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Synthesis of Vinylnaphthofurans and NMR Analysis of their Photoswitching

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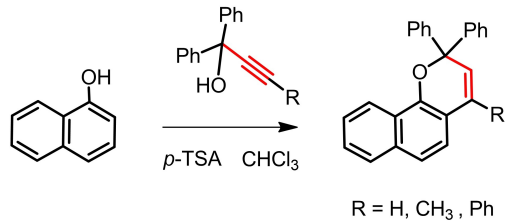
An easy synthesis of photochromic vinylnaphthofurans by the acid-catalyzed one-pot reaction of naphthols with but-2-yne-1,4-diols is described. These uncolored polyaromatic compounds are activated by UV light, at room temperature, and converted through a stilbene-type electrocyclization into a thermally stable orange species, which can be switched back using visible light. The behavior of these photoswitches was elucidated using NMR, which allowed to identify the photoisomers and some side-products, formed after prolonged UV irradiation.

Introduction

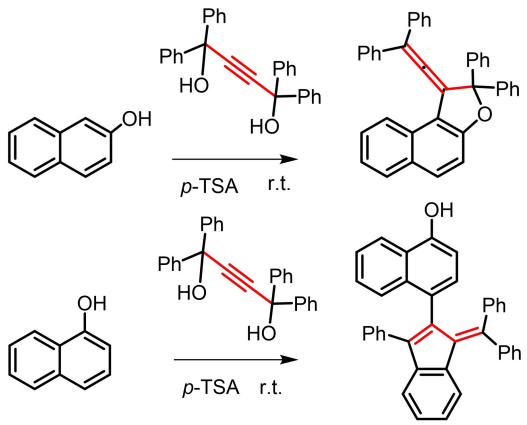
The one-pot acid-catalyzed reaction of naphthols with 1,1-diarylprop-2-yn-1-ols has been extensively used in the preparation of a wide range of naphthopyrans which show photochromic properties.[1] In this cascade transformation the terminal hydrogen atom of the alkyne ends up in the pyran double bond but the reaction is not limited to terminal alkynols. The use of 1,1-diarylbut-2-yn-1-ols or 1,1,3-triarylprop-2-yn-1-ols allows also to prepare naphthopyrans substituted with methyl or phenyl groups in the pyran double bond which, however, show weak photochromic properties (Scheme 1).[2]

Nevertheless, the introduction of a reactive hydroxymethyl group in the terminal position of the alkyne changes significantly its reactivity. For instance, the reaction of symmetrical tetraarylbut-2-yne-1,4-diols with 2-naphthols affords directly vinylidene-naphthofurans, which show also photochromic activity,[3–5] while the reaction with 1-naphthols originates colored 1H-indenes (Scheme 2).[6] The first reaction follows initially the same mechanism that leads to the naphthopyrans, but the presence of the terminal tertiary alcohol in the alkyne opens a different reaction pathway leading to the vinylidene-naphthofurans. The second reaction follows a different mechanism involving an electrophilic aromatic substitution in the 4th position of the naphthol followed by an intramolecular Nazarov electrocyclization.

Notwithstanding, the presence of a terminal hydroxymethyl group in the propynol has some advantages for the synthesis of naphthopyrans since it can be used to form, *in situ*, a lactone ring. For instance, the reaction of methyl 4-hydroxy-6-methoxy-2-naphthoate with 1,1-diphenylbut-2-yne-1,4-diol, at room temperature, under acid catalysis, gives directly a naphthopyran with a fused lactone ring (Scheme 3).[7,8]



Scheme 1. Synthesis of naphthopyrans from 1-naphthol and diarylpropynols.



Scheme 2. Reaction of naphthols with tetraphenylbut-2-yne-1,4-diol.

Contrary to common thermally reversible photochromic naphthopyrans used in the ophthalmic lenses industry, which generate two colored species, with different thermal stability, under sunlight, these lactone-fused naphthopyrans can only form a single colored photoisomer and thus exhibit a faster color decay in the dark.[9,10] However, we observed that the ester group in the *meta* position of the naphthol is essential for the formation of the pyranic ring. In this paper, we describe that in the absence of the ester group, the reaction of naphthols with

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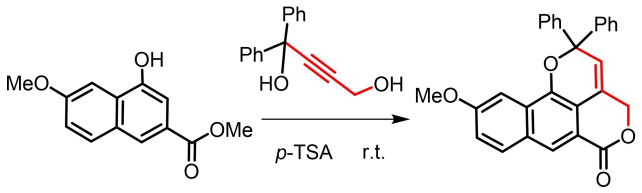


Scheme 3. One-pot synthesis of a lactone-fused naphthopyran.

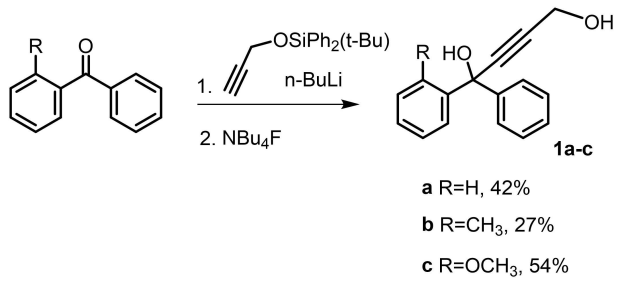
1,1-diarylbut-2-yne-1,4-diols leads to new vinylnaphthofurans which show photochemically reversible photochromic properties at room temperature.

Results

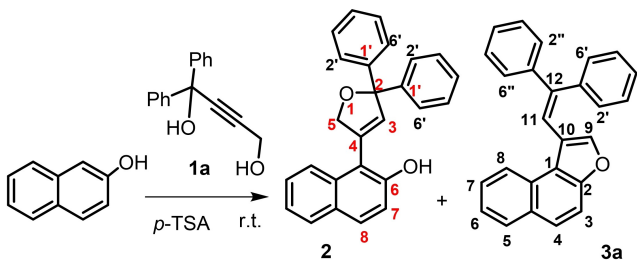
Synthesis

The 1,1-diarylbut-2-yne-1,4-diols **1a–c** were easily prepared through the reaction of benzophenones with *tert*-butyldiphenyl (prop-2-yn-1-yloxy)silane, in the presence of *n*-BuLi, followed by deprotection with NBu_4F (Scheme 4).[8] Alternatively, the 1,1-diphenylbut-2-yne-1,4-diol **1a** could be prepared in higher yield (60%) through the reaction of 1,1-diphenylprop-2-yn-1-ol with *n*-BuLi followed by the addition of paraformaldehyde.

The reaction of 2-naphthol with 1,1-diphenylbut-2-yne-1,4-diol **1a**, at room temperature, under acid catalysis, gave compound **2** as the major product (54%) along with a small amount of the less polar compound **3a** (4%). Compound **2**, with the molecular formula $C_{26}H_{21}O_2$, has a phenolic function



Scheme 4. Synthesis of 1,1-diarylbut-2-yne-1,4-diols **1a-c** from benzophenones.



Scheme 5. Reaction of 2-naphthol with 1,1-diphenylbut-2-yne-1,4-diol **1a** at room temperature.

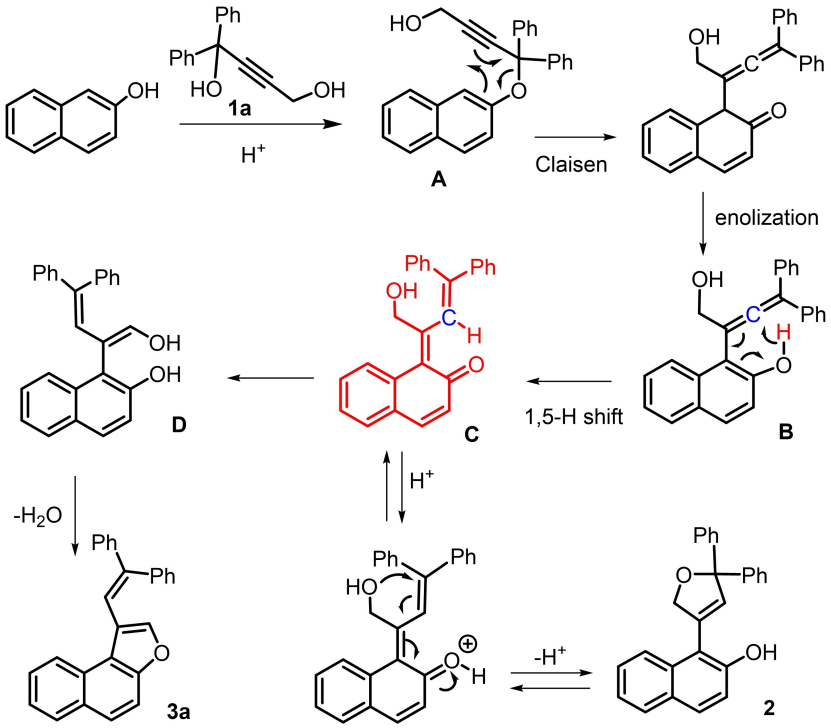
(IR: 3320 cm^{-1}) while the molecular formula of the minor compound **3a** ($C_{26}H_{19}O$) indicates the loss of water. Both were unambiguously structurally identified by NMR as the 1-(5,5-diphenyl-4,5-dihydrofuran-3-yl)naphthalen-2-ol **2** and the 1-(2,2-diphenylvinyl)naphtho[2,1-*b*]furan **3a** (Scheme 5)[11–13].

More particularly, in the ^1H NMR spectrum of **2** (Figure S1), the poor-resolved signal at 5.40 ppm is the phenolic OH-6, the doublet at 5.10 ppm and the triplet at 6.64 ppm correspond to the CH_2-5 and the H-3, respectively, with their common coupling constant $^4J = 2.2$ Hz. In the ^{13}C spectrum (Figure S2) the important signals at 95.7 ppm and 76.7 ppm were assigned to the quaternary C-2 and secondary C-5 carbon atoms. The 2D COSY spectrum (Figure S3) shows correlations between the protons H-3 and H-5, and H-7 and H-8 while in the ^1H-^{13}C HMBC experiment (Figure S4), the long-range correlations between the protons H-2′/6′ at 7.50 ppm and the carbon C-2 at 95.7 ppm, and between the protons CH_2-5 and carbon atoms C-1′ at 145.0 ppm and C-2 confirmed the dihydrofuran structure.

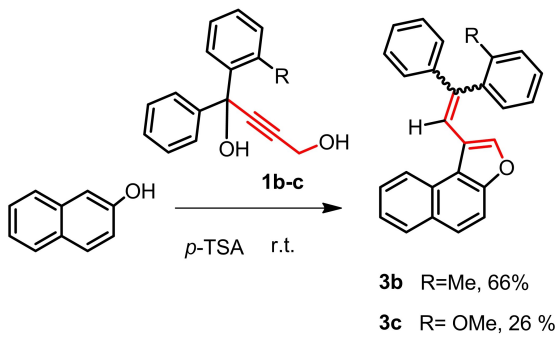
The ^1H NMR spectrum of **3a**, (Figure S5) displays two doublet signals at 7.00 and 7.48 ppm ($^4J = 1.2$ Hz) assigned respectively to protons H-9 in the furan ring and H-11 in the ethylenic bridge. The 2D COSY spectrum (Figure S7) shows scalar correlations: H-3 at 7.61 ppm↔H-4 at 7.75 ppm, H-5 at 8.00 ppm↔H-6 at 7.51 ppm↔H-7 at 7.59 ppm↔H-8 at 8.53 ppm, and H9↔H-11. The ^1H-^{13}C HBMC experiment (Figure S8) evidences long-range correlations between i) the carbon C-1 at 121.6 ppm and H-3, H-11, H-9 and H-8, ii) the carbon C-2 at 152 ppm and H-9, H-3 and H-4, iii) the carbon C-10 at 120.2 ppm with H-9 and H-11 and iv) the carbon C-9 at 142.8 ppm (correlated in ^1H-13 C HSQC with H-9, (Figure S9)) with H-11 which confirms the vinylnaphtho[2,1-*b*]furan structure.

The dihydrofuran **2** was completely converted into the vinylnaphthofuran **3a** upon heating for 10 min, in toluene, at reflux, in the presence of *p*-TSA. These observations can be rationalized considering the known mechanism that leads to naphthopyrans (Scheme 6). Thus, the reaction between 2-naphthol and the 1,1-diphenylbut-2-yne-1,4-diol **1a** affords initially the ether **A** that after a Claisen rearrangement, enolization, and 1,5-Hydrogen shift is transformed into the conjugated and colored species **C**. In the absence of the hydroxymethyl group this species would be converted through an electrocyclization into the known naphtho[2,1-*b*]pyran, however, the free hydroxymethyl enables two new reaction pathways: 1) the acid-catalyzed intramolecular 1,6-conjugated addition of the alcohol to the conjugated system in the intermediate **C** may form the dihydrofuran **2**; 2) **C** may isomerize to the diol **D** that performs an irreversible intramolecular ether formation leading to the vinylnaphthofuran **3a** (Scheme 6). Since the dihydrofuran **2** is in thermal equilibrium with the colored opened form **C**, the latter can be converted, at a higher temperature, into the vinylnaphthofuran **3a**, which is thermodynamically more stable.

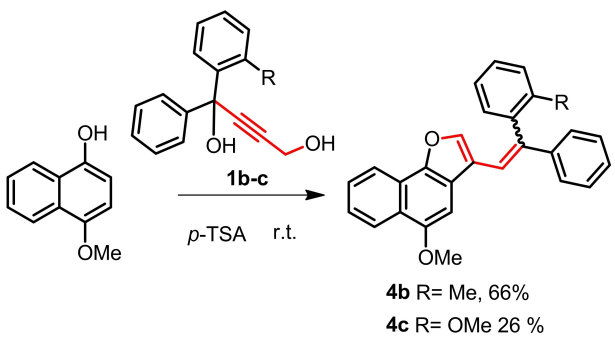
Under the same conditions, the reaction of 2-naphthol with the diols **1b–c** performed in $CHCl_3$, at room temperature, gave directly the vinylnaphthofurans **3b–c**. However, since the two aromatic groups in the diols **1b–c** are not the same, the



Scheme 6. Proposed mechanism for the reaction of 2-naphthol with 1,1-diphenylbut-2-yne-1,4-diol **1a**.



Scheme 7. One-pot synthesis of naphthofurans **3b–c** from 2-naphthol and 1,1-diarylbut-2-yne-1,4-diols **1b–c**.



Scheme 8. One-pot synthesis of naphthofurans **4b–c** from 4-methoxynaphth-1-ol and 1,1-diarylbut-2-yne-1,4-diols **1b–c**.

corresponding vinylnaphthofurans **3b–c** were isolated as a mixture of two E–Z isomers (Scheme 7). The main isomer is *Z* with an amount of 88% for **3b** and 93% for **3c** (Figures S10–S13). The excess of the Z-isomer is probably due to the faster intramolecular 1,5-H shift to the less hindered face of the allenic carbon atom in the corresponding intermediate **B**.

This reaction was also attempted with 1-naphthols. Although the treatment of 1-naphthol with 1,1-diphenylbut-2-yne-1,4-diol **1a** provided a complex mixture of unidentified compounds, the reaction of 4-methoxynaphth-1-ol with 1,1-diarylbut-2-yne-1,4-diols **1b–c**, proceeded smoothly, at room temperature, and gave directly the vinylnaphthofurans **4b–c** (Scheme 8). As observed previously with the naphthofurans **3b–c**, because of the inequivalence of both aryl groups, the naphthofurans **4b-c** were isolated as a mixture of two *E-Z* isomers. The main isomer is again the *Z* with an amount of 78% for **4b** and 87% for **4c** (Figure S14-S17).

The compounds **3a-c** and **4b-c** have a partial structure of diarylethene (2-furyl-1,1-diphenylethene) and thus are candidates to perform a photochemical 6π-electrocyclization.

Photochromic behaviour under UV and Vis irradiation

Vinylnaphthofurans **3a-c** and **4b-c** are uncolored compounds with strong absorption in the UV region below 360 nm ($CHCl_3$ 1.0×10^{-3} M). Continuous UV light irradiation (150 W ozone free Xe lamp) of $CHCl_3$ solutions, at 20 °C, using a Schott 011FG09 ($259<\lambda<388$ nm with $\lambda_{max}=330$ nm and $T=79\%$) filter leads

to the development of an orange colouration with a maximal absorption between 455–470 nm (Figure 1)

The absorbance at the maximal absorption wavelength increased with time but the photostationary state was not achieved even after 6 min of UV irradiation. When the UV irradiation was turned off, the absorbance decreased very slowly underlining the formation of relatively stable colored species. The return to the uncolored state could be achieved in few minutes under visible irradiation (>420 nm) (Figure 2). However, the UV/vis irradiation cycles were not reproducible suggesting the possibility of a secondary reaction. To clarify the photochromic behavior of these compounds and identify the structure of the photoproducts, their behavior was further studied by NMR.[14]

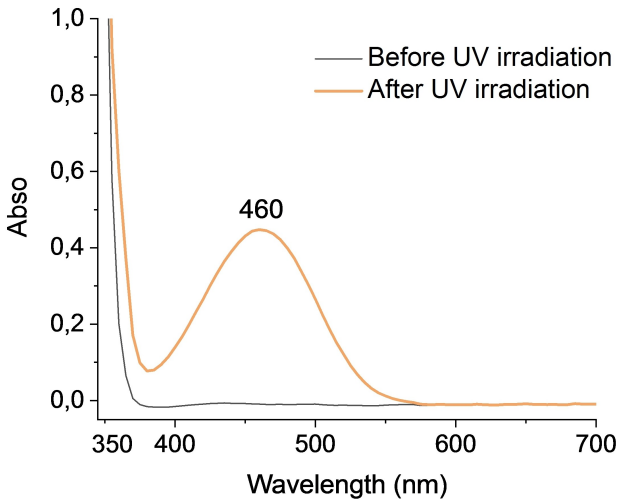


Figure 1. UV-vis spectra of vinylnaphthofuran **3a** ($CHCl_3$ 1.0×10^{-3} M) before (black) and after exposure to the UV light (orange)

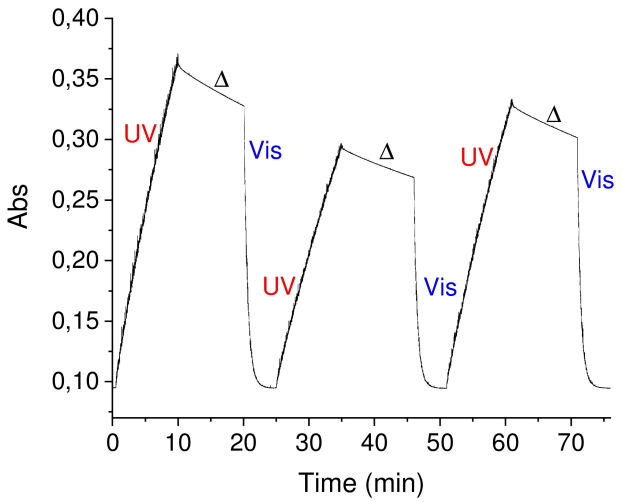


Figure 2. Successive cycles of UV/Vis irradiation for the vinylnaphthofuran **3a** in $CHCl_3$ measured at 460 nm.

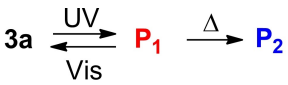
NMR analysis of the photochromism of vinylnaphthofuran 3a

NMR studies on naphthofurans **3**–**4**, in toluene-d_8 solutions (5×10^{-3} M), were carried out before and after UV irradiation with filtered UV-band at 313 nm.

The ^{1}H NMR spectra of naphthofuran **3a** in Figure 3a features a set of aromatic protons resonating between 7–8.6 ppm. Upon UV-irradiation, two sets of signals assigned to photoproducts $\mathbf{P_1}$ and $\mathbf{P_2}$ are observed (Figure 3b). The time evolution of the system was followed by measuring the peak-intensities of the three species after 5, 10, 15, and 20 minutes of irradiation (Figure S25). During the first irradiation period, compound **3a** was converted almost concomitantly into $\mathbf{P_1}$ and $\mathbf{P_2}$, then upon prolonged UV irradiation, $\mathbf{P_1}$ decreased progressively while $\mathbf{P_2}$ increased, becoming the major product in solution (Figure 3c).

The thermal time-evolution of the concentrations of compounds **3a**, $\mathbf{P_1}$ and $\mathbf{P_2}$, were recorded after UV irradiation for 3 minutes of a fresh solution of **3a** (Figure S26). The concentration of **3a** remained constant while the conversion of $\mathbf{P_1}$ into $\mathbf{P_2}$ was observed.

In parallel, the photochemical bleaching with visible light at 436 nm was also conducted on a fresh solution of **3a** (Figure S27) preliminary UV-irradiated for 3 minutes. The photoproduct $\mathbf{P_1}$ is bleached into **3a**, while $\mathbf{P_2}$ remained almost constant. These results suggest the following general mechanism:



Structural elucidation of photoproducts P_1 and P_2

The photoproduct P_1 is characterized by a set of signals in the ^{1}H NMR spectrum (Figure 3b) between 4.0 and 6.8 ppm underlining the loss of aromaticity of a part of the molecule. In fact, protons 9, 2′, 3′, 4′, 5′, 6′ (Scheme 9) are all shifted upfield and the scalar correlation between H-2′ at 4.03 ppm and H-9 at 5.44 ppm with a coupling constant of $^3J=24$ Hz, confirms the formation of a chemical bond between one of the phenyl groups and the furan ring (Figure 3b). The value of the coupling constant could appear surprisingly and uncommonly high, but it is not unprecedented as the isolation of persistent dihydrophenanthrenes with a ^{3}J coupling constant of 20.7 Hz has been recently reported.[15] The scalar couplings in the 2D-COSY experiment (Figure S18) evidences the connections H-9↔H-2′↔H-3′ at 6.29 ppm↔H-4′ at 6.02 ppm↔H-5′ at 5.71 ppm↔H-6′ at 6.53 ppm. Also, the HSQC experiment (Figure S19) confirms the aliphatic character of the carbon atoms C-2′ at 42.2 ppm and C-9 at 86.0 ppm by direct correlations with H-2′ and H-9 respectively. P_1 is then deduced to be the *trans*-12-phenyl-7a,7b-dihydrodinaphtho[1,2-*b*:1′,2′-*d*]furan (Scheme 9).

The photoproduct $\mathbf{P_2}$ is characterized by a set of signals between 7.0 and 8.7 suggesting an oxidation process with the loss of hydrogen atoms $H_{2'}$ and H_9 leading to the formation of a polyaromatic system (Figure 3c). To assign the aromatic pro-

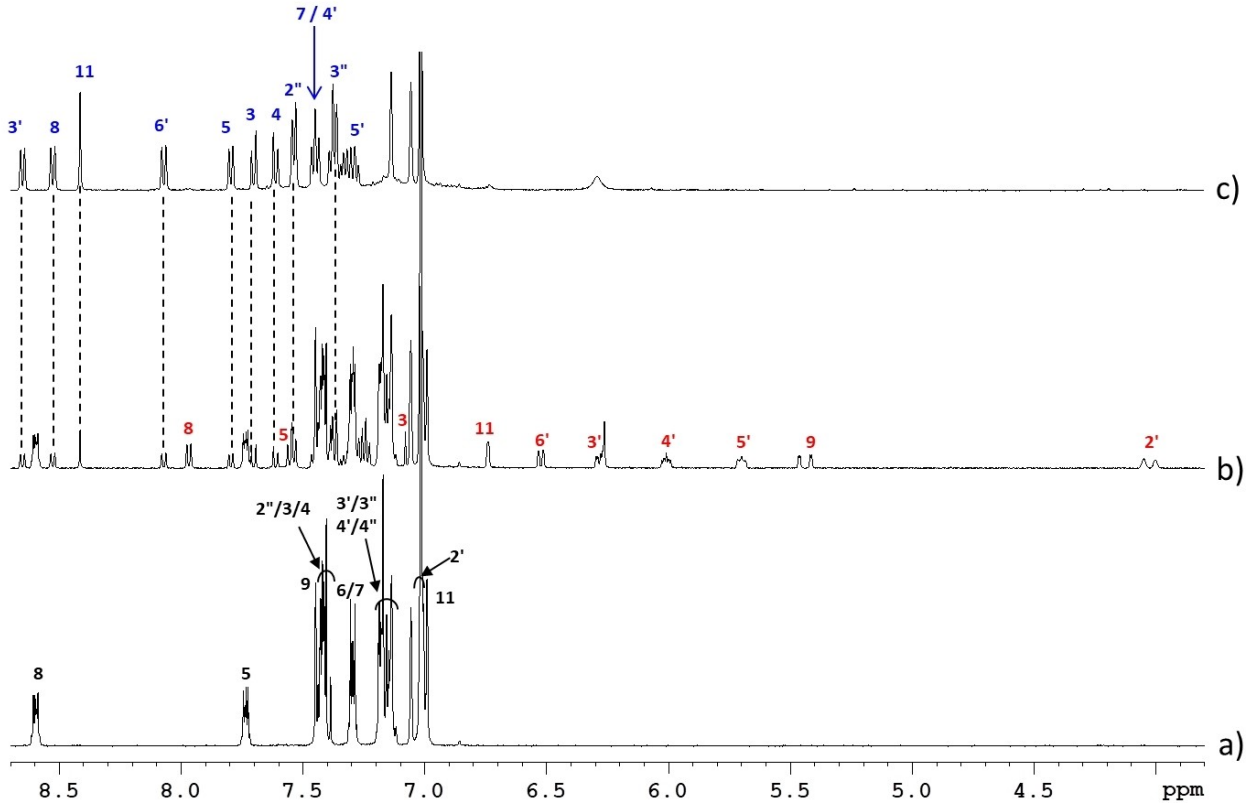
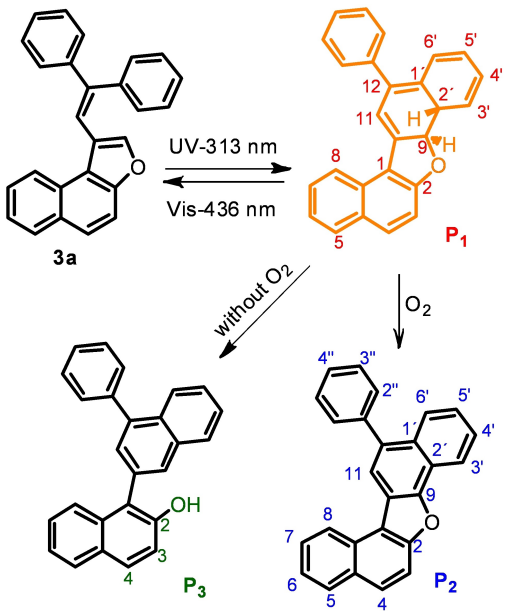


Figure 3. ^{1}H NMR spectra of naphthofuran **3a** in toluene-d_8 (5×10^{-3} M), **a)** before hv, **b)** after 5 min of UV irradiation at 313 nm, and **c)** after 20 min of UV irradiation at 313 nm. Assignment in black, red, and blue are referred to **3a**, $\mathbf{P_1}$ and $\mathbf{P_2}$, respectively.



Scheme 9. General mechanism for the photochromic behavior of vinylnaphthofuran **3a**.

tons, a series of TOCSY-1D experiments (Figure S20) and a 2D-COSY (Figure S21) have been acquired. The scalar couplings allow to identify the connections i) H-3′ at 5.44 ppm↔H-4′ at 7.45 ppm↔H-5′ at 7.29 ppm↔H-6′ at 8.07 ppm, ii) H-8 at 8.53 ppm↔H-7 at 7.45 ppm↔H-6 at 7.36 ppm↔H-5 at 7.80 ppm, iii) H-2″ at 7.54 ppm↔H-3″ at 7.32 ppm↔H-4″ at 7.32 ppm. In the HMBC experiment (Figure S22), long-range correlations between C-2 at 154.0 ppm with H-4 at 7.61 ppm and between C-9 at 151.9 ppm with H-11 at 8.41 ppm and H-3′ at 8.65 ppm are observed. The two quaternary carbon atoms of the pyran ring between 150 and 155 ppm confirm the polyaromatic system with the loss of hydrogen atoms H-9 and H-2. $\mathbf{P_2}$ is then identified to the 12-phenyldinaphtho[1,2-*b*:1′,2′-*d*]furan.

Thus, $\mathbf{P_1}$ is formed through a UV-promoted stilbene-type electrocyclic reaction with the formation of a 6-membered ring system that, in the presence of oxygen, is irreversibly oxidized to $\mathbf{P_2}$ (Scheme 9).[16–21]

The experiment was repeated in degassed toluene solution. **3a** was anew converted into $\mathbf{P_1}$ (Figure 4b). After 1 day of thermal evolution, the ^{1}H NMR spectrum (Figure 4c) evidenced the disappearance of the signals of $\mathbf{P_1}$ and the appearance of a singlet signal at 5.0 ppm assigned to an OH function and a new set of aromatic signals suggesting that $\mathbf{P_1}$ had evolved thermally and irreversibly to a new product $\mathbf{P_3}$ (Scheme 9).[22,23]

$\mathbf{P_3}$ was characterized (Figures S23 and S24) as a phenolic structure obtained by the cleavage of the furan ring via a *syn*-elimination. In the HMBC experiment, long-range correlations between C-2 at 150.8 ppm and H-4 at 7.61 ppm, H-3 at

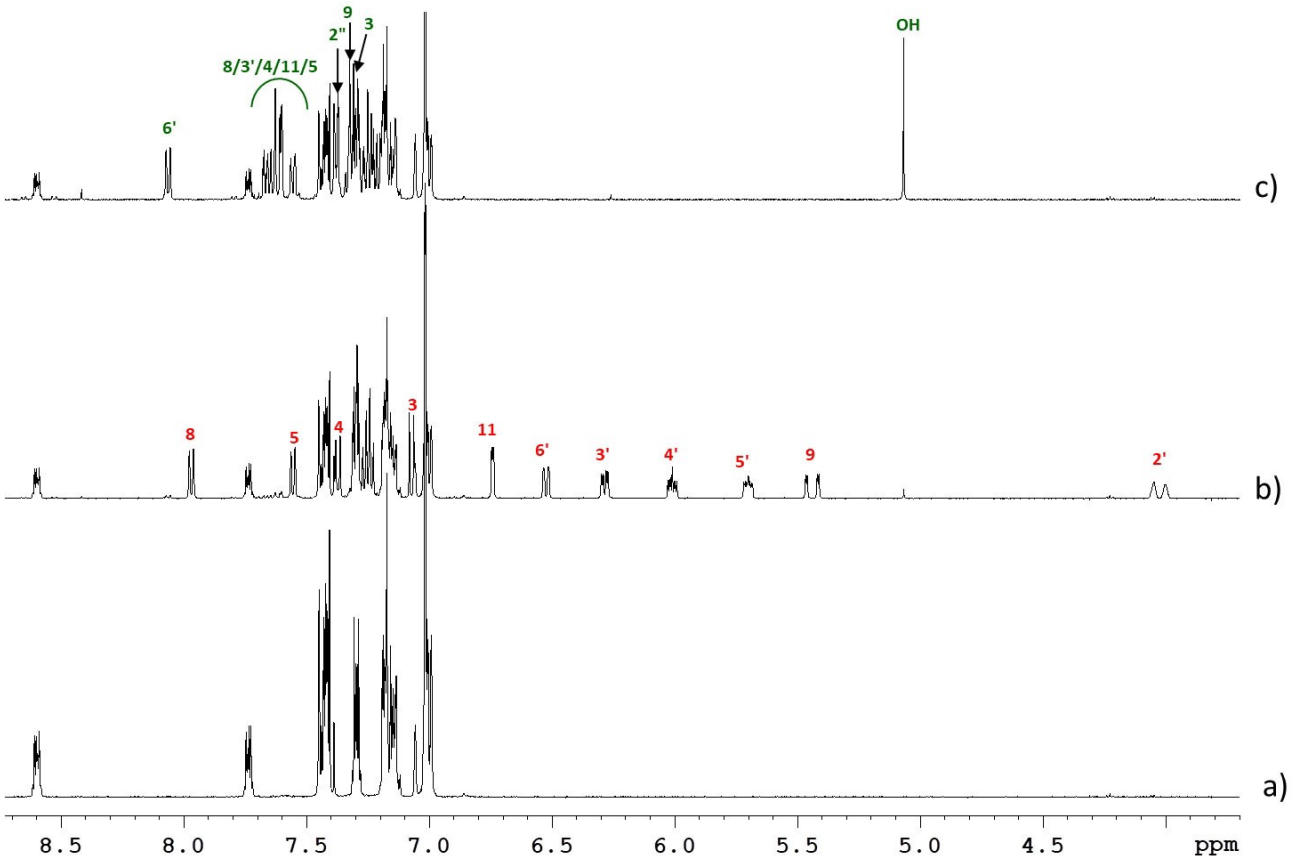


Figure 4. ^{1}H NMR spectra of naphthofuran **3a** in a degassed toluene-d8 solution (5×10^{-3} M), **a)** before hv, **b)** after UV irradiation and **c)** after thermal evolution for 1 day.

7.30 ppm, and OH at 5.07 ppm confirm the phenolic group attached to the carbon C-2. $\mathbf{P_3}$ is then identified as the 4′-phenyl-[1,2′-binaphthalen]-2-ol (Figure S28).

These side reactions leading to $\mathbf{P_2}$ and $\mathbf{P_3}$, explain the poor repeatability that was observed during the successive cycles of UV/Vis irradiation (Figure 2).

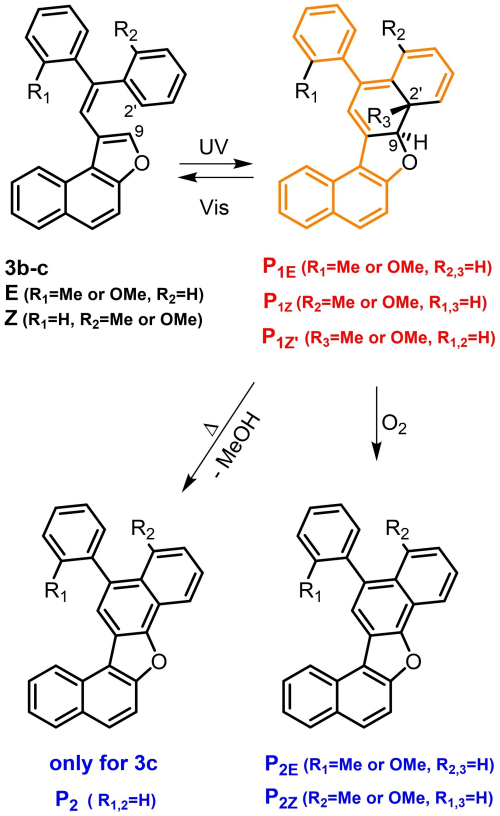
NMR analysis of the photochromism of vinylnaphthofurans 3b–c and 4b–c

The presence of methyl or methoxy groups at the *ortho* position of one of the phenyl rings in diols **1b–c**, led to the formation of a mixture of two *Z/E* diastereoisomeric forms of vinylnaphthofurans **3b–c** and **4b–c**, the *Z* isomer being largely majority. Although this brings an extra level of complexity, the NMR analysis showed that the presence of these substituents in the phenyl group involved in the cyclization reaction (*Z*-isomer) changed the chemical behavior of the photocyclized forms regarding the oxidation process.

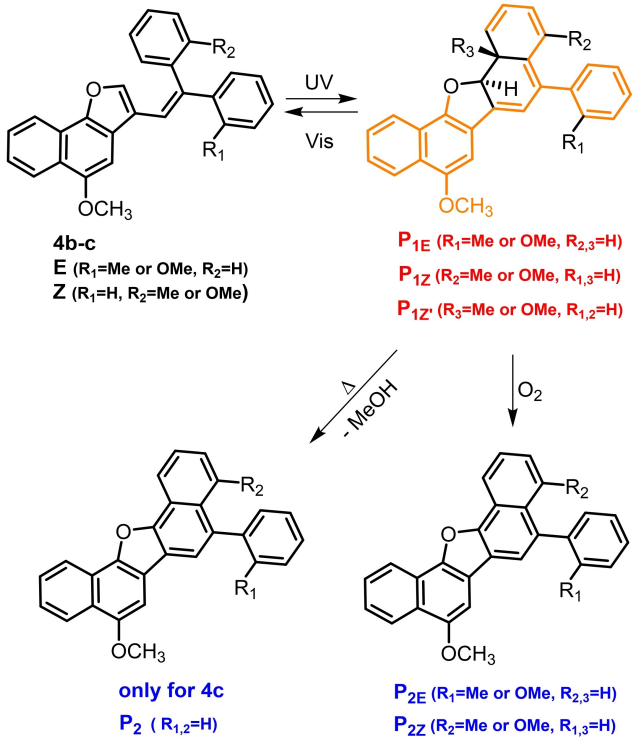
UV irradiation of a toluene-d_8 solution of **3b** led to the appearance of 3 isomers of the cyclohexadiene structure ($\mathbf{P_{1E}}$,$\mathbf{P_{1Z}}$ and $\mathbf{P_{1Z'}}$) (Scheme 10, Figure S29). The cyclization of the *E* isomer of **3b** (R_1 = Me) gave the minor product $\mathbf{P_{1E}}$ (R_1 = Me).

The two other products ($\mathbf{P_{1Z}}$ and $\mathbf{P_{1Z'}}$) are obtained from the *Z* isomer of **3b** (R_2 = Me) (Scheme 10) and involve the cyclization of the *o*-tolyl group. $\mathbf{P_{1Z'}}$ (R_3 = Me) with the methyl group attached to the carbon involved in the new ring (C-2′) is thermally stable and cannot oxidize while $\mathbf{P_{1E}}$ (R_1 = Me) and $\mathbf{P_{1Z}}$ (R_2 = Me), in the presence of oxygen, lead as expected, to the oxidized compounds $\mathbf{P_{2E}}$ and $\mathbf{P_{2Z}}$. Irradiation with 436 nm visible light-induced the conversion of $\mathbf{P_{1Z'}}$ back into the initial **3b** (Scheme S30).

For **3c** (*Z* isomer, R_1 = OMe and *E* isomer, R_2 = OMe) with the anisole group, the cyclohexadienyl photoproducts obtained after UV irradiation ($\mathbf{P_{1E}}$ (R_1 = OMe) and $\mathbf{P_{1Z}}$ (R_2 = OMe), Scheme 10, Figures S31-33) are unstable and quickly oxidized to the aromatic $\mathbf{P_{2E/Z}}$. A third photoproduct was also detected, identified as the aromatic unsubstituted cyclized structure $\mathbf{P_{2'}}$, identical to the structure of $\mathbf{P_2}$ in Scheme 9. In contrast with **3b**, here no $\mathbf{P_{1Z'}}$ (R_3 = OMe) was detected. However, $\mathbf{P_{1Z'}}$ must be effectively produced, but its thermal stability is certainly so short that it rapidly converts into $\mathbf{P_2}$ after a concomitant release of methanol. When the solution is degassed, no oxidation of $\mathbf{P_{1Z}}$ occurred ($\mathbf{P_{1E}}$ was not detected), but the formation of $\mathbf{P_2}$ and methanol was still observed (Figures S32-33). Then, as the degassed solution of **3c** at the end of irradiation is only



Scheme 10. General mechanism for the photochromic behavior of vinylnaphthofurans **3b–c**.



Scheme 11. General mechanism for the photochromic behavior of vinylnaphthofurans **4b–c**.

constituted by P_2, this means that a photochemical equilibrium exists between P_{1Z} and $P_{1Z'}$ through **3c**.

The photochromic behavior of the substituted vinylnaphthofurans **4b-c** is similar to that of **3b-c** (Scheme 11, Figure S34-37). The presence of the *ortho* methyl group limits the oxidation of the *Z* isomer, but not of the *E* isomer. A solution to this problem would be the introduction of methyl groups in each of the four *ortho* positions, however, the 2,2′,6,6′-tetramethylbenzophenone did not react with the *tert*-butyldiphenyl(prop-2-yn-1-yloxy)silane, in the presence of *n*-BuLi, which made it difficult the synthesis of the corresponding tetramethylnaphthofuran.

Conclusion

The acid-catalyzed one-pot condensation of diarylbut-2-yne-1,4-diols with naphthols at room temperature gives directly vinylnaphthofurans which shows photochromic properties. NMR analysis, before and after irradiation, and in the presence or absence of oxygen, allowed to elucidate the chemical processes involved in this reversible transformation.

Under UV light these uncolored polyaromatic compounds undergo an intramolecular electrocyclization with the formation of a colored 7a,7b-dihydrodinaphtho[1,2-*b*:1′,2′-*d*]furan system. This photoproduct can be switched back using visible light, but in the presence or absence of oxygen, a part is irreversibly converted into aromatic compounds. The introduction of methyl or methoxy groups at the *ortho*-position of one of the phenyl rings led to the formation of a mixture of two *E/Z* isomers. The methoxy group does not change significantly the photochromic behavior, however, the presence of a methyl group in the same position can prevent, partially, the irreversible degradation: while the minor *E* isomer shows a similar behavior as the unsubstituted compound, the major *Z* isomer cyclizes into a thermally stable photoisomer which does not oxidize and can be switched back with visible light.

Experimental section

General Methods. The reactions were monitored by thin-layer chromatography (TLC) on aluminum plates precoated with silica gel 60 F254 (0.25 mm). Column chromatography was performed on silica gel 60 (70–230 mesh). FTIR spectrometer, with diamond crystal cell ATR was used to acquire the absorption spectra of the compounds (wavenumbers in cm^{-1}). HRMS spectra were recorded on an ESI-TOF mass spectrometer. NMR spectra were recorded using a Bruker NEO 500 MHz spectrometer (^1H 500 MHz and ^{13}C 125 MHz), equipped with TXI probe, using standard sequences. Data sets were processed using Bruker Topspin 4,2 software. Samples in toluene-d8 were irradiated directly in the NMR tube (5 mm), thermo-regulated, using a 1000 W Xe–Hg HP filtered short-arc lamp (Oriel) equipped with a filter for UV irradiation (Schott UG11, $295 < \lambda < 800$ nm + 313 nm interferential filter). For visible irradiation, a Schott KG1, $295 < \lambda < 800$ nm + 436 nm interferential

filter was used. After irradiation had been stopped, the samples were transferred to the thermoregulated NMR probe. When required, degassing of toluene-d_8 solution was performed by the technique of freeze-pump-thaw cycles (five cycles at 2,25×10–6 Torr) directly in the J. Youngvalve NMR sample tubes (Wilmad 507-JY-7). Chemical shifts (δ) are reported in parts per million

General procedure for the synthesis of diols 1 a–c

n-Butyllithium (2 eq., 1.6 M in hexane) was added dropwise to a solution of *tert*-butyldiphenyl(prop-2-yn-1-yloxy)silane (1 eq.) in dry THF (25 mL) at 0 °C. After complete addition, the cold mixture was maintained under constant stirring for 1 h. The respective benzophenone (1 eq.) was added at once to the solution, and the resulting mixture was stirred at room temperature for 20–24 hours. Water (25 mL) was added, and the aqueous phase was extracted with ethyl acetate (3×30 mL). The combined organic phases were dried using Na_2SO_4 and the solvent was removed under reduced pressure. To a solution of the final residue in dry THF was added tetra-*n*-butylammonium fluoride (2 eq), with stirring, at room temperature. After 24 h, HCl (5%, 25 mL) was added and the aqueous phase was extracted with ethyl acetate (2×30 mL). The resulting organic phase was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The resulting oil was purified by recrystallization or column chromatography.

1,1-Diphenylbut-2-yne-1,4-diol 1 a

Obtained from *tert*-butyldiphenyl(prop-2-yn-1-yloxy)silane (200 mg, 0.680 mmol) and benzophenone (124 mg, 0.680 mmol). The resulting residue was purified by recrystallization from CH_2Cl_2 / ethyl acetate/ petroleum ether affording 65 mg of diol **1 a** (white crystals), 42% yield. Mp:142–143 °C. IR (cm^{-1}): 3315, 2985, 2319, 1488, 1446, 1337, 1190, 1134, 1077, 1002, 974, 898, 765, 751, 699, 605. ^{1}H NMR (400 MHz, $CDCl_3$): 7.61 (d, J=7.3 Hz, 4H), 7.36 (t, J=7.3 Hz, 4H), 7.33–7.24 (m, 4H), 4.45 (s, 2H), 2.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.60, 128.33, 127.85, 126.02, 88.38, 85.46, 77.34, 77.02, 76.70, 74.40, 51.34. ESI-MS (TOF) *m/z* (%): 261 ($[M+H+Na]^+$, 7), 221 ($[M+H\text{-}H_2O]^+$, 100), 203 (7), 193 (17), 145 (13), 134 (37), 132 (80), 115 (6). HRMS calcd for $C_{16}H_{13}O$: 221.0961 $[M+H\text{-}H_2O]^+$. Found: 221.0968.

1-Phenyl-1-(*o*-tolyl)but-2-yne-1,4-diol 1 b

Obtained from *tert*-butyldiphenyl(prop-2-yn-1-yloxy)silane (1 g, 3.40 mmol) and 2-methylbenzophenone (667 g, 3.40 mmol) and purified by column chromatography (20% ethyl acetate / petroleum ether) affording 220 mg of diol **1 b** (white crystals), 27% yield. Mp:144-145 °C. IR (cm^{-1}): 3204, 2991, 2899, 2320, 1489, 1448, 1379, 1356, 1186, 1140, 1095, 1025, 988, 906, 773, 750, 695, 644, 617. ^{1}H NMR (400 MHz, $CDCl_3$): 7.96 (dd, J=7.2, 2.3 Hz, 1H), 7.58–7.45 (m, 2H), 7.42–7.19 (m, 7H), 7.18–7.09 (m, 1H), 4.43 (s, 2H), 2.72 (s, 1H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.70, 141.20, 136.28, 132.12, 128.36, 128.17, 127.96, 126.42, 126.06, 125.54, 87.48, 85.73, 77.32, 77.00, 76.68, 74.11, 51.34, 21.01. ESI-MS (TOF) *m/z* (%): 275 ($[M+H+Na]^+$, 27), 235 ($[M+H\text{-}H_2O]^+$, 100), 190 (12), 182 (7), 151 (8), 150 (10), 149 (15), 147 (16), 145 (34), 141 (17), 134 (16), 132 (37). HRMS calcd for $C_{17}H_{15}O$: 235.1117 $[M+H\text{-}H_2O]^+$. Found: 235.1122.

1-(2-Methoxyphenyl)-1-phenylbut-2-yne-1,4-diol 1 c

Obtained from *tert*-butyldiphenyl(prop-2-yn-1-yloxy)silane (853 mg, 2.90 mmol) and 2-methoxybenzophenone (615 mg, 2.90 mmol) and purified by recrystallization from CH_2Cl_2 / ethyl acetate / petroleum ether affording 418 mg of diol **1 c** (white crystals), 54% yield. Mp:80-82 °C. IR (cm^{-1}): 3287, 2905, 2376, 1597, 1483, 1432, 1360, 1285, 1243, 1186, 1134, 1091, 1025, 997, 969, 907, 765, 756, 695, 614. ^{1}H NMR (400 MHz, $CDCl_3$): 7.42 (s, 3H), 7.20 (q, J=12.2, 9.6 Hz, 5H), 6.87 (t, J=7.5 Hz, 1H), 6.81 (d, J=8.0 Hz, 1H), 4.89 (s, 1H), 4.22 (s, 2H), 3.60 (s, 3H), 2.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 156.60, 144.35, 132.02, 129.48, 128.39, 127.90, 127.42, 126.01, 120.86, 112.16, 87.15, 85.50, 77.32, 77.00, 76.68, 74.40, 55.74, 51.06. ESI-MS (TOF) *m/z* (%): 291 ($[M+H+Na]^+$, 3), 251 ($[M+H\text{-}H_2O]^+$, 75), 223 (7), 150 (10), 147 (9), 145 (16), 134 (42), 132 (100), 122 (7). HRMS calcd for $C_{17}H_{15}O_2$: 251.1067 $[M+H\text{-}H_2O]^+$. Found: 251.1070.

Alternatively, the 1,1-diphenylbut-2-yne-1,4-diol 1 a can be obtained using the following protocol

n-Butyllithium (15 mL, 1.6 M in hexane, 24.0 mmol) was added dropwise to a solution of 1,1-diphenylprop-2-yn-1-ol (2.5 g, 12.0 mmol) in dry THF (25 mL) at 0 °C under stirring. 1 hour after complete addition, paraformaldehyde (2.2 g, 72.0 mmol) was added at once to the solution, and the resulting mixture stirred at room temperature for 20 hours. Water (25 mL) and HCl (5%, 5 mL) were added, and the aqueous phase was extracted with ethyl acetate (3×30 mL). The combined organic phases were washed several times with water and then dried using Na_2SO_4. The solvent was removed under reduced pressure. The resulting residue was purified by recrystallization from CH_2Cl_2 / ethyl acetate / petroleum ether affording 1.7 g of diol **1 a** (white crystals), 60% yield.

Synthesis of naphthofuran 3 a

Reaction between 2-naphthol and diphenylbut-2-yne-1,4-diol 1 a at room temperature

p-TSA (catalytic) was added to a solution of 2-naphthol (150 mg, 1.04 mmol) and 1,1-diphenylbut-2-yne-1,4-diol **1 a** (248 mg, 1.04 mmol) in $CHCl_3$ (15 mL). After stirring for 1 h at room temperature, water (25 mL) was added, and the aqueous phase extracted with ethyl acetate (3×10 mL). The combined organic phases were dried (Na_2SO_4), filtered, and the solvent removed under reduced pressure. The residue was purified by column chromatography (5% ethyl acetate / petroleum ether) affording: 205 mg of 1-(5,5-diphenyl-4,5-dihydrofuran-3-yl)naphthalen-2-ol **2** (yellowish crystals), 54% yield: Mp:62–63 °C. IR (cm^{-1}): 3320, 3056, 2315, 1597, 1507, 1446, 1271, 1025, 808, 746, 695. ^{1}H NMR (300 MHz; $CDCl_3$): 7.80 (d, J=8.0 Hz, 1H), 7.77 (d, J=9.2 Hz, 1H), 7.68 (d, J=8.2 Hz, 1H), 7.50 (d, J=7.8 Hz, 4H), 7.47-7.30 (m, 8H), 7.19 (d, J=9.1 Hz, 1H), 6.64 (t, J=2.2 Hz, 1H), 5.40 (s, 1H), 5.13 (d, J=2.2 Hz, 2H). ^{13}C NMR (75 MHz; $CDCl_3$):150.5, 145.0, 135.4, 134.7, 132.7, 130.1, 129.0, 128.6, 128.3, 127.6, 127.1, 126.3, 123.9, 123.6, 117.3, 112.2, 95.7, 76.7. EI-MS (TOF) *m/z* (%): 365 ($[M+H]^+$, 100), 364 (M^+, 24), 363 (62), 351 (29), 347 (11), 183 (20). HRMS calcd for $C_{26}H_{21}O_2$: 365.1536 $[M+H]^+$. Found: 365.1550.

and 14 mg of 1-(2,2-diphenylvinyl)naphtho[2,1-*b*]furan **3 a** (yellowish crystals), 4% yield. Mp:102–104 °C. IR (cm^{-1}): 2919, 2845, 1442, 1386, 1204, 1108, 995, 882, 803, 752, 690, 610. EI-MS (TOF) *m/z* (%): 347 $[M+H]^+$, 4), 346 (M^+, 1), 257 (9), 145 (19), 134 (40), 132 (100). ^{1}H NMR (300 MHz; $CDCl_3$): 8.54 (d, J=8.3 Hz, 1H), 8.00 (dd, J=8.0 Hz, J=1.4 Hz, 1H), 7.75 (d, J=8.9 Hz, 1H), 7.60 (d, J=8.9 Hz, 1H), 7.59 (ddd, J=8.3 Hz, J=7.0 Hz, J=1.6 Hz, 1H), 7.52 (ddd, J=8.1 Hz, J=7.0 Hz, J=1.5 Hz, 1H), 7.51-7.37 (m, 6H), 7.34-7.26 (m, 5H), 7.00 (d, J=1.2 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$):152.6, 144.6, 142.8, 142.5, 140.3, 130.9, 130.1, 129.0, 128.8, 128.5, 128.4, 127.8, 127.7, 127.5, 126.5, 125.6, 124.4, 123.6, 121.6, 120.2, 118.0, 112.6. HRMS calcd for $C_{26}H_{19}O$: 347.1430 $[M+H]^+$. Found: 347.1427.

Compound **2** was converted into **3a** after heating for 10 min in toluene, in the presence of *p*-TSA.

General procedure for the synthesis of naphthofurans 3b–c, and 4b–c

p-TSA (catalytic) was added to a solution of naphthol (1 eq) and diol (1 eq) in $CHCl_3$ (15 mL). After stirring for 0.5–5 h, at room temperature, water (25 mL) was added, and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic phases were dried (Na_2SO_4), filtered, and the solvent removed under reduced pressure.

(Z)-1-(2-Phenyl-2-(o–tolyl)vinyl)naphtho[2,1-b]furan 3b

Obtained from 2-naphthol (43 mg, 0.298 mmol) and 1-phenyl-1-(*o*-tolyl)but-2-yne-1,4-diol **1b** (75 mg, 0.298 mmol). After 1.30 h, an extra 0.5 eq of 1-phenyl-1-(*o*-tolyl)but-2-yne-1,4-diol **1b** were added to the mixture. The residue was purified by column chromatography (petroleum ether) affording 71 mg of naphthofuran **3b** (slightly yellow crystals), 66% yield. Mp:113–114 °C. IR (cm^{-1}): 3021, 2919, 1493, 1442, 1386, 1119, 995, 882, 809, 752, 731, 690, 610. ^{1}H NMR (300 MHz; $CDCl_3$): 8.56 (d, J=8.4 Hz, 1H), 7.99 (d, J=8.0 Hz, 1H), 7.73 (d, J= 8.9 Hz, 1H), 7.67 (s, 1H), 7.63 (t, J= 8.0 Hz, 1H), 7.56 (d, J=9.0 Hz, 1H), 7.55-7.45 (m, 3H), 7.42 (t, J=7.0 Hz, 2H), 7.35 (t, J=7.0 Hz, 1H), 7.30-7.16 (m, 5H), 6.84 (s, 1H), 2.11 (s, 3H)H). ^{13}C NMR (75 MHz; $CDCl_3$):152.5, 142.7, 142.6, 141.4, 139.7, 136.3, 130.9, 130.6, 130.1, 129.1, 128.8, 128.6, 127.8, 127.6, 126.7, 126.5, 126.3, 125.6, 124.3, 123.5, 121.0, 120.1, 118.1, 112.6, 19.6. EI-MS (TOF) *m/z* (%): 361 ($[M+H]^+$, 51), 360 (M^+, 11), 311 (10), 258 (48), 213 (13), 150 (14), 145 (21), 134 (39), 132 (100), 114 (17). HRMS calcd for $C_{27}H_{21}O$: 361.1587 $[M+H]^+$. Found: 361.1585.

(Z)-1-(2-(2-Methoxyphenyl)-2-phenylvinyl)naphtho[2,1-b]furan 3c

Obtained from 2-naphthol (40 mg, 0.277 mmol) and 1-(2-methoxyphenyl)-1-phenylbut-2-yne-1,4-diol **1c** (75 mg, 0.277 mmol). After 1.30 h, an extra 0.5 eq of 1-(2-methoxyphenyl)-1-phenylbut-2-yne-1,4-diol **1c** were added to the mixture. The residue was purified by column chromatography (petroleum ether) affording 27 mg of naphthofuran **3c** (slightly yellow crystals), 26% yield. Mp:150–151 °C. IR (cm^{-1}): 2921, 1489, 1462, 1388, 1241, 1108, 1025, 883, 800, 759, 690, 608. ^{1}H NMR (300 MHz; $CDCl_3$): 8.56 (d, J=8.1 Hz, 1H), 7.98 (d, J=8.0 Hz, 1H), 7.72 (d, J=8.9 Hz, 1H), 7.61 (t, J=7.0 Hz, 1H), 7.58 (d, J=8.9 Hz, 1H), 7.57 (d, J=1.3 Hz, 1H), 7.55-7.48 (m, 3H), 7.45-7.29 (m, 4H), 7.16 (dd, J=7.7 Hz, J=1.9 Hz, 1H), 7.06 (d, J= 1.2 Hz, 1H), 6.96-6.89 (m, 2H), 3.53 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$):157.4, 152.5, 142.2, 141.7, 140.7, 131.3, 130.8, 129.2, 129.1, 128.9, 128.8, 128.4, 127.5, 126.7, 126.4, 125.4, 124.3, 123.9, 121.5, 120.9, 120.4, 118.9, 112.5, 111.3, 55.5. EI-MS (TOF) *m/z* (%): 377 ($[M+H]^+$, 100), 376 (M^+, 7), 368 (39), 327 (14), 311 (45), 299 (58), 274 (20), 257 (41), 145 (22), 132 (15). HRMS calcd for $C_{27}H_{21}O_2$: 377.1536 $[M+H]^+$. Found: 377.1528.

(Z)-5-Methoxy-2-(2-phenyl-2-(o–tolyl)vinyl)naphtho[1,2-b]furan 4b

Obtained from 4-methoxy-1-naphthol (52 mg, 0.299 mmol) and 1-phenyl-1-(*o*-tolyl)but-2-yne-1,4-diol **1b** (75 mg, 0.299 mmol). After 1.30 h, an extra 0.5 eq of 1-phenyl-1-(*o*-tolyl)but-2-yne-1,4-diol **1b** were added to the mixture. The residue was purified by column chromatography (0.5% ethyl acetate/petroleum ether) affording 85 mg of naphthofuran **4b**, 73% yield. Mp:75–76 °C. IR (cm^{-1}): 2971, 2900, 1592, 1446, 1379, 1262, 1214, 1111, 1053, 827, 756, 723, 695, 605. ^{1}H NMR (300 MHz; $CDCl_3$): 8.33 (ddd, J=8.4 Hz, J=1.3 Hz, J= 0.7 Hz, 1H), 8.14 (ddd, J=8.2 Hz, J=1.1 Hz, J=0.8 Hz, 1H), 7.59 (ddd, J=8.2 Hz, J=6.9 Hz, J=1.2 Hz, 1H), 7.53–7.45 (m, 3H), 7.43–7.20 (m, 8H), 7.02 (s, 1H), 6.50 (d, J=0.7 Hz, 1H), 4.10 (s, 3H), 2.15 (s, 3H)). ^{13}C NMR (75 MHz; $CDCl_3$):152.3, 144,9, 142.0, 141.5, 141.0, 140.3, 136.2, 131.0, 129.5, 128.5, 128.1, 127.5, 127.0, 127.0, 126.3, 124.6, 124.2, 123.0, 122.4, 121.7, 119.6, 119.0, 115.8, 95.0, 56.0, 19.4. EI-MS (TOF) *m/z* (%): 391 ($[M+H]^+$, 19), 197 (28), 145 (17), 134 (42), 132 (100). HRMS calcd for $C_{28}H_{23}O_2$: 391.1693 $[M+H]^+$. Found: 391.1681.

(Z)-5-Methoxy-2-(2-(3-methoxyphenyl)-2-phenylvinyl)naphtho[1,2-b]furan 4c

Obtained from 4-methoxy-1-naphthol (49 mg, 0.281 mmol) and 1-(2-methoxyphenyl)-1-phenylbut-2-yne-1,4-diol **1c** (75 mg, 0.281 mmol). The residue was purified by column chromatography (1% ethyl acetate/petroleum ether) affording 46 mg of naphthofuran **4c** (yellow crystals), 40% yield. Mp:109-113 °C. IR (cm^{-1}): 2933, 2829, 1639, 1592, 1488, 1455, 1432, 1247, 1219, 1106, 1025, 907, 827, 751, 732, 695, 638, 605. ^{1}H NMR (300 MHz; $CDCl_3$): 8.31 (ddd, J=8.4 Hz, J=1.3 Hz, J=0.8 Hz, 1H), 8.14 (ddd, J=8.2 Hz, J=1.2 Hz, J=0.8 Hz, 1H), 7.58 (ddd, J=8.2 Hz, J=7.0 Hz, J=1.2 Hz, 1H), 7.53-7.41 (m, 4H), 7.40-7.28 (m, 3H), 7.25 (d, J=0.7 Hz, 1H), 7.24 (dd, J= 7.9 Hz, J=1.4 Hz, 1H), 7.14-7.03 (m, 2H), 6.97 (s, 1H), 6.76 (d, J= 0.7 Hz, 1H), 4.05 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$):157.0, 152.1, 145.0, 141.9, 141.7, 139.3, 131.1, 129.7, 129.5, 128.3, 127.3, 126.9, 126.3, 124.5, 124.1, 123.0, 122.5, 121.7, 121.6, 119.7, 119.4, 116.7, 112.0, 95.4, 55.9, 55.8. EI-MS (TOF) *m/z* (%): 407 ($[M+H]^+$, 61), 406 (M^+, 5), 301 (22), 279 (18), 235 (18), 213 (34), 203 (27), 147 (48), 145 (100), 134 (18), 132 (44). HRMS calcd for $C_{28}H_{23}O_3$: 407.1642. $[M+H]^+$ Found: 407.1625.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Electrocyclization · One-pot synthesis · Photochromism · Naphthofurans · NMR

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