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Synthesis of Photochromic Spirooxazines from 1-Amino-2-Naphthols

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Abstract: A synthetic access to photochromic spirooxazines is developed through the condensation of methylene-substituted azaheterocycles on 1-amino-2-naphthols in presence of an oxidizing agent. Compared to usual preparation of this kind of compounds (*via* 1-nitroso-2-naphthols), yields are generally good and approaches to further spiroheterocyclic oxazines are possible.

Photochromism[1,2] has attracted much attention in the last decades due to a variety of practical applications[3]. In this field, spirooxazines[4] have undergone considerable development owing to good photochromic properties associated to high fatigue resistance.

By now the only known method to synthesize spironaphthoxazines consists in the condensation of a methylenic base (for instance 1,3,3-trimethyl-2-methyleneindoline, Fischer's base) with 1-nitroso-2-naphthols, although precursors for the latter can be of various origin (method A, scheme 1). The main problems encountered with this method are related to :

- The nitrosation reaction of 2-naphthols leading to satisfying yields only in a few cases despite numerous modifications brought;[5]

- Oximation reactions of 1,2-naphthoquinones[6] giving rise to loss of materials, especially due to the low stability of 1,2-naphthoquinones and the formation of two possible isomers (1-oximino-2-naphthoquinone et 2-oximino-1-naphthoquinone), the separation of which is difficult;[7]

- The condensation reaction itself leading generally to low yields of spirocompounds[4] even if optimization of experimental conditions (especially by solvent modifications) allowed to improve them in some cases.[6,8]

In 1988 Japanese researchers pointed out in a patent application the formation of spirooxazines through the reaction of 2-hydroxyiminomethyl-1,3,3-trimethylindoleninium perchlorate with 1-amino-2-naphthol hydrochloride in the presence of triethylamine[9] (method B, scheme 2). Although the mechanism of the reaction was not described, the involvement of an intermediate carbonyl derivative is probable. No other new method for spirooxazine formation was proposed till the patent of Minkin *et al* [10] in which the reactive carbonyl intermediate (supposed to be a ketene) was generated by oxidization of the Fischer's base (method C, scheme 3). Various oxidizing agents like selenium dioxide, pyridinium chlorochromate and dimethylsulfoxide (DMSO) activated with sodium hydrogencarbonate were used by the Russian authors. This work is certainly an important contribution in the field because of the good yields reported for the spirooxazine synthesis. Nevertheless, in this preliminary work, only 1-alkyl(or benzyl)substituted-2-methyleneindoline and some substituted 1-amino-2-naphthols were used as precursors. The limited range of substitutions and structure variations don't allow to conclude about the generality of the method.

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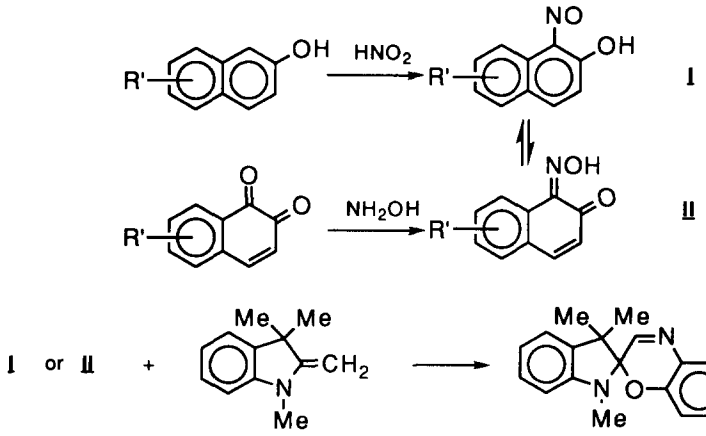
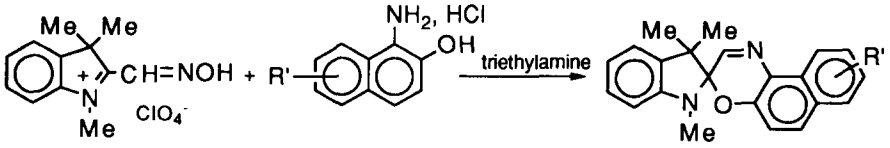
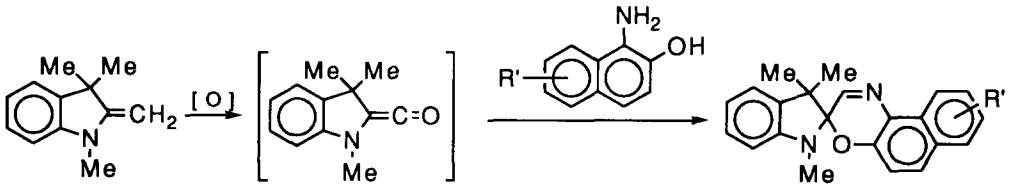


Scheme 1. Method A



Scheme 2. Method B

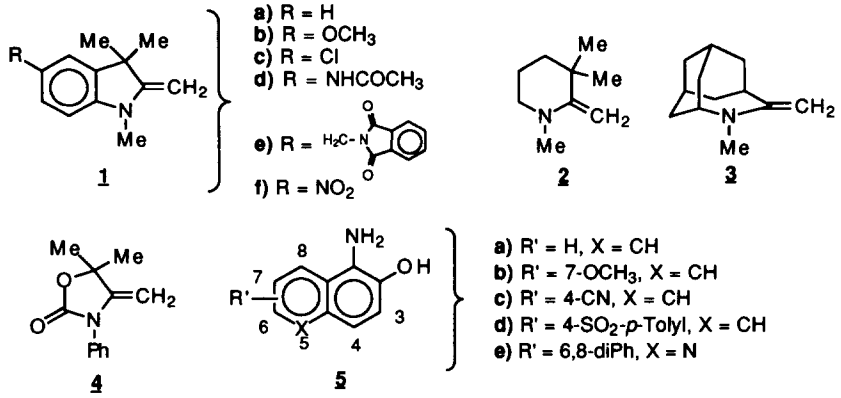


Scheme 3. Method C

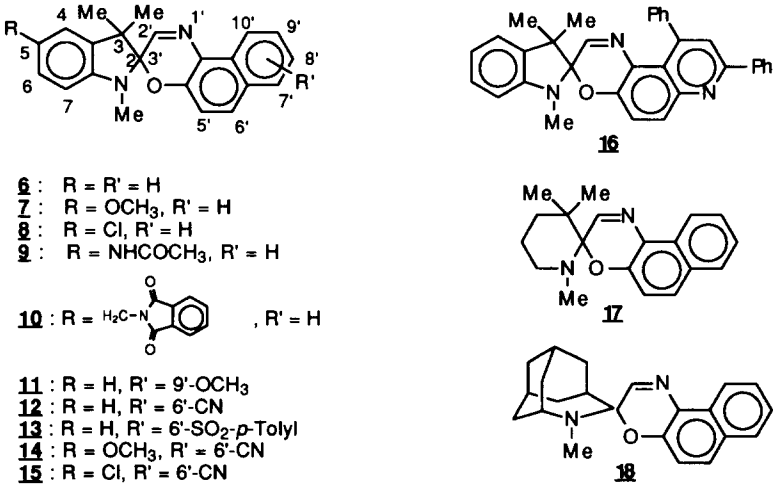
We decided to widen the reaction to a large set of precursors in order to evaluate the general validity of the method and to show its advantages and limitations.

Results and discussion

The condensation reaction (method C, scheme 3) was studied using different methylenic bases belonging to indoline (**1**), piperidine (**2**), homoazaadamantane (**3**), 1,3-oxazolidine-2-one (**4**) series and five substituted 1-amino-2-naphthols or 5-amino-6-quinolinol (**5**) (scheme 4). From the experimental procedure using DMSO as oxidizing agent[10], we prepared twelve spirooxazines (**7**- **18** , scheme 5) including eight new compounds (**2**, **10**, **12** - **16**, **18**). Among them 6'-cyano- or 6'-arylsulfonylspiro[indoline-naphthoxazines] (**12**- **15**) and spiro[homoazaadamantane-naphthoxazine] (**18**) exhibited interesting photochromic properties justifying patent applications.[11,12] In a typical experiment, a mixture of the methylenic base and 1-amino-2-naphthol,



Scheme 4. Precursors for the synthesis of spirooxazines according to method C



Scheme 5. Spirooxazines prepared according to method C

dimethylsulfoxide, sodium hydrogencarbonate and magnesium sulfate was heated in toluene as solvent. Base and aminonaphthol can be generated *in situ* from corresponding salts by addition of triethylamine. The yields of the isolated spirooxazines are reported in table 1. The unsubstituted parent compound (**6**) is given as reference. For spirooxazines **9**, **10**, **18**, yields we obtained according to the usual method A (condensation of 2-methyleneindolines with nitrosonaphthols) are given for comparison.

The first observation is that the studied method can be applied to a large set of substitutions, as well for the 'left' heterocyclic part as for the oxazinic part. Regarding whole data, one can notice that the yields obtained by the new method C are generally slightly higher than those obtained with the method A, but the increase is not

really significant. Nevertheless, the studied condensation method leads to better results when non conjugated methylenic bases (**2**, **3**) are used. Probably, the mild experimental conditions of method C prevent side reactions due to the fragility of this kind of bases.

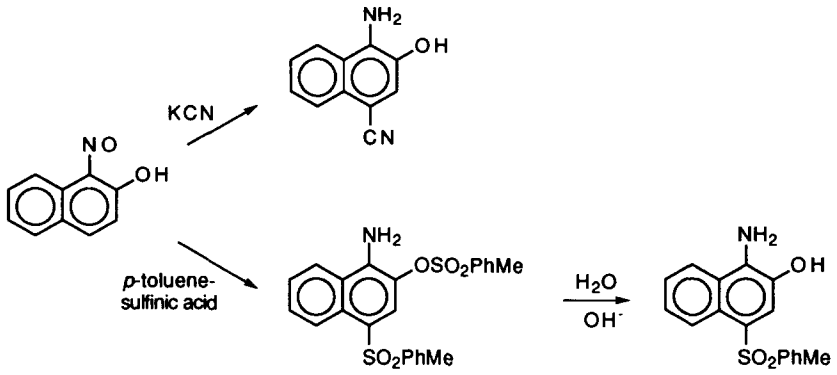
Table 1. Experimental Conditions for the Synthesis and Physical Properties of Spirooxazines.

Compound	Precursors	Reaction Temperature (°C)	Reaction Time (°C)	Yield (%) Method C (Method A)	Melting Point (°C) (lit.)
6	1a, 5a	80	12	75[10] (53)[10]	125[10]
7	1b, 5a	80	12	45 (40)[13]	130-132 (130-131)[13]
8	1c, 5a	80	12	36 (31)	177-178 (175-176)[13]
9	1d, 5a	60	4	69 (58)	229-230
10	1e, 5a	60	24	52 (35)	210-212
11	1a, 5b	60	24	48 (53)[14]	185-186 (184)[14]
12	1a, 5c	80	12	58	159
13	1a, 5d	80	16	17	204-205
14	1b, 5c	80	12	65	128
15	1c, 5c	80	12	50	175
16	1a, 5e	80	12	36	191-192
17	2, 5a	60	4	28 (10)[15]	105-106 (104-105)[15]
18	3,5a	50	5	26 (12)	108

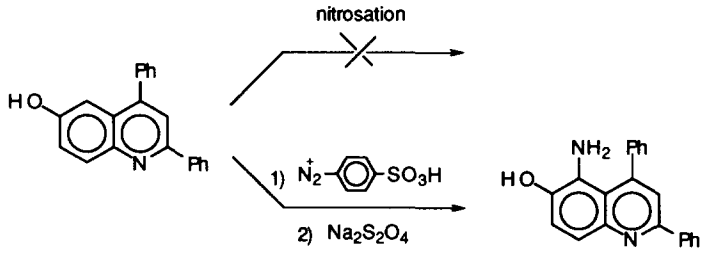
But the main interest and the complementary role of this method is highlighted regarding examples **12** to **15**. In this cases, it is effectively difficult to imagine other synthetic approach. Indeed, 1-amino-4-cyano-2-naphthol and 1-amino-4-*p*-tolylsulfonyl-2-naphthol are easily obtained from 1-nitroso-2-naphthols[16] (scheme 6), even though the synthesis of the corresponding 4-substituted nitroso-derivatives seems to be restricted. The example of synthesis of compound **16** is also interesting. We failed in the direct nitrosation of the 2,4-diphenyl-6-hydroxyquinoline despite many variations of the experimental conditions. In contrast, we were able to prepare the 5-amino-2,4-diphenyl-6-hydroxyquinoline in two steps *via* the azo compounds followed by a reduction reaction (scheme 7), allowing then to synthesize the corresponding spirooxazine.

On the other hand, the condensation reaction through the aminonaphthol failed starting from the methylenic bases **1f** and **4**, certainly due to the high stability of the latest toward oxidization reaction. Different

attempts using other oxidizing agents described in reference[10] were also unsuccessful. The low reactivity of these methylenic bases is confirmed by the lack of reaction of **4** with the 1-nitroso-2-naphthol and the low yield (10%) obtained with **1f** in these conditions.[13]



Scheme 6



Scheme 7

In summary, the preparation of spirooxazines through the condensation of methylene-substituted heterocyclic bases with 1-amino-2-naphthols in presence of an oxidizing agent can be applied to a large set of substitutions. It is particularly interesting when the used methylenic base is fragile or when 1-nitroso-2-naphthols (acting as synthons in the usual synthesis of spirooxazines) are less accessible than the corresponding amino-derivatives.

EXPERIMENTAL PART

Solvents (SDS Company, France) were used without further purification and dried on molecular sieves if necessary.

^1H and ^{13}C NMR spectra were recorded on a Bruker BM 250 spectrometer (250 MHz and 62.5 MHz respectively for ^1H and ^{13}C) using tetramethylsilane as internal standard. Chemical shifts are given in ppm and coupling constants in Hz.

Melting points (°C) were measured in capillary tubes on a Buchi 510 apparatus and are uncorrected.

Column chromatographies were performed on silica gel Merck 60 (70-230 mesh) and flash chromatographies on silica gel Merck 60H (5-50 mesh).

Elemental analysis were performed by the Microanalytical Centre of the University of Aix-Marseille III.

The identification of previously reported reaction products was made by ^1H NMR and melting points comparison with literature data.

Starting materials

Compounds **1a**, **5a** (Aldrich), **1b** (Chroma Chemicals Inc., USA), **1c** (BASF, Germany) were commercially available.

Compounds **1d**[17], **1e**[18], **1f**[19], **2**[20], **3**[21], **4**[22], **5c**[16], **5d**[16] were prepared according to previously described methods.

*7-Methoxy-1-amino-2-naphthol hydrochloride (**5b**)* was obtained according to the method described for the synthesis of the 1-amino-2-naphthol hydrochloride.[23] Isolated as colorless needles (from water). Mp 210° (decomposition). NMR ^1H (DMSO d_6): 3.85 (3H, s, OCH_3) ; 6.97 (1H, dd, J = 8.9 and 2.2, 6-H) ; 7.12 (1H, d, J = 8.8, 3-H) ; 7.35 (1H, d, J = 2.2, 8-H) ; 7.62 (1H, d, J = 8.8, 4-H) ; 7.73 (1H, d, J = 8.9, 5-H).

*6-Hydroxy-2,4-diphenylquinoline (**19**).*- A mixture of 6-methoxy-2,4-diphenylquinoline[24] (1.8 g, 5.8 mmol), 15 ml of acetic acid and 10 ml of aqueous solution (48%) of HBr were refluxed for 24 hours. After cooling, ice was added. The precipitate was filtered off, washed with water and then dissolved in 100 ml of an aqueous solution (5 %) of NaOH. The solution was washed with CH_2Cl_2, treated with active charcoal and acidified. After filtering off and drying, 1.2 g (70 % yield) the wished compound was isolated as a pale yellow solid. Mp 210-212 (from chloroform). NMR ^1H ($CDCl_3$): 6.37 (1H, broad s, OH) ; 7.17 (1H, d, J = 2.7, 5-H) ; 7.29 (1H, dd, J = 9 and 2.7, 7-H) ; 7.38-7.52 (8H, m, arom.-H) ; 7.72 (1H, s, 3-H) ; 8.08 (2H, m, arom.-H) ; 8.12 (1H, d, J = 9, 8-H). Anal. calc. for $C_{21}H_{15}NO$: C 84.82, H 5.08, N 4.71; found : C 84.78, H 5.12, N 4.80.

*5-Amino-6-hydroxy-2,4-diphenylquinoline (**5e**).*- Sulfanilic acid (0.52 g, 3 mmol) mixed with Na_2CO_3 (0.16 g, 1.5 mmol) was diazotized in standard conditions[23] with sodium nitrite (0.23 g, 3.3 mmol) and concentrated HCl (0.53g, 7.5 mmol) in water (10 ml) at 0°C. The suspension of diazonium salt was mixed at 0°C with a solution of 6-hydroxy-2,4-diphenylquinoline (0.89 g, 3 mmol) and NaOH (0.32 g, 8 mmol) in water (8 ml). Standing (30 min) at room temperature, the precipitated red-orange dye was filtered off and washed with water. A solution of the dye in 20 ml aqueous solution of NaOH (5%) was reduced with $Na_2S_2O_4$ (1.64 g, 8 mmol) and stirred at 40°C during 10 min. The solution was then acidified (pH 6-7) and extracted with CH_2Cl_2. The organic phase was washed with water and dried with $MgSO_4$. Removing of the solvent gives 0.35 g (37 % yield) of the expected compound **5e** as yellow powder. **5e** was used without purification for the synthesis of the spirooxazine **16**. Due to difficulties to obtain a perfectly pure sample, the compound was characterized as

triacetyl derivative : colorless needles, Mp. 181-183 (from ethanol). ^{1}H NMR ($CDCl_3$): 1.9 (6H, s, N-acetyl); 2.25 (3H, s, O-acetyl); 7.27 (2H, m, arom.-H); 7.43-7.55 (6H, m, arom.-H); 7.66 (1H, d, J = 9.2, 7-H); 7.69 (1H, s, 3-H); 8.15 (2H, m, arom.-H); 8.38 (1H, d, J = 9.2, 8-H). NMR ^{13}C ($CDCl_3$): 20.7 (q), 26.6 (q), 123.4 (d), 123.7 (s), 125,4 (d), 126.5 (s), 127.5 (d), 127.6 (d), 128.2 (d), 128.5 (d), 129.0 (d), 133.0 (d), 138.4 (s), 140.0 (s), 146.0 (s), 147.2 (s), 147.9 (s), 156.4 (s), 168.4 (s), 172.2 (s). Anal.calc. for $C_{27}H_{22}N_2O_4$: C 73.96, H 5.06, N 6.39, found : C 74.04, H 5.11, N 6.45.

General method for synthesis of spirooxazines (Method C)[10]

A mixture of 1 mmol of methylenic base, 1.1 mmol of aminonaphthol, 0.25 g (3 mmol) of DMSO, 0.3 g of $MgSO_4$, 0.4 g of $NaHCO_3$ in 15 ml of toluene was heated. Time and temperature are indicated in table 1. If hydroiodide of the methylenic base or(and) hydrochloride of the aminonaphthol are used, 1.5 equivalent of triethylamine are added *per* acid equivalent. The solution was filtered off and concentrated under vacuum. The expected spirooxazines are purified by column chromatography or flash chromatography on silica gel.

Larger scale experiments can be performed. For instance, starting from 20 mmol of Fischer 's base **1a** and 22 mmol of aminonaphthol **5a**, 12.4 mmol of spirooxazine **6** were isolated (62% yield).

5-Methoxy-1,3,3-trimethylspiro [indoline-2,3'-[3H] naphth [2,1-b][1,4] oxazine] (7): purification by column chromatography, eluent CH_2Cl_2 / hexane (70/30); crystallisation in heptane.

5-Chloro-1,3,3-trimethylspiro [indoline-2,3'-[3H] naphth [2,1-b][1,4] oxazine] (8): purification by column chromatography, eluent CH_2Cl_2 / hexane (70/30); crystallisation in heptane.

5-Acetylamino-1,3,3-trimethylspiro [indoline-2,3'-[3H] naphth [2,1-b][1,4] oxazine] (9): purification by column chromatography, eluent CH_2Cl_2 / ethyl acetate (70/30); pale brown solid (from ethanol). NMR ^{1}H ($CDCl_3$): 1.32 (3H, s, 3-CH_3) ; 1.36 (3H, s, 3-CH_3) ; 2.16 (3H, s, $COCH_3$) ; 2.72 (3H, s, 1-CH_3) ; 6.49 (1H, d, J = 8.2, 7-H) ; 6.99 (1H, d, J = 8.9, 5'-H) ; 7.13 (1H, broad s, NH) ; 7.21 (1H, dd, J = 8.2 and 2.0, 6-H) ; 7.30 (1H, d, J = 2.0, 4-H) ; 7.39 (1H, dd, J = 7.0, 8'-H) ; 7.57 (1H, dd, J = 8.4, 9'-H) ; 7.73 (1H, s, 2'-H) ; 7.75 (1H, d, J = 7.0, 7'-H) ; 8.55 (1H, d, J = 8.4, 10'-H). NMR ^{13}C ($CDCl_3$): 20.6 (q) ; 24.3 (q) ; 25.3 (q) ; 29.8 (q) ; 51.8 (s) ; 98.7 (s) ; 107.0 (d) ; 115.5 (d) ; 116.7 (d) ; 120.7 (d) ; 121.5 (d) ; 124.2 (d) ; 127.1 (d) ; 127.8 (d) ; 129.2 (s) ; 130.3 (d) ; 130.6 (s) ; 136.5 (s) ; 143.8 (s) ; 144.7 (s) ; 150.5 (d) ; 168.1 (s). Anal.calc. for $C_{24}H_{23}N_3O_2$: C 74.78, H 6.01, N 10.90; found C 74.70, H 6.07, N 10.85.

5-(N-phthalimidomethyl)-1,3,3-trimethylspiro [indoline-2,3'-[3H] naphth [2,1-b][1,4] oxazine] (10): purification by column chromatography, eluent CH_2Cl_2, pale yellow solid (from ethanol /CH_2Cl_2 1:1). NMR ^{1}H ($CDCl_3$): 1.33 (6H, s, 3-CH_3) ; 2.73 (3H, s, 1-CH_3) ; 4.80 (2H, s, CH_2) ; 6.50 (1H, d, J = 8.0, 7-H) ; 6.98 (1H, d, J = 8.9, 5'-H) ; 7.19 (1H, d, J = 1.6, 4-H) ; 7.34 (1H, dd, J = 8.0 and 1.6, 6-H) ; 7.39 (1H, ddd, J = 7.6 and 1.2, 8'-H) ; 7.57 (1H, ddd, J = 7.6 and 1.2, 9'-H) ; 7.64 (1H, d, J = 8.9, 6'-H) ; 7.69-7.75 (4H, m, 2'-H, 7'-H and *meta* -H of phthalimido ring) ; 7.82-7.87 (2H, m, *ortho*-H of phthalimido ring) ; 8.54 (1H, d, J = 8.5, 10'-H). NMR ^{13}C ($CDCl_3$) : 20.8 (q) ; 25.4 (q) ;29.7 (q) ; 41.7 (t) ; 51.8 (s) ; 98.7 (s) ; 107.0 (d) ; 116.8 (d) ; 121.5 (d) ; 122.7 (d) ; 122.9 (s) ; 123.3 (d) ; 124.2 (d) ; 127.2 (d) ; 127.8 (d) ; 128.0 (s); 129.2 (d) ; 129.3 (s) ; 130.3 (d) ; 130.8 (s) ; 132.3 (s) ; 133.9 (d) ; 136.4 (s) ; 144.0 (s) ; 147.4 (s) ; 150.6 (d) ; 168.2 (s). Anal.calc. for $C_{31}H_{25}N_3O_3$: C 76.37, H 5.17, N 8.62 ; found C 76.39, H 5.19, N 8.60.

9'-Methoxy-1,3,3-trimethylspiro [indoline-2,3'-[3H] naphth [2,1-b][1,4] oxazine] (11): purification by column chromatography, eluent CH_2Cl_2 / hexane (70/30); crystallisation in heptane.

6'-Cyano-1,3,3-trimethylspiro [indoline- 2,3'-[3H]naphth[2,1-b][1,4]oxazine] (12): purification by flash chromatography, eluent hexane / ethyl acetate (90/10); yellow cristals (from heptane). NMR ^{1}H ($CDCl_3$): 1.34

(3H, s, 3-CH_3) ; 1.37 (3H, s, 3-CH_3) ; 2.76 (3H, s, 1-CH_3) ; 6.59 (1H, d, J = 7.6, 7-H) ; 6.93 (1H, dd, J = 7.2, 5-H) ; 7.09 (1H, d, J = 7.2, 4-H) ; 7.24 (1H, dd, J = 7.6, 6-H) ; 7.46 (1H, s, 5'-H) ; 7.59 (1H, ddd, J = 7.0 and 1.2, 8'-H) ; 7.69 (1H, ddd, J = 7.0 and 1.2, 9'-H) ; 7.89 (1H, s, 2'-H) ; 8.14 (1H, d, J = 8.0, 7'-H) ; 8.66 (1H, d, J = 8.5, 10'-H). NMR ^{13}C ($CDCl_3$): 20.7 (q) ; 25.4 (q) ; 29.6 (q) ; 52.2 (s) ; 99.0 (s) ; 107.3 (d) ; 111.1 (s) ; 117.0 (s) ; 120.3 (d) ; 121.5 (d) ; 122.4 (d) ; 123.2 (d) ; 125.1 (d) ; 126.6 (d) ; 126.7 (s) ; 128.2 (d) ; 128.4 (d) ; 128.5 (s) ; 130.6 (s) ; 135.3 (s) ; 143.0 (s) ; 147.2 (s) ; 154.4 (d). Anal.calc. for $C_{23}H_{19}N_3O$: C 78.17, H 5.42, N1 1.89 ; found C 78.21, H 5.51, N 11.79.

6'-p-Tolylsulfonyl-1,3,3-trimethylspiro [indoline-2,3'-[3H]naphth[2,1-b][1,4]oxazine](**13**)*:* purification by flash chromatography, eluent : hexane / ethyl acetate (90/10); pale yellow crystals (from ethanol /diethylether 1:1). NMR ^1H ($CDCl_3$): 1.34 (3H, s, 3-CH_3) ; 1.35 (3H, s, 3-CH_3) ; 2.39 (3H, s, CH_3) ; 2.73 (3H, s, 1-CH_3) ; 6.58 (1H, d, J = 7.8, 7-H) ; 6.91 (1H, dd, J = 7.2, 5-H) ; 7.08 (1H, d, J = 7.2, 4-H) ; 7.19-7.26 (3H, m, 6-H and *meta*-H of tolyl ring) ; 7.46 (1H, ddd, J = 7.0 and 1.2, 8'-H) ; 7.58 (1H, ddd, J = 7.0 and 1.2, 9'-H) ; 7.82 (2H, d, J = 8.3, *orho*-H of tolyl ring) ; 7.87 (1H, s, 2'-H) ; 8.05 (1H, s, 5'-H) ; 8.57 (1H, d, J = 8.5, 7'-H) ; 8.66 (1H, d, J = 8.3, 10'-H). NMR ^{13}C ($CDCl_3$): 20.96 (q) ; 21.66 (q) ; 25.52 (q) ; 29.79 (q) ; 52.23 (s) ; 99.10 (s) ; 107.4 (d) ; 120.4 (d) ; 120.9 (d) ; 121.6 (d) ; 122.8 (d) ; 124.5 (d) ; 124.6 (s) ; 126.3 (d); 127.3 (s) ; 127.7 (d) ; 127.8 (d) ; 128.3 (d) ; 130.0 (d) ; 131.9 (s) ; 135.5 (s) ; 137.9 (s) ; 138.4 (s) ; 142.6 (s) ; 144.4 (s) ; 147.3 (s) , 154.5 (d). Anal.calc. for $C_{29}H_{26}N_2O_3S$: C 72.18, H 5.43, N 5.81, S 6.64 ; found C 72.21, H 5.39, N 5.74, S 6.81.

6'-Cyano-5-methoxy-1,3,3-trimethylspiro[indoline-2,3'-[3H]naphth[2,1-b][1,4]oxazine](**14**)*:* purification by flash chromatography, eluent : hexane / ethyl acetate (90/10) ; yellow crystals (from heptane). NMR ^1H ($CDCl_3$): 1.33 (3H, s, 3-CH_3) ; 1.38 (3H, s, 3-CH_3) ; 2.69 (3H, s, 1-CH_3) ; 3.81 (3H, s, OCH_3) ; 6.50 (1H, d, J = 8.2, 7-H) ; 6.72-6.78 (2H, m, 4-H and 6-H) ; 7.47 (1H, s, 5'-H) ; 7.59 (1H, ddd, J = 6.9 and 1.2, 8'-H) ; 7.70 (1H, ddd, J = 6.9 and 1.2 , 9'-H) ; 7.88 (1H, s, 2'-H) ; 8.13 (1H, d, J = 8.1, 7'-H) ; 8.66 (1H, d, J = 8.1, 10'-H). NMR ^{13}C ($CDCl_3$): 20.9 (q) ; 25.6 (q) ; 30.2 (q) ; 52.5 (s) ; 56.2 (q) ; 99.6 (s); 107.8 (d) ; 109.6 (d) ; 111.3 (s) ; 112.2 (d) ; 117.3 (s) ; 122.7 (d) ; 123.5 (d) ; 125.3 (d) ; 126.8 (d) ; 127.0 (s) ; 128.7 (d) ; 128.8 (s) ; 130.9 (s) ; 137.2 (s) ; 141.6 (s) ; 143.3 (s) ; 154.5 (d) , 154.8 (s). Anal.calc. for $C_{24}H_{21}N_3O_2$: C 75.18, H 5.52, N 10.96 ; found C 75.16, H 5.62, N 10.87.

5-Chloro-6'-cyano-1,3,3-trimethylspiro [indoline-2,3'-[3H]naphth[2,1-b][1,4]oxazine](**15**)*:* purification by flash chromatography, eluent : hexane / ethyl acetate (90/10) ; yellow crystals (from heptane). NMR ^1H ($CDCl_3$): 1.32 (3H, s, 3-CH_3) ; 1.37 (3H, s, 3-CH_3) ; 2.73 (3H, s, 1-CH_3) ; 6.49 (1H, d, J = 8.3, 7-H) ; 7.04 (1H, d, J = 2.0, 4-H) ; 7.18 (1H, dd, J = 8.3 and 2.0, 6-H) ; 7.46 (1H, s, 5'-H) ; 7.60 (1H, ddd, J = 8.3 and 1.2, 8'-H) ; 7.70 (1H, ddd, J = 8.3 and 1.2, 9'-H) ; 7.87 (1H, s, 2'-H) ; 8.14 (1H, d, J = 8.3, 7'-H) ; 8.65 (1H, d, J = 8.3, 10'-H). NMR ^{13}C ($CDCl_3$): 20.6 (q) ; 25.2 (q) ; 29.7 (q) ; 52.2 (s) ; 98.9 (s) ; 108.2 (d) ; 111.3 (s) ; 117.0 (s) ; 122.1 (d) ; 122.5 (d) ; 123.0 (d) ; 125.1 (d) ; 126.7 (d) ; 127.9 (d) ; 128.5 (d) ; 130.6 (s) ; 137.2 (s) ; 142.7 (s) ; 145.9 (s) ; 153.7 (d) Anal.calc. for $C_{23}H_{18}N_3ClO$: C 71.22, H 4.68, N 10.83 ; found C 71.20, H 4.70, N 10.75.

8'10'-Diphenyl-1,3,3-trimethylspiro[indoline-2,3'-[3H]pyrido[3,2f][1,4]benzoxazine](**16**) *:* purification by column chromatography, eluent CH_2Cl_2; yellow cristals (from heptane / CH_2Cl_2 1:1). NMR ^1H ($CDCl_3$): 1.26 (3H, s, 3-CH_3) ; 1.33 (3H, s, 3-CH_3) ; 2.74 (3H, s, 1-CH_3) ; 6.55 (1H, d, J = 7.7, 7-H) ; 6.88 (1H, dd, J = 7.2, 5-H) ; 7.05 (1H, d, J = 7.2, 4-H) ; 7.20 (1H, dd, J = 7.7 , 6-H) ; 7.20 (1H, s, 2'-H) ; 7.29 (1H, d, J = 9.2, 5'-H) ; 7.42-7.57 (8H, m, arom.-H) ; 7.78 (1H, s, 9'-H) ; 8.08 (1H, d, J = 9.2, 6'-H) ; 8.15 (2H, m, arom.-H). NMR ^{13}C ($CDCl_3$): 21.7 (q) ; 25.3 (q) ; 29.8 (q) ; 52.1 (s) ; 98.1 (s) ; 107.3 (d) ; 120.1 (d) ;

120.8 (d) ; 121.7 (d) ; 122.7 (d) ; 123.4 (s) ; 124.6 (s) ; 127.6 (d) ; 128.3 (d) ; 129.1 (d) ; 129.4 (d) ; 132.6 (d) ; 135.8(s) ; 139.6 (s) ; 143.1 (s) ; 145.4 (s) ; 146.0 (s) ; 147.6 (s) ; 148.0 (s) ; 148.6 (d) ; 154.9 (s). Anal.calc. for $C_{33}H_{27}N_3O$: C 82.3, H 5.65, N 8.73 ; found C 82.4, H 5.63, N 8.68.

1',3',3'-Trimethylspiro [3H]-naphth [2,1-b][1,4] oxazine-3,2'- piperidine] (**17**)*:* purification by flash chromatography, eluent pentane ; crystallisation in methanol.

4-Methylspiro-[4-azahomoadamantane-5,3'-[3H]naphth[2,1-b][1,4]oxazine](**18**)*:* purification by flash chromatography, eluent : pentane/ether (95/5) ; colorless needles (from heptane). NMR ^1H ($CDCl_3$): 1.36-1,45 (1H, m) ; 1.59 (2H, m) ; 1.67-2.14 (8H, m) ; 2.39-2.47 (2H, m) ; 2.53 (3H, s, CH_3) ; 3.11 (1H, m, 3-H) ; 7.10 (1H, d, J = 8.2, 5'-H) ; 7.34 (1H, ddd, J = 8.2 and 1.1, 8'-H) ; 7.51 (1H, ddd, J = 8.4 and 1.1,9'-H) ; 7.63 (1H, d, J = 8.8, 6'-H) ; 7.67 (1H, s, 2'-H) ; 7.72 (1H, d, J = 8.4, 10'-H). NMR ^{13}C ($CDCl_3$) : 26.9 (d); 27.0 (d) ; 30.0 (t) ; 30.8 (t) ; 33.5 (t) ; 36.2 (t) ; 37.7 (d) ; 39.7 (q) ; 39.9 (t) ; 58.7 (d) ; 93.9 (s) ; 117.9 (d) ; 121.6 (d) ; 123.7 (s) ; 123.8 (d) ; 126.9 (d) ; 127.8 (d) ; 129.1 (s) ; 129.3 (d) ; 130.9 (s) ; 144.9 (s) ; 158.8 (d). Anal.calc. for $C_{22}H_{24}N_2O$: C 79.48, H 7.28, N 8.43 ; found C 79.42, H 7.32, N 8.52.

Spirooxazines (**2**), (**10**) ***and*** (**18**) were also synthesized according to the ***method A***

A solution of 1 mmol of the corresponding methylenic base and 1.1 mmol of 1-nitroso-2-naphthol in 20 ml ol trichloroethylene was refluxed for 5 hours. After removing of the solvent under vacuum, compounds were purified as described above. Physical characteristics and NMR spectra are identical whatever the method used.

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