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BENZOPHENONE SENSITIZED REARRANGEMENT OF FURYLIDENTETRALONES

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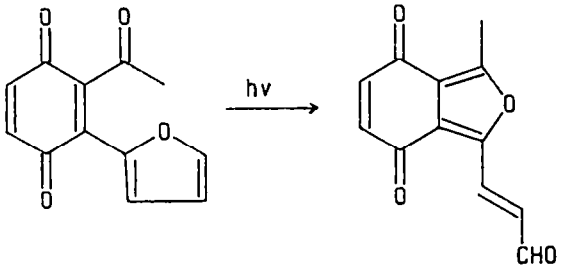
Abstract - Benzophenone sensitized rearrangement of furylidentetralones into dihydronaphthofuran derivatives was described. All the obtained compounds (**6a**, **b**, **c**, **d**, **f**) showed a trans-double bond in α-position on the furan ring. Only using the methoxy derivative **5e** the formation of a little amount of cis-isomer was observed. Furylidenacetone, furylidenacetophenone, and furylidenindanone did not show this reaction in agreement with the hypothesis that the observed intramolecular rearrangement is strictly related to the presence of tetralone moiety. An explanation of this behaviour on the basis of steric hindrance to conjugation in the starting materials was reported.

Twenty years ago Weisgerber and Eugster reported that the irradiation of 2-(2-furyl)-3-acetyl-1,4-benzoquinone (**1**) gave the product **2** deriving from an intramolecular rearrangement[1].



1 2

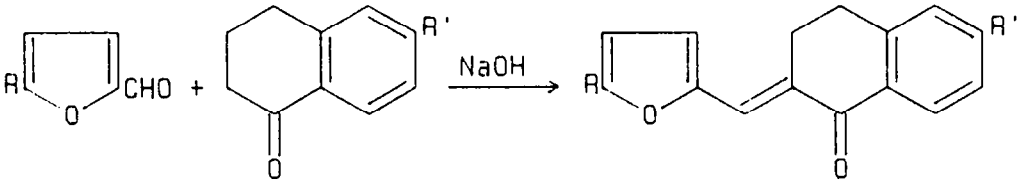
After this paper there were only few communications about similar reactivity using other furan compounds: the irradiation of 3-aroyl-2-(2-furyl)chromones afforded low yields of the corresponding isomerization products: in fact, irradiation on a preparative scale of a 10^{-2} M solution of the starting material in benzene afforded the recovery of the substrate

in the range 86-97%[2]. Nevertheless an application of this type of susbstrates as photoactivable fluorphores on the basis of the above described rearrangement appeared[3]: photoactivable fluorphores serve as useful probes to study the transport and diffusion of macromolecules by the technique fluorescence photoactivation and dissipation.

In our plan devoted to study the photochemical reactivity of furan derivatives, we decided to test the reactivity of some other furyl acrylic derivatives in order to understand if the rearrangement was strictly related to the presence of quinone moiety. In this context we decided to test the reactivity of furylidentetralones. The rearrangement of these starting materials could be a useful synthetic method because it allows to obtain both the skeleton of eudesmanolides[4] and some other biologically active compounds with antihelmintic activity[5].

Results and Discussion

Starting materials were obtained through Claisen-Schmidt condensation between furan-2-carbaldehydes **3** and α-tetralones **4**[6].



3 4 5

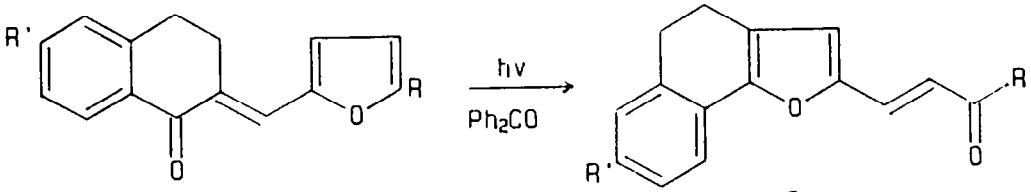
a: R = H a: R' = H

b: R = CH_3 b: R' = OCH_3

c: R = OCH_3

The irradiation of a benzene solution of **5** did not give any reaction. Change of the solvent (i. e. acetonitrile) did not modify the photochemical behaviour. However Huffman reported that photoisomerization of 3-aroyl-2-(2-furyl)chromones occurred via a triplet sensitized mechanism

using benzophenone as sensitizer[2]. In fact, the irradiation of **5** in acetonitrile as solvent in the presence of a small amount of benzophenone allowed to obtain the compound **6** in good yields (Table 1): when R = R′ = H, we obtained a product which showed in the NMR spectrum an aldehydic signal at 9.59 ppm as a doublet with a coupling constant of 8 Hz, an olefinic proton at 6.61 ppm coupled with the aldehydic proton and with an olefinic proton at 7.17 ppm (J = 15.5 Hz), and a singlet at 6.69 ppm (the ß-proton on the furan ring).



5 6

Table 1 - Photochemical intramolecular rearrangement of furylidentetralones

Entry	Substrate	R	R′	Reaction time (h)	Product	Yield(%)[a]
1	**5a**	H	H	6	**6a**	60
2	**5b**	CH_3	H	8	**6b**	57
3	**5c**	H	OCH_3	3	**6c**	56
4	**5d**	CH_3	OCH_3	5	**6d**	58
5	**5e**	OCH_3	H	4.5	**6e**[b]	8
					6f[b]	52

a) All the yields refer to isolated chromatographically pure products.
b) The product was obtained as a cis/trans mixture. **6e** is the cis-isomer, while **6f** is the trans-isomer.

The stereochemistry of the double bond was trans as clearly demonstrated by the coupling constant of 15.5 - 15.8 Hz observed in our products. Only using 5-methoxy-2-furyliden-α-tetralone (**5e**) we obtained the formation of a small amount (8%) of the cis-isomer (Table 1).

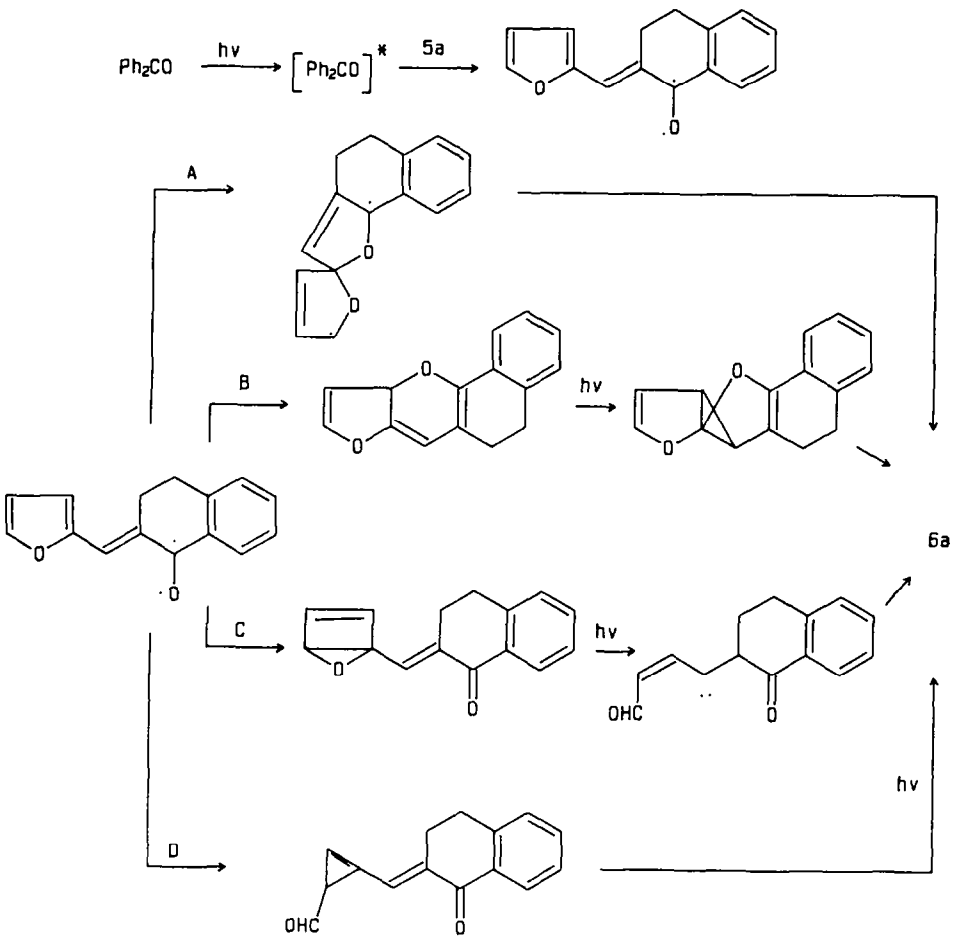
On the basis of the reported data (Table 1), the substitution on both the furan ring and the tetralone moiety does not modify the reactivity of the substrate: in all the experiments conversions of 56-60% were obtained.

Several mechanisms were proposed to justify this type of conversion[1,2]. On the basis of these hypotheses, after the triplet sensitization by benzophenone, four paths for the conversion **5** --> **6** can be depicted as in Scheme 1. Paths C and D can be eliminated in our scheme because a) photochemical isomerization to Dewar furan is not so common in solution[7]; b) photoisomerization to cyclopropenyl derivatives is possible but normally this type of reaction has been described in gas phase, and, in solution, there is not any result confirming the formation of this intermediate in the presence of a conjugated carbonyl group[8,9]; furthermore, it is noteworthy that using thiophene derivatives this type of reaction is completely inhibited in the presence of a carbonyl group[10]; c) the formation of both Dewar furan and cyclopropenyl isomer had to lead to isomeric furan substituted in ß-position[11,12], but we did not observe the formation of any isomeric product of this type; d) the reaction of a carbene intermediate can be excluded on the basis of our experimental results: in the presence of this intermediate, there is competing attack of the carbene at the acrolein carbonyl to regenerate the starting material. In this case the amount of regenerate starting material will depend on the competition between the attack of the carbene on the two carbonyl groups. This competition can be effected by the electron density on the carbonyl groups: however, in the presence of substituents that increase or decrease the electron density on the carbonyl groups we did not observe any modification of the reactivity.

Path B requires an initial ß-attack of the carbonyl group on the furan as described in the intramolecular reaction of a carbonyl compound with simple

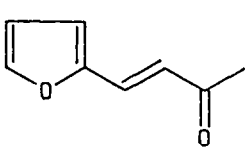
olefins[13]: however, it is known that the addition of a carbonyl group on furan occurs with high stereoselectivity on the basis of an initial α-attack of the carbonyl group on furan[14].

SCHEME 1



In conclusion only path A, involving the α-attack of the carbonyl group on the furan ring and subssequently ring opening, seems to be useful to explain our reactivity pattern.

The quantum yield of the conversion **5** --> **6** was determinated on **5b** as substrate in a Rayonet apparatus at 350 nm, by using phenylglyoxylic acid as actinometer[15]: the obtained value was 0.040 ± 0.005, in agreement with the reported one for the rearrangement of 3-aroyl-2-(2-furyl)chromones[2] (Φ = 0.044). One of the questions is then why did we obtaine reasonable chemical yields of the corresponding isomerization product while Huffman[2] reported very low yields for the same type of conversion. To obtain informations about this problem we have tested the reactivity under our photochemical conditions of furylidenacetone (**7**). It showed a completely different behaviour giving dimerization products[16]. The irradiation of furylidenacetophenone (**8**) did not give any isomerization product with the exception of cis/trans isomerization. These negative results pointed out the required presence of a cyclic ketone to obtain the intramolecular rearrangement. However, the irradiation of furylidenindanone (**9**) did not give the corresponding isomerization product.



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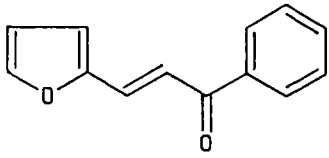

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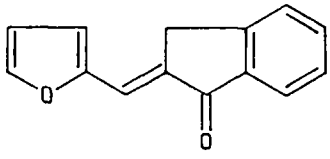

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To understand this behaviour, some informations can be obtained from the examination of the uv spectra of **8**, **9**, and **5b**, showed in table 2. In fact, the presence of an α-alkyl substituent on **9** in comparison with **8** induces a

bathochromic shift (14 nm) in agreement with calculated value of 10 nm. On the contrary, the difference between absorption maxima in **5b** and **9** (15 nm)

Table 2 - UV spectra of some furan acrylic derivatives

Compound	λ_{max}, nm[a]	log ε
8	343	4.39
5b	372	4.27
	259	4.13
9	357	4.46
	270	4.00

a) All the spectra were determined in EtOH as solvent.

can be due to steric hindrance to conjugation. In fact, while furylidenindanone shows a completely planar structure, cyclohexyl ring of tetralone in **5** has some difficulties to maintain a planar structure of the unsaturated system, due to the presence of two sp^3 carbons in the skeleton with four sp^2 carbons. Furthermore this situation changes in the product: both Dreiding models and nmr spectra ($J_{CH2-CH2}$ in **5a** = 7.0 Hz, $J_{CH2-CH2}$ in **6a** = 7.8 Hz) show a modification in the relative positions of CH_2 groups. This steric effect can be considered the driving force for the conversion (**5** --> **6**).

Experimental

Melting points were obtained with a Mettler FP81 MBC cell equipped with a Mettler FP80 central processor. ^{1}H-NMR spectra were recorded with a Varian Gemini 200 instrument using $CDCl_3$ as solvent. IR spectra were obtained on a Perkin-Elmer 457 spectrometer. Mass spectra were obtained with a Hewlett-Packard 5971A mass selective detector connected with a Hewlett-Packard 5890 gas chromatographic instrument and with a Hewlett-Packard 9000 central processor. Uv spectra were recorded with a Varian DMS-90 spectrophotometer.

Starting materials

All the starting materials were obtained from the corresponding 2-furylcarbaldehyde **3a-c** by reaction with α-tetralones **4a-b** in aqueous-

alcoholic sodium hydroxide as described in Ref. 6.

2-Furyliden-α-tetralone 5a. M.p. 75-76°C. ^{1}H-NMR ($CDCl_3$, δ): 8.08 (dd, 1 H, J_1 = 7.7 Hz, J_2 = 1.4 Hz), 7.57 (m, 1 H), 7.54 (d, 1 H, J = 1.6 Hz), 7.46 (ddd, 1 H, $J_1 = J_2$ = 7.7 Hz, J_3 = 1.6 Hz), 7.33 (ddd, 1 H, $J_1 = J_2$ = 7.7 Hz, J_3 = 1.4 Hz), 7.24 (d, 1 H, J = 7.7 Hz), 6.69 (d, 1 H, J = 3.4 Hz), 6.50 (dd, 1 H, J_1 = 3.4 Hz, J_2 = 1.8 Hz), 3.31 (t, 2 H, J = 7.0 Hz), 2.98 (t, 2 H, J = 7.0 Hz). IR ($CHCl_3$) ν_{max} 1670, 1610, 1598, 1550, 1480, 1435, 1390, 1335, 1320, 1300, 1155, 1135, 1090, 1075, 1020, 1000, 970, 950, 920, 885 cm^{-1}. MS: m/z 224 (M^+).

α-(5-Methyl-2-furyliden)-tetralone 5b. ^{1}H-NMR ($CDCl_3$, δ): 8.08 (d, 1 H, J = 7.7 Hz), 7.52 (s, 1 H), 7.46 (dd, 1 H, $J_1 = J_2$ = 7.7 Hz), 7.32 (dd, 1 H, $J_1 = J_2$ = 7.7 Hz), 7.24 (d, 1 H, J = 7.7 Hz), 6.60 (d, 1 H, J = 3.2 Hz), 6.11 (d, 1 H, J = 3.2 Hz), 3.28 (t, 2 H, J = 7.0 Hz), 2.97 (t, 2 H, J = 7.0 Hz), 2.37 (s, 3 H). IR ($CHCl_3$) ν_{max} 1670, 1610, 1570, 1460, 1440, 1375, 1360, 1335, 1320, 1300, 1160, 1135, 1020, 950, 930, 880 cm^{-1}. MS: m/z 238 (M^+).

2-Furyliden-6-methoxy-α-tetralone 5c. M.p. 104-105°C. ^{1}H-NMR ($CDCl_3$, δ): 8.06 (d, 1 H, J = 8.7 Hz), 7.53 (s, 2 H), 6.84 (dd, 1 H, J_1 = 8.7 Hz, J_2 = 2.6 Hz), 6.69 (d, 1 H, J = 2.6 Hz), 6.65 (d, 1 H, J = 3.4 Hz), 6.48 (dd, 1 H, J_1 = 3.4 Hz, J_2 = 1.9 Hz), 3.84 (s, 3 H), 3.29 (t, 2 H, J = 7.0 Hz), 2.74 (t, 2 H, J = 7.0 Hz). IR ($CHCl_3$) ν_{max} 1665, 1610, 1600, 1550, 1465, 1445, 1335, 1318, 1295, 1270, 1155, 1135, 1095, 1020, 970, 955, 920, 890, 850 cm^{-1}. MS: m/z 254 (M^+).

α-(5-Methyl-2-furyliden)-6-methoxy-tetralone 5d. ^{1}H-NMR ($CDCl_3$, δ): 8.06 (d, 1 H, J = 8.7 Hz), 7.47 (s, 1 H), 6.84 (dd, 1 H, J_1 = 8.7 Hz, J_2 = 2.6 Hz), 6.69 (d, 1 H, J = 2.6 Hz), 6.57 (d, 1 H, J = 3.3 Hz), 6.10 (d, 1 H, J = 3.3 Hz), 3.85 (s, 3 H), 3.26 (t, 2 H, J = 6.2 Hz), 2.94 (t, 2 H, J = 6.2 Hz), 2.37 (s, 3 H). IR ($CHCl_3$) ν_{max} 1660, 1610, 1600, 1580, 1445, 1370, 1330, 1315, 1295, 1260, 1130, 1020, 950, 930, 870, 850 cm^{-1}. MS: m/z 268 (M^+).

α-(5-Methoxy-2-furyliden)-tetralone 5e. ^{1}H-NMR ($CDCl_3$, δ): 8.04 (d, 1 H, J = 7.4 Hz), 7.41 (s, 1 H), 7.41 (dd, 1 H, $J_1 = J_2$ = 7.4 Hz), 7.29 (dd, 1 H, $J_1 = J_2$ = 7.4 Hz), 7.20 (d, 1 H, J = 7.4 Hz), 6.61 (d, 1 H, J = 3.4 Hz), 5.31 (d, 1 H, J = 3.4 Hz), 3.88 (s, 3 H). IR ($CHCl_3$) ν_{max} 1660, 1600, 1560, 1530, 1455, 1430, 1390, 1320, 1295, 1130, 1050, 1020, 1000, 965, 920, 905, 875 cm^{-1}. MS: m/z 254 (M^+).

2-Furylidenacetophenone 8. B.p. 178-179°C (7 mmHg). ^{1}H-NMR ($CDCl_3$, δ): 7.92 (m, 1 H), 7.89 (d, 1 H, J = 1.8 Hz), 7.50 (d, 1 H, J = 15.6 Hz), 7.37 (m, 5 H), 6.55 (d, 1 H, J = 3.4 Hz), 6.32 (dd, 1 H, J_1 = 3.4 Hz, J_2 = 1.8 Hz). IR ($CHCl_3$) ν_{max} 1660, 1600, 1575, 1550, 1470, 1440, 1385, 1325, 1195, 1180, 1010, 970, 880 cm^{-1}.

2-Furyliden-α-indanone 9. ^{1}H-NMR ($CDCl_3$, δ): 7.85 (d, 1 H, J = 7.7 Hz), 7.60 (d, 1 H, J = 1.8 Hz), 7.55 (m, 2 H), 7.43 (m, 2 H), 6.74 (d, 1 H, J = 3.5 Hz), 6.53 (dd, 1 H, J_1 = 3.5 Hz, J_2 = 1.8 Hz), 4.01 (s, 2 H). IR ($CHCl_3$) ν_{max} 1695, 1630, 1590, 1470, 1390, 1325, 1300, 1260, 1155, 1100, 1070, 1020, 970, 960, 910, 890 cm^{-1}.

Isomerization of furylidentetralones - General procedure

2-Furyliden-α-tetralone (**5**, 1 g) was dissolved in acetonitrile (300 ml) in

the presence of benzophenone (100 mg). The solution was outgassed with nitrogen for 1 h and then irradiated in an immersion apparatus with a 500 W high-pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water jacket. At the end of the reaction (Table 1) the removal of the solvent under reduced pressure yielded a crude product that was chromatographed on silica gel (Eluents: **6a**, $CHCl_3$ - n-hexane 6:1; **6b**, benzene - Et_2O 9:1; **6c**, n-hexane - Et_2O 1:1; **6d**, n-hexane - AcOEt 3:1; **6e**, **6f**, $CHCl_3$ - n-hexane 3:2).

2-[3-oxo-1-(E)-propenyl]-4,5-dihydronaphtho[1,2-b]furan 6a. ^{1}H-NMR ($CDCl_3$,): 9.59 (d, 1 H, J = 8.0 Hz), 7.54 (d, 1 H, J = 6.6 Hz), 7.3 - 7.15 (m, 3 H), 7.17 (d, 1 H, J = 15.5 Hz), 6.69 (s, 1 H), 6.61 (dd, 1 H, J_1 = 15.5 Hz, J_2 = 8.0 Hz), 2.97 (t, 2 H, J = 7.8 Hz), 2.74 (t, 2 H, J = 7.8 Hz). ^{13}C-NMR ($CDCl_3$, δ): 193.45, 150.42, 138.17, 136.50, 128.73, 127.57, 127.5, 125.19, 124.8, 122.92, 120.94, 118.81, 28.87, 20.79. IR ($CHCl_3$) ν_{max} 1665, 1620, 1605, 1585, 1560, 1480, 1440, 1420, 1300, 1280, 1135, 1100, 1005, 985, 955, 900, 880 cm^{-1}. MS: m/z 225 (16), 224 (100), 223 (12), 206 (26), 205 (11), 196 (11), 195 (24), 183 (10), 181 (17), 178 (10), 170 (44), 169 (11), 167 (21), 166 (12), 165 (42), 153 (12), 152 (31), 141 (21), 139 (15), 128 (12), 118 (36), 115 (27), 90 (22), 89 (20), 83 (11), 82 (15), 81 (23), 77 (10), 63 (21).

2-[3-oxo-1-(E)-butenyl]-4,5-dihydronaphtho[1,2-b]furan 6b. ^{1}H-NMR ($CDCl_3$,): 7.54 (d, 1 H, J = 7.0 Hz), 7.34 (s, 2 H), 7.25 (d, 1 H, J = 15.7 Hz), 7.19 (m, 1 H), 6.67 (d, 1 H, J = 15.7 Hz), 6.60 (s, 1 H), 2.96 (t, 2 H, J = 7.8 Hz), 2.73 (t, 2 H, J = 7.8 Hz), 2.33 (s, 3 H). IR ($CHCl_3$) ν_{max} 1665, 1625, 1605, 1585, 1565, 1485, 1450, 1425, 1360, 1305, 1255, 1170, 1125, 1090, 1000, 970, 910, 885 cm^{-1}. MS: m/z 238 (M^+).

2-[3-oxo-1-(E)-propenyl]-4,5-dihydro-7-methoxy-naphtho[1,2-b]furan 6c. ^{1}H-NMR ($CDCl_3$, δ): 9.57 (d, 1 H, J = 8.0 Hz), 7.48 (d, 1 H, J = 7.7 Hz), 7.15 (d, 1 H, J = 15.6 Hz), 6.78 (d, 1 H, J = 7.7 Hz), 6.76 (s, 1 H), 6.68 (s, 1 H), 6.57 (dd, 1 H, J_1 = 15.6 Hz, J_2 = 8.0 Hz), 3.81 (s, 3 H), 2.94 (t, 2 H, J = 7.6 Hz), 2.72 (t, 2 H, J = 7.6 Hz). IR ($CHCl_3$) ν_{max} 2720, 1670, 1630, 1615, 1560, 1485, 1430, 1335, 1315, 1285, 1145, 1110, 1050, 1010, 960, 905, 870, 860 cm^{-1}. MS: m/z 254 (M^+).

2-[3-oxo-1-(E)-butenyl]-4,5-dihydro-7-methoxy-naphtho[1,2-b]furan 6d. ^{1}H-NMR ($CDCl_3$, δ): 7.47 (d, 1 H, J = 8.8 Hz). 7.23 (d, 1 H, J = 15.8 Hz), 6.77 (dd, 1 H, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 6.75 (s, 1 H), 6.62 (d, 1 H, J = 15.8 Hz), 6.58 (s, 1 H), 3.80 (s, 3 H), 2.93 (t, 2 H, J = 7.8 Hz), 2.70 (t, 2 H, J = 7.8 Hz), 2.31 (s, 3 H). IR ($CHCl_3$) ν_{max} 1665, 1605, 1595, 1560, 1490, 1470, 1450, 1430, 1360, 1280, 1250, 1155, 1125, 1100, 1040, 1000, 970, 910, 870, 855 cm^{-1}. MS: m/z 268 (M^+).

2-[2-carbomethoxy-1-(Z)-ethenyl]-4,5-dihydronaphtho[1,2-b]furan 6e. ^{1}H-NMR ($CDCl_3$, δ): 7.76 (s, 1 H), 7.50 (d, 1 H, J = 6.6 Hz), 7.22 (d, 1 H, J = 6.6 Hz), 7.17 (s, 2 H), 6.84 (d, 1 H, J = 12.8 Hz), 5.69 (d, 1 H, J = 12.8 Hz), 3.76 (s, 3 H), 2.96 (t, 2 H, J = 7.7 Hz), 2.75 (t, 2 H, J = 7.7 Hz). IR ($CHCl_3$) ν_{max} 1715, 1640, 1630, 1615, 1595, 1490, 1440, 1420, 1340, 1310, 1270, 1170, 1120, 1095, 1010, 970, 920, 890, 860 cm^{-1}. MS: m/z 254 (M^+).

2-[2-carbomethoxy-1-(E)-ethenyl]-4,5-dihydronaphtho[1,2-b]furan 6f. ^{1}H-NMR ($CDCl_3$, δ): 7.78 (d, 1 H, J = 7.7 Hz), 7.49 (m, 2 H), 7.40 (d, 1 H, J = 15.6 Hz), 7.24 (m, 1 H), 6.53 (s, 1 H), 6.35 (d, 1 H, J =15.6 Hz), 3.77 (s, 3 H), 2.95 (t, 2 H, J = 8.0 Hz), 2.71 (t, 2 H, J = 8.0 Hz). IR ($CHCl_3$) ν_{max} 1705, 1640, 1620, 1595, 1490, 1440, 1300, 1270, 1170, 1130, 1090, 975, 910, 890, 860 cm^{-1}. MS m/z 254 (M^+).

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