One-Pot Synthesis of 6′-Amino-Substituted Spirooxazines

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Abstract: A one-pot synthesis of 6′-amino-substituted spiroindolinonaphth[2,1-*b*][1,4]oxazines is developed through the condensation of 2-methylene-1,3,3-trimethylindoline derivatives and 1-amino-2-naphthol in the presence of different secondary amines and oxidizing agents using methanol or toluene as the solvent. The main advantage of the method is its simplicity, and starting from readily accessible reagents, it allows the preparation of amino derivatives of spironaphthoxazine with good yields under mild reaction conditions.

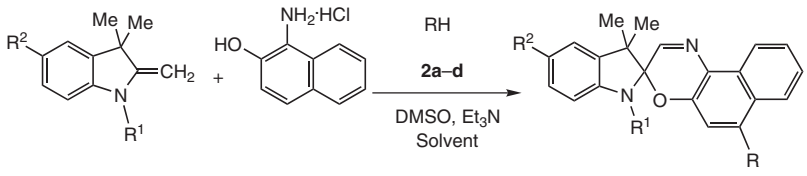
Key words: spiroindolinonaphth[2,1-*b*][1,4]oxazine, 2-methylene-1,3,3-trimethylindoline, 1-amino-2-naphthol, one-pot synthesis

Spirooxazines have UV activation properties and thermal bleaching properties that are convenient for practical applications.[1–5] By now, the widely applied procedures for the synthesis of spirooxazines consist in the condensation of nitrogen-containing heterocycles with hydroxynitroso compounds.[3] Unfortunately, this method affords spirooxazines in low yields, even if optimization of experimental conditions allowed to improve it in some cases.[3,6] The spirooxazine molecule can be constructed also by using 1-amino-2-naphthol as the starting material.[7–12]

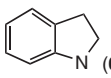
Most of the structural modifications of the oxazine fragment in spiro compounds are based on the substitution on the naphthalene ring. The required group is most commonly introduced into this fragment already in the preparation of the starting 1-nitroso-2-naphthol. Rickwood and co-workers used some secondary amines as nucleophiles for the preparation of 6′-amino-substituted spironaphthoxazines.[13–16] It was assumed that the reaction involves the nucleophilic addition of secondary amine at position 4 of the quinone oxime tautomer of 1-nitroso-2-naphthol. Subsequent oxidation of intermediate can occur under the action of a second 1-nitroso-2-naphthol molecule, which partially accounts for the low yield.

In this paper we describe the synthesis of the 6′-amino-subsituted spirooxazines by one-pot condensation of 1-amino-2-naphthol with substituted 2-methyleneindolines in the presence of different secondary amines and oxidizing agent using methanol or toluene as the solvent (Scheme 1). To evaluate the general validity of the method and to show its advantages and limitations we varied the substituents in indoline molecules **1a–d** and used different secondary cyclic amines **2a–d**.

Our experiments showed that alicyclic/aliphatic secondary amines did not participate in the condensation reaction. In the presence of diethylamine or bis(2-methoxyethyloxy)amine the condensation of **1a** with 1-amino-2-naphthol results in the formation of unsubstituted spiroindolinonaphth[2,1-*b*][1,4]oxazine. In contrast, the method was successfully applied for the preparation of spirooxazines **3a–c**, **4a**, **5**, and **6** with cyclic amine substit-



1a–d **3a–d**, **4a**,**b**, **5**, **6**

1a, **2a**, **3a**, **4a**, **5**, **6**: R^1 = Me, R^2 = H, R =  (**2a**, **3a**),  (**4a**),  (**5**),  (**6**);

1b, **2b**, **3b**: R^1 = $C_{16}H_{33}$, R^2 = H, R =  , **4b**: R =  ;

1c, **2c**, **3c**: R^1 = Me, R^2 = MeO, R =  ; **1d**, **2d**, **3d**: R^1 = Me, R^2 = Cl, R = 

Scheme 1

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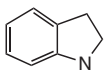
uents at the 6′-position as shown in Table 1. In a typical experiment, a mixture of reagents and dimethyl sulfoxide was heated in toluene or methanol up to 40 °C. 1-Amino-2-naphthol and in some experiments bases **1a–c** were generated in situ from the corresponding salts by addition of Et_3N.

Table 1 6′-Amino-Substituted Spirooxazines **3a–d**, **4a**,**b**, **5**, and **6** Prepared

Product	R	R^1, R^2	Yield (%) in MeOH	Yield (%) in Toluene
3a		R^1 = Me, R^2 = H	81 (60)[a]	15
3b		$R^1 = C_{16}H_{33}$, R^2 = H	46[a]	15
3c		R^1 = Me, R^2 = Cl	15 (17)[b]	0 (12)[b]
3d		R^1 = Me, R^2 = OMe	45	0
4a		R^1 = Me, R^2 = H	13	10
4b		R^1 = Me, R^2 = Cl	13	0
5		R^1 = Me, R^2 = H	39	17
6		R^1 = Me, R^2 = H	19	10

[a] Compound was prepared from the corresponding heterocyclic salts, the bases were generated in situ by addition of Et_3N.
[b] Dess–Martin reagent was used as the oxidizing agent.[17]

Regarding the data of Table 1, one can conclude that the procedure can be employed for the preparation of amino-substituted spirooxazines starting from readily accessible reagents. Another important advantage of the procedure is that the reactions can be carried out under mild conditions.

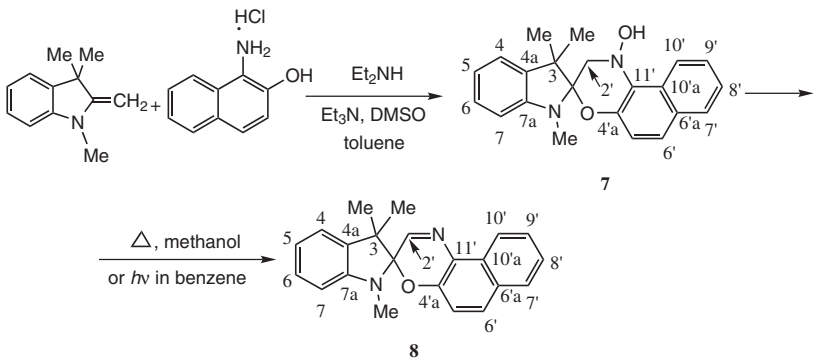
The nature of the solvent and the nature and structure of the amine component have a substantial influence on the course of the one-pot formation of the 6′-amino-substituted spirooxazines. In principle, during the course of the reaction, the intermediates formed by the condensation of 1-amino-2-naphthol with substituted 2-methyleneindolines, as well as spiroindolinonaphth[2,1-*b*][1,4]oxazines are able to react with secondary amines by the Michael addition mechanism;[14] the step in which the amino group is inserted into the molecule remains an open point for future investigation.

In the formation of 6′-amino-substituted spironaphthoxazines, DMSO was used as oxidizing agent.[8] In our experiment to improve the yield of the product **3c**, the commercially available oxidizing reagent Dess–Martin was used.[17] As shown in Table 1, more substantial increase of the yield was found in toluene as the reaction medium.

Although in the mechanism of the reaction, formation of spironaphthoxazine from the 1-amino-2-naphthol and Fisher's base has not been described, the involvement of an intermediate carbonyl derivative was proposed.[7] The mild reaction conditions allowed us to isolate compound **7** whose structure was established by NMR (^1H, ^{13}C) spectroscopy, COSY and NOESY (^1H,^{13}C) methods (Scheme 2). The NMR investigation showed that, in comparison with spiroindolinonaphth[2,1-*b*][1,4]oxazine **8**, in the aromatic region of **7** the singlet of CH=N group of oxazine ring is absent. In aliphatic region a new broad singlet at 4.25 ppm and 2 doublets at 3.6 ppm and 3.8 ppm had appeared. From NMR analysis, the singlet corresponds to the proton of the hydroxy group at N atom. Two doublets that form AB system correspond to the protons connected with $C^{2'}$.

The transformation of compound **7** to the final spironaphthoxazine was studied in benzene and methanol. Compound **7** is stable enough in benzene even upon heating at 80 °C for 6 hours. The transformation of **7** to **8** in benzene is possible only upon irradiation with light at 365 nm.

Compound **7** is not stable in methanol. The dissolution of **7** in methanol results in the formation of **8**. Figure 1a shows the NMR spectrum of **7** in methanol (proton signals of compound **7** are marked by 'i', proton signals of compound **8** are marked by 's'). Keeping **7** in methanol causes the spontaneous transformation into the spirooxazine **8**. Figures 1b,c show the spectra of **7** after keeping of solution during 7 and 14 days. The intensity of proton signals of spironaphthoxazine **8** increases with simultaneous decreases of proton signals of **7**. After 14 days, the solution contains practically pure spirooxazine **8** (Figure 1c).



7

8

Scheme 2

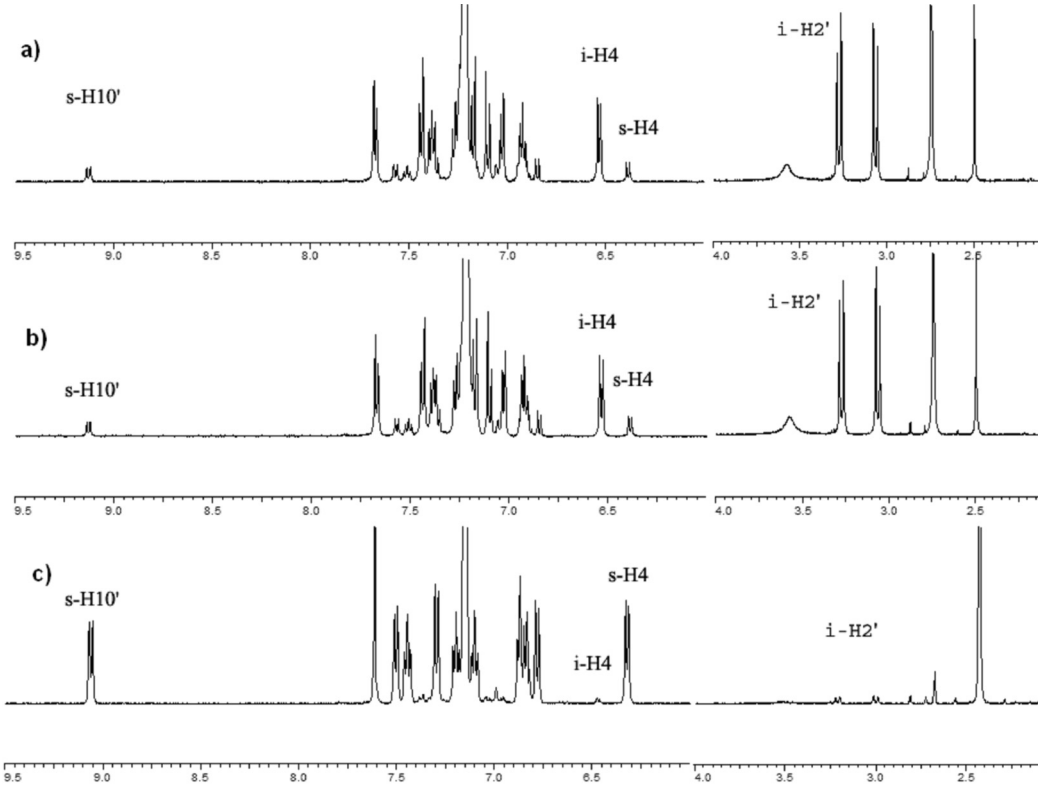


Figure 1 ^{1}H NMR spectra (Bruker, 25 °C, 500 Hz) of compound **7** in CD_3OD: a) freshly prepared; b) after keeping for 7 days in CD_3OD; c) after keeping for 14 days in CD_3OD.

Thus, compound **7** can be considered as the direct precursor of the spirooxazine **8**. The formation of **7** in course of the reaction condensation is an important fact for understanding the mechanism of the spironaphthoxazine formation. Evidently, the reaction includes the oxidation of the 1-amino-2-naphthol, condensation of the oxidation product with Fisher's base to form **7**, and thermal or photo-induced dehydration of **7** resulting in the formation of the spironaphthoxazine **8**. The possibility of **7** for easy transformation under irradiation or heating to photochromic compound **8** can be considered as promising for practical applications.

In summary, the condensation of methylene-substituted heterocyclic bases with 1-amino-2-naphthol in presence of cyclic secondary amines and oxidizing agent can be successfully applied to the synthesis of spirooxazines substituted by cyclic amine at 6′-position. The yields of the products depend on the nature and structure of the secondary cyclic amines. The method is simple, starts from readily accessible reagents, and allows to prepare amino derivatives in moderate to good yields.

Compounds **1a–d, 2a–d** and Dess–Martin periodinane were commercially available (Aldrich). Solvents were used without future purification and dried on molecular sieves, if necessary.

^{1}H NMR spectra were recorded on Bruker BM 250 P spectrometer (250 MHz) and on a Bruker DRX500 instrument (500.13 MHz, respectively) as solutions in $CDCl_3$, DMSO-d_6 or CD_3CN using the solvent as an internal reference (7.27, 2.50 and 1.96 ppm for ^{1}H, respectively); 2D homonuclear NOESY spectra was used to assign the proton and carbon signals. Chemical shifts are expressed in parts per million downfield from was used as solvent for all probes.

Melting points (°C) were measured in capillary tubes on a Büchi 510 apparatus and are uncorrected. TLC was performed on 0.2 mm precoated plates of Silica gel 60 F-254 (Merck). Visualization was made with UV (254 and 365 nm). Silica gel 60 Merck with 0.06–0.20 mm particle size was used for preparative column chromatography. Elemental analyses were performed by the Microanalytical Center of the University of Aix-Marseille III.

The identification of previously reported reaction products were made by ^{1}H NMR spectroscopy and melting points comparison with literature data. Elemental analyses data are presented also for known compounds for which these data have not been given in the literature.

Spirooxazines 3a–d, 4a,b, 5, 6; General Procedure

Indoline base **1a–d** (1 mmol), 1-aminonaphthol hydrochloride (1.1 mmol), secondary amine **2a–d** (1.2 mmol), Et_3N (1.1 mmol) and DMSO (or Dess–Martin reagent, 3 mmol) were dissolved in MeOH or toluene (15 mL). If the bases were generated in situ from corresponding salts, Et_3N (1.5 equiv) was added per acid equivalent. The mixture was stirred for 20 h at 40 °C. After the reaction was over, the product was purified by column chromatography on silica gel using pentane–Et_2O mixture as eluent (Table 1).

1,3,3-Trimethyl-6′-morpholinospiro(indolino-2,3′-[3*H*]naphth[2,1-*b*]oxazine) (3a)

Mp 198–200 °C (Lit.[14] mp 196 °C).

1-Hexadecyl-3,3-dimethyl-6-morpholinospiro(indolino-2,3′-[3*H*]naphth[2,1-*b*]oxazine) (3b)

Violet oil.

^{1}H NMR ($CDCl_3$, 30 °C, 250 MHz): δ = 0.88 (t, 3 H, CH_3, *J* = 6.5 Hz), 1.23 (m, 26 H, 13 CH_2), 1.34 [s, 6 H, $C(CH_3)_2$], 1.63 (m, 2 H, CH_2), 3.07 [m, 4 H, $N(CH_2)_2$], 3.14 (d, 2 H, NCH_2, *J* = 7.5 Hz), 3.95 [m, 4 H, $O(CH_2)_2$], 6.59 (m, 2 H, H-5′, H-7), 6.87 (dd, 1 H, H-5, *J* = 7.3, 7.4 Hz), 7.08 (d, 1 H, H-4, *J* = 7.1 Hz), 7.19 (dd, 1 H, H-6, *J* = 7.6, 7.6 Hz), 7.38 (ddd, 1 H, H-8′, *J* = 8.2, 8.2, 1.3 Hz), 7.55 (ddd, 1 H, H-9′, *J* = 8.4, 8.1, 1.3 Hz), 7.65 (s, 1 H, H-2′), 8.04 (d, 1 H, H-7′, *J* = 8.1 Hz), 8.54 (d, 1 H, H-10′, *J* = 8.4 Hz).

Anal. Calcd for $C_{41}H_{57}N_3O_2$: C, 78.93; H, 9.21; N, 6.73. Found: C, 78.84; H, 9.30; N, 6.69.

5-Chloro-1,3,3-trimethyl-6′-morpholinospiro(indolino-2,3′-[3*H*]naphth[2,1-*b*]oxazine) (3c)
Mp 205–207 °C (Lit.[14] mp 196 °C).

^{1}H NMR ($CDCl_3$, 30 °C, 250 MHz): δ = 1.34 [s, 6 H, $C(CH_3)_2$], 2.73 (s, 3 H, NCH_3), 3.08 [m, 4 H, $N(CH_2)_2$], 3.95 [m, 4 H, $O(CH_2)_2$], 6.48 (d, 1 H, H-7, *J* = 8.2 Hz), 6.59 (s, 1 H, H-5′), 7.04 (d, 1 H, H-4, *J* = 2.1 Hz), 7.16 (dd, 1 H, H-6, *J* = 8.2, 2.2 Hz), 7.39 (ddd, 1 H, H-8′, *J* = 8.2, 8.2, 1.2 Hz), 7.57 (ddd, 1 H, H-9′, *J* = 8.2, 8.2, 1.2 Hz), 7.62 (s, 1 H, H-2′), 8.05 (d, 1 H, H-7′, *J* = 8.1 Hz), 8.55 (d, 1 H, H-10′, *J* = 8.4 Hz).

Anal. Calcd for $C_{26}H_{26}ClN_3O_2$: C, 69.71; H, 5.85; N, 9.38. Found: C, 69.63; H, 5.91; N, 9.35.

5-Methoxy-1,3,3-trimethyl-6′-morpholinospiro(indolino-2,3′-[3*H*]naphth[2,1-*b*]oxazine) (3d)
Mp 170–172 °C (Lit.[14] mp 172–173 °C).

^{1}H NMR ($CDCl_3$, 30 °C, 250 MHz): δ = 1.35 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 2.70 (s, 3 H, NCH_3), 3.06 [m, 4 H, $N(CH_2)_2$], 3.80 (s, 3 H, OCH_3), 3.94 [m, 4 H, $O(CH_2)_2$], 6.48 (d, 1 H, H-7, *J* = 8.7 Hz), 6.63 (s, 1 H, H-5′), 6.74 (m, 2 H, H-4, H-6), 7.38 (dd, 1 H, H-8′, *J* = 7.2, 7.8 Hz), 7.57 (dd, 1 H, H-9′, *J* = 7.6, 7.3 Hz), 7.64 (s, 1 H, H-2′), 8.05 (d, 1 H, H-7′, *J* = 8.3 Hz), 8.55 (d, 1 H, H-10′, *J* = 8.6 Hz).

Anal. Calcd for $C_{27}H_{29}N_3O_3$: C, 73.11; H, 6.59; N, 9.47. Found: C, 73.01; H, 6.68; N, 9.39.

1,3,3-Trimethyl-6′-piperidinospiro(indolino-2,3′-[3*H*]naphth[2,1-*b*]oxazine) (4a)
Mp 213–215 °C (Lit.[14] mp 238–239 °C).

^{1}H NMR ($CDCl_3$, 30 °C, 250 MHz): δ = 1.35 [s, 6 H, $C(CH_3)_2$], 1.62 (m, 2 H, CH_2) 1.80 (m, 4 H, 2 CH_2) 2.76 (s, 3 H, NCH_3) 3.01 [m, 4 H, $N(CH_2)_2$], 6.57 (m, 2 H, H-5′, H-7), 6.89 (dd, 1 H, H-5, *J* = 7.4, 8.1 Hz), 7.09 (d, 1 H, H-4, *J* = 7.1 Hz), 7.22 (ddd, 1 H, H-6, *J* = 7.7, 7.6, 1.3 Hz), 7.37 (ddd, 1 H, H-8′, *J* = 8.2, 8.2, 1.3 Hz), 7.54 (ddd, 1 H, H-9′, *J* = 8.2, 8.2, 1.3 Hz), 7.62 (s, 1 H, H-2′), 8.02 (d, 1 H, H-7′, *J* = 8.2 Hz), 8.53 (d, 1 H, H-10′, *J* = 8.5 Hz).

Anal. Calcd for $C_{27}H_{29}N_3O$: C, 78.80; H, 7.10; N, 10.21. Found: C, 78.93; H, 7.04; N, 10.19.

5-Chloro-1,3,3-trimethyl-6′-piperidinospiro(indolino-2,3′-[3*H*]naphth[2,1-*b*]oxazine) (4b)
Mp 227–229 °C (Lit.[14] mp 220–222 °C).

^{1}H NMR ($CDCl_3$, 30 °C, 250 MHz): δ = 1.34 [s, 6 H, $C(CH_3)_2$], 1.62 (m, 2 H, CH_2), 1.80 [m, 4 H, $N(CH_2)_2$], 2.72 (s, 3 H, NCH_3), 2.99 (m, 4 H, 2 CH_2), 6.46 (d, 1 H, H-7, *J* = 8.2 Hz), 6.55 (s, 1 H, H-5′), 7.02 (d, 1 H, H-4, *J* = 2.1 Hz), 7.15 (dd, 1 H, H-6, *J* = 8.2, 2.1 Hz), 7.37 (ddd, 1 H, H-8′, *J* = 8.2, 6.9, 1.3 Hz), 7.51 (m, 2 H, H-9′, H-2′), 8.03 (d, 1 H, H-7′, *J* = 8.3 Hz), 8.51 (d, 1 H, H-10′, *J* = 8.3 Hz).

Anal. Calcd for $C_{27}H_{28}ClN_3O$: C, 72.71; H, 6.33; N, 9.42. Found: C, 72.58; H, 6.41; N, 9.38.

1,3,3-Trimethyl-6′-thiomorpholinospiro(indolino-2,3′-[3*H*]naphth[2,1-*b*]oxazine) (5)
Mp 188–189 °C (Lit.[14] mp 184–185 °C).

^{1}H NMR ($CDCl_3$, 30 °C, 250 MHz): δ = 1.35 [s, 6 H, $C(CH_3)_2$], 2.75 (s, 3 H, NCH_3), 2.89 [m, 4 H, $N(CH_2)_2$], 3.29 [m, 4 H, $S(CH_2)_2$], 6.59 (m, 2 H, H-7, H-5′), 6.90 (dd, 1 H, H-5, *J* = 7.4, 7.3 Hz), 7.09 (d, 1 H, H-4, *J* = 7.1 Hz), 7.22 (ddd, 1 H, H-6, *J* = 7.6, 7.6, 1.3 Hz), 7.41 (ddd, 1 H, C-8′, *J* = 7.1, 7.0, 1.2 Hz), 7.55 (ddd, 1 H, H-9′, *J* = 7.1, 7.0, 1.2 Hz), 7.65 (s, 1 H, H-2′), 8.01 (d, 1 H, H-7′, *J* = 8.2 Hz), 8.53 (d, 1 H, H-10′, *J* = 8.2 Hz).

Anal. Calcd for $C_{26}H_{27}N_3OS$: C, 72.69; H, 6.34; N, 9.78. Found: C, 72.41; H, 6.43; N, 9.71.

6′-Indolino-1,3,3-trimethylspiro(indolino-2,3′-[3*H*]naphth[2,1-*b*]oxazine) (6)
Mp 250–252 °C (Lit.[14] mp 231–233 °C) .

^{1}H NMR ($CDCl_3$, 30 °C, 250 MHz): δ = 1.36 [s, 6 H, $C(CH_3)_2$], 2.77 (s, 3 H, NCH_3), 3.17 (m, 2 H, CH_2), 3.90 (m, 2 H, NCH_2), 6.28 (d, 1 H, H-7″, *J* = 7.7 Hz), 6.58 (d, 1 H, H-7, *J* = 7.7 Hz), 6.74 (dd, 1 H, H-5″, *J* = 6.5, 6.5 Hz), 6.92 (m, 3 H, H-5, H-5′, H-4″), 7.09 (d, 1 H, H-4, *J* = 8.1 Hz), 7.21 (dd, 2 H, H-6, H-6″, *J* = 8.0, 7.6 Hz), 7.34 (ddd, 1 H, H-8′, *J* = 8.4, 8.2, 1.3 Hz), 7.60 (ddd, 1 H, H-9′, *J* = 8.1, 8.3, 1.3 Hz), 7.69 (s, 1 H, H-2′), 7.96 (d, 1 H, H-7′, *J* = 8.1 Hz), 8.61 (d, 1 H, H-10′, *J* = 8.4 Hz).

Anal. Calcd for $C_{30}H_{27}N_3O$: C, 80.87; H, 6.11; N, 9.43. Found: C, 80.72; H, 6.18; N, 9.39.

Compound 7
2-Methylene-1,3,3-trimethylindoline (1 mmol), 1-aminonaphthol hydrochloride (1.1 mmol), diethylamine (1.2 mmol), Et_3N (1.1 mmol) and DMSO (3 mmol) were dissolved in toluene (15 mL). The mixture was stirred for 20 h at r.t. After the reaction was over, the product was purified by column chromatography on silica gel (Merck 60 with 0.06–0.20 mm particles) using pentane–Et_2O mixture as eluent; yield: 26%; mp 167–169 °C (dec.).

^{1}H NMR ($CDCl_3$, 30 °C, 500 MHz): δ = 1.40 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 2.94 (s, 3 H, NCH_3), 3.60 (d, 1 H, H-2′, *J* = 11.8 Hz), 3.80 (d, 1 H, H-2′, *J* = 11.8 Hz), 4.25 (br s, 1 H, NOH), 6.65 (d, 1 H, H-7, *J* = 7.4 Hz), 6.88 (ddd, 1 H, H-5, *J* = 6.9, 6.7 Hz, 0.9 Hz), 7.11 (m, 2 H, H-4, H-5′), 7.19 (ddd, 1 H, H-6, *J* = 7.4, 7.1, 1.3 Hz), 7.31 (d, 1 H, H-6′, *J* = 8.6 Hz), 7.38 (ddd, 1 H, H-8′, *J* = 7.1, 6.6, 1.4 Hz), 7.49 (ddd, 1 H, H-9′, *J* = 6.7, 7.1, 1.3 Hz), 7.72 (d, 1 H, H-10′, *J* = 8.0 Hz), 7.8 (d, 1 H, H-7′, *J* = 7.6 Hz).

^{14}C NMR ($CDCl_3$, 30 °C, 500 MHz): δ = 21.47 (CH_3), 25.43 (CH_3), 29.34 (NCH_3), 42.97 (C-2′), 49.18 (C-3), 99.60 (C-2), 106.99 (C-7), 118.32 (C-5′), 118.67 (C-10′), 118.98 (C-5), 119.95 (C-6′), 121.31 (C-4), 123.19 (C-8′), 123.84 (C-10′a), 124.93 (C-11′), 125.28 (C-9′), 127.66 (C-6), 128.57 (C-7′), 128.94 (C-6′a), 137.29 (C-4a), 141.63 (C-4′a), 149.09 (C-7a).

MS: *m*/*z* (%) = 369 (30, [$M^+ - H_2O$]), 329 (25), 291 (2), 277 (100), 259 (1), 241 (7), 223 (10), 215 (8), 201 (2), 196 (4).

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