

Article

Cyclization of Hydrazones of 2-Acetyl-1-naphthol and 1-Acetyl-2-naphthol with Triphosgene. Synthesis of Spiro Naphthoxazine Dimers

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Abstract: Cyclization of hydrazones derived from 2-acetyl-1-naphthol and 1-acetyl-2-naphthol with triphosgene gave naphtho[1,2-e]-1,3-oxazines, naphtho[2,1-e]-1,3-oxazines or their spiro dimers depending on the molar ratio of triphosgene used for the cyclization.

Keywords: 2-acetyl-1-naphthol; 1-acetyl-2-naphthol; triphosgene; naphthoxazine, spiro naphthoxazine

Introduction

Triphosgene (bis(trichloromethyl)carbonate) has been repeatedly used in the literature for the construction of a variety of heterocyclic systems. It holds an advantage over other similar reagents, such as phosgene and diphosgene, of being a safe and easy to handle solid. Examples of important heterocyclic systems prepared using this reagent include benzothiadiazepines [1], quinazolines [2], diazolidines [3], imidiazolidines [4] and azetidines [5]. We have recently reported the use of triphosgene in the cyclization of hydrazones and Schiff bases of 2-hydroxy- and 2-aminoacetophenones to give 1,3-benzoxazines [6,7], spiro 1,3-benzoxazine dimmers [8], quinazolines and spiro quinazoline dimers [9].

We would like to report here results obtained from the cyclization of hydrazones of 2-acetyl-1-naphthol and 1-acetyl-2-naphthol with triphosgene.

Results and Discussion

Hydrazones of 2-acetyl-1-naphthol and 1-acetyl-2-naphthol were obtained in very good yields from the reaction of these compounds with aromatic hydrazines (Scheme 1, Table 1).

Scheme 1. Synthesis of hydrazones of 2-acetyl-1-naphthol and 1-acetyl-2-naphthol.

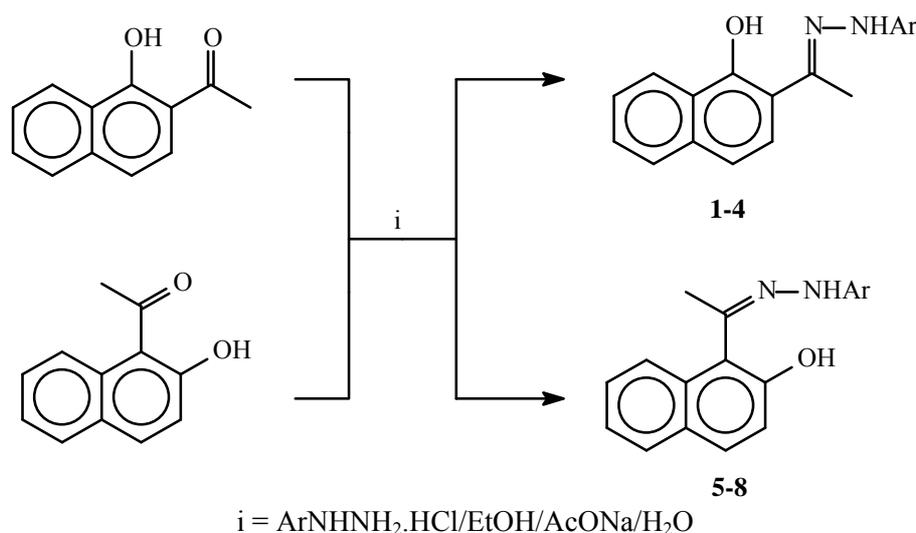


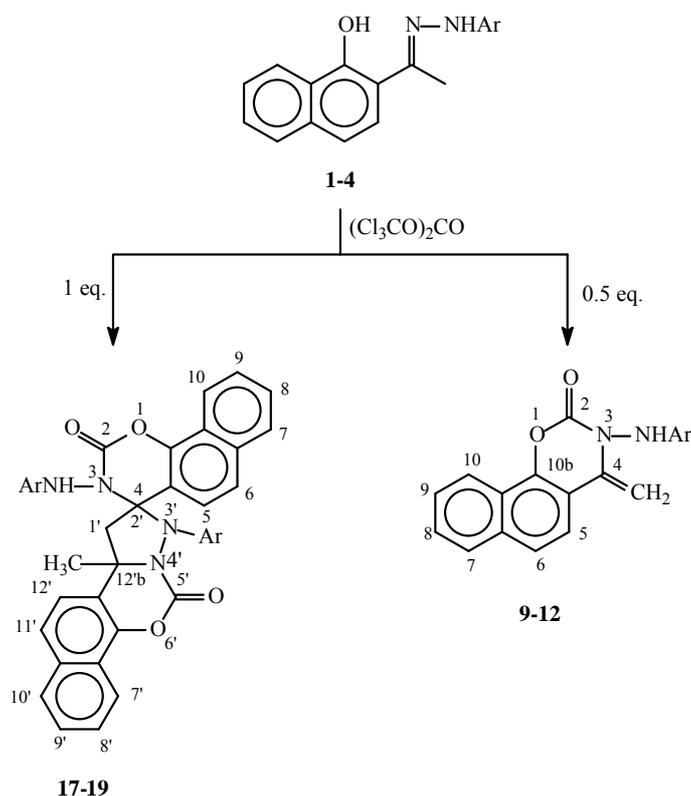
Table 1. Hydrazones **1-8**.

Compound	Ar	Yield (%)
1	Phenyl	92
2	4-ClC ₆ H ₄	82
3	4-BrC ₆ H ₄	79
4	4-CH ₃ C ₆ H ₄	91
5	Phenyl	75
6	4-ClC ₆ H ₄	80
7	4-BrC ₆ H ₄	68
8	4-CH ₃ C ₆ H ₄	68

The hydrazones **1-8** show in their IR spectra absorbances for the C=N group in the 1,614-1,636 cm⁻¹ range and for the OH and NH groups at about 3,400 cm⁻¹ and 3,350 cm⁻¹, respectively. The ¹H-NMR spectra of compounds **1-8** show in each case two distinct doublets which have been assigned to the H₃ and H₄ positions. In the spectra of **1-4** these two doublets appear at δ 7.04-7.16 and δ 7.68-7.76. The lower field signal in this case was assigned to H₃ as it is deshielded by the hydrazone moiety. In contrast, for compounds **5-8**, where the two doublets appear at δ 6.80-6.90 and δ 7.63-7.66 the signal at the higher field was assigned to H₃ as in this case this position is shielded by the OH group. It is also worth mentioning here that in the ¹³C-NMR spectra of the above compounds, the methyl group of the hydrazones of the 2-acetyl derivatives **1-4** absorbs at higher fields (δ 12.22-13.04)

than those of the 1-acetyl derivatives **5-8** (δ 18.29-18.55). The rest of the spectral data is shown in the Experimental section. Treatment of the hydrazones **1-8** with triphosgene gave the 4-methylenenaphthoxazines **9-16** or the spiro naphthoxazine dimers **17-20**, depending on the molar ratio of triphosgene used in the cyclizations (Schemes 2 and 3, Table 2).

Scheme 2. Reaction of hydrazones 1-4 with triphosgene.



Scheme 3. Reaction of hydrazones 5-8 with triphosgene.

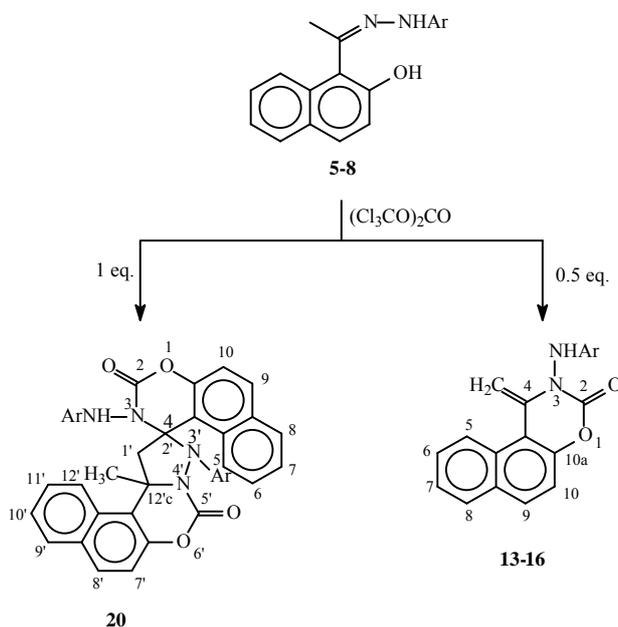


Table 2. 4-Methylenenaphthoxazines **9-16** and spiro naphthoxazine dimmers **17-20**.

Compound	Ar	Yield (%)
9	Phenyl	69
10	4-ClC ₆ H ₄	74
11	4-BrC ₆ H ₄	71
12	4-CH ₃ C ₆ H ₄	73
13	Phenyl	62
14	4-ClC ₆ H ₄	61
15	4-BrC ₆ H ₄	64
16	4-CH ₃ C ₆ H ₄	60
17	Phenyl	69
18	4-ClC ₆ H ₄	72
19	4-BrC ₆ H ₄	71
20	4-CH ₃ C ₆ H ₄	55

These results are in agreement with our previous reports on the reaction of hydrazones of 2-hydroxyacetophenones with triphosgene. It was observed then that the use of 0.5 equivalents of triphosgene gave the 4-methylene-1,3-benzoxazines, while the spiro 1,3-benzoxazine dimers were obtained when 1.0 equivalent of triphosgene was used [8]. The structures of those compounds were established based on X-ray crystal structure and spectroscopic studies [8,9]. As a result, we are showing here partial spectroscopic data for compounds **9-16** (Tables 3 and 4) and **17-20** (Table 5). In these tables, signals that can be easily attributed to structurally related positions, and with significance to the elucidation of the structures of the new compounds are shown for matter of comparison, while the complete data is given in the experimental section.

Table 3. Partial IR and NMR data for compounds **9-16**.

Compound	IR (cm ⁻¹)		¹ H-NMR (ppm)	
	C=O	=CH ₂	=CH ₂	Aromatic
9	1,727	1,620	5.02 (d, <i>J</i> = 2.2 Hz, 1H) 5.13 (d, <i>J</i> = 2.2 Hz, 1H)	6.80 (d, <i>J</i> = 8.1 Hz, 2H, H _{2,6,Ar}) 7.61 (d, <i>J</i> = 8.8 Hz, 1H, H ₆) 7.66 (d, <i>J</i> = 8.8 Hz, 1H, H ₅)
10	1,732	1,621	5.02 (d, <i>J</i> = 2.2 Hz, 1H) 5.09 (d, <i>J</i> = 2.2 Hz, 1H)	6.78 (d, <i>J</i> = 9.0 Hz, 2H, H _{2,6,Ar}) 7.23 (d, <i>J</i> = 9.0 Hz, 2H, H _{3,5,Ar}) 7.67 (d, <i>J</i> = 8.8 Hz, 1H, H ₅)
11	1,741	1,621	4.96 (d, <i>J</i> = 2.0 Hz, 1H) 5.01 (d, <i>J</i> = 2.0 Hz, 1H)	6.73 (d, <i>J</i> = 8.8 Hz, 2H, H _{2,6,Ar}) 7.24 (d, <i>J</i> = 8.8 Hz, 2H, H _{3,5,Ar})
12	1,737	1,612	4.92 (d, <i>J</i> = 2.0 Hz, 1H) 5.14 (d, <i>J</i> = 2.0 Hz, 1H)	6.71 (d, <i>J</i> = 8.1 Hz, 2H, H _{2,6,Ar}) 7.02 (d, <i>J</i> = 8.1 Hz, 2H, H _{3,5,Ar}) 7.84 (d, <i>J</i> = 8.8 Hz, 1H, H ₆) 7.91 (d, <i>J</i> = 8.8 Hz, 1H, H ₅)
13	1,725	1,620	5.04 (d, <i>J</i> = 2.2 Hz, 1H) 5.15 (d, <i>J</i> = 2.2 Hz, 1H)	6.97 (d, <i>J</i> = 8.8 Hz, 2H, H _{2,6,Ar}) 7.67 (d, <i>J</i> = 8.1 Hz, 1H, H ₉)

Table 3. Cont.

14	1,732	1,620	5.05 (d, $J = 1.5$ Hz, 1H)	6.84 (d, $J = 8.8$ Hz, 2H, H _{2,6,Ar})
			5.15 (d, $J = 1.5$ Hz, 1H)	7.23 (d, $J = 8.8$ Hz, 2H, H _{3,5,Ar})
				7.70 (d, $J = 8.1$ Hz, 1H, H ₉)
15	1,733	1,616	5.05 (d, $J = 2.2$ Hz, 1H)	6.90 (d, $J = 8.0$ Hz, 2H, H _{2,6,Ar})
			5.14 (d, $J = 2.2$ Hz, 1H)	7.29 (d, $J = 8.0$ Hz, 2H, H _{3,5,Ar})
16	1,741	1,615	5.04 (d, $J = 2.2$ Hz, 1H)	6.81 (d, $J = 8.8$ Hz, 2H, H _{2,6,Ar})
			5.14 (d, $J = 2.2$ Hz, 1H)	7.08 (d, $J = 8.8$ Hz, 2H, H _{3,5,Ar})
				7.66 (d, $J = 8.8$ Hz, 1H, H ₉)

Table 4. Partial ¹³C-NMR data for **9-16**.

	9	10	11	12	13	14	15	16
C _{1,Ar}	143.05	143.46	143.35	143.34	143.53	143.48	143.53	142.88
C _{2,6,Ar}	113.03	115.70	114.89	113.07	113.97	115.33	113.96	114.12
C _{3,5,Ar}	129.30	132.33	131.99	130.03	129.45	129.44	129.47	129.96
C ₂	148.05	147.99	147.35	147.21	148.07	148.01	148.08	148.10
C ₄	138.69	138.26	138.54	138.99	138.46	138.30	138.45	138.48
=CH ₂	88.60	88.55	88.58	88.97	88.53	88.53	88.54	88.50
C ₅ (C ₁₀)	122.93	121.48	121.52	121.50	(120.33)	(120.25)	(120.33)	(120.34)
C ₆ (C ₉)	120.69	120.24	120.73	121.05	(128.12)	(128.23)	(128.13)	(128.10)
C _{10b} (C _{10a})	146.16	144.45	145.60	144.14	(145.29)	(143.95)	(145.29)	(143.53)
C ₂	148.05	147.99	147.35	147.21	148.07	148.01	148.08	148.10

Table 5. Partial ¹H and ¹³C-NMR data for the spiro compounds **17-20**.

	¹ H		¹³ C				
	CH ₃	C _{1'}	CH ₃	C _{1'}	C _{2'}	C _{12'b}	C=O
17	2.12	3.58 (d, $J = 14.70$ Hz, 1H)	32.15	59.65	85.55	66.06	149.24
		3.69 (d, $J = 14.70$ Hz, 1H)					149.90
18	2.10	3.49 (d, $J = 14.70$ Hz, 1H)	32.08	60.07	85.47	66.05	149.01
		3.60 (d, $J = 14.70$ Hz, 1H)					149.07
19	2.09	3.44 (d, $J = 14.70$ Hz, 1H)	32.04	60.11	85.41	65.96	148.95
		3.54 (d, $J = 14.70$ Hz, 1H)					149.15
20	2.51	3.41 (d, $J = 14.65$ Hz, 1H)	17.20	27.87	97.68	(88.06)*	148.60
		3.54 (d, $J = 14.65$ Hz, 1H)					149.01

*(C_{12'c}).

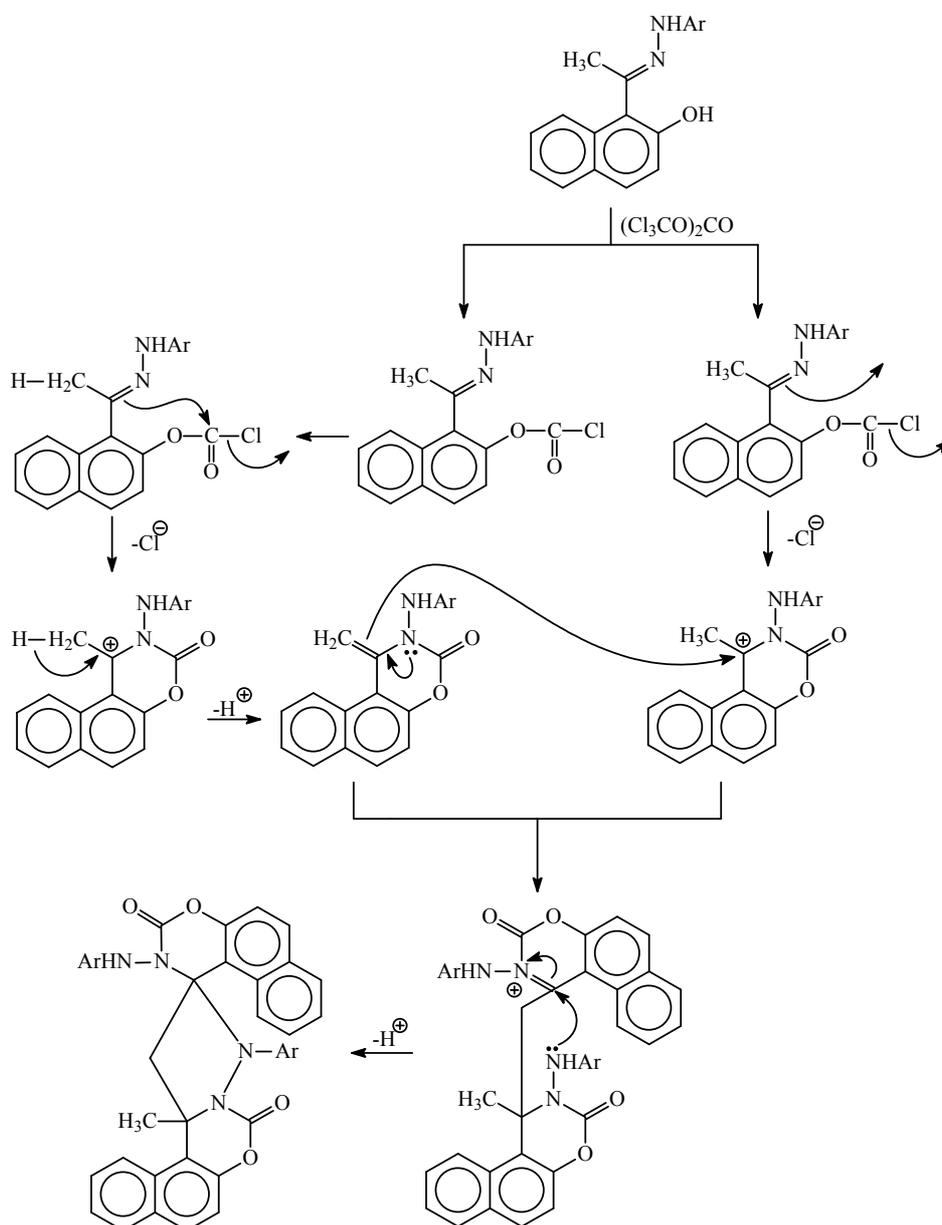
It can be seen from Table 3 that there is a noticeable difference in the ¹³C-NMR spectra of **17-19** compared with **20**. In the latter compound the CH₃ group and position C_{1'} absorb at higher fields than those in **17-19**, while positions C_{2'} and C_{12'c} absorb at lower fields than positions C_{2'} and C_{12'b} in **17-19**. This might be speculated as a result of the orientation of the aromatic rings in respect to these positions, which needs further studies. In addition, the above results for compounds **17-19** are in close

resemblance to these reported for the spiro 1,3-benzoxazine dimmers which might suggest that they have similar steric environment for the 1,3-benzoxazines[8].

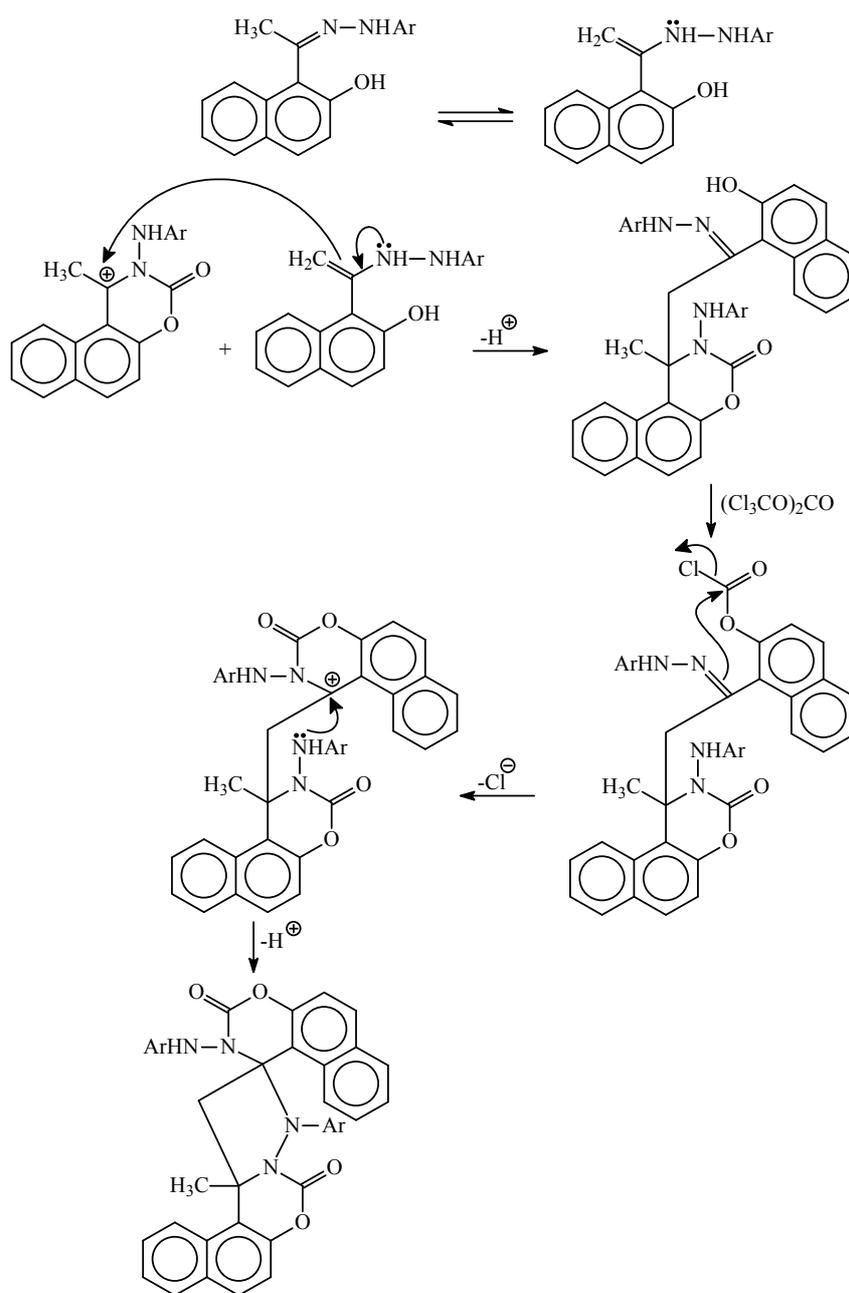
The EIMS spectra of the spiro compounds **17-20** did not show the expected molecular ions. They appear to fragment at the spiro junction to give fragments at $m/z = M^+ - \text{ArN}_2\text{CO}$ and $m/z = M^+ - \text{ArN}_2\text{CO}_2$. For example, compound **18** shows in its EIMS spectra fragment peaks at m/z 505 and 489, arising from the loss of $\text{ClC}_6\text{H}_4\text{N}_2\text{CO}$ and $\text{ClC}_6\text{H}_4\text{N}_2\text{CO}_2$, respectively. This type of fragmentation was previously observed with analogous spiro compounds[8,9].

Finally, it is worth mentioning here that although the formation of the 4-methylene-naphthoxazines **9-16** would be expected to proceed via a similar reaction mechanism to that previously reported for the cyclization of hydrazones of 2-hydroxyacetophenone and acetophenone [6,10], the mechanism for formation of the spiro naphthoxazine dimmers is not clear to us with regards to at what stage does the dimerization occurs to form the final spiro naphthoxazines.

Scheme 4. Proposed mechanism for the formation of the spiro compounds **17-20**.



Scheme 4. Cont.



The use of 1.0 equivalents of triphosgene is necessary to form the latter products because in its reactions it gives an equivalent of three moles of phosgene (COCl_2), so the formation of naphthoxazines (where one CO group is introduced) would require only 0.5 equivalent of triphosgene (1.5 equivalent of COCl_2 , a slight excess is usually used in these kinds of cyclizations) while the spiro dimers (where two CO groups are introduced) would require double this amount. In Scheme 4, a speculative mechanism for the formation of the spiro products is shown with two pathways; in the first one the dimerization occurs after the formation of the two naphthoxazine nuclei, while in the second one the dimerization takes place before the formation of the second naphthoxazine ring.

Experimental

Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer as KBr pellets and expressed as ν in cm^{-1} . NMR spectra were recorded on JEOL ECP 400 (400 MHz) in CDCl_3 and chemical shifts are expressed as δ in ppm. MS spectra were recorded on Shimadzu QP 5050A GC/MS system.

2-Acetyl-1-naphthol phenylhydrazone (1): To a solution of 2-acetyl-1-naphthol (2.0 g, 10.8 mmol) in ethanol (50 mL) was added a solution of phenylhydrazine hydrochloride (1.9 g, 12.9 mmol) and sodium acetate (1.0 g, 12.2 mmol) in a mixture of ethanol (30 mL) and water (10 mL). The above solution was refluxed for 5 hours and then evaporated under vacuum. The resulting solid was washed with water (50 mL) and then recrystallized from ethanol-chloroform (8:2). Yield 92%, red solid, mp 162°C ; IR: 3,410 (OH), 3,334 (NH), 1,620 (C=N); $^1\text{H-NMR}$: 1.81 (s, 3H), 6.17 (t, $J = 7.3$ Hz, 1H), 6.46 (d, $J = 7.7$ Hz, 2H), 6.62 (m, 3H), 6.77 (m, 2H), 6.88 (d, $J = 8.8$ Hz, 1H), 7.06 (m, 1H), 7.64 (m, 1H); $^{13}\text{C-NMR}$: 13.04, 112.42, 114.49, 117.42, 119.49, 122.49, 123.58, 124.66, 126.51, 126.75, 128.60, 128.84, 133.41, 144.69, 148.03, 154.09; MS: m/z (%) 276 (M^+ , 100), 261 (7), 260 (18), 295 (38), 230 (6), 183 (25), 168 (6), 141 (13), 128 (10), 115 (49), 77 (8); Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}$: C, 78.23; H, 5.83; N, 10.13. Found: C, 77.96; H, 5.71; N, 10.28.

2-Acetyl-1-naphthol 4-chlorophenylhydrazone (2): This compound was prepared from 2-acetyl-1-naphthol and 4-chlorophenylhydrazine using the procedure described for **1**. Yield, 82%, brownish solid, mp 175°C ; IR: 3,420 (OH), 3,331 (NH), 1,636 (C=N); $^1\text{H-NMR}$: 2.38 (s, 3H), 6.98 (d, $J = 8.8$ Hz, 2H), 7.26 (d, $J = 8.8$ Hz, 2H), 7.32 (m, 2H), 7.49 (m, 2H), 7.73 (m, 1H), 8.40 (m, 1H); $^{13}\text{C-NMR}$: 12.28, 112.67, 114.27, 118.24, 123.22, 123.51, 125.37, 125.67, 127.15, 127.34, 129.49, 134.28, 142.68, 149.27, 155.67; MS: m/z (%) 312 ($\text{M}+2$, 21), 310 (M^+ , 65), 296 (5), 294 (10), 293 (51), 258 (17), 184 (30), 183 (41), 169 (10), 168 (9), 143 (22), 141 (25), 134 (45), 127 (100), 114 (37), 76 (6); Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{ClN}_2\text{O}$: C, 69.56; H, 4.86; N, 9.01. Found: C, 69.72; H, 4.77; N, 8.88.

2-Acetyl-1-naphthol 4-bromophenylhydrazone (3): This compound was prepared from 2-acetyl-1-naphthol and 4-bromophenylhydrazine using the procedure described for **1**. Yield, 79%, brownish solid, mp 182°C ; IR: 3,412 (OH), 3,348 (NH), 1,632 (C=N); $^1\text{H-NMR}$: 2.40 (s, 3H), 6.94 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.8$ Hz, 1H), 7.41 (d, $J = 8.8$ Hz, 1H), 7.48 (d, $J = 8.1$ Hz, 2H), 7.53 (m, 2H), 7.74 (m, 1H), 8.41 (m, 1H); $^{13}\text{C-NMR}$: 12.29, 112.92, 113.20, 118.20, 121.12, 123.32, 123.63, 125.33, 125.38, 127.23, 127.30, 129.70, 134.27, 144.11, 148.52, 155.12; MS: m/z (%) 356 ($\text{M}+2$, 70), 354 (M^+ , 71), 340 (11), 339 (54), 338 (12), 337 (49), 258 (21), 185 (15), 183 (56), 173 (63), 156 (10), 128 (18), 115 (100), 91 (35), 76 (6); Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{BrN}_2\text{O}$: C, 60.86; H, 4.25; N, 7.88. Found: C, 60.67; H, 4.15; N, 7.75.

2-Acetyl-1-naphthol 4-methylphenylhydrazone (4): This compound was prepared from 2-acetyl-1-naphthol and 4-methylphenylhydrazine using the procedure described for **1**. Yield, 91% brownish solid, mp 164°C ; IR: 3,424 (OH), 3,350 (NH), 1,614 (C=N); $^1\text{H-NMR}$: 2.01 (s, 3H), 2.19 (s, 3H), 6.76 (d, $J = 8.1$ Hz, 2H), 6.80 (d, $J = 8.1$ Hz, 2H), 7.02 (m, 1H), 7.17 (m, 2H), 7.24 (m, 1H), 7.45 (m, 1H), 8.06 (m, 1H); $^{13}\text{C-NMR}$: 12.22, 20.73, 113.03, 113.31, 118.13, 118.42, 123.31, 123.62, 125.01,

125.32, 127.22, 127.49, 130.15, 134.21, 141.96, 148.05, 155.06; MS: m/z (%) 290 (M^+ , 85), 275 (14), 273 (54), 185 (15), 168 (12), 128 (6), 115 (37), 107 (100), 93 (6), 76 (25); Anal. Calcd. for $C_{19}H_{18}N_2O$: C, 78.59; H, 7.95; N, 12.27. Found: C, 78.38; H, 7.85; N, 12.12.

1-Acetyl-2-naphthol phenylhydrazone (5): This compound was prepared from 1-acetyl-2-naphthol and phenylhydrazine hydrochloride using the procedure described for **1**. Yield, 75%, pale yellow solid, mp 125°C; IR: 3,418 (OH), 3,335 (NH), 1,617 (C=N); 1H -NMR: 2.49 (s, 3H), 6.93 (t, $J = 7.3$ Hz, 1H), 7.12 (d, $J = 7.3$ Hz, 2H), 7.21 (d, $J = 8.8$ Hz, 1H), 7.29 (d, $J = 7.3$ Hz, 2H), 7.33 (m, 1H), 7.44 (m, 1H), 7.79 (d, $J = 8.1$ Hz, 1H); ^{13}C -NMR: 18.41, 113.18, 116.32, 118.64, 121.13, 123.15, 124.52, 126.50, 128.97, 129.26, 129.63, 130.77, 131.66, 144.24, 144.76, 153.43; MS: m/z (%) 276 (M^+ , 69), 260 (21), 259 (100), 184 (22), 169 (6), 141 (9), 128 (7), 115 (28), 93 (33), 77 (9); Anal. Calcd. for $C_{18}H_{16}N_2O$: C, 78.23, H, 5.73, N, 10.13. Found: C, 78.11; H, 5.73, N, 10.08.

1-Acetyl-2-naphthol 4-chlorophenylhydrazone (6): This compound was prepared from 1-acetyl-2-naphthol and 4-chlorophenylhydrazine using the procedure described for **1**. Yield, 80%, pale yellow solid, mp 154°C; IR: 3,422 (OH), 3,355 (NH), 1,619 (C=N); 1H -NMR: 2.47 (s, 3H), 7.04 (d, $J = 9.2$ Hz, 2H), 7.21 (d, $J = 9.2$ Hz, 2H), 7.24 (d, $J = 8.8$, 1H), 7.33 (m, 1H), 7.44 (m, 1H), 7.66 (d, $J = 8.4$ Hz, 1H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.77 (d, $J = 7.7$ Hz, 1H); ^{13}C -NMR: 18.42, 114.36, 116.29, 118.57, 123.24, 124.44, 126.60, 129.00, 129.05, 129.30, 129.51, 130.94, 131.65, 142.93, 143.11, 153.30; MS: m/z (%) 312 ($M+2$, 21), 310 (M^+ , 62), 296 (7), 295 (34), 294 (23), 293 (100), 184 (45), 183 (18), 169 (16), 168 (9), 141 (24), 127 (74), 76 (6); Anal. Calcd. for $C_{18}H_{15}ClN_2O$: C, 69.56; H, 4.86; N, 9.01. Found: C, 69.42; H, 4.73; N, 9.12.

1-Acetyl-2-naphthol 4-bromophenylhydrazone (7): This compound was prepared from 1-acetyl-2-naphthol and 4-bromophenylhydrazine using the procedure described for **1**. Yield, 68%, yellow solid, mp 153°C; IR: 3,436 (OH), 3,354 (NH), 1,619 (C=N); 1H -NMR: 2.49 (s, 3H), 7.01 (d, $J = 8.8$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 1H), 7.34 (m, 1H), 7.39 (d, $J = 8.8$ Hz, 2H), 7.45 (m, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.73 (d, $J = 8.8$ Hz, 1H), 7.78 (d, $J = 8.4$ Hz, 1H); ^{13}C -NMR: 18.29, 112.86, 114.66, 116.23, 118.48, 123.14, 124.35, 126.49, 128.90, 129.20, 130.82, 131.54, 132.31, 143.29, 145.04, 153.19; MS: m/z (%) 356 ($M+2$, 71), 354 (M^+ , 75), 340 (19), 339 (97), 338 (22), 337 (100), 258 (8), 210 (17), 185 (12), 183 (27), 173 (44), 169 (67), 115 (87), 76 (7); Anal. Calcd. for $C_{18}H_{15}BrN_2O$: C, 60.86; H, 4.25; N, 7.88. Found: C, 60.73; H, 4.38; N, 7.93.

1-Acetyl-2-naphthol 4-methylphenylhydrazone (8): This compound was prepared from 1-acetyl-2-naphthol and 4-methylphenylhydrazine using the procedure described for **1**. Yield, 68%, yellow solid, mp 132 °C; IR: 3,417 (OH), 3,360 (NH), 1,618 (C=N); 1H -NMR: 2.29 (s, 3H), 2.49 (s, 3H), 7.02 (d, $J = 8.1$ Hz, 2H), 7.09 (d, $J = 8.1$ Hz, 2H), 7.21 (d, $J = 8.8$ Hz, 1H), 7.32 (m, 1H), 7.44 (m, 1H), 7.68 (d, $J = 8.1$ Hz, 1H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.78 (d, $J = 7.3$ Hz, 1H); ^{13}C -NMR: 18.55, 20.69, 113.38, 116.22, 118.66, 123.15, 124.51, 126.51, 128.96, 129.24, 130.09, 130.62, 130.81, 131.65, 142.05, 143.11, 153.54; MS: m/z (%) 290 (M^+ , 89), 273 (100), 184 (30), 169 (7), 141 (11), 128 (8), 115 (35), 107 (57), 106 (36), 105 (46), 91 (6), 76 (25); Anal. Calcd. for $C_{19}H_{18}N_2O$: C, 78.59; H, 7.95; N, 12.27. Found: C, 78.41; H, 7.81; N, 12.18.

4-Methylene-3-(N-phenylamino)-3,4-dihydro-2H-naphth[2,1-e]-1,3-oxazine-2-one (**9**): To a stirred solution of 0.20 g (0.72 mmol) of **1** and triethylamine (1 mL) in dichloromethane (30 mL) was added dropwise under N₂ atmosphere a solution of 0.5 equivalent (0.12 g, 0.36 mmol) of triphosgene in dichloromethane (10 mL). The mixture was refluxed for 4 hours and then washed with water. The organic layer was dried over magnesium sulfate and evaporated under vacuum. The resulting solid was recrystallized from a mixture of benzene-ethanol (1:1). Yield, 69%, colorless solid, mp 196°C; IR: 3,306 (NH), 1,727 (C=O), 1,620 (=CH₂); ¹H-NMR: 5.02 (d, *J* = 2.2 Hz, 1H), 5.13 (d, *J* = 2.2 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 2H), 7.02 (m, 3H), 7.55 (m, 2H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.83 (m, 1H), 8.20 (m, 1H), 8.33 (bs, 1H); ¹³C-NMR: 88.60, 111.50, 113.03, 120.69, 121.57, 122.93, 125.18, 127.46, 127.89, 128.12, 128.60, 129.30, 134.57, 138.69, 143.05, 146.16, 148.05; MS: *m/z* (%) 302 (M⁺, 13), 260 (25), 259 (100), 232 (11), 230 (23), 182 (18), 168 (11), 140 (9), 139 (17), 128 (25), 92 (13), 77 (9); Anal. Calcd. for C₁₉H₁₄N₂O₂: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.13; H, 4.50; N, 9.63.

4-Methylene-3-[N-(4-chlorophenyl)amino]-3,4-dihydro-2H-naphth[2,1-e]-1,3-oxazine-2-one (**10**): Prepared from **2** and triphosgene using the procedure described for **9**. Yield, 74%, pale yellow solid, mp 182°C; IR: 3,260 (NH), 1,732 (C=O), 1,621 (=CH₂); ¹H-NMR: 5.02 (d, *J* = 2.2 Hz, 1H), 5.09 (d, *J* = 2.2 Hz, 1H), 6.57 (bs, 1H), 6.78 (d, *J* = 9.0 Hz, 2H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.59 (m, 3H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.85 (m, 1H), 8.30 (m, 1H); ¹³C-NMR: 88.55, 111.09, 114.46, 115.70, 120.24, 121.48, 123.03, 125.36, 127.53, 127.70, 128.22, 132.33, 134.68, 138.26, 143.46, 144.45, 147.99; MS: *m/z* (%) 338 (M+2, 6), 336 (M⁺, 17), 301 (24), 296 (9), 295 (32), 294 (23), 293 (91), 259 (28), 258 (100), 230 (17), 182 (53), 140 (18), 128 (74), 115 (21), 98 (31), 76 (10); Anal. Calcd. for C₁₉H₁₃Cl N₂O₂: C, 67.76; H, 3.89; N, 8.31. Found: C, 67.47; H, 3.71; N, 8.19.

4-Methylene-3-[N-(4-bromophenyl)amino]-3,4-dihydro-2H-naphth[2,1-e]-1,3-oxazine-2-one (**11**): Obtained from **3** and triphosgene using the procedure described for **9**. Yield, 71%, brownish solid, mp 185°C; IR: 3,281 (NH), 1,741 (C=O), 1,621 (=CH₂); ¹H-NMR: 4.96 (d, *J* = 2.0 Hz, 1H), 5.01 (d, *J* = 2.0 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.54 (m, 4H), 7.83 (m, 1H), 8.17 (m, 1H), 8.69 (bs, 1H); ¹³C-NMR: 88.58, 111.33, 112.06, 114.89, 120.73, 121.52, 122.88, 125.27, 127.53, 127.95, 128.21, 131.99, 134.59, 138.54, 143.35, 145.60, 147.35; MS: *m/z* (%) 382 (M+2, 12), 380 (M⁺, 13), 354 (12), 340 (16), 339 (74), 337 (72), 301 (44), 259 (36), 258 (100), 230 (26), 182 (58), 128 (74), 115 (33), 91 (43), 76 (11); Anal. Calcd. for C₁₉H₁₃BrN₂O₂: C, 59.86; H, 3.43; N, 7.34. Found: C, 59.73; H, 3.33; N, 7.43.

4-Methylene-3-[N-(4-methylphenyl)amino]-3,4-dihydro-2H-naphth[2,1-e]-1,3-oxazine-2-one (**12**): Obtained from **4** and triphosgene using the procedure described for **9**. Yield, 73%, brownish solid, mp 150°C; IR: 3,260 (NH), 1,737 (C=O), 1,612 (=CH₂); ¹H-NMR: 2.19 (s, 3H), 4.92 (d, *J* = 2.0 Hz, 1H), 5.14 (d, *J* = 2.0 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 7.69 (m, 2H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 8.04 (m, 1H), 8.17 (m, 1H), 8.67 (bs, 1H); ¹³C-NMR: 20.72, 88.97, 111.70, 113.07, 121.50, 122.80, 125.43, 128.10, 128.43, 128.62, 129.14, 130.03, 134.66, 138.99, 143.34, 144.14, 147.21; MS: *m/z* (%) 316 (M⁺, 24), 274 (20), 273 (100), 244

(10), 182 (13), 128 (23), 105 (61), 76 (31); Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.85. Found: C, 75.81; H, 5.15; N, 8.77.

4-Methylene-3-(N-phenylamino)-3,4-dihydro-2H-naphth[1,2-e]-1,3-oxazine-2-one (**13**): Obtained from **5** and triphosgene using the procedure described for **9**. Yield, 62%, colorless solid, mp 166 °C; IR: 3,297 (NH), 1,725 (C=O), 1,620 (=CH₂); ¹H-NMR: 5.04 (d, *J* = 2.2 Hz, 1H), 5.15 (d, *J* = 2.2 Hz, 1H), 6.53 (bs, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.25 (m, 3H), 7.58 (m, 3H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.84 (m, 1H), 8.32 (m, 1H); ¹³C-NMR: 88.53, 111.24, 113.97, 120.33, 121.90, 122.27, 123.10, 125.23, 127.44, 127.67, 128.12, 129.45, 134.66, 138.46, 143.53, 145.29, 148.07; MS: *m/z* (%) 302 (M⁺, 7), 258 (100), 182 (16), 128 (5), 115 (7), 92 (5), 77 (6); Anal. Calcd. for $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.24; H, 4.71; N, 9.18.

4-Methylene-3-[N-(4-chlorophenyl)amino]-3,4-dihydro-2H-naphth[1,2-e]-1,3-oxazine-2-one (**14**): Obtained from **6** and triphosgene using the procedure described for **9**. Yield, 61%, brownish solid, mp 187°C; IR: 3,260 (NH), 1,732 (C=O), 1,620 (=CH₂); ¹H-NMR: 5.05 (d, *J* = 1.5 Hz, 1H), 5.15 (d, *J* = 1.5 Hz, 1H), 6.52 (bs, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.51 (m, 3H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.86 (m, 1H), 8.31 (m, 1H); ¹³C-NMR: 88.53, 111.10, 115.33, 120.25, 121.87, 123.04, 125.37, 127.22, 127.54, 127.71, 128.23, 129.44, 134.69, 138.30, 143.48, 143.95, 148.01; MS: *m/z* (%) 338 (M+2, 5), 336 (M⁺, 14), 301 (24), 295 (29), 259 (29), 258 (100), 230 (14), 182 (60), 128 (68), 115 (21), 99 (36), 76 (9); Anal. Calcd. for $C_{19}H_{13}ClN_2O_2$: C, 67.76; H, 3.89; N, 8.32. Found: C, 67.59; H, 3.95; N, 8.25.

4-Methylene-3-[N-(4-bromophenyl)amino]-3,4-dihydro-2H-naphth[1,2-e]-1,3-oxazine-2-one (**15**): Obtained from **7** and triphosgene using the procedure described for **9**. Yield, 64%, colorless solid, mp 203°C; IR: 3,353 (NH), 1,733 (C=O), 1,616 (=CH₂); ¹H-NMR: 5.05 (d, *J* = 2.2 Hz, 1H), 5.14 (d, *J* = 2.2 Hz, 1H), 6.53 (bs, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.60 (m, 3H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.82 (m, 1H), 8.12 (m, 1H); ¹³C-NMR: 88.54, 111.24, 113.96, 116.78, 120.33, 121.90, 125.24, 127.16, 127.45, 127.68, 128.13, 129.47, 134.66, 138.45, 143.53, 145.29, 148.08; MS: *m/z* (%) 382 (M+2, 18), 380 (M⁺, 16), 301 (35), 259 (30), 258 (100), 230 (35), 210 (18), 184 (49), 182 (48), 139 (45), 126 (69), 115 (72), 101 (35), 76 (19); Anal. Calcd. for $C_{19}H_{13}BrN_2O_2$: C, 59.86; H, 3.44; N, 7.35. Found: C, 59.98; H, 3.18; N, 7.12.

4-Methylene-3-[N-(4-methylphenyl)amino]-3,4-dihydro-2H-naphth[1,2-e]-1,3-oxazine-2-one (**16**): Obtained from **8** and triphosgene using the procedure described for **9**. Yield 60%, yellowish solid, mp 160°C; IR: 3,245 (NH), 1,741 (C=O), 1,615 (=CH₂); ¹H-NMR: 2.26 (s, 3H), 5.04 (d, *J* = 2.20 Hz, 1H), 5.14 (d, *J* = 2.20 Hz, 1H), 6.47 (bs, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.58 (m, 3H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.85 (m, 1H), 8.32 (m, 1H); ¹³C-NMR: 20.71, 88.50, 111.28, 114.12, 120.34, 121.91, 123.10, 125.19, 127.43, 127.67, 128.10, 129.96, 131.73, 134.63, 138.48, 142.88, 143.53, 148.10; MS: *m/z* (%) 316 (M⁺, 13), 274 (17), 273 (100), 182 (11), 139 (15), 128 (20), 106 (52), 76 (36); Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.85. Found: C, 75.75; H, 5.22; N, 8.73.

3'-Phenyl-3-(phenylamino)-1',12'-b-dihydro-12'-b-methylspiro{4H-naphth[2,1-e]-1,3-oxazine-4,2'-(3'H)-[5H]pyrazolo[1,5-c]naphth[2,1-e]-1,3-oxazine}-2,5'-dione (**17**): Obtained from **1** and one equivalent of triphosgene using the procedure described for **9**. Yield 69%, reddish solid, mp 207 °C; IR: 3,256 (NH), 1,748, 1,755 (2C=O); ¹H-NMR: 2.12 (s, 3H), 3.58 (d, *J* = 14.70 Hz, 1H), 3.65 (d, *J* = 14.70 Hz, 1H), 6.72 (m, 4H), 6.97 (m, 4H), 7.11 (m, 5H), 7.58 (m, 5H), 7.91 (m, 2H), 8.40 (m, 2H); ¹³C-NMR: 32.15, 59.65, 66.06, 85.55, 112.48, 112.93, 113.91, 116.47, 116.80, 119.92, 120.36, 121.68, 122.19, 122.23, 124.96, 125.49, 127.55, 127.68, 128.81, 129.19, 133.56, 133.86, 134.09, 141.92, 142.46, 142.78, 143.18, 145.29, 145.42, 145.69, 149.24, 149.90; MS: m/z (%) 471 (M⁺ - C₆H₅N₂CO, 20), 455 (M⁺ - C₆H₅N₂CO₂, 14), 440 (57), 423 (28), 351 (12), 302 (21), 259 (100), 258 (17), 230 (34), 185 (29), 168 (39), 128 (21), 115 (38), 93 (70), 77 (51), 63 (35); Anal. Calcd. for C₃₈H₂₈N₄O₄: C, 75.48; H, 4.66; N, 9.26. Found: C, 75.21; H, 4.71; N, 9.19.

3'-(4-Chlorophenyl)-3-[(4-chlorophenyl)amino]-1',12'-b-dihydro-12'-b-methylspiro{4H-naphth[1,2-e]-1,3-oxazine-4,2'-(3'H)-[5H]pyrazolo[1,5-c]naphth[2,1-e]-1,3-oxazine}-2,5'-dione (**18**): This compound was obtained from **2** and one equivalent of triphosgene using the procedure described for **9**. Yield, 72%, mp 267°C; IR: 3,219 (NH), 1,724, 1,753 (2C=O); ¹H-NMR: 2.10 (s, 3H), 3.49 (d, *J* = 14.70 Hz, 1H), 3.60 (d, *J* = 14.70 Hz, 1H), 6.35 (m, 3H), 6.65 (m, 4H), 6.93 (m, 4H), 7.66 (m, 5H), 7.82 (m, 2H), 8.40 (m, 2H); ¹³C-NMR: 32.08, 60.07, 66.05, 85.47, 111.88, 114.22, 117.91, 119.62, 121.02, 121.54, 122.16, 122.56, 123.11, 125.25, 125.57, 126.45, 127.18, 127.40, 127.47, 127.66, 127.78, 127.93, 128.81, 128.84, 128.91, 133.47, 134.31, 141.39, 141.81, 143.90, 145.61, 149.61, 149.01, 149.07; MS: m/z (%) 505 (M⁺ - ClC₆H₄N₂CO, 22), 489 (M⁺ - ClC₆H₄N₂CO₂, 100), 410 (7), 336 (13), 295 (12), 259 (21), 230 (10), 168 (26), 139 (24), 127 (28), 115 (21), 99 (9), 90 (5), 76 (15), 63 (12); Anal. Calcd. for C₃₈H₂₆Cl₂N₄O₄: C, 67.76; H, 3.89; N, 8.32. Found: C, 67.46; H, 3.68; N, 8.54.

3'-(4-Bromophenyl)-3-[(4-bromophenyl)amino]-1',12'-b-dihydro-12'-b-methylspiro{4H-naphth[2,1-e]-1,3-oxazine-4,2'-(3'H)-[5H]pyrazolo[1,5-e]naphth[2,1-e]-1,3-oxazine}-2,5'-dione (**19**): Obtained from **3** and one equivalent of triphosgene using the procedure described for **9**. Yield, 71%, mp 246 °C; IR: 3,232 (NH), 1,730, 1,745 (2C=O); ¹H-NMR: 2.09 (s, 3H), 3.44 (d, *J* = 14.70 Hz, 1H), 3.54 (d, *J* = 14.70 Hz, 1H), 6.28 (m, 3H), 6.60 (m, 3H), 6.85 (m, 2H), 7.04 (m, 2H), 7.52 (m, 6H), 7.78 (m, 2H), 8.34 (m, 2H); ¹³C-NMR: 32.04, 60.11, 65.96, 85.41, 111.75, 113.97, 114.67, 115.87, 117.98, 118.21, 119.56, 121.00, 121.53, 122.16, 122.55, 123.11, 125.31, 127.42, 127.48, 127.69, 127.79, 127.95, 128.94, 131.70, 131.74, 132.05, 133.66, 134.31, 141.78, 141.88, 144.40, 148.95, 149.15; MS: m/z (%) 549 (M⁺ - BrC₆H₄N₂CO, 6), 533 (M⁺ - BrC₆H₄N₂CO₂, 100), 409 (15), 382 (20), 380 (17), 340 (24), 339 (85), 258 (86), 202 (24), 196 (51), 168 (74), 129 (59), 115 (84), 99 (51), 91 (49), 90 (52), 76 (71), 63 (84); Anal. Calcd. for C₃₈H₂₆Br₂N₄O₄: C, 59.86; H, 3.43; N, 7.34. Found: C, 59.73; H, 3.49; N, 7.42.

3'-(4-Chlorophenyl)-3-[(4-chlorophenyl)amino]-1',12'-b-dihydro-12'-b-methylspiro{4H-naphth[1,2-e]-1,3-oxazine-4,2'-(3'H)-[5H]pyrazolo[1,5-c]naphth[1,2-e]-1,3-oxazine}-2,5'-dione (**20**): Obtained from **6** and one equivalent of triphosgene using the procedure described for **9**. Yield, 55%; mp 227 °C; IR: 3,338 (NH), 1,730, 1,755 (2C=O); ¹H-NMR: 2.51 (s, 3H), 3.41 (d, *J* = 14.65 Hz, 1H),

3.54 (d, $J = 14.65$ Hz, 1H), 7.07 (m, 3H), 7.25 (m, 4H), 7.51 (m, 5H), 8.11 (m, 4H), 8.29 (m, 2H), 8.61 (m, 2H); $^{13}\text{C-NMR}$: 17.20, 27.87, 88.06, 97.68, 114.00, 114.31, 114.46, 115.89, 116.26, 120.55, 123.56, 124.20, 124.87, 125.67, 125.73, 127.89, 128.57, 128.72, 128.87, 128.93, 129.76, 131.21, 131.32, 131.66, 131.77, 131.80, 136.60, 138.88, 143.81, 144.17, 145.50, 147.04, 148.60, 149.01; MS: m/z (%) 505 (M^+ - $\text{ClC}_6\text{H}_4\text{N}_2\text{CO}$, 20), 489 (M^+ - $\text{ClC}_6\text{H}_4\text{N}_2\text{CO}_2$, 100), 410 (7), 336 (21), 319 (15), 295 (21), 293 (44), 258 (31), 230 (14), 139 (29), 127 (44), 115 (35), 75 (20), 63 (16); Anal. Calcd. for $\text{C}_{38}\text{H}_{26}\text{Cl}_2\text{N}_4\text{O}_4$: C, 67.76; H, 3.89; N, 8.32. Found: C, 67.53; H, 3.93; N, 8.46.

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Sample Availability: Samples of the compounds are available from the authors.