.1 (d, C-ar), 128.0 (d, C-ar), 127.6 (d), 126.7 (d), 126.4 (d), 126.1 (d), 124.9 (d), 116.4 (d), 115.4 (t), 11.3 (q); HRMS (MALDI-TOF/TOF) for $C_{20}H_{17}NO$ $(M+H)^+$ calcd 288.1383, found 288.1377.

trans-4-phenyl-5-methyl-[2-(2-vinylphenyl)ethenyl]oxazole (***trans*-1b** with 15% impurity), oil: R_f (PE/E = 5:1) 0.44; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 328 (22303), 253 (23408); IR ν_{max}/cm^{-1}: 2922, 2359, 2160, 1599, 1495, 1186, 962, 895, 696, 484; ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 7.79 (d, 1H, J_{et} = 16.3 Hz, H-et), 7.70-7.68 (m, 2H, H-ar), 7.59-7.58 (m, 1H, H-ar), 7.51-7.49 (m, 1H, H-ar), 7.45-7.43 (m, 2H, H-ar), 7.34-7.31 (m, 3H, H-ar), 7.15 (dd, 1H, $J_{a,c}$ = 17.3 Hz, $J_{b,c}$ = 10.0 Hz, H-c), 6.87 (d, 1H, J_{et} = 16.3 Hz, H-et), 5.68 (dd, 1H, $J_{a,c}$ = 17.3 Hz, $J_{a,b}$ = 1.2 Hz, H-a), 5.43 (dd, 1H, $J_{c,b}$ = 10.0 Hz, $J_{a,b}$ = 1.2 Hz, H-b), 2.60 (s ,3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 143.4 (s), 136.7 (s), 135.7 (s), 134.1 (d), 133.3 (s), 132.2 (d), 131.8 (s), 128.4 (s), 128.1 (d), 127.5 (d), 126.9 (d), 126.4(d), 126.2 (d), 125.8 (d), 116.9 (t), 115.2 (d), 30.9 (d), 29.7 (d), 29.2 (t), 11.5 (q); MS *m/z* (%, fragment) (EI): 187 (100%, M^+), 103 (25%).

4,5-diphenyl-2[2-(2-vinylphenyl)ethenyl]oxazole (1c). By column chromatography on silica gel using petroleum ether/ether (variable ratio) as eluent afforded 0.64 g (61%) of mixture of *cis*/*trans*= 1:4 isomers of compound **1c**. The isomers were separated by repeated column chromatography on silica gel.

Cis-4,5-diphenyl-2[2-(2-vinylphenyl)ethenyl]oxazole (***cis*-1c**), oil: R_f (PE/E = 10:1) = 0.26; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 330 (10630), 279 (18025), 228 (28575); ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.67 (m, 1H, H-Ar), 7.46 (1H, H-Ar), 7.11 (d, 1H, $J_{et1,et2}$ = 12.2

Hz, H-et$_1$/et$_2$), 6.92 (dd, 1H, $J_{c,b}$ = 17.4 Hz, $J_{c,a}$ = 11.0 Hz, H-c), 6.65 (d, 1H, $J_{et1,et2}$ = 12.2 Hz, H-et1/et2), 5.67 (dd, 1H, $J_{a,c}$ = 17.4 Hz, $J_{a,b}$ = 1.1 Hz, 1H, H-a), 5.26 (dd, 1H, $J_{b,c}$ = 11.0 Hz, $J_{b,a}$ = 1.1 Hz, 1H, H-b); ^{13}C NMR ($CDCl_3$, 600 MHz): δ/ppm 158.8 (s), 145.2 (s), 136.3 (s), 135.1 (s), 135.6 (d), 135.3 (s), 134.8 (d), 132.5 (s), 129.3 (d), 128.5 (s), 128.3 (d), 128.2 (d), 128.1 (d), 128.1 (d), 127.9 (d), 127.3 (d), 126.8 (d), 125.9 (d), 125.4 (d), 117.2 (d), 116.0 (t). HRMS (MALDI-TOF/TOF) for $C_{25}H_{19}NO$ $(M-e)^-$ calcd 349.146115, found 349.149054.

Trans-4,5-diphenyl-2[2-(2-vinylphenyl)ethenyl]oxazole (***trans*-1c**); yellow powder: mp 106.5-107°C; R_f (PE/E = 10:1) = 0.24; UV (EtOH) λ_{max}/nm (ε / $dm^3mol^{-1}cm^{-1}$): 345 (21234), 280 (19127), 234 (20621); IR ν_{max}/cm^{-1} (KBr): 1620, 1590, 1525, 1495, 1465, 1435, 1175, 1150, 1060, 1015, 960, 910; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.91 (d, J_{et} = 16.1 Hz, 1H, H-et), 7.68 (m, H-Ar), 7.61 (m, H-Ar), 7.51 (m, H-Ar), 7.15 (dd, $J_{c,a}$ = 17.4 Hz, $J_{c,b}$ = 11.0 Hz, 1H, H-c), 6.94 (d, J_{et} = 16.1 Hz, 1H, H-et), 5.69 (dd, $J_{a,c}$ = 17.4 Hz, $J_{a,b}$ = 0.9 Hz, 1H, H-a), 5.44 (dd, $J_{b,c}$ = 11.0 Hz, $J_{a,b}$ = 0.9 Hz, 1H, H-b); ^{1}H NMR (C_6D_6, 600 MHz): δ/ppm 8.08 (d, J_{et} = 16.2 Hz, 1H, H-et), 7.92 (m, 2H, H-Ar), 7.62 (m, 2H, H-Ar), 7.33 (m, 2H, H-Ar), 6.93 (d, J_{et} = 16.2 Hz, 1H, H-et), 5.46 (dd, $J_{a,b}$ = 1.4 Hz, $J_{a,c}$ = 17.2 Hz, 1H, H-a), 5.11 (dd, $J_{a,b}$ = 1.4 Hz, $J_{b,c}$ = 11.0 Hz, 1H, H-b); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 160.1 (s), 145.3 (s), 137.3 (s), 137.0 (s), 134.6 (d), 133.8 (d), 133.7 (s), 132.5 (s), 129.1 (d), 128.9 (s), 128.7 (d), 128.7 (d), 128.6 (d), 128.3 (d), 128.1 (d), 127.0 (d), 126.7 (d), 126.5 (d), 117.6 (t), 115.9 (d); MS, *m/z* (M^+, %): 349 (40), 348 (58), 221 (88), 193 (75), 165 (100), 77 (89).

Irradiation experiments

Irradiation of 5-(4-methylphenyl)-2-[2-(2-vinylphenyl)ethenyl]oxazole (1a).

In a vessel 0.086 g (4.5×10^{-3} mol/L) a mixture of *cis*- and *trans*-**1a** dissolved in benzene was purged for 20 minutes with argon in a Rayonet reactor at 350 nm with varying irradiation times. After removal of the solvent, ^{1}H NMR spectra show at shorter irradiation times (≈ 30

minutes) only *trans-cis* isomerization and at longer period of irradiation (≈ 9h) only tarry material.

Irradiation of 5-methyl-4-phenyl-2-[2-(2-vinylphenyl)ethenyl]oxazole (1b). In a vessel 0.060 g (3×10^{-3} mol/L) a mixture of *cis*- and *trans*-**1b** dissolved in benzene and purged with argon for 20 minutes was irradiated at 350 nm for 5h. After removal of the solvent the crude product based on ^{1}H NMR contains only **3b** (See Supporting Information 1).

12-methyl-13-phenyl-15-oxa-14-azatetracyclo[10.2.1.0^{1,10}.0^{4,9}]pentadeca-2,4,6,8,13-pentaene (**3b**): ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.75-7.73 (m, 2H, H-Ar), 7.49-7.21 (m, 8H, H-Ar), 7.15 (d, J_{Ar} = 7.5 Hz, 1H, H-Ar), 6.90 (d, $J_{E,F}$ = 9.8 Hz, 1H, H-E/F), 6.52 (d, $J_{E,F}$ = 9.8 Hz, 1H, H-E/F), 3.24 (dd, $J_{A,X}$ = 8.7 Hz, $J_{B,X}$ = 4.5 Hz, 1H, H-X), 2,40 (dd, $J_{A,B}$ = 11.7 Hz, $J_{A,X}$ = 8.7 Hz, 1H, H-A), 2.02 (dd, $J_{B,X}$ = 4.5 Hz, $J_{A,B}$ = 11.7 Hz, 1H, H-B), 1.88 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm:142.6 (s), 137.1 (s), 133.8 (d), 131.3 (s), 131.0(d), 130.5 (s), 130.3 (d), 128.2 (d), 128.0 (d), 127.6 (d), 127.5 (d), 126.9 (d), 122.3 (d), 98.3 (s), 84.6 (s), 42.4 (d), 37.5 (t), 16.8 (q, $\underline{C}H_3$); HRMS (MALDI-TOF/TOF) for $C_{20}H_{17}NO$ $(M+H)^+$ calcd 288.1388, found 288.1378.

When the crude product was purified by column chromatography on silica gel 0.43 g (72%) of **6b** was isolated.

2-methyl-3-phenyl-1*H*,4*H*-benzo[*f*]quinoline (**6b**): colorless powder: mp 58-61 °C; R_f (CH_2Cl_2) = 0.28; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 333 (5054), 273 (15836), 251 (14360), 218 (20098); IR ν_{max}/cm^{-1}: 3400 (NH), 3055, 2930, 1650, 1444, 1137; ^{1}H NMR ($CDCl_3$ 600 MHz): δ/ppm 8.03-8.00 (m, 3H, H-Ar), 7.88 (d, J_{Ar} = 8.4 Hz, 1H, H-Ar), 7.81 (d, $J_{E,F}$ = 8.5 Hz, 1H, H-E/F), 7.69 (d, $J_{E,F}$ = 8.5 Hz, 1H, H-E/F), 7.57-7.54 (m, 1H, H-5c), 7.49-7.46 (m, 4H, H-Ar), 3.45 (d, $J_{A,B}$ = 16.4 Hz, 1H, H-A/B), 3.31 (d, $J_{A,B}$ = 16.4 Hz, 1H, H-A/B), 2.09 (brs, 1H, N$\underline{H}$), 1.54 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 172.7 (s), 140.2 (s), 136.0 (s), 132.4 (s), 130.8 (s), 129.5 (d), 128.3 (d), 128.2 (d), 127.7 (d), 127.3 (d),

126.0 (d), 126.0 (d), 125.2 (d), 123.0 (d), 120.9 (s), 70.8 (s), 37.4 (t), 24.9 (q); MS *m/z* (%, fragment) (EI): 270 (100%, $(M+H)^+$); HRMS (MALDI-TOF/TOF) for $C_{20}H_{17}N$ $(M-H)^-$ calcd 270.1288, found 270.1284.

Irradiaton of 4,5-diphenyl-2[2-(2-vinylphenyl)ethenyl]oxazole (1c).

In a vessel 0.079 g (2.27×10^{-3} mol/L) a mixture of *cis*- and *trans*-**1c** dissolved in benzene and purged with argon for 20 minutes was irradiated at 350 nm for 6.5 h. After removal of the solvent crude product was purified by column chromatography on silica gel using dichloromethane as eluent and gave 0.029 g (37.5%) of 12,13-diphenyl-15-oxa-14-azatetracyclo[10.2.1.$0^{1,10}$.$0^{4,9}$]pentadeca-2,4,6,8,13-pentaene (**3c**) as colorless powder: mp 198-199 °C; R_f (CH_2Cl_2) = 0.37; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 259 (19414), 335 (1889); IR ν_{max}/cm^{-1}: 2924, 1610, 1447, 1159, 1005, 696, 608; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.55-7.53 (m, 2H, H-Ar), 7.44-7.42 (m, 2H, H-Ar), 7.37-7.33 (m, 2H, H-Ar), 7.24-7.19 (m, 2H, H-Ar), 6.92 (d, $J_{E,F}$ = 9.8 Hz, 1H, H-E/F), 6.64 (d, $J_{E,F}$ = 9.8 Hz, 1H, H-E/F), 3.37 (dd, $J_{B,X}$ = 8.6 Hz, $J_{A,X}$ = 4.3 Hz, 1H, H-X), 2.76 (dd $J_{B,X}$ = 8.6 Hz, $J_{A,B}$ = 11.4 Hz, 1H, H-A/B), 2.54 (dd, $J_{A,B}$ = 11.4, $J_{A,X}$ = 4.3 Hz, 1H, H-A/B); ^{1}H NMR (C_6D_6, 600 MHz) δ/ppm: 7.52-7.50 (m, 2H, H-Ar), 7.30-7.28 (m, 2H, H-Ar), 6.90-6.89 (m, 4H, H-Ar), 6.86-6.83 (m, 1H, H-Ar) 6.80-6.76(m, 2H, H-Ar), 6.68 (d, $J_{E/F}$ = 9.6 Hz, 1H, H-E/F), 6.47 (d, $J_{E,F}$ = 9.6 Hz, 1H, H-E/F), 3.12 (dd, $J_{B,X}$ = 8.4 Hz, $J_{A,X}$ = 4.8 Hz, 1H, H-X), 2.12 (dd $J_{A/B,X}$ = 4.8 Hz, $J_{A,B}$ = 11.3 Hz, 1H, H-A), 2.08 (dd, $J_{A,B}$ = 11.4, $J_{A/B,X}$ = 8.4 Hz, 1H, H-B); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 176.5(s), 169.6 (s), 136.9 (s), 135.6 (s), 130.6 (s), 98.9 (s), 88.5 (s), 134.1 (d, C-E/F), 130.4 (d), 128.4 (d), 128.2 (d), 128.1 (d), 128.0 (d), 127.9 (d), 127.7 (d), 127.5 (d), 126.2 (d), 122.1 (d, C-E/F), 42.4 (d, C-X), 34.4 (t, C-A,B);); MS *m/z* (%, fragment) (EI): 349 (100%, M^+), 321 (20%), 247 (32%), 167 (65%); HRMS (MALDI-TOF/TOF) for $C_{25}H_{19}NO$ $(M+H)^+$ calcd 350.1539, found 350.1524.

Ring opening of the oxa-bridged derivate 3c. The photoproduct **3c** (0.015 g) is refluxed in acidic ethanol (two drops of HCl p.a. in 10 mL of ethanol) for 1h. After cooling the mixture is neutralized with NaOH, extracted with ether, dried over anhydrous magnesium sulphate, filtered and the solvent is removed under reduced pressure. The crude product is purified by column chromatography on silica gel with dichloromethane as eluent and 0.011 g (74%) of **6c** is gained. 2,3-Diphenyl-1*H*,4*H*-benzo[*f*]quinoline **(6c):** colorless powder mp 104-106 °C; R_f (CH_2Cl_2) = 0.40; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 273 (2876), 283 (2750), 338 (1198); IR ν_{max}/cm^{-1}: 3379, 3059, 1447, 1215, 908, 698; ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 7.86 (d, 1H, J_{Ar} = 8.4 Hz, H-H-Ar), 7.81 (d, 2H, $J_{E/F}$ = 8.58, H-E/F), 7.77 (d, 1H, $J_{E/F}$ = 8.58, H-E/F), 7.66 (m, 2H, H-Ar), 7.48-7.33 (m, 7H, H-Ar), 7.25-7.19 (m, 3H), 3.77 (d, 1H, $J_{A,B}$ = 16.7 Hz, H-A/B), 3.63 (d, 1H, $J_{A,B}$ = 16.7 Hz, H-A/B), 2.65 (s, 1H, NH); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 169.1 (s), 142.0 (s), 140.4 (s), 136.4 (s), 132.6 (s), 130.6 (s), 129.5 (d), 128.3 (d), 128.1 (d), 127.9 (d), 127.9 (d), 127.4 (d), 126.0 (d), 125.9 (d), 125.2 (d), 124.5 (d), 123.0 (d), 119.8 (s), 74.0 (s), 39.3 (t, A,B); HRMS (MALDI-TOF/TOF) for $C_{25}H_{19}N$ (M-e)$^-$ calcd 333.1508, found 333.1512.

Computational Details

A key step in preparation of novel benzo[*f*]quinoline derivatives – transformation of 2-(2-vinylstyryl)oxazoles (**1**) to epoxy derivatives (**3**) was rationalized by DFT calculations using M06 density functional.[35] The restricted method was used for all closed shell species while we employed the unrestricted method for the open shell species. The stationary structures in the singlet ground state and the lowest triplet state were optimized by using 6-31+G(d) basis set. The nature of stationary points was investigated by a full vibrational analysis at the same theoretical level used for geometry optimization. Harmonic frequencies were used to compute zero-point energies. The total energies were further recalculated using M06-2X density functional and larger 6-311++G(2d,p) basis set. Also, TD-DFT approach was used for the

single point calculation of the first excited singlet state energies in all stationary points found on the S_0 and T_1 PESs as well as for the search of stationary points in the S_1 excited state. All calculations were carried out using the Gaussian09 suite of programs[43] on the Isabella cluster (Isabella.srce.hr) at the University of Zagreb Computing Center (SRCE) and visualized by the VEGA-ZZ[44] and Molden[45] programs.

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Supporting Information

Spectral data (^{1}H NMR, ^{13}C NMR, IR and UV) of synthesized compounds **1**-**7** are given in the Supporting Information 1 (SI 1). Detailed description of computational methods and analysis of the theoretical results are given in the Supporting Information 2 (SI 2). This material is available free of charge via the Internet at http://pubs.acs.org.

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