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Synthesis of Naphthoxazoles by Photocyclization of 4-/5-(phenylethenyl)oxazoles

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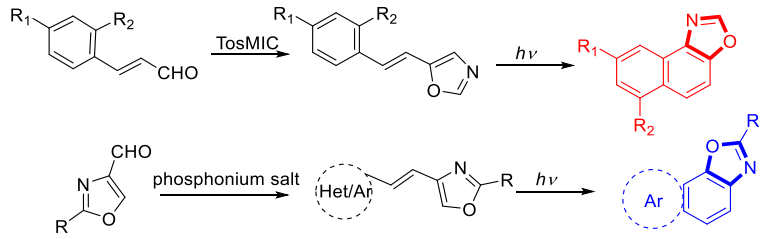
Abstract graphic



Abstract

Promising test results on biological activity of our previously described naphtho[1,2-*d*]oxazoles and heterobenz[1,2-*d*]oxazoles, obtained by photochemical cyclization of 5-phenylethenyl- and 5-heteroarylethenyloxazoles, prompted us to continue with the photochemical synthesis of diverse substituted naphtho[1,2-*d*]oxazoles and extend the photochemical cyclization to naphtho/heterobenz[2,1-*d*]oxazoles going from 4-(aryl/heteroarylethenyl)oxazoles. Required *p*- and *o*-phenyl-substituted 5-arylethenyloxazoles were prepared from the corresponding α,β-unsaturated aldehydes and the TosMIC reagent by Van Leusen reaction. For the preparation of the substituted 4-(aryl/heteroarylethenyl)oxazoles the Wittig reaction was used starting from the selected diverse phosphonium salts and the 2-H/methyl-4-oxazolecarbaldehydes.

Keywords: polycyclic oxazoles, photocyclization, biological activity, Van Leusen, Wittig reaction

Introduction

Benzoxazoles and naphthoxazoles as subunits are important moieties in the synthesis of biologically active molecules[1-7] and there is a vast number of ground state synthetic approaches leading to these fused oxazole polycyclic compounds.[8-15] One of the excited state approaches for the formation of polycycles would be the photocyclization reaction. In the specific case of heterobenzoxazoles and naphthoxazoles the required substrates would have to be stilbene-type compounds. Earliest studies on excited state reactivity of stilbene were done on the photochemical isomerization and cyclization reactions. Synthetically efficient photocyclization became feasible in 1964, when *F. Mallory* discovered that iodine can catalyze

this oxidation.[16] Over the preceding years there has been a lot of developments and applications[17] of the Mallory photocyclization of heterostilbene-type analogues. The photocyclization of heterostilbene-type compounds that would have an oxazole ring incorporated into it was not described until our paper appeared covering photochemical transformations of 5-arylethenyl-/5-heteroarylethenyloxazoles.[18] In the published Note an easy and clean photochemical path to new fused naphtho[1,2-*d*]oxazoles as well as heterobenzoxazoles was given. Since this paper was published some of the naphtho[1,2-*d*]oxazoles as well as heterobenzoxazoles (**A**-**G**; figure 1) that were synthesized were tested for antioxidant activity as well as acetylcholinesterase and butyrylcholinesterase inhibitory activity.[19] These compounds have shown a high cholinesterase inhibition rate and antioxidant activity greater than that of vitamin C. As acetylcholinesterase and butyrylcholinesterase hyper production along with oxidative stress play a big role in different stages of Alzheimer's disease some of the tested compounds could potentially become promising hits in the search for a drug.

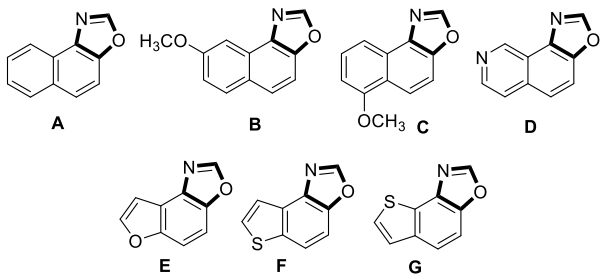


Figure 1. Biologically active naphtho[1,2-*d*]oxazoles and heterobenzoxazoles.

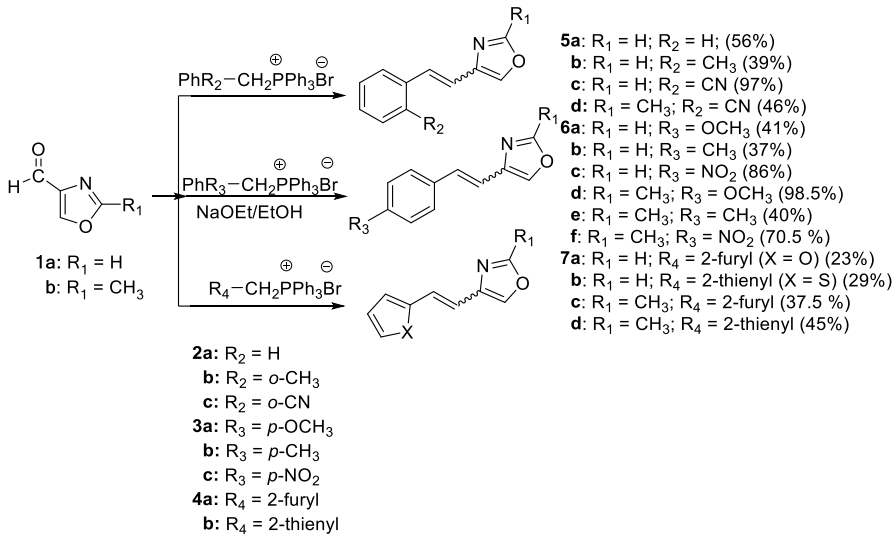
These previously synthesized fused oxazole compounds are also being tested for additional biological activity, lipophilicity as well as metabolic stability.[20] Having in mind that these structures are showing such positive results it was our goal to significantly broaden the scope of this easy and fast photochemical synthesis by adding selected, new, naphtho[1,2-*d*]oxazoles as well as a series of new naphtho[2,1-*d*]oxazoles and fused heterobenzoxazoles to the library of compounds.

Results and discussion

Synthesis of the 4-/5-(phenylethenyl)oxazoles

The plan was to synthesize new 4-styryl/heteroaryl-oxazoles that would further be photochemically transformed to heterobenz/naphtho[2,1-*d*]oxazole products. For the synthesis of these 4-aryl/furyl/thienylethenyloxazoles Wittig reaction[21] was utilized. Selected phosphonium salts (**2**-**4**) were combined with the oxazole-4-carbaldehyde (**1a)**[22] or 2-methyl-oxazole-4-carbaldehyde (**1b**)[23] with sodium ethoxide as base (scheme 1). Aldehydes **1a** and

1b were prepared from commercially available esters by DIBAL-H reduction following the procedure[23] for oxazole-4-carbaldehyde (**1a**).



Scheme 1. Synthesis of 4-styryloxazoles (**5a-c; 6a-c; 7a,b)** and 4-(2-methylstyryl)oxazoles (**5d; 6d-f; 7c,d**).

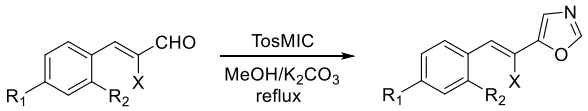
Required phosphonium salts were synthesized from the corresponding bromides and triphenylphosphine.[24-28] Phosphonium salt with the methoxy group in the *para* position on the phenyl ring was used to give compounds **6a** and **6d** and the 2-furyl and 2-thienyl salts to give compounds **7a-d**, respectively. Salt with the methyl group in both the *ortho* and the *para* position was used for the synthesis of compounds **5b**, **6b** and **6e**, respectively. As biologically active compounds containing heterocycles which are bearing nitro groups are well known[29] a salt with the nitro group in the *para* position of the phenyl ring was used for the synthesis of compounds **6c** and **6f**. One of the groups that is also a proven pharmacophore is the nitrile group.[30] Nitriles often play a key role as hydrogen bond acceptors thus bonding with the amino acids or water which are bound to the protein backbone.[31,32] This group is also quite robust and is not readily metabolized so it passes through the body unchanged and the release of the cyanide from aromatic carbons has never been observed.[33] This prompted us to synthesize compounds **5c** and **5d** where phosphonium salt with the *o*-nitrile group was utilized.

All of the Wittig reactions gave mixtures of *trans* and *cis* isomers in diverse ratios. The geometry of the resulting alkene that is formed in the Wittig reaction depends partially on the reactivity of the ylide. The formed ylide can be stabilized by bearing an electron withdrawing group and not as reactive as when it has an electron donating group or an alkyl group. [34-36] The overall stereoselectivity of the Wittig reaction is believed to be the result of steric effects

that develop as the ylide and carbonyl compound approach one another. The three phenyl substituents on phosphorus impose large steric demands that govern the formation of the diastereomeric adducts. Reactions of unstabilized phosphoranes are believed to to be selective for the *cis*-alkene. Ultimately the precise stereoselectivity is dependent on a number of variables, including reactant structure, the base used for ylide formation, the presence of other ions, solvent, and temperature. [37]

Wittig reaction with the (2-cyanobenzyl)triphenylphosphonium bromide (**2b**) was stereoselective and only *cis*-**5c** and *cis*-**5d** were formed, respectively. While the (4-nitrobenzyl)triphenylphosphonium bromide (**3c**) gave only *trans*-**6c** and *trans*-**6f**, respectively. Both the cyano and the nitro group are by itself electron withdrawing, but when they are present as substituents on the phenyl ring there are numerous electronic and steric effects that come into consideration, and direct the Wittig reaction towards stereoselectivity. All of the other salts, that were used, gave mixtures of isomers as products, with variable *cis*/*trans* ratios. New 4-styryloxazoles **5-7** were obtained in good to excellent yields (23 – 98.5 %). Mixtures of isomers, that had the R_f values different enough, were separated by multiple column and thin layer chromatographies on silica gel with petroleumether/diethyl ether as eluent and they were completely characterized (See experimental part and SI).

To further broaden the library of naphtho[1,2-*d*]oxazoles new 5-(arylethenyl)oxazoles were synthesized, as described,[18] in one step by Van Leusen reaction[38,39] from the corresponding aryl-substituted α,β-unsaturated aldehydes (**9a-e**) with tosylmethyl-isocyanide (TosMIC) (scheme 2).

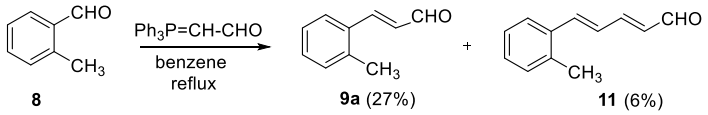


9a: R_1 = H; R_2= CH_3; X = H
b: R_1 = $N(CH_3)_2$; R_2 = H, X = H
c: R_1 = Cl; R_2 = H, X = H
d: R_1 = F; R_2 = H, X = H
e: R_1 = H; R_2 = H; X = Cl

10a: R_1 = H; R_2 = CH_3, X = H, (33%)
b: R_1 = $N(CH_3)_2$; R_2 = H, X = H (22%)
c: R_1 = Cl; R_2 = H, X = H (92%)
d: R_1 = F; R_2 = H, X = H (92%)
e: R_1 = H; R_2 = H; X = Cl (94%)

Scheme 2. Synthesis of 5-(arylethenyl)oxazoles **10a-e**.

After the solvent was evaporated and the crude reaction mixture purified by column chromatography on silica gel, substituted 5-styryloxazoles (*trans*-**10a-e**) were isolated in yields ranging from 22% to 94%. The *trans*-3-(*o*-tolyl)acrylaldehyde[40] (**9a**), that was not commercially available, was synthesized by Wittig reaction from the *o*-methylbenzaldehyde (**8**) and formylmethylenetriphenylphosphorane by a procedure described in literature for the synthesis of (*E*)-3-(pyridyl)acrylaldehydes[41] (scheme 3).



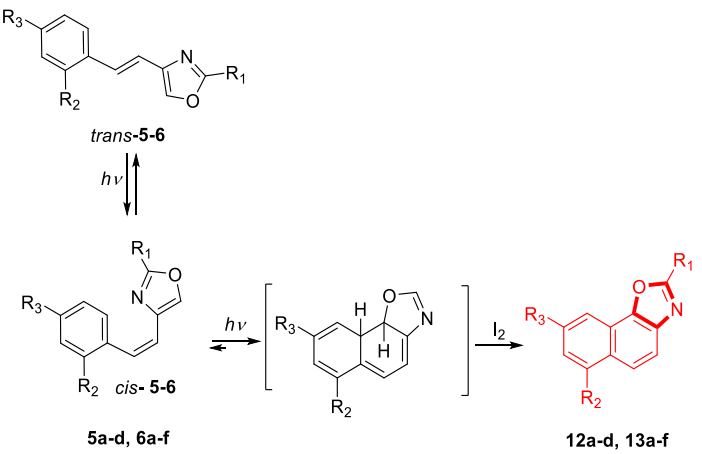
8 **9a** (27%) **11** (6%)

Scheme 3. Synthesis of *trans*-3-(*o*-tolyl)acrylaldehyde (*trans*-**9a**).

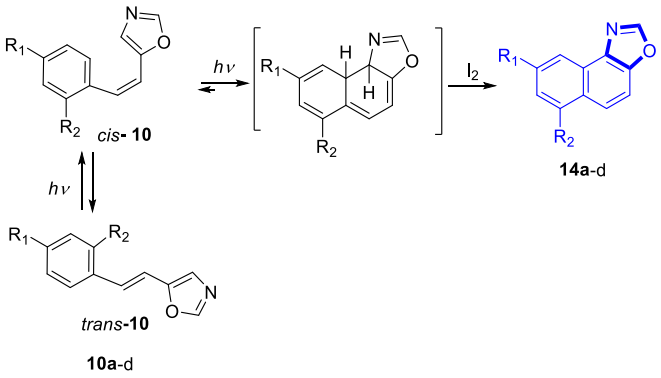
The stereoselectivity leading exclusively to *trans*-**9a** was directed by the electron withdrawing CHO group on the ylide. With 1.3 equiv of the starting phosphorane the yield on the product **9a** was 27% and an increase of the phosphorane added to the reaction (up to 3 equiv) gave no rise in the yields of neither the desired product *trans*-3-(*o*-tolyl)acrylaldehyde (*trans*-**9a)** nor the byproduct *trans,trans*-5-(2-methylphenyl)penta-2,4-dienal (*trans,trans*-**11**). Reduced reactivity of the *o*-methylbenzaldehyde (**8**) can be explained by the steric hindrances of the substituent in the *ortho* position. We have observed this effect of the *ortho* group in one of our previous papers.[42] In that case the vinyl group was in the *ortho* position to the aldehyde and that resulted in both a lower yield of formation of the acrylaldehyde as well as in formation of the double addition byproduct. The selected new 5-styryloxazoles (**10**) were synthesized in order to transform them to naphtho[1,2-*d*]oxazoles with chlorine, fluorine and dimethyl-amino groups, as potential pharmachophores.[43,44] Fluorine and dimethyl-amino groups have been extensively investigated as substituents in drug research as they can enhance biological activity as well as chemical and metabolic stability.[45,46] As all of the α,β-unsaturated aldehydes (**9**) were in *trans*-configuration, when entering the Van Leusen reaction, all of the synthesized compounds **10a-e** were obtained in pure *trans*-form (See Experimental and SI).

*Photochemical transformation of oxazole derivatives **5-10***

From our previous studies on the photo-physical properties of 2/4/5-styryloxazoles[47,48] it is evident that in the case of 4- and 5-styryl-oxazoles, the initial process in nitrogen purged solutions is the *trans-cis* isomerization followed by the electrocyclization process to naphthoxazoles *via* dihydro-intermediates. The electrocyclization process is accelerated in solutions that are aerated, which is expected. Formation of the desired cyclization products in preparative conditions with iodine present is fast and efficient because the iodine acts as a hydrogen-trapping agent. This makes the photocyclization reaction of 4- and 5-styryloxazoles useful and economic as a synthetic tool. Preparative irradiation experiments of **5-10** were performed in toluene solutions with the addition of small amounts of iodine (≈1-3 mg) in the Rayonet reactor equipped with 300 and 350 nm lamps, respectively (scheme 4). The irradiations were performed until full consumption of the starting 4/5-(arylethenyl)oxazoles (schemes 4 and 5).



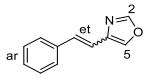
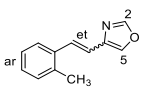
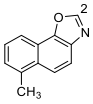
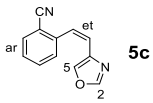
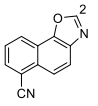
Scheme 4. Photocyclization of 4-(arylethenyl)oxazoles to naphtho[2,1-*d*]oxazoles **12-13**.

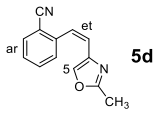
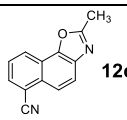
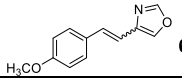
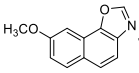
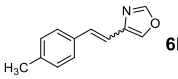
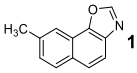
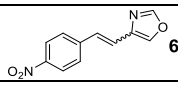
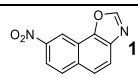
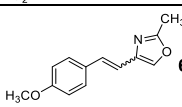
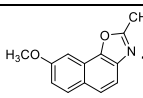
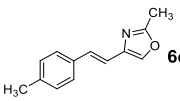
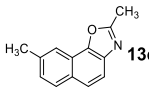
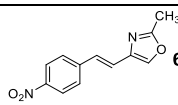
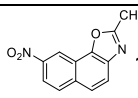


Scheme 5. Photocyclization of 5-(arylethenyl)oxazoles to naphtho[1,2-*d*]oxazoles **14.**

Synthesized 4-(arylethenyl)oxazoles **5a-d** and **6a-e** as well as 5-(arylethenyl)oxazoles **10a-d** gave the photocyclization products **12-14** in very good to excellent yields, ranging from 30% to 99%. Tables 1 and 2 give a summary of the starting compounds, cyclization products, reaction conditions and the photocyclization reaction yields. All of the cyclization products were isolated and completely characterized by spectroscopic methods (See Experimental part and SI).

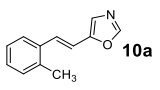
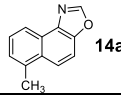
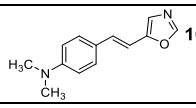
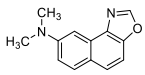
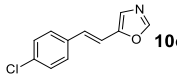
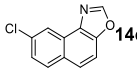
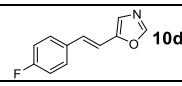
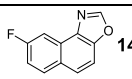
Table 1. Cyclization products **12-13** of 4-(arylethenyl)oxazoles **5** and **6**.

Starting Compound	Product	t_{irr}/h	λ_{irr}/nm	Yield (%)
 **5a**	 **12a**	4	300	92[a]
 **5b**	 **12b**	4	300	49
 **5c**	 **12c**	11	300	90

 **5d**	 **12d**	11	300	35
 **6a**	 **13a**	7	300	90
 **6b**	 **13b**	4	300	65
 **6c**	 **13c**	16	350	86
 **6d**	 **13d**	7	300	45
 **6e**	 **13e**	7	300	53
 **6f**	 **13f**	24	350	42

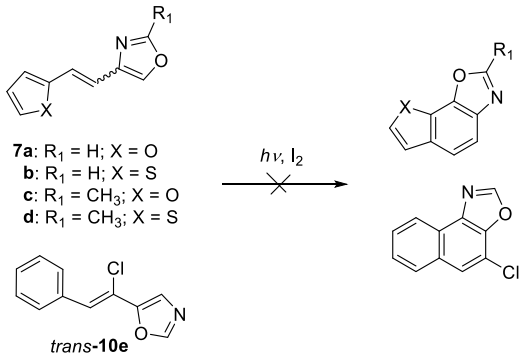
[a] Lit. yield 14%[51]

Table 2. Cyclization products **14** of 5-(arylethenyl)oxazoles **10**.

Starting Compound	**Product**	t_{irr}/ h	λ_{irr}/nm	**Yield (%)**
 **10a**	 **14a**	7	300	99
 **10b**	 **14b**	24	350	33
 **10c**	 **14c**	11	300	77
 **10d**	 **14d**	7	300	30

On irradiation of 4-(heteroarylethenyl)oxazoles **7a-d** the resulting photo-mixtures showed only *trans-cis* isomerization, in shorter irradiation times, and high molecular weight products on prolonged irradiations. No photocyclization products were detected, not even in trace amounts (scheme 6). As opposed to the formerly studied 5-(heteroarylethenyl)oxazoles[18] new 4-(heteroarylethenyl)oxazoles **7a-d** obviously do not cyclize under the same conditions. Modification of the irradiation time, concentration, wavelength or the amount of iodine that was added gave no improvement. Photocyclization reactivity of the 5- *versus* 4-(heteroarylethenyl)oxazoles is comparable to the reactivity of the 1,2-di-(2-thienyl)ethene and 1,2-di-(3-thienyl)ethene where the 2-thienyl derivative gave the fused cyclization product in 70% yield and the 3-thienyl derivative gave no product.[49] It can also be compared to the difference in reactivity of our previously published 5-(heteroarylethenyl)oxazole compounds

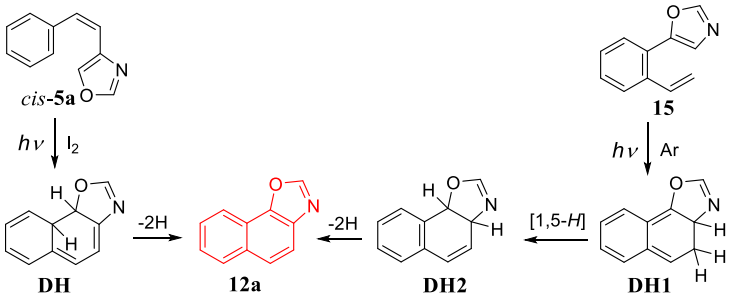
where the 5-(3-thienylethenyl)oxazole had a lower cyclization yield (41%) than the 5-(2-thienylethenyl)oxazole (59%).[18] The position of the heteroatoms (4-oxazole *vs* 5-oxazole) in the stilbene-type compounds has an effect on the overall distribution of electrons in the excited state of the system and consequently this impacts the general reactivity. Recently, [50] the stilbene-type derivatives with furan and thiophene moieties were studied under base conditions. In the present paper we haven't explored photocyclization conditions beyond neutral. The compound **10e** (scheme 6) with the α-substituted chlorine atom also reacted by giving high molecular weight products and traces of a large number of unidentified products.



Scheme 6. Attempted photocyclization of **7a-d** and **10e**.

At this time the cause of this unreactivity was not investigated further and these starting compounds were proclaimed to be synthetically ineffective, but future study into their non-reactivity is not excluded.

In an attempt to further open new routes for the formation of polycyclic heterocycle containing compounds, 5-(2-vinylphenyl)oxazole (**15**) was synthesized by Van Leusen reactions starting from 2-vinylbenzaldehyde (**16**). This compound, in which the middle double bond of the hexatriene system is a part of a benzene ring, has a hypsochromic shift in UV spectrum (See SI) when compared to the 2/4/5-styryloxazoles where the middle double bond of the hexatriene system is a part of a conjugated system, as expected. Photocyclization reaction of compound **15** gave the identical product as the photocyclization of the 4-styryloxazole (**5a**) but *via* a different cyclization route (scheme 7). We hypothesized that electrocyclization proceeds *via* DH1 and DH2 followed by loss of hydrogen.



Scheme 7. Plausible mechanism for the photocyclization of **15**.

Conditions of this photocyclization reaction were considerably different. The irradiation was performed in argon purged solutions without addition of iodine. The yield was smaller (16%) than the one gained by photocyclization from **5a** (92%) but never the less it is a new option for insertion of oxazole ring into the polycyclic compounds.

CONCLUSION

In conclusion, new 4-(aryl/heteroarylethenyl)- (**5-7**) and 5-(arylethenyl)oxazoles (**10**) have been synthesized and photochemically cyclized to various naphtho[2,1-*d*]oxazoles **12-13** and naphtho[1,2-*d*]oxazoles **14**, respectively. For the synthesis of the starting 4-aryl-/5-heteroarylethenyloxazoles two synthetic methods were utilized, the Wittig reaction and the Van Leusen reaction. All of the starting 4-aryl-/5-heteroarylethenyloxazoles are new compounds and are completely characterized. The described photochemical method to substituted naphtho[1,2-*d*]oxazoles and naphtho[2,1-*d*]oxazoles was proven to be applicable for the synthesis of a broad spectrum of fused polycycles with the oxazole ring incorporated into the system to be tested for biological activity. We have demonstrated that 4-(heteroarylethenyl)oxazoles with furan and thiophene moiety behave radically different. Additionally, we have presented a potential new photochemical route to naphtho[2,1-*d*]oxazole on irradiation of 5-(*o*-vinylphenyl)oxazole.

Experimental section

General procedures. 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, 0,5 mm, Kieselgel 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 600 MHz. All NMR spectra were measured in $CDCl_3$ using tetramethylsilane as reference. 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 UHPLC/MS system with the QTOF mass spectrometer operating at Dual AJS ESI, 2 GHz, Ext dynamic range and 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 closed quartz vessels in benzene or toluene solutions in a photochemical reactor equipped with 300 and 350 lamps, respectively.

Synthesis of 4-styryloxazoles (5-6) and 4-(heteroarylethenyl)oxazoles (7)

Phosphonium salt (0.00217 mol) was dissolved in 50 mL of dry ethanol. In a funnel sodium ethoxide was prepared by dissolving 0.06 g of sodium (1.2 eq, 0.0026 mol) in 20 mL of ethanol and added dropwise to the reaction mixture, simultaneously with the 2-methyl-oxazole-4-carbaldeyhde (**1a**)/oxazole-4-carbaldeyhde (**1b**) (1 eq, 0.00217 mol,), from a syringe. The reaction mixture was left to stir for 24 h. Solvent was removed under reduced pressure and the residue was dissolved in water and extracted with toluene (6 × 20 mL). Organic layers were dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure. Isomers were purified and separated by multiple column and thin layer chromatographies.

4-styryloxazole (**5a**)[39] (0.255 g, 56%))

***cis*-4-styryloxazole** (*cis*-**5a**, with 11% of *trans*-**5a** as impurity) as oil: R_f (PE/E = 3:1) = 0.41; IR ν_{max}/cm^{-1}: 3024, 1517, 1097, 1065, 910; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 275 (8719); ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.78 (s, 1H, H-2), 7.38-7.33 (m, 5H, H-ar), 7.28 (s, 1H, H-5), 6.72 (d, 1H, J_{et} = 12.0 Hz, H-et), 6.44 (d, J_{et} = 12.0 Hz, 1H, H-et); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 150.1 (d, C-2), 137.6 (s), 136.7 (s), 136.2 (d, C-5), 132.2 (d, C-et), 128.5 (d, C-Ar), 128.3 (d, C-Ar), 127.6 (d, C-Ar), 120.0 (d, C-Ar); HRMS(MALDI-TOF/TOF) za $C_{11}H_9NO$: $(M+K)^+_{calcd}$ = 210.0316, $(M+H)^+_{found}$ = 210.0311.

***trans*-4-styryloxazole** (*trans*-**5a**) (Values are taken out of a spectra of mixture of the two isomers) as oil: R_f (PE/E=3:1) = 0.40; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.88 (s, 1H, H-2), 7.68 (s, 1H, H-5), 7.50 (d, J_{ar} = 7.3 Hz, 1H, H-ar), 7.38-7.33 (m, 2H, H-ar), 7.36 (d, J_{et} = 16.0 Hz, H-et), 7.29-7.28 (m, 1H, H-ar), 6.94 (d, J_{et} = 12.0 Hz, 1H, H-et).

4-(2-methylstyryl)oxazole (**5b**) (0.157 g, 39%)

***cis*-4-(2-methylstyryl)oxazole** (*cis*-**5b**) as oil: R_f (PE/CH_2Cl_2 = 3:1) = 0.40; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 271 (5488); ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 7.73 (s, 1H, H-2),

7.24-7.18 (m, 3H, H-Ar), 7.19-7.17 (m, 1H, H-Ar), 6.88 (s, 1H, H-5), 6.74 (d, J_{et} = 11.9 Hz, 1H, H-et), 6.54 (d, J_{et} = 11.9 Hz, 1H, H-et), 2.24 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 149.4 (d, C-2), 137.0 (s), 136.3 (s), 135.4 (d, C-5), 135.1 (s), 131.0 (d, C-et), 129.8 (d, C-Ar), 127.6 (d, C-Ar), 127.3 (d, C-Ar), 125.6 (d, C-Ar), 120.8 (d, C-et), 19.1 (q, $\underline{C}H_3$); MS *m/z* (%, fragment): 185 (100%, M^+), 168 (18%), 156 (27%); HRMS(MALDI-TOF/TOF) za $C_{12}H_{11}NO$: $(M+H)^+_{calcd}$ = 186.0913, $(M+H)^+_{found}$ = 186.0916.

***trans*-4-(2-methylstyryl)oxazole** (*trans*-**5b)** as oil: R_f (PE/CH_2Cl_2 = 3:1) = 0.45; IR ν_{max}/cm^{-1}: 3022, 1695, 1516, 1186, 1066; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 283 (12819); ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.87 (s, 1H, H-2), 7.65 (s, 1H, H-5), 7.58 (d, 1H, J_{et} = 15.8 Hz, H-et), 7.55-7.54 (m, 1H, H-ar), 7.24-7.16 (m, 3H, H-ar), 6.83 (d, 1H, J_{et} = 15.8 Hz, H-et), 2.44 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 150.7 (d, C-2), 138.5 (s), 135.6 (s), 135.3 (s), 134.9 (d, C-5), 130.0 (d, C-ar), 128.2 (d, C-6/7), 127.3 (d, C-ar), 125.6 (d, C-ar), 124.7 (d, C-ar), 116.7 (d, C-6/7), 19.4 (q, $\underline{C}H_3$); MS *m/z* (%, fragment): 185 (100%, M^+), 168 (18%), 156 (27%).

4-(2-cyanostyryl)oxazole (**5c**) (0.415, 97%)

***cis*-4-(2-cyanostyryl)oxazole** (*cis*-**5c**) as white powder: mp 99-101^{0}C, (PE/E = 5:1) = 0.55, UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 228 (12847), 272 (5402), 301 (Sh 3552), IR ν_{max}/cm^{-1} (NaCl): 3147, 3112, 2924, 2228, 1736, 1519, 1478, 1450, 1090, ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.76 (s, 1H, H_{ox2}), 7.69 (d, $J_{3/4}$= 7.6 Hz, 1H, H_{ar4}), 7.62 (d, $J_{1/2}$ = 7.7 Hz, 1H, H_{ar1}), 7.55 (dd, $J_{2/3}$ = 7.6 Hz, $J_{1/2}$ = 7.7 Hz, 1H, H_{ar2}), 7.37 (t, $J_{3/4}$ = $J_{2/3}$ = 7.6 Hz, 1H, H_{ar3}), 7.35 (s, 1H, H_{ox5}) 6.80 (d, J_{et} = 12.1 Hz, 1H, H_{et}), 6.66 (d, J_{et} = 12.2 Hz, 1H, H_{et}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 150 (d, C-2), 140.7 (s), 136.7 (d), 132.2 (d), 131.8 (d), 129. 2 (d), 127.4 (d), 126.7 (d), 122.2 (d), 117.2 (s), 111.8 (s); MS *m/z* (%, fragment): 196 (100%, $(M+H)^+$); HRMS (Q-TOF) for $C_{12}H_8N_2O$: $(M+H)^+_{calcd}$ = 197.0637$_{found}$ = 197.0707.

2-methyl-4-(2-cyanostyryl)oxazole (**5d**) (0.210, 46 %)

***cis*-2-methyl-4-(2-cyanostyryl)oxazole** (*cis*-**5d**) as oil: R_f (PE/E = 5:1) = 0.60; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 284 (4406); IR ν_{max}/cm^{-1} (NaCl): 2926, 2224, 1589, 1109; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.67 (t, J_{ar} = 8.8 Hz, 2H, $H_{ar1/4}$), 7.55-7.52 (m, 1H, H_{ar2-3}), 7.37 (t, J_{ar} = 8.8 Hz, 1H, $H_{ar2/3}$), 7.16(s, 1H, H_{ox}), 6.74 (d, $J_{e\,t}$= 12.1 Hz, 1H, H_{et}), 6.58 (d, J_{et} = 12.1 Hz, 1H, H_{et}), 2.38 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 160.5 (s), 140.8 (s), 136.2 (d, C-ar), 132.3 (d, C-ar), 131.8 (d, C-ar), 129.2 (d, C-ar), 127.3 (d, C-ar), 126.0 (d, C-et), 122.9 (d, C-et), 117.3 (s(, 111.8 (s), 13.3 (q, $\underline{C}H_3$); MS *m/z* (%, fragment): 211 (100%, $(M+H)^+$); HRMS (Q-TOF) for $C_{14}H_{10}N_2O$: $(M+H)^+_{calcd}$ = 211.0793, $(M+H)^+_{found}$ = 211.0866.

4-(4-methoxystyryl)oxazole (6a) (0.180 g, 41%)

***cis*-4-(4-methoxystyryl)oxazole** (*cis*-**6a**) as oil: R_f (PE/E = 20:1) = 0.63, UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 272 (6306); IR ν_{max}/cm^{-1} (NaCl): 2933, 1607, 1509, 1252,^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.79 (s, 1H, H_{ox2}), 7.38 (s,1H, H_{ox5}), 7.34 (d, J_{ar} = 8.7 Hz, 2H, H_{ar2}), 6.87 (d, J_{ar1} = 8.7 Hz, 2H, H_{ar1}), 6.63 (d, J_{et} = 12.1 Hz, 1H, H_{et}), 6.34 (d, J_{et} =12.1 Hz, 1H, H_{et}), 3.83 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 159.1 (s), 151.1 (s), 150.1 (d, C-ox2), 136.9 (s), 136.1 (d, C-et), 131.8 (d, C-ox5), 130.0 (d, C-ar2), 118.5 (d, C-et), 113.8 (d, C-Ar1), 55.2 (q, O<u>C</u>H$_3$); MS *m/z* (%, fragment): 201 (100%), $(M+H)^+$); HRMS (Q-TOF) for $C_{12}H_{11}NO_2$: $(M+H)^+_{calcd}$ = 202.0790, : $(M+H)^+_{found}$ = 202.0863.

***trans*-4-(4-methoxystyryl)oxazole** (*trans*-**6a**) as white powder: mp 95-101 ^{0}C, R_f (PE/E = 20:1) = 0.55; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 292 (8199); IR ν_{max}/cm^{-1}(NaCl): 2913, 1733, 1606, 1511, 1249; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.86 (s, 1H, H_{ox2}), 7.64 (s, 1H, H_{ox5}), 7.43 (d, J_{ar}= 8.6 Hz, 2H, H_{ar2}), 7.29 (d, J_{et} = 15.9 Hz, 1H, H_{et}), 6.89 (d, J_{ar} = 8.6 Hz, 2H, H_{ar1}), 6.81 (d, J_{et} = 15.9 Hz, 1H, H_{et}), 3.83 (s, 3H, O<u>C</u>H$_3$), MS *m/z* (%, fragment): 201 (100%, M^+).

4-(4-methylstyryl)oxazole (**6b**) (0.150 g, 37%)

4-(4-methylstyryl)oxazole) as an inseparable mixture of *cis* and *trans*-isomer: R_f (PE/E = 20:1) = 0.60; IR ν_{max}/cm^{-1}(NaCl): 3023, 1694, 1514, 1090; ^{1}H NMR ($CDCl_3$, 600 MHz, from mixture for *cis*-**6b**): δ/ppm 7.87 (s, 1H, H_{ox2}), 7.66 (s, 1H, H_{ox5}), 7.39 (d, J_{et} = 7.7 Hz, 2H, H_{ar}), 7.32 (d, J_{ar} = 16.0 Hz, 1H, H_{et}), 7.16 (dd, J_{ar} = 7.2 Hz, 2H, H_{ar}), 6.88 (d, J_{ar} = 16.0 Hz, 1H, H_{et}), 2,36 (s, 3H, C<u>H</u>$_3$); ^{1}H NMR ($CDCl_3$, 600 MHz, from mixture for *trans*-**6b**): δ/ppm ppm 7.78 (s, 1H, H_{ox2}), 7.34 (s, 1H, H_{ox5}), 7.27 (d, J_{et} = 7.2 Hz, 2H, H_{ar}), 7.16 (dd, J_{ar} = 7.2 Hz, 2H, H_{ar}), 6.67 (d, J_{et} = 11.6 Hz, 1H, H_{et}), 6.39 (d, J_{ar} = 11.6 Hz, 1H, H_{et}), 2,36 (s, 3H, C<u>H</u>$_3$; MS *m/z* (%, fragment): 185 (100%, M^+), 168 (18%), 156 (27%); HRMS(Q-TOF) for $C_{12}H_{11}NO$: $(M+H)^+_{calcd}$ = 186.0841, $(M+H)^+_{found}$ = 186.0914.

4-(4-nitrostyryl)oxazole (6c) (0.402 g, 86%)

***cis*-4-(4-nitrostyryl)oxazole** (*cis*-**6c**) as yellow powder: mp 171-178^{0}C, (PE/E = 20:1) = 0.43; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 328 (8320); IR ν_{max}/cm^{-1}(NaCl): 3125, 2925, 2854, 1596, 1508, 1341, 1090, ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.19 (d, J_{ar} = 8.8 Hz, 2H, H_{ar2}), 7.82 (s, 1H, H_{ox2}), 7.63 (d, J_{ar} = 8.8 Hz, 2H, H_{ar1}), 7.49 (s, 1H, H_{ox5}), 6.67 (d, J_{et} = 12.6 Hz, 1H, H_{et2}), 6.57 (d, J_{et} = 12.6 Hz, 1H, H_{et1}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 150.7 (d, C_{ox2}), 146.9 (s), 143.9 (s), 137.5 (d, C_{ox2}), 136.5 (s), 129.8 (d, C_{ar1}), 129.4 (d, C_{et1}), 124.2 (d, C_{ar2}),

121.5 (d, C_{et2}); MS *m/z* (%, fragment): 216 (100%); $(M+H)^+$); HRMS (Q-TOF) for $C_{11}H_8N_2O_3$: $(M+H)^+$ calcd 217.0535, found 217.0610.

***trans*-4-(4-nitrostyryl)oxazole** (*trans*-**6c**) as oil: (PE/E = 20:1) = 0.15; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 339 (9634); IR ν_{max}/cm^{-1}(NaCl):2923, 1735, 1594, 1507, 1341, ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.21(d, J_{ar} = 8.7 Hz, 2H, H_{ar}), 7.91 (s, 1H, H_{ox2}), 7.76 (s, 1H, H_{ox5}), 7.61 (d, J_{ar} = 8.7 Hz, 2H, H_{ar}), 7.41 (d, J_{et} = 15.6 Hz, 1H, H_{et}), 7.10 (d, J_{et} = 15.6 Hz, 1H, H_{et}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 146.6 (d, C-ox2), 142.7 (s), 135.4 (s), 129.3 (s), 128.0 (d, C-et), 126.5 (d, C-ar), 123.6 (d, C-ar), 122.1 (d, C-ox5), 119.9 (d), 112.0 (d); MS *m/z* (%, fragment): 216 (100%); $(M+H)^+$.

2-methyl-4-(4-methoxystyryl)oxazole (6d) (0.460 g, 98.5 %)

***cis*-2-methyl-4-(4-methoxystyryl)oxazole** (*cis*-**6d**) as oil: R_f (PE/E = 20:1) = 0.80; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 284 (6796), 394 (Sh 850); IR ν_{max}/cm^{-1}(NaCl): 2887, 1605, 1516, 1343, 1228; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.35 (d, J_{ar} = 8.7 Hz, 2H, H_{ar2}), 7.25 (s, 1H, H_{ox}), 6.86 (d, J_{ar} = 8.7 Hz, 2H, H_{ar1}), 6.56 (d, J_{et} = 12.4 Hz, 1H, H_{et}), 6 27 (d, J_{et} = 12.4 Hz, 1H, H_{et}), 3.83 (s, 3H, O$\underline{C}H_3$), 2.41 (s, 3H, $C\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 159.9 8 (s), 158.5 (s), 136.7 (s), 135.1 (d, C-ox), 130.6 (d, C-et), 129.5 (s), 129.3 (d, C-ar), 118.6 (d, C-et), 113.3 (d, C-ar), 54.7 (q, O$\underline{C}H_3$), 13.3 (q, $\underline{C}H_3$); MS *m/z* (%, fragment): 216 (100%); $(M+H)^+$.

***trans*-2-methyl-4-(4-methoxystyryl)oxazole** (*trans*-**6d**) as white powder: mp 113-117 ^{0}C; R_f (PE/E = 20:1) = 0.23; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 286 (Sh 10088), 293 (10348), 310 (Sh 6869), 322 (Sh 4381); IR ν_{max}/cm^{-1} (NaCl): 2924, 1605, 1510, 1247; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.49 (s, 1H, H_{ox}), 7.41 (d, J_{ar} = 8.7 Hz, 2H, H_{ar}), 7.22 (d, J_{et} = 15.9 Hz, 1H, H_{et}), 6.87 (d, J_{ar} = 8.7 Hz, 2H, H_{ar}), 6.74 (d, J_{et} = 15.9 Hz, 1H, H_{et}), 3,82 (s, 3H, O$\underline{C}H_3$), 2.48 (s, 3H, $C\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 161.3 (s), 158.9 (s), 138.9 (s), 134.1 (d, C-5), 129.3 (s), 129.1 (d-et), 127.2 (d-ar), 113.6 (d-et), 113.3 (d-ar), 54.8 (q, O$\underline{C}H_3$), 13.5 (q, $\underline{C}H_3$). MS *m/z* (%, fragment): 216 (100%), $(M+H)^+$).

2-methyl-4-(4-methylstyryl)oxazole (6e) (0.172 g, 40%)

***cis*-2-methyl-4-(4-methylstyryl)oxazole** (*cis*-**6e**) as oil: (PE/E = 20:1) = 0.40; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 308 (2224); ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.28 (d, J_{ar} = 8.0 Hz, 2H, H-ar), 7.19 (s, 1H, H-5), 7,13 (d, J_{ar} = 8.0 Hz, 2H, H-ar), 6.60 (d, J_{et} = 12.5 Hz, 1H, H_{et}), 6.31 (d, J_{et} = 12.5 Hz, 1H, H_{et}) 2.40 (s, 3H, $C\underline{H}_3$), 2.35 (s, 3H, $C\underline{H}_3$); MS *m/z* (%, fragment): 199 (100%, M^+); HRMS (Q-TOF) for $C_{13}H_{13}NO$: $(M+H)^+_{calcd}$ = 200.0997, $(M+H)^+_{found}$ = 200.1071.

***trans*-2-methyl-4-(4-methylstyryl)oxazole** (*trans*-**6e**) as white powder: mp 99-101 ^{0}C, (PE/E = 20:1) = 0.43; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 282 (27358), 290 (28184), 311 (Sh 14359); IR ν_{max}/cm^{-1} (NaCl): 3088, 1726, 1591, 1097, 963; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.51 (s, 1H, H_5), 7.37 (d, J_{ar} = 7.9 Hz, 2H, H_{ar}), 7.23(d, J_{et} = 16.1 Hz, 1H, H_{et}), 7.14 (d, J_{ar} = 7.9 Hz, 2H, H_{ar}), 6.83 (d, J_{et} = 16.1 Hz, 1H, H_{et}), 2.48 (s, 3H, C$\underline{H}_3$), 2.35 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 138.8 (s), 137.1 (s), 134.4 (d,C-5), 133.7 (s), 129.5 (d, C-et), 128.9 (d, C-ar), 125.9 (d, C-ar), 115.0 (d, C-et), 20.7 (q), 13.5 (q); MS *m/z* (%, fragment): 199 (100%, M^+).

2-methyl-4-(4-nitrostyryl)oxazole (**6f**) (0.352, 70.5 %)

***trans*-2-methyl-4-(4-nitrostyryl)oxazole** (*trans*-**6f**) as yellow powder, mp 181-199 ^{0}C, (PE/E = 20:1) = 0.15; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 238 (7592), 343 (10915); IR ν_{max}/cm^{-1} (NaCl): 2950, 1600, 1520, 1350; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.20 (d, J_{ar} = 8.8 Hz, 2H, H_{ar2}), 7.62 (s, 1H, H_5), 7.59 (d, J_{ar} = 8.8 Hz, 2H, H_{ar1}), 7.33 (d, J_{et} = 16.0 Hz, 1H, H_{et1}), 7.04 (d, J_{et} = 16.0 Hz, 1H, H_{et2}), 2.51(s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 162.3 (s), 146.9 (s), 138.5 (s), 136.7 (d, C-ox), 129.8 (s), 127.7 (d, C-et1), 126.8 (d, C-ar1), 124.1 (d, C-ar2), 120.9 (d, C-et2), 29.7 (C$\underline{H}_3$); MS *m/z* (%, fragment): 230 (100%), $(M+H)^+$); HRMS (Q-TOF) for $C_{13}H_{10}N_2O_3$: $(M+H)^+_{calcd}$ = 231.0691, $(M+H)^+_{found}$ = 231.0760.

4-(2-furostyryl)oxazole (7a) (0.097 g, 23 %)

***cis*-4-(2-furostyryl)oxazole** (*cis*-**7a**) as oil: (PE/E = 20:1) = 0.35; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 305 (9623), 315 (8325); ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm ppm 8.32 (s, 1H, H_2), 7.87 (s, 1H, H_5), 7.49 (d, J_f = 1.3 Hz, 1H, H_{f1}), 6.65 (d, J_f = 3.3 Hz, 1H, H_{f3}), 6.46-6.45 (m, 1H, H_{f2}), 6.37 (d, J_{et} = 13.2 Hz, H_{et}), 6.26 (d, J_{et} = 13.2 Hz, H_{et}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 152.1 (s), 150.1 (d), 142.3 (d), 137.7 (d), 136.7 (s), 117.3 (d), 115.5 (d), 112.1 (d), 111.8 (d); MS *m/z* (%, fragment): 161 (100%), $(M)^+$); HRMS (Q-TOF) for $C_9H_7NO_2$: $(M+H)^+_{calcd}$ = 162.0477, $(M+H)^+_{found}$ = 162.0552.

***trans*-4-(2-furostyryl)oxazole** (*trans*-**7a**) (from mixture of *cis* : *trans* = 1:1) (PE/E = 20:1) = 0.34; IR ν_{max}/cm^{-1}(NaCl): 3583, 1666,01595, 1359; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.85 (s, 1H, H_2), 7.65 (s, 1H, H_5), 7.40 (d, J_f = 1.3 Hz, 1H, H_{f1}), 7.13 (dd, J_{et} = 15.7 Hz, H_{et}), 6.42-6.41 6.86 (d, J_{et}= 15.7 Hz, 1H, H_{et}), 6.39-6.38 (m, 1H, H_{f2t}), 6.36 (s, 1H, H_{f3}); MS *m/z* (%, fragment): 16 (100%).

4-(2-thienostyryl)oxazole (**7b**) (0.111 g, 29%)

***cis*-4-(4-thienostyryl)oxazole** (*cis*-**7b** with 30% of *trans*-**7b** as impurity) as oil: (PE/E = 20:1) = 0.41; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 287 (Sh 4665), 299 (5119), 314 (Sh 3909); IR

ν_{max}/cm^{-1}(NaCl): 2965, 1692, 1484, 1068; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.32 (s, 1H, H_2), 7.86 (s, 1H, H_5), 7.49 (brs, 1H, H_{tf1}), 6.46 (d, J_{tf} = 3.3 Hz, 1H, H_{tf3}), 7.41-7.40 (m, 1H, H_{tf2}), 6.37 (d, J_{et} = 13.1 Hz, 1H, H_{et}), 6.25 (d, J_{et} = 13.1 Hz, 1H, H_{et}); 6.80 (d, J_{et} = 12.1 Hz, 1H, H_{et}), 6.66 (d, J_{et} = 12.2 Hz, 1H, H_{et}); MS *m/z* (%, fragment): 161 (100%), $(M)^+$).

***trans*-4-(4-thienostyryl)oxazole** (*trans*-**7b**) as white powder: mp 100-103 ^{0}C, (PE/E = 20:1) = 0.40, UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 285 (Sh 8276), 293 (10907), 310 (Sh 8890); ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.85 (s, 1H, H_2), 7.64 (s, 1H, H_5), 7.39 (d, J_{tf} = 1.7 Hz, 1H, H_{tf1}), 7.55 (d, J_{et}= 15.8 Hz, 1H, H_{et}), 6.85 (d, J_{et}= 15.8 Hz, 1H, H_{et}), 6.42-6.41 (m, 1H, H_{tf2}), 6.35 (d, J_{tf} = 3.3 Hz, 1H, H_{tf3}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm152.3 8d), 150.7(s), 141.5 (d), 148.5 (s), 134.8 (d), 118.2 (d), 114.0 (d), 111.1 (d), 108.9 (d); MS *m/z* (%, fragment): 161 (100%), $(M)^+$).

2-methyl-4-(2-furostyryl)oxazole (**7c**) (0.170 g, 37.5 %)

***cis*-2-methyl-4-(4-furostyryl)oxazole** (*cis*-**7c**) as oil: (PE/E = 20:1) = 0.39; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 290 (Sh 7821), 302 (9591), 316 (7325); IR ν_{max}/cm^{-1}(NaCl): 3047, 2930, 1759;^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.16 (s, 1H, H_5), 7.46 (d, J_f = 1.5 Hz, 1H, H_{f1}), 6.67 (d, J_f = 3.3 Hz, 1H, H_{f3}), 6.45-6.44 (m, 1H, H_{f2}), 6.31 (d, J_{et} = 12.9 Hz, 1H, H_{et}), 6.17 (d, J_{et} = 12.9 Hz, 1H, H_{et}), 2.47 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 160.5 (s), 152.3 (s), 142.1 (d), 137.3 (d), 137.0 (s), 116.8 (d), 115.8 (d), 111.8 (d), 111.7 (d), 13.7 (q); MS *m/z* (%, fragment): 175 (100%), $(M)^+$); HRMS (Q-TOF) for $C_{10}H_9NO_2$: $(M+H)^+_{calcd}$ = 176.0633, $(M+H)^+_{found}$ = 176.0703.

***trans*-2-methyl-4-(4-furostyryl)oxazole** (*cis*-**7c**) as oil: (PE/E = 20:1) = 0.45, UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 286 (13774), 298 (18327), 312 (14789); ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.50 (s, 1H, H_5), 7.37 (d, J_f = 1.3 Hz, 1H, H_{f1}), 7.06 (d, J_{et} = 15.9 Hz, 1H, H_{et}), 6.79 (d, J_{et} = 15.9 Hz, 1H, H_{et}), 6.40-6.39 (m, 1H, H_{f2}), 6.31 (d, J_f = 3.1 Hz, 1H, H_{f3}), 2.48 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 157.0 (s), 155.2 (s), 142.2 (s), 138.9 (s), 135.2 (d), 117.9 (d), 114.9 (d), 111.6 (d), 109.0 (d), 13.9 (q); MS *m/z* (%, fragment): 175 (100%), $(M)^+$).

2-methyl-4-(2-thienostyryl)oxazole (**7d**) (0.111 g, 45%)

***cis*-2-methyl-4-(4-thienostyryl)oxazole** (*cis*-**7d**)(from a mixture of isomers, *cis* : *trans* = 3 : 1) as oil: (PE/E = 20:1) = 0.23; IR ν_{max}/cm^{-1}(NaCl): 3104, 1672, 1587, 1371, 1105; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.63 (s, 1H, H_5), 7.28 (d, J_{tf} = 3.6 Hz, 1H, H_{tf1}), 7.25 (d, J_{tf} = 6.0 Hz, 1H, H_{tf3}), 7.0-6.97 (m, 1H, H_{tf2}), 6.65 (d, J_{et} = 12.3 Hz,

1H, H_{et}), 6.23 (d, J_{et} = 12.3 Hz, 1H, H_{et}), 2.48 (s, 3H, CH_3); MS *m/z* (%, fragment): 192 (100%), $(M+H)^+$); HRMS (Q-TOF) for $C_{10}H_9NOS$: $(M+H)^+_{calcd}$ = 192.0405, $(M+H)^+_{found}$ = 192.0480.

***trans*-2-methyl-4-(4-thienostyryl)oxazole** (*trans*-**7d**) (from a mixture of isomers, *cis* : *trans* = 3 : 1) as oil: (PE/E = 20:1) = 0.23; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.50 (s, 1H, H_5), 7.17 (d, J_{tf} = 5.0 Hz, 1H, H_{tf1}), 7.04 (d, J_{tf} = 3.3 Hz, 1H, H_{tf3}), 7.0-6.97 (m, 1H, H_{tf2}), 6.69 (d, J_{et} = 15.7 Hz, 1H, H_{et}), 6.39 (d, J_{et} = 15.7 Hz, 1H, H_{et}), 2.48 (s, 3H, CH_3).

Synthesis of 9a

trans-3-(2-methylphenyl)prop-2-enal (**9a**) was prepared from the *o*-methylbenzaldehyde and formylmethylenetriphenylposphorane by the Wittig reaction described in literature.[41] Formylmethylenetriphenylposphorane (1,3 eq, 0,026 mol) and aldehyde (1 eq, 0,02 mol) were mixed in dry benzene and heated to reflux under a stream of nitrogen for 24h. After removal of the solvent the crude residue was extracted with cold ether and the ether extracts were dried over anhydrous $MgSO_4$ after which the solvent was evaporated. The crude mixture contained the compound **9** as well as the byproduct *trans,trans*-5-(2-methylphenyl)penta-2,4-dienal **11** and was purified by column chromatography on silica gel using petroleum ether/diethyl ether (variable ratio) as eluent.

(0.79 g, 27%) *trans*-3-(2-methylphenyl)prop-2-enal[40] (*trans*-**9a**) as oil: R(f) (PE/E = 50:1) = 0.20; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 292 (18898), 224 (9193); IR ν_{max}/cm^{-1}: 1677 (C=O), 1616, 1460, 1117; ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 9.73 (d, $J_{CHO,2}$ = 7.6 Hz, 1H, C<u>H</u>O), 7.78 (d, $J_{2,3}$ = 15.8 Hz, 1H, H-3), 7.59 (d, J_{ar} = 7.8 Hz, 1H, H-Ar), 7.33 (dd, J_{ar} = 7.6 Hz, J_{ar} = 7.2 Hz, 1H, H- Ar), 7.26 (dd, J_{ar} = 7.6 Hz, J_{ar} = 7.8 Hz, 2H, H-Ar), 6.67 (dd, $J_{CHO,2}$ = 7.6 Hz, $J_{2,3}$ = 15.8 Hz, 1H, H-2), 2.48 (s, 3H, C<u>H</u>$_3$); ^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 193.3 (d, <u>C</u>HO), 149.7 (d, C-3), 137.4 (s), 132.4 (s), 130.5 (d, C-ar), 129.2 (d, C-2), 126.3 (d, C-ar), 126.1 (d, C-ar), 19.2 (q, CH_3); MS *m/z* (EI) = 147 (100, M^+); HRMS(MALDI-TOF/TOF) for $C_{10}H_{10}O$: $(M+H)^+_{calcd}$ = 147.0804, $(M+H)^+_{found}$ = 147.0801.

(0.098 g, 6%) *trans,trans*-5-(2-methylphenyl)penta-2,4-dienal (*trans*-**11**) as oil: R(f) (PE/E=25:1) = 0.10; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 329 (27012), 238 (6519); IR ν_{max}/cm^{-1}: 3020, 1680 (C=O), 1616, 1599, 1157, 1119; ^{1}H NMR ($CDCl_3$, 600 MHz) : δ/ppm 9.63 (d, $J_{CHO,2}$ = 7.9 Hz, 1H, C<u>H</u>O), 7.58 (d, J_{ar} = 7.8 Hz, 1H, H-ar), 7.31 (dd, $J_{2,3}$ = 15.4 Hz, $J_{3,4}$ = 11.0 Hz 1H, H-3), 7.28 (d, $J_{4,5}$ = 15.4 Hz, 1H, H-5), 7.25 – 7.18 (m, 3H, H-ar), 6.93 (dd, $J_{3,4}$ = 11.0 Hz, $J_{4,5}$ = 15.4 Hz, 1H, H-4), 6.28 (dd, $J_{2,3}$ = 15.4 Hz, $J_{CHO,2}$ = 7.9 Hz, 1H, H-2), 2.42 (s, 3H, H-C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 193.0 (d, <u>C</u>HO), 151.8 (d, C-3), 139.5 (d, C-

5), 136.4 (s), 134.0 (s), 131.0 (d, C-2), 130.3 (d, C-ar), 129.0 (d, C-ar), 126.7 (d, C-4), 125.9 (d, C-ar), 125.4 (d, C-ar), 19.2 (q, $\underline{C}H_3$); HRMS (MALDI-TOF/TOF) for $C_{12}H_{12}O$: $(M\text{-}e)^-_{calcd}$ = 172.0883 $(M\text{-}e)^-_{found}$ = 172.0878.

Synthesis of 5-(aryl/heteroarylethenyl)oxazoles (**10a-e)** and **15**

Compounds **10a-e** were prepared from the corresponding acrylaldehydes **9a-e** and 4 -toluenesulfonylmethyl isocyanide (TosMIC) as described in the literature for 5-phenyloxazole.[38] For the compound **15** the starting aldehyde was the *o*-vinylbenzaldehyde. 4-Toluenesulfonylmethylisocyanide (1 eq, 0.005 mol), aldehyde (1 eq, 0.005 mol), and potassium carbonate (1 eq, 0.005 mol) in 30 mL of methanol were heated under reflux for 3-4 h. After removal of the solvent the residue was worked up with ice-water and extracted with cold ether. Ether extracts were dried over anhydrous $MgSO_4$. Evaporation under reduced pressure afforded the crude product, which was further purified by column chromatography on silica gel using petroleum ether/diethyl ether (variable ratio) as eluent.

***trans*-5-(2-methylstyryl)oxazole** (*trans*-**10a**)

(0.31 g, 33%), as oil: R_f (PE/E=10:1) = 0.15; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 300 (12646), 318 (11021), 329 (6440); IR ν_{max}/cm^{-1}: 3020, 2924, 1689, 1460, 1090, 955; ^{1}H NMR (CDCl3, 600 MHz): δ/ppm 7.82 (s, 1H, H-2), 7.51 – 7.5 (m, 1H, H-Ar), 7.33 (d, J_{et} = 16.2 Hz, 1H, H-et), 7.20 -7.14 (m, 3H, H-ar), 7.04 (s, 1H, H-4), 6.80 (d, J_{et} = 16.2 Hz, 1H, H-et), 2.43 (s, 3H, H-CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 150.6 (d, C-2), 150.2 (s,), 136.0 (s), 135.0 (d,C-ar), 128.2 (d, C-ar), 127.9 (d, C-et), 126.2 (d, C-ar), 125.0 (d, C-ar), 123.8 (d, C-5), 113.8 (d, C-et), 19.7 (s); HRMS(MALDI-TOF/TOF) for $C_{12}H_{11}NO$: $(M+H)^+_{calcd}$ = 186.0913, $(M+H)^+_{found}$ = 186.0914.

***trans*-5-(4-*N*,*N*-dimethylaminostyryl)oxazole** (*trans*-**10b**)

(0.235 g, 22 %) as yellow crystals: mp 139-141 °C; R_f (PE/E=1:1) = 0.20; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 357 (27584); IR ν_{max}/cm^{-1}: 2853, 2218, 1600, 1380, 1270; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.80 (s, 1H, H-2), 7.38 (d, J_{ar} = 8.7 Hz, 2H, H-ar), 7.03 (d, J_{et} =16.3 Hz, 1H, H-et), 6.98 (s, 1H, H-4), 6.72 (d, J_{et} =16.3 Hz, 1H, H-et), 6.27-6.70 (m, 1H, H-ar), 3.00 (s, 6H, N-($C\underline{H}_3$)$_2$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm151.3 (s), 149.7 (s), 149.6 (d), 130.6 (d), 127.8 (d), 122.4 (d), 112.3 (d), 108.6 (s), 40.3 (q), 31.2 (q); MS *m/z* (EI) = 214 (100, M^+); HRMS(Q-TOF) for $C_{13}H_{14}N_2O$: $(M+H)^+_{calcd}$ = 215.1106, $(M+H)^+_{found}$ = 215.1176.

***trans*-5-(4-chlorostyryl)oxazole** (*trans*-**10c**)

(0.946 g, 92 %) as colorless crystals: mp 78-81°C; R_f (PE/E=10:1) = 0.55; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 299 (27977), 312 (29351), 326 (20895); IR ν_{max}/cm^{-1}: 1697, 1610, 1491,

1089; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.84 (s, 1H, H-2), 7.40 (dd, J_{ar}= 8.5 Hz, J_{ar}= 6.6 Hz, 2H, H-ar), 7.33 (dd, J_{ar}= 8.5 Hz, J_{ar}= 6.6 Hz, 2H, H-ar), 7.08 (s, 1H, H-4), 7.04 (d, J_{et} = 16.2 Hz, 1H, H-et), 6.88 (d, J_{et} = 16.2 Hz, 1H, H-et); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 149.9 (d, C-2), 149.7 (s), 134.2 (s), 133.5 (s), 128.5 (d), 128.4 (d), 127.2 (d), 124.0 (d), 112.9 (d); MS *m/z* (EI) = 205 (100, M^+); HRMS(Q-TOF) for $C_{11}H_8ClNO$: $(M+H)^+_{calcd}$ = 206.0294, $(M+H)^+_{found}$ = 206.0369.

***trans*-5-(4-fluorostyryl)oxazole** (*trans*-**10d**)

(0.728 g, 92 %) as colorless crystals: mp 73-76 °C; R_f (PE/E=10:1) = 0.65; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 274 (10817), 284 (12200); IR ν_{max}/cm^{-1}: 1645, 1534, 1457, 1361; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.85 (s, 1H, H-2), 7.47-7.44 (m, 2H, H-ar), 7.08-7.05 (m, 4H, H-ar, et, 4), 6.84 (d, J_{et} = 16.1 Hz, 1H, H-et); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 163.1 (d), 161.4 (s), 149.8 (s), 131.9 (s), 128.6 (d), 127.7 (d), 123.5 (d), 115.3 (d), 115.2 (d), 112.2 (d); MS *m/z* (EI) = 189 (100, M^+); HRMS(Q-TOF) for $C_{11}H_8FNO$: $(M+H)^+_{calcd}$ = 190.0590, $(M+H)^+_{found}$ = 190.0666.

***trans*–5–(1–chloro-2-phenylvinyl)oxazole** (*trans*-**10e**)

(1.01 g, 94 %) as yellow crystals: mp 62.3-62.4 °C; R_f (PE/E=10:1) = 0.14, UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 225 (7646), 291 (23972), 303 (25341), 318 (15546); IR ν_{max}/cm^{-1}: 3126, 1443, 974, 829, 633; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.88 (s, 1H, H-2), 7.75 (d, $J_{9,10}$ = 7.4 Hz, 2H, H-9), 7.41 (t, $J_{9,10}$ = $J_{10,11}$ = 7.4 Hz, 2H, H-10), 7.35 (d, $J_{10,11}$ = 7.4 Hz, 1H, H-11), 7.31 (s, 1H, H-4), 7.26 (s, 1H, H-7); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 150.9 (d, C-2), 149.6 (s), 133.8 (s), 129.7 (d), 128.8 (d), 128.5 (d), 128.4 (s), 125.3 (d), 117.8 (s); HRMS(MALDI-TOF/TOF) for $C_{11}H_8ClNO$: $(M+H)^+_{calcd}$ = 206.0367, $(M+H)^+_{found}$ = 206.0374.

Synthesis of 5-(2-vinylphenyl)oxazole (15)

(0.513 g 60 %) as oil: R_f (PE/E = 5:1) = 0.44; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 265 (14159), 235 (20436); IR ν_{max}/cm^{-1}: 3128, 1501, 1317, 1103, 914, 639; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.95 (s, 1H, H-2), 7.63 – 7.61 (m, 1H, H-Ar), 7.58–7.56 (m, 1H, H-Ar), 7.38 – 7.35 (m, 2H, H-Ar), 7.23 (s, 1H, H-4), 7.00 (dd, $J_{a,c}$ = 17.40 Hz, $J_{b,c}$ = 10.95 Hz, 1H, H-c), 5.72 (dd, $J_{a,c}$ = 17.40 Hz, $J_{a,b}$ = 1.26 Hz, 1H, H-a), 5.39 (dd, $J_{b,c}$ = 10.95 Hz, $J_{a,b}$ = 1.26 Hz, 1 Hz, H-b); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 150.60 (d), 150.15 (s), 136.23 (s), 135.39 (d), 128.97 (d), 127.90 (d), 127.50 (d), 127.19 (d), 125.92 (s), 125.34 (d), 117.03 (t); HRMS(MALDI-TOF/TOF) for $C_{11}H_9N_2O$: $(M+H)^+_{calcd}$ = 172.0757, $(M+H)^+_{found}$ = 172.0760.

Photochemistry of 4-/5-(aryl/heteroarylethnyl)oxazoles

A quartz vessel was charged with 4/5-styryl/heteroaryl-oxazoles (**5-10**) (0.0009 mol) in 300 mL of benzene with addition of small amount of iodine and was irradiated at 300 nm and 350 nmin Rayonet reactor for 4h, 7h, 11h, 24h. After irradiation the solvent was removed in vacuum and the residue chromatographed on silica gel column using petroleum ether/diethyl ether (variable ratio) as eluent.

naphtho[2,1-*d*]oxazole (12a)[51] (0.140 g, 92 %, lit[51] 14 %) as colorless crystals : mp 50-51 °C; R_f (PE/E=10:2) = 0.43; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 222 (29823), 233 (31946), 311 (1545), 326 (2098); IR ν_{max}/cm^{-1}: 3099, 2921, 1498, 1261, 1087, 1066; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.26 (d, J_{ar} = 8.6 Hz, 1H, H-ar), 8.25 (s, 1H, H-2), 8.00 (d, J_{ar} = 8.2 Hz, 1H, H-ar), 7.86 (d, J_{et}= 8.7 Hz, 1H, H-et), 7.82 (d, J_{et}= 8.7 Hz, 1H, H-et), 7.67-7.64 (m, 1H, H-ar), 7.59-7.56 (m, 1H, H-ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 151.2 (d), 145.6 (s), 136.1 (s), 131.4 (s), 128.1 (d), 126.5 (d), 125.5 (d), 125.0 (d), 120.0 (s), 119.8 (d), 118.4 (d).

Irradiation without the presence of oxygen and iodine

0.154 g (c = 3 × 10^{-3} mol/L) of 5-(2-vinylphenyl)oxazole (**15**) in 300 mL of benzene (purged with argon for 30 min) at 300 nm was irradiated for 76h. After removal of the solvent and purification 0.025 g (16 %, lit.[51] 14%) of naphtho[2,1-*d*]oxazole (**12a**) was obtained.

6-methylnaphtho[2,1-*d*]oxazole (12b) (0.081 g, 49 %) as yellow crystals: mp 62–64 °C; R_f (PE/E=10:1) = 0.15; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 238 (24720), 270 (3775), 281 (3480), 293 (2296), 314 (1522), 329 (2185); IR ν_{max}/cm^{-1}: 2972, 1531. 1504, 1379, 1263; ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm 8.22 (s, 1H, H-2), 8.13 (d, J_{ar} = 8.2 Hz, 1H, H-10/12), 7.98 (d, $J_{6,7}$ = 8.9 Hz, H-6/7), 7.88 (d, $J_{6,7}$ = 8.9 Hz, 1H, H-6/7), 7.53 (dd, J_{ar} = 8.2 Hz, J_{ar} = 7.0 Hz, 1H, H-11), 7.41 (d, J_{ar} = 7.0 Hz, 1H, H-10/12), 2.77 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ/ppm 151.7 (d, C-2), 136.3 (s), 135.4 (s), 131.0 (s), 126.9 (d), 126.7 (d, C), 124.5 (s), 121.6 (d), 120.6 (s), 118.5 (d), 118.4 (d), 20.2 (q, $\underline{C}H_3$); MS *m/z* (EI): 183 (100, M$^+$); HRMS(MALDI-TOF/TOF) za $C_{12}H_9NO$: $(M+H)^+_{calcd}$ = 184.0757, $(M+H)^+_{measured}$ = 184.0756.

naphthho[2,1-*d*]oxazole-6-carbonitrile (**12c**) (0.158 g, 90 %) as yellow powder: mp 158-165 °C, R_f (PE/E = 20:1) = 0.19; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 220 (2140), 247 (3150), 253 (3972), 300 (349); IR ν_{max}/cm^{-1} (NaCl): 2919, 2228, 1079; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.53 (d, $J_{2,3}$ = 7.5 Hz, 1H, H_3), 8.31(s, 1H, H_{ox}), 8.25 (d, $J_{4,5}$=8.5 Hz, 1H, $H_{4/5}$), 8.09 (d, $J_{4,5}$ = 8.6 Hz, 1H, $H_{4/5}$), 8.00 (d, $J_{1,2}$= 7.5 Hz, 1H, H_1), 7.72 (t, $J_{1,2}$ = $J_{2,3}$ = 7.5 Hz, 1H, H_2); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 225.6 (s, CN), 152.1 (d), 131.8 (d), 130.3 (s), 129.3 (s), 122.1 (d), 121.4 (d), 121.3 (d), 121.1 (d), 119.9 (s), 117.0 (s), 97.2 (s); MS *m/z* (EI): 194 (100, M$^+$).

2-methyl-naphtho[2,1-*d*]oxazole-6-carbonitrile (**12d**) (0.066 g, 35 %) as oil: R_f (PE/E = 20:1) = 0.12; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}):303 (3260), 338 (Sh 1784); IR ν_{max}/cm^{-1} (NaCl): 3011, 2230, 1109; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.45 (d, J_{ar} = 8.8 Hz, 1H, $H_{ar1/3}$), 8.19 (d, J_{ar} = 9.9 Hz, 1H, $H_{ar5/6}$), 7.98 (d, J_{ar} = 9.9 Hz, 1H, $H_{ar5/6}$), 7.96 (dd, J_{ar} = 7.4 Hz, J_{ar} = 1.1 Hz, 1H, $H_{ar1/3}$), 7.68 (dd, J_{ar} = 8.8 Hz, J_{ar} = 7.4 Hz, 1H, H_{ar2}), 2.80 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 163.7 (s), 146.1 (s), 138.7 (s), 131.3 (d), 129.6 (s), 125.3 (d), 124.6 (d), 121.5 (d), 120.8 (d), 119.6 (s), 117.2 (s), 110.6 (s), 14.13 (q, $\underline{C}H_3$); MS *m/z* (EI): 208 (100, M^+).

8-metoxynaphto[2,1-*d*]oxazole (**13a**) (0.160 g, 90 %) as yellow powder: mp 131-141^{0}C; R_f (PE/E = 20:1) = 0.43; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 225 (9427), 246 (11694), 280 (1681), 316 (626); ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.22 (s, 1H, H_{ox}), 7.88 (d, $J_{2/3}$ = 8.8 Hz, 1H, H_3), 7.73 (d, $J_{4,5}$ = 8.5 Hz, 1H, $H_{4/5}$), 7.70 (d, $J_{4,5}$ = 8.5 Hz, 1H, $H_{4/5}$), 7.52 (d, $J_{1,2}$ = 2.5 Hz, 1H, H_1), 7.20 (dd, $J_{1,2}$ = 2.5 Hz, $J_{2,3}$ = 8.8 Hz, 1H, H_2), 4.00 (s, 3H, OC$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 158.1 (s), 151.1 (s), 136.6 (s), 129.8 (d), 126.7 (s), 124.7 (d), 124.2 (d), 121.0 (s), 117.8 (d), 115.7 (d), 98.6 (d), 55.0 (q); MS *m/z* (EI): 200 (100, $(M+H)^+$); HRMS (Q-TOF) for $C_{12}H_9NO_2$: $(M+H)^+_{calcd}$ = 200.0633, $(M+H)^+_{found}$ = 200.0705.

8-methylnaphtho[2,1-*d*]oxazole (**13b**) (0.107 g, 65 %) as yellow powder: mp 121-129 ^{0}C; R_f (PE/E = 20:1) = 0.45; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 224 (35106), 241 (39824), 280 (4554), 312 (1207), 326 (1694); IR ν_{max}/cm^{-1} (NaCl): 3096, 1497, 1261, 1091; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.21 (s, 1H, H_{ox}), 8.01 (brs, 1H, H_1), 7.87 (d, $J_{2,3}$ = 8.4 Hz, 1H, H_3), 7.76 (d, $J_{4,5}$ = 8.8 Hz, 1H, $H_{4/5}$), 7.75 ($J_{4,5}$ = 8.8 Hz, 1H, $H_{4/5}$), 7.39 (dd, $J_{2,3}$ = 8.4 Hz, $J_{1,2}$ = 1.5 Hz, 1H, H_2), 2.59 (s, 3H, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 151.1 (d, C-ox), 145 2 (s), 136.6 (s), 136.1 (s), 129.7 (s), 127.9 (d, C-3), 127.7 (d, C-2), 124.7 (d, C-4/5), 118.8 (d, C-1), 117.3 (d, C-4/5), 21.4 ($\underline{C}H_3$); MS *m/z* (EI): 183 (100, M^+); HRMS(Q-TOF) za $C_{12}H_9NO$: $(M+H)^+_{calcd}$ = 184.0684, $(M+H)^+_{found}$ = 184.0755.

8-nitronaphtho[2,1-*d*]oxazole (**13c**) (0.165 g, 86 %) as colorless powder: 84-96 ^{0}C; R_f (PE/E = 20:1) = 0.11; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}):258 (1116), 270 (Sh 928), 300 (511); IR ν_{max}/cm^{-1} (NaCl): 3584, 2913, 1600, 1509, 1344, 1275; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 9.21 (d, $J_{1,2}$ = 2.2 Hz, H_1), 8.35 (s, 1H, H_{ox}), 8.34 (dd, $J_{1,2}$ = 2.2 Hz, $J_{2,3}$ = 8.9 Hz, 1H, H_2), 8.14 (d, $J_{2/3}$ = 8.9 Hz, 1H, H_3), 8.07 (d, $J_{4,5}$ = 8.7 Hz, 1H, H_4), 7.93 (d, $J_{4,5}$ = 8.7 Hz, 1H, H_5); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 152.2 (s), 133.7 (s), 129.8 (d), 129.2 (d), 124.8 (d), 122.4 (d), 121.0 (s), 118.9 (d), 118.8 (s), 117.4 (s), 116.7 (d); MS *m/z* (EI): 214 (100, M^+); HRMS (Q-TOF) for $C_{11}H_6N_2O_3$: $(M+H)^+_{calcd}$ = 215.0378, $(M+H)^+_{found}$ = 215.0450.

2-methyl-8-methoxynaphtho[2,1-*d*]oxazole (13d) (0.080 g, 45 %) as white powder: 122-125 ^{0}C; R_f (PE/E = 20:1) = 0.44; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 227 (28292), 246 (43332), 254 (35544); IR ν_{max}/cm^{-1} (NaCl): 2923, 2225, 1450, 1225, 1023; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.84 (d, $J_{2,3}$ = 8.9 Hz, 1H, H_3), 7.66 (d, $J_{4,5}$ = 8.5 Hz, 1H, $H_{4/5}$), 7.59 (d, $J_{4,5}$ = 8.5 Hz, 1H, $H_{4/5}$), 7.44 (d, $J_{1,2}$ = 2.3 Hz, 1H, H_1), 7.15 (dd, $J_{1,2}$ = 2.3 Hz, $J_{2,3}$ = 8.9 Hz, 1H, H_2), 3.98(s, 3H, O$\underline{C}H_3$), 2.74(s, 3H, $C\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 162.9 (s), 158.5 (s), 146.2 (s), 138.3 (s), 130.3 (d), 126.7 (s), 124.5 (d), 121.2 (s), 117.8 (d), 115. 7(d), 55.5 (q, O$\underline{C}H_3$), 14.6 (q, $\underline{C}H_3$); MS *m/z* (EI): 213 (100, M$^+$); HRMS (Q-TOF) for $C_{13}H_{11}NO_2$: $(M+H)^+_{calcd}$ = 214.0790, $(M+H)^+_{measured}$ = 214.0860.

2-methyl-8-methylnaphtho[2,1-*d*]oxazole (**13e**) (0.094 g, 53 %) as yellow powder: mp 71-75 ^{0}C; R_f (PE/E = 20:1) = 0.70; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}):272 (5973); IR ν_{max}/cm^{-1} (NaCl): 3110, 1517, 1251; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 7.95 (d, $J_{1,2}$ = 0.9 Hz, 1H, H_1), 7.84 (d, $J_{2,3}$ = 7.8 Hz, 1H, H_3), 7.69 (J_{et} = 9.0 Hz, 1H, H_{et}), 7.66 (J_{et} = 9.0 Hz, 1H, H_{et}), 7.34 (dd, $J_{1,2}$ = 0.9 Hz, $J_{2,3}$ = 7.8 Hz, 1H, H_2), 2.73 (s, 3H, $C\underline{H}_3$), 2.58 (s, 3H, $C\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 162.8 (s), 148.3 (s), 137.9 (s), 136.7 (s), 129.6 (s), 128.4 (d), 127.5 (d), 124.5 (d), 120.4 (s), 118.9 (d), 117.3 (d), 21.8 (q), 14.6 (q); MS *m/z* (EI): 197 (100, M$^+$); HRMS(Q-TOF) za $C_{13}H_{11}NO$: $(M+H)^+_{calcd}$ = 198.0841, $(M+H)^+_{measured}$ = 198.0911.

2-methyl-8-nitronaphtho[2,1-*d*]oxazole (**13f**) (in a mixture with 40% of unknown impurity with the same R_f value) (0.086, 42%) as yellow powder: 91 - 105 ^{0}C; R_f (PE/E = 20:2) = 0.15; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 9.15 (d, J_{ar} = 2.3 Hz, 1H, H-ar1), 8.32 (d, J_{ar} = 7.6 Hz, 1H, H-ar2), 8.10 (d, J_{ar} = 9.3 Hz, 1H, H-ar4), 7.97 (d, J_{ar} = 7.6 Hz, 1H, H-ar3), 7.86 (d, J_{ar} = 7.6 Hz, 1H, H-ar5), 2.81 (s, 3H, CH_3); MS *m/z* (EI): 228 (100, M$^+$); HRMS (Q-TOF) for $C_{12}H_8N_2O_3$: $(M+H)^+_{calcd}$ = 229.0535, $(M+H)^+_{measured}$ = 229.0605.

6-methylnaphtho[1,2-*d*]oxazole (14a) (0.163 g, 99 %) as yellow crystals: mp 107.5–107.8 ^{0}C; R_f (PE/E=10:3) = 0.20; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 225 (36251), 280 (6150), 290 (5888), 311 (2975), 319 (2529), 325 (4491); IR ν_{max}/cm^{-1}: 3129, 1531, 1505, 1391, 1241, 1031; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.40 (d, $J_{10,11}$ = 8.2 Hz, 1H, H-10), 8.21 (s, 1H, H-2), 8.00 (d, $J_{6,7}$ = 9.2 Hz, 1H, H-6/7), 7,74 (d, $J_{6/7}$ = 9.2 Hz, 1H, H-6/7), 7.56 (dd, $J_{10,11}$= 8.2 Hz, $J_{11,12}$= 7.1 Hz, 1H, H-11), 7.40 (d, $J_{11,12}$= 7.1 Hz, 1H, H-12), 2.77 (s, 3H, $C\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 151.5 (d, C-2), 147.3 (s), 135.9 (s), 135.1 (s), 130.3 (s), 127.1 (d, C-11), 126.9 (s), 126.5 (d, C-12), 122.8 (d, C-6/7), 120.4 (d, C-10), 110.5 (d, C-6/7), 20.1 (q, $\underline{C}H_3$); MS *m/z* (EI): 183 (100, M$^+$), 155 (10%), 126 (9%), 102 (7%); HRMS(Q-TOF) za $C_{12}H_9NO_2$: $(M+H)^+_{calcd}$ = 184.0757, $(M+H)^+_{measured}$ = 184.0759.

8-*N*,*N*-dimethylamino-naphtho[2,1-*d*]oxazole (**14b**) (0.063 g, 33 %) as orange powder: 61-64 ^{0}C; R_f (PE/E = 20:1) = 0.15; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 254 (17936), 316 (7040), 350 (4879); IR ν_{max}/cm^{-1} (NaCl): 2950, 2300, 1590, 1410, 1266; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.08 (s, 1H, H-2ox), 7.74 (d, J_{ar} = 8.8 Hz, 1H, H-et), 7.60 (d, $J_{ar2,3}$ = 9.0 Hz, 1H, H-3), 7.46 (d, $J_{ar1,2}$ = 2.5 Hz, 1H, H-1), 7.08 (dd, $J_{ar1,2}$ = 2.5 Hz, $J_{ar2,3}$ = 9.0 Hz, 1H, H-2), 3.07 (s, 6H, 2xC<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 150.6 (d, C-2ox), 149.5 (s), 148.2 (s), 129.5 (d), 128.4 (s), 127.8 (s), 126.3 (d), 123.8 (s), 114.7 (d), 106.4 (d), 100.6 (d), 40.7 (q, 2x<u>C</u>H3); MS *m/z* (EI): 212 (100, M$^+$); HRMS (Q-TOF) for $C_{13}H_{12}N_2O$: (M+H)$^+_{calcd}$ = 213.0950, (M+H)$^+_{measured}$ = 213.1024.

8-chloronaphtho[2,1-*d*]oxazole (**14c**) (0.141 g, 77 %) as white powder: mp 121-125 ^{0}C; R_f (PE/E = 20:1) = 0.80; UV (EtOH) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 288 (5142), 322 (1850); IR ν_{max}/cm^{-1} (NaCl): 1690, 1620, 1451; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.50 (d, J_{ar}= 2.1 Hz, H-1), 8.23 (s, 1H, H-ox2), 7.91 (d, J_{ar}= 8.7 Hz, 1H, H-3), 7.81 (d, J_{ar}= 9.0 Hz, 1H, H-et), 7. 81 (d, J_{ar}= 9.0 Hz, 1H, H-et), 7.50 (dd, J_{ar} = 8.7 Hz, J_{ar} = 2.1 Hz, 1H, H-2); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 151.8 (d), 148.1 (s), 134.9 (s), 133.5 (s), 130.1 (d), 129.4 (s), 127.4 (s), 126.5 (d), 126.4 (d), 121.4 (d), 111.2 (d); MS *m/z* (EI): 203 (100, M$^+$); HRMS (Q-TOF) for $C_{11}H_6ClNO$: (M+H)$^+_{calcd}$ = 204.0138, (M+H)$^+_{measured}$ = 204.0212.

8-fluoronaphtho[2,1-*d*]oxazole (**14d**) (0.050 g, 33 %) as white powder: mp 89-91 ^{0}C; R_f (PE/E = 20:1) = 0.82; IR ν_{max}/cm^{-1} (NaCl): 1705, 1599, 1561, 1101; ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm 8.22 (s, 1H, H-2ox), 8.10 (dd, J_{ar} = 2.4 Hz, J_{ar} = 9.4 Hz H-1), 7.96 (dd, J_{ar} = 8.8 Hz, J_{ar} = 9.4 Hz H-2), 7.82 (d, J_{ar}= 8.8 Hz, 1H, H-et), 7.68 (d, J_{ar}= 8.8 Hz, 1H, H-et), 7.32 (dd, J_{ar} = 8.8 Hz, J_{ar} = 2.4 Hz, 1H, H_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm 162.5 (s), 160.9 (s), 151.6 (d), 148.1 (s), 135.4 (s), 127.9 (s), 126.5 (d), 115.5 (d), 110.4 (d), 106.2 (d); MS *m/z* (EI): 187 (100, M$^+$); HRMS (Q-TOF) for $C_{11}H_6FNO$: (M+H)$^+_{calcd}$ = 188.0433, (M+H)$^+_{measured}$ = 188.0501.

Supporting Information

This file contains all of the ^{1}H and ^{13}C spectra along with UV and 2D HETCOR spectra of some compounds.

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Text for the TOC

Biological activity of naphtho[1,2-*d*]oxazoles and heterobenz[1,2-*d*]oxazoles, prompted the further photochemical synthesis of substituted naphtho[1,2-*d*/2,1-*d*]xazoles. Required *p*- and *o*-phenyl-substituted 5-arylethenyloxazoles were prepared by Van Leusen reaction. For the preparation of the substituted 4-(aryl/heteroarylethenyl)oxazoles the Wittig reaction was utilized.

Key topic

Oxazole photochemistry