142. Synthesis of Thiophene-Substituted Spiropyrans and Spirooxazines, Precursors of Photochromic Polymers

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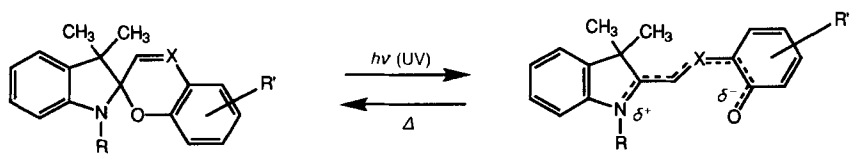
(28.IV.95)

The synthesis of spiropyrans **11** and **12** and spirooxazines **13**–**17** containing a thiophene moiety is described. Two different synthetic approaches were used. The spectrokinetic properties of these new compounds are reported.

Introduction. – In the general context of organic conductors, thiophene oligomers received considerable attention in recent years [1–5]. Their processability by *Langmuir-Blodgett* or vacuum-sublimation techniques led to several interesting applications in the field of nonlinear optics, electronic devices [6] [7], or, more recently, of electroluminescent diodes [8]. The modification of the optical, electronic, and electrochemical properties of these materials is the main goal of research efforts. Thus, the synthesis of new precursor structures to prepare new conducting materials remains a current challenge for organic chemists. The typical photochromic compounds such as spiropyrans and spirooxazines are well-known for their photosensitive properties [9] [10] (*Scheme 1*). The exposure of these organic compounds to UV light results in a color change. This transformation between the closed form, which is colorless, and the colored open form (photomerocyanine) proves attractive to affect potentially the polymer properties.

In this paper, we report the synthesis of spiro[benzopyran-indoles] and spiro[indole-naphthoxazines] containing a thiophene moiety. The introduction of this heterocycle must allow subsequently to access to new molecular materials by electrochemical poly-

Scheme 1. *Photochromic Equilibrium between Closed Form and Open Form*



Closed form
absorption in the UV region
spiro[2*H*-benzopyran-2,2′(3′*H*)-[1*H*]indole] X = CH
spiro[2*H*-1,4-benzoxazine-2,2′(3′*H*)-[1*H*]indole] X = N

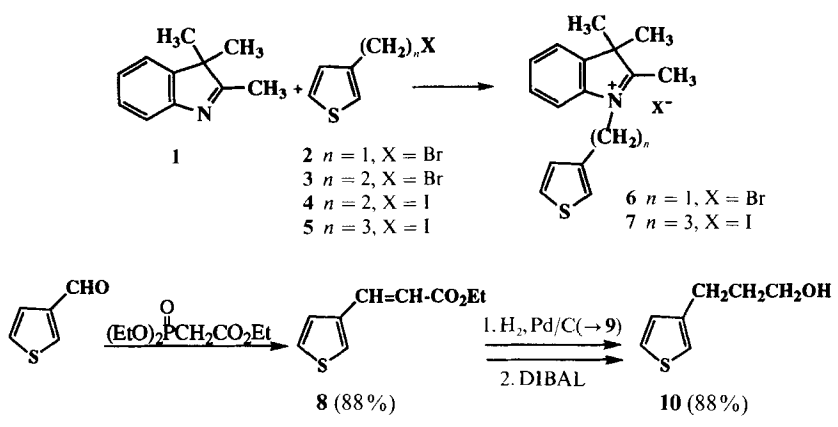
Open form
absorption in the VIS region

merization or copolymerization [11–14]. Both series are interesting candidates because of their different oxidation potentials. This characteristic can be a deciding factor in the final step of electrochemical polymerization or copolymerization [15].

Results and Discussion. – *Synthesis.* We used two different procedures, *A* and *B*, to obtain the photochromic compounds. *Procedure A* is a classical synthetic method, involving the condensation of a heterocyclic iminium salt with 2-hydroxy-3-methoxy-5-nitrobenzaldehyde or 1-nitrosonaphthalen-2-ol in basic medium. Piperidine abstracts an H-atom of the quaternary salt to generate *in situ* a dehydrobase, which then reacts with 2-hydroxy-3-methoxy-5-nitrobenzaldehyde or 1-nitrosonaphthalen-2-ol to lead to a spiro[benzopyran-indole] or spiro[indole-naphthoxazine], respectively.

The quaternary salts **6** and **7** are obtained by a nucleophilic substitution of 2,3,3-trimethyl-3*H*-indole (**1**) on (halogenoalkyl)thiophene (*Scheme 2*). The halogenated compounds **2**–**4** are easily accessible from commercially available alcohols by bromination and iodination. Thus, PBr_3 reacts with thiophene-3-methanol and thiophene-3-ethanol to afford the brominated products **2** and **3** in 89 and 53% yield, respectively. Halogen exchange on **3** using NaI in acetone leads to **4**. The synthesis of thiophene-3-propanol (**10**), precursor of **5** requires three steps from commercial thiophene-3-carboxaldehyde

Scheme 2

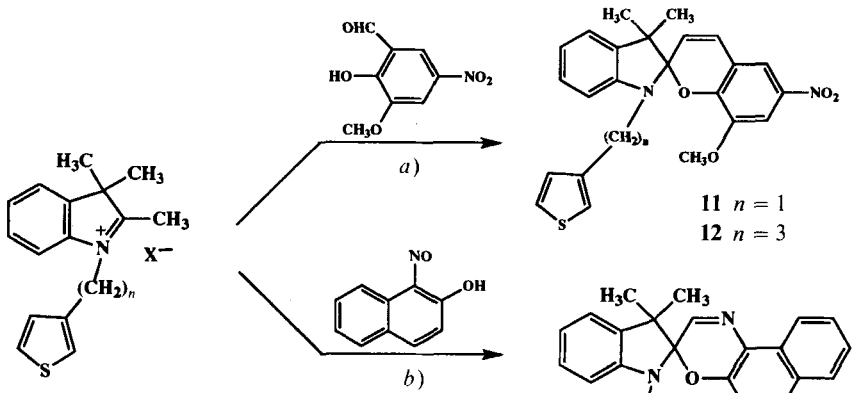


(*Scheme 2*). Using a *Wadsworth-Emmons* reaction [16–18], the enolate ylide obtained from NaH and 2-(diethoxyphosphoryl)ethylacetate reacts with this aldehyde to lead to ethyl 3-(thien-3-yl)acrylate (**8**) in 88% yield. The C=C bond is quantitatively hydrogenated at 60° in the presence of a Pd/C catalyst, and reduction of ethyl thiophene-3-propanoate (**9**) by diisobutylaluminium hydride DIBAL (H) [19] gives the desired **10** in 88% yield. Bromination of **10** and then iodination as already described afford **5** (51% overall yield).

The three halogenated compounds **2**, **4**, and **5** are reacted with 2,3,3-trimethyl-3*H*-indole (**1**) in a sealed tube under vacuum at 80–110°, **2** and **5** giving the quaternary salts **6** and **7** as hygroscopic solids in 61 and 91% yield, respectively. The quaternary salt cannot be obtained from **4**; the formation of a black residue is observed. Apparently, for **4**,

elimination becomes preponderant over nucleophilic substitution at high temperatures, and an ionic polymerization is induced. Finally, the quaternary salts **6** and **7** react with the substituted salicylaldehyde in refluxing EtOH to give the spiropyrans **11** and **12** (62 and 87% yield), respectively, or with the 1-nitrosonaphthalen-2-ol in refluxing trichloroethylene to give the spirooxazines **13** and **14** (42 and 55% yield), respectively (*Scheme 3*).

Scheme 3

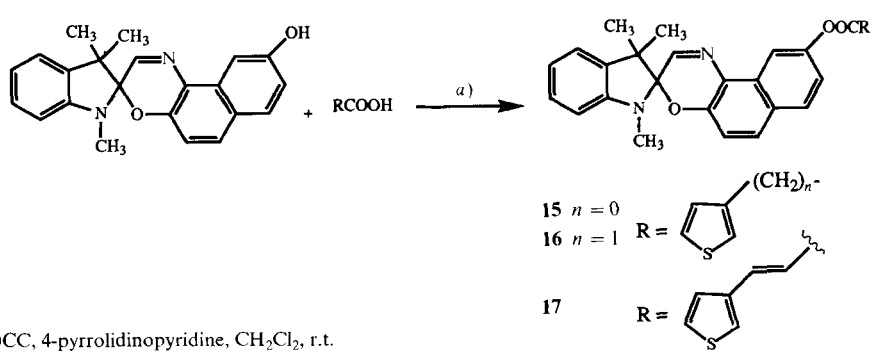


6 $n = 1$, X = Br
7 $n = 3$, X = I

a) Piperidine, EtOH, Ar, reflux.
b) Piperidine, trichloroethylene, Ar, reflux.

Procedure B is based on a mild 'one-pot' esterification [20] of a carboxylic acid containing a thiophene moiety with 1,3,3-trimethylspiro[1*H*-indole-2(3*H*),3′-[3*H*]-naphth[2,1-*b*][1,4]oxazin-9′-ol] [21] (*Scheme 4*). This reaction takes place at room temperature under neutral conditions. According to this approach, the new compounds **15**–**17** are obtained in yields over 70%. Regular esterification methods, using drastic experimental conditions, induce a chemical degradation of the photochromic part.

Scheme 4



a) DCC, 4-pyrrolidinopyridine, CH_2Cl_2, r.t.

Spectrokinetic Measurements. The photochromic properties are described by three main parameters [22] [23]: the fading rate and the wavelength of absorption of the colored form (k_Δ and λ_{max}, resp.), and its 'colorability' defined as the initial absorbance (A_o) obtained at λ_{max} just after the photoactivation. The spectra of photomerocyanines in toluene at 298 K and the rate constants of thermal ring closure k_Δ were determined using a flash-photolysis apparatus (*Nortech*; flash energy 6 kV) coupled to a *Warner* and *Swasey* fast scanning spectrometer [22] [23]. Concentrations used were $2.5 \cdot 10^{-5}$ M in toluene as solvent. The results are reported in the *Table*.

Table. *Fading Rate* k_Δ *and Absorption Wavelength* λ_{max} *of the Colored Form and 'Colorability'* (initial absorbance A_o)

	11	**12**	**13**	**14**	**15**	**16**	**17**
k_Δ [s^{-1}]	0.05	0.023	0.5	0.58	0.28	0.29	0.30
λ_{max} [nm]	608	605	(560)589	(554)593	(562)597	(569)598	(565)598
A_o	3.45	2.70	1.30	1.08	0.99	0.88	0.97

As expected, the colored forms of spiropyrans **11** and **12** are more stable than the colored forms of spirooxazines **13–17**. The open form of compound **12** presents a better thermal stability than the open form of compound **11**, due to the stereoelectronic effects (increasing of the inductive effect and decreasing of the steric hindrance). This result is compatible with the zwitterionic character of photomerocyanines [24].

In the spirooxazine series, this effect is not observed, because the corresponding open forms have a quinone or polyene structure. The presence of an ester functionality at C(9′) of **15–17** stabilizes the colored forms without influencing the absorption wavelengths. The variations of the 'colorability' are quite low. As one might expect, the spiropyrans show a better colorability than the spirooxazines [10]; nevertheless, spirooxazines are well known for their better resistance to photodegradation [25].

Conclusion. – It is shown in this paper, that spiropyrans and spirooxazines containing one thiophene entity are quite accessible. The introduction of the thiophene moiety does not affect appreciably spectrokinetic properties, so these compounds will be good precursors to prepare new molecular materials by electrochemical polymerization or copolymerization.

The *Belgium National Bank* is gratefully acknowledged for its financial support.

Experimental Part

1. *General.* Solvents were dried by distillation on drying agents as follows: THF, benzene, toluene (Na metal); CH_2Cl_2 (CaH_2). Abs. EtOH and acetone were purchased from *Carlo-Erba Co.* Column chromatography (CC): silica gel *60* (*Merck 7734*). Melting points: capillary tubes, *Büchi-510* apparatus; uncorrected. *Fourier* transform IR spectra: *Matson-Polaris* spectrophotometer; in cm^{-1}. NMR Spectra: in $CDCl_3$ soln.; *Bruker-AW-80, -BM-250,* or *-AMX-400* spectrophotometers; chemical shifts δ in ppm downfield from ($SiMe_4 = 0$ ppm), coupling constants J in Hz.

2. *(Halogenoalkyl)thiophene. 3-(Bromomethyl)thiophene* (**2**). To a soln. of thiophene-3-methanol (4 g, 3.5 mmol) in dry benzene (40 ml) was added PBr_3 (9.5 g, 3.5 mmol). The mixture was stirred at r.t. for 3 h (TLC monitoring). After evaporation of the benzene, the residue was poured into cold H_2O and 2.0M aq. NaOH was

added until pH 11 was reached. The mixture was extracted with CH_2Cl_2 (2 × 30 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the crude product purified by CC (silica gel, $CHCl_3$): 5.5 g (89%) of **2**. Lachrymatory oil. ^{1}H-NMR (80 MHz): 4.46 (*s*, 2 H); 6.80–7.35 (*m*, 3 H).

3-(2-Bromoethyl)thiophene (**3**). PBr_3 (24 g, 88 mmol) was slowly added to a soln. of thiophene-3-ethanol in dry benzene (150 ml) and the mixture stirred at r.t. for 5 h. Workup as described for **2** (no CC) gave 9 g (53%) of **3** (> 95% pure by ^{1}H-NMR) which was used without further purification in the next step. IR (film): 540. ^{1}H-NMR (80 MHz): 3.15 (*t*, *J* = 7.2, 2 H); 3.40 (*t*, *J* = 7.3, 2 H); 6.80–7.25 (*m*, 3 H).

3-(2-Iodoethyl)thiophene (**4**). A mixture of NaI (21 g, 0.47 mol) and **3** (9 g, 0.14 mol) in dry acetone (60 ml) was stirred at 50° for 4 d. After cooling, the mixture was filtered, the filtrate evaporated, and the crude product purified by CC (silica gel, $CHCl_3$): 10.27 g (92%) of **4**. IR (film): 560. ^{1}H-NMR (80 MHz): 2.95–3.45 (*m*, 4 H); 6.65–7.40 (*m*, 3 H).

Ethyl 3-(Thien-3-yl)prop-2-enoate (**8**). Ar, NaH (0.902 g, 80% dispersion in mineral oil, 39 mmol) was washed with hexane and then suspended in THF (15 ml). To this suspension at 0° (ice bath), a soln. of 2-(diethoxyphosphoryl)ethylacetate (8.79 g, 39 mmol) in dry THF (40 ml) was added dropwise. The soln. was stirred at 0° for 30 min and then allowed to warm to r.t. Within *ca.* 30 min, thiophene-3-carboxaldehyde (4 g, 36 mmol) in dry THF (40 ml) was slowly added, and the mixture was stirred at r.t. for 16 h (TLC (pentane/AcOEt 1:1) monitoring). After evaporation of the THF, the residue was poured into 150 ml of H_2O, the mixture extracted with $CHCl_3$ (3 × 50 ml), the combined org. phase washed with H_2O, sat. aq. $NaHCO_3$ soln., and brine, dried ($MgSO_4$), and evaporated and the residue purified by CC (silica gel, pentane/Et_2O 100:0→40:60): 5.70 (88%) of **8**. IR (film): 1705, 1637. ^{1}H-NMR (250 MHz): 1.32 (*t*, *J* = 7.1, 3 H); 4.25 (*q*, *J* = 7.1, 2 H); 6.25 (*d*, *J* = 15.9, 1 H); 7.27–7.34 (*m*, 2 H); 7.48 (*dd*, *J* = 1.2, 2.8, 1 H); 7.66 (*d*, *J* = 15.9, 1 H). Anal. calc. for $C_9H_{10}O_2S$: C 59.31, H 5.53, S 17.5; found: C 59.28, H 5.50, S 17.5.

Ethyl 3-(Thien-3-yl)propanoate (**9**). A soln. of **8** (4 g, 22 mmol) in abs. EtOH (40 ml) was hydrogenated at 60° under H_2 (1 atm) in the presence of 1 g of Pd/C. After 4 d, the mixture was purged with N_2 and filtered through *Celite*. The *Celite* was washed with abs. EtOH and the filtrate evaporated 4 g (*ca.* 100%) of **9**. IR (film): 1734, 1184. ^{1}H-NMR (250 MHz): 1.23 (*t*, *J* = 7.1, 3 H); 2.61 (*t*, *J* = 7.6, 2 H); 2.96 (*t*, *J* = 7.6, 2 H); 4.13 (*q*, *J* = 7.1, 2 H); 6.92–6.97 (*m*, 2 H); 7.23 (*dd*, *J* = 3.0, 4.8, 1 H). Anal. calc. for $C_9H_{12}O_2S$: C 58.66, H 6.56, S 17.4; found: C 58.64, H 6.49, S 17.4.

Thiophene-3-propanol (**10**). A soln. of **9** (4 g, 22 mmol) in toluene (20 ml) was cooled to 0° (ice bath), and 65 ml of 1.0M DIBAH in toluene was added by syringe. The mixture was stirred at 0° for 3 h, then toluene/MeOH 1:1 (20 ml) was slowly added, followed by 20 ml of 2.0M aq. HCl. The mixture was stirred at 0° for 30 min, the solid filtered off, the org. layer separated, and the aq. layer extracted with Et_2O (2 × 20 ml). The combined org. phase was dried (K_2CO_3) and evaporated and the residue chromatographed (silica gel, pentane/AcOEt 1:1): 2.71 g (88%) of **10**. IR (film): 3550–3100, 1055, 774. ^{1}H-NMR (80 MHz): 1.82–1.93 (*m*, 2 H); 1.96 (*s* large, 1 H); 2.71 (*t*, *J* = 7.6, 2 H); 3.64 (*t*, *J* = 6.4, 2 H); 6.87–7.25 (*m*, 2 H). Anal. calc. for $C_9H_{10}O_2S$: C 59.11, H 7.09, S 22.5; found: C 59.15, H 7.02, S 22.5.

3-(3-Bromopropyl)thiophene. PBr_3 (2.28 g, 8.4 mmol) was slowly added to a soln. of **10** (1.2 g, 8.4 mmol) in dry benzene (20 ml) and the mixture stirred at r.t. for 2 h. Workup as described for **2** (2 × 15 ml of CH_2Cl_2, no CC) gave 1.20 g (68%) of the bromide (> 95% pure by ^{1}H-NMR) which was used without further purification in the next step. IR (film): 560. ^{1}H-NMR (80 MHz): 2.03–2.14 (*m*, 2 H); 2.74 (*t*, *J* = 7.2, 2 H); 3.33 (*t*, *J* = 6.5, 2 H); 6.86–7.20 (*m*, 3 H).

3-(3-Iodopropyl)thiophene (**5**). As described for **4**, with NaI (2.61 g, 17.4 mmol), 3-(3-bromopropyl)thiophene (1.19 g, 5.8 mmol), and acetone (30 ml; at 40° for 47 h). CC (silica gel, pentane) yielded 1.10 g (75%) of **5**. IR (film): 540. ^{1}H-NMR (80 MHz): 2.04–2.15 (*m*, 2 H); 2.73 (*t*, *J* = 7.1, 2 H); 3.12 (*t*, *J* = 6.5, 2 H); 6.87–7.23 (*m*, 3 H).

3. *Quaternizations. 2,3,3-Trimethyl-1-[(thien-3-yl)methyl]-3H-indol-1-ium Bromide* (**6**). A mixture of 2,3,3-trimethyl-3*H*-indole (**1**; 4.95 g, 31 mmol) and **2** (5.5 g, 31 mmol) was sealed under vacuum and heated in an oven at 80° for 18 h. The suspension was filtered and the solid washed with pentane: 6.4 g (61%) of **6**. Hygroscopic pink-orange solid. M.p. 58–59°. ^{1}H-NMR (80 MHz): 1.62 (*s*, 6 H); 3.12 (*s*, 3 H); 5.20 (*s*, 2 H); 6.93–7.90 (*m*, 7 H).

2,3,3-Trimethyl-1-[3-(thien-3-yl)propyl]-3H-indol-1-ium Iodide (**7**). As described for **6**, with **5** (1.83 g, 7.2 mmol, at 110° for 16 h): 2.72 g (91%) of **7**. Hygroscopic orange solid. M.p. 83–84°. ^{1}H-NMR (80 MHz): 1.60 (*s*, 3 H); 2.34 (*t*, *J* = 7.9, 2 H); 2.93 (*t*, *J* = 7.1, 2 H); 3.04 (*s*, 3 H); 4.69 (*dd*, *J* = 7.9, 7.1, 1 H); 6.94–7.89 (*m*, 7 H).

4. *Photochromic Compounds*. 4.1. *Procedure A. Compounds* **11** *and* **12**: A soln. of 2-hydroxy-3-methoxy-5-nitrobenzaldehyde (1.5 mmol), the quaternary salt (1.5 mmol), and piperidine (1.5 mmol) in abs. EtOH (30 ml) was refluxed under Ar. After evaporation of EtOH, the residue was purified by CC (silica gel, pentane/AcOEt 100:0→40:60). Recrystallization form pentane/Et_2O gave crystalline material.

Compounds **13** *and* **14**: A soln. of 1-nitrosonaphthalin-2-ol (1.5 mmol), the quaternary salt (1.5 mmol), and piperidine (1.5 mmol) in trichloroethylene (40 ml) was refluxed under Ar. The solvent was evaporated and the residue purified by CC (silica gel, CH_2Cl_2/Et_2O 100:0→50:50). Recrystallization from pentane/Et_2O gave crystalline material.

4.2. *Procedure B. Compounds* **15–17**: A soln. of carboxylic acid (10 mmol), *N,N*-dicyclohexylcarbodiimide (DCC; 11 mmol), 1,3,3-trimethylspiro[1*H*-indole-2(3*H*),3′-[3*H*]naphth[2,1-*b*][1,4]oxazin]-9′-ol (11 mmol) and 4-pyrrolidinopyridine (1 mmol) in CH_2Cl_2 (30–40 ml) was allowed to stand at r.t. until esterification was complete (TLC (pentane/AcOEt 1:1) monitoring). The *N,N*-dicyclohexylurea was filtered off and washed with CH_2Cl_2. The filtrate was evaporated and the residue purified by CC (silica gel, pentane/CH_2Cl_2 100:0→0:100) to give the corresponding ester.

4.3. *Compounds* **11–14**. *8-Methoxy-3′,3′-dimethyl-6-nitro-1′-[(thien-3-yl)methyl]spiro[2*H*-benzopyran-2,2′(3′*H*)-[1*H*]indole]* (**11**). After 17 h, yield 62%. M.p. 78°. IR (KBr): 1651, 1608, 1578, 1455, 1113, 1091. ^{1}H-NMR (400 MHz): 1.21 (*s*, 3 H); 1.29 (*s*, 3 H); 3.71 (*s*, 3 H); 4.40 (*AB*, J_{AB} = 16.3, $\Delta\nu$ = 30.3, 2 H); 5.86 (*d*, *J* = 10.3, 1 H); 6.41 (*d*, *J* = 7.7, 1 H); 6.82 (*d*, *J* = 10.3, 1 H); 6.86 (*dd*, *J* = 7.4, 0.8, 1 H); 6.95 (*dd*, *J* = 4.9, 1.2, 1 H); 7.04–7.10 (*m*, 3 H); 7.21 (*dd*, *J* = 4.9, 3.0, 1 H); 7.59 (*d*, *J* = 2.6, 1 H); 7.66 (*d*, *J* = 2.6, 1 H). ^{13}C-NMR (62.5 MHz): 19.87 (Me); 26.32 (Me); 43.36 (CH_2N); 52.66 (C); 56.17 (MeO); 106.34 (C); 107.61 (CH); 107.80 (CH); 115.28 (CH); 118.29 (C); 119.63 (CH); 121.01 (CH); 121.63 (2 CH); 125.93 (CH); 126.68 (CH); 127.59 (CH); 128.40 (CH); 136.02 (C); 139.63 (C); 140.47 (C); 146.82 (C); 147.36 (C); 149.20 (C). Anal. calc. for $C_{24}H_{22}N_2O_4S$: C 66.34, H 5.10, N 6.44, S 7.4; found: C 66.35, H 5.28, N 6.44, S 7.3.

*8-Methoxy-3′,3′-dimethyl-6-nitro-1′-[3-(thien-3-yl)propyl]spiro[2*H*-benzopyran-2,2′(3′*H*)-[1*H*]indole]* (**12**). After 16 h, yield 87%. M.p. 58–59°. IR (KBr): 1607, 1618, 1480, 1455, 1092. ^{1}H-NMR (250 MHz): 1.16 (*s*, 3 H); 1.27 (*s*, 3 H); 1.87–2.00 (*m*, 2 H); 2.58–2.67 (*m*, 2 H); 3.17–3.27 (*m*, 2 H); 3.70 (*s*, 3 H); 5.78 (*d*, *J* = 10.3, 1 H); 6.48 (*d*, *J* = 7.6, 1 H); 6.77–7.23 (*m*, 7 H); 7.59 (*d*, *J* = 2.5, 1 H); 7.66 (*d*, *J* = 2.5, 1 H). ^{13}C-NMR (62.5 MHz): 20.48 (Me); 26.77 (Me); 28.42 (CH_2); 29.96 (CH_2); 43.55 (CH_2N); 53.14 (C); 56.81 (MeO); 107.14 (CH); 108.41 (CH); 115.99 (CH); 118.84 (C); 119.72 (CH); 120.68 (CH); 122.29 (CH); 122.48 (CH); 126.02 (CH); 128.19 (CH); 128.57 (CH); 128.65 (CH); 136.60 (C); 140.90 (C); 142.46 (C); 147.53 (C); 147.93 (C); 149.94 (C). Anal. calc. for $C_{26}H_{22}N_2O_4S$: C 67.50; H 5.66, N 6.05, S 6.9; found: C 67.56, H 5.67, N 6.01, S 6.8.

*3,3-Dimethyl-1-[(thien-3-yl)methyl]spiro[1*H*-indole-2(3*H*),3′-[3*H*]naphth[2,1-b][1,4]oxazine]* (**13**). After 24 h, yield 42%. M.p. 78–79°. IR (KBr): 1651, 1608, 1578, 1455, 1281, 1113, 1091. ^{1}H-NMR (400 MHz): 1.35 (*s*, 3 H); 1.39 (*s*, 3 H); 4.36 (*AB*, J_{AB} = 16.3, $\Delta\nu$ = 30.3, 2 H); 6.46 (*t*, *J* = 7.4, 1 H); 6.88 (*t*, *J* = 7.4, 1 H); 6.97 (*d*, *J* = 8.9, 1 H); 6.98 (*d*, *J* = 4.9, 1 H); 7.04 (*m*, 1 H); 7.07–7.12 (*m*, 2 H); 7.22 (*dd*, *J* = 3.0, 4.9, 1 H); 7.37 (*t*, *J* = 7.6, 1 H); 7.54 (*dd*, *J* = 8.4, 7.6, 1 H); 7.63 (*d*, *J* = 8.9, 1 H); 7.72 (*d*, *J* = 7.6, 1 H); 7.73 (*s*, 1 H); 8.51 (*d*, *J* = 8.4, 1 H). ^{13}C-NMR (62.5 MHz): 20.70 (Me); 25.50 (Me); 44.22 (CH_2N); 52.21 (C); 98.89 (C); 107.86 (CH); 107.86 (CH); 116.70 (CH); 120.00 (CH); 121.39 (CH); 121.50 (2 CH); 122.67 (C); 124.15 (CH); 126.13 (CH); 126.72 (CH); 127.07 (CH); 127.70 (CH); 127.86 (CH); 129.22 (C); 130.23 (CH); 130.73 (C); 135.66 (C); 139.22 (C); 143.79 (C); 146.98 (C); 150.81 (CH). Anal. calc. for $C_{26}H_{22}N_2OS$: C 76.06, H 5.40, N 6.82, S 7.8; found: C 75.92, H 5.41, N 6.49, S 7.7.

*3,3-Dimethyl-1-[3-(thien-3-yl)propyl]spiro[1*H*-indole-2(3*H*),3′-[3*H*]naphth[2,1-b][1,4]oxazine]* (**14**). After 22 h, yield 55%. M.p. 123–124°. IR (KBr): 1605, 1592, 1240, 1032, 745. ^{1}H-NMR (400 MHz): 1.32 (*s*, 6 H); 1.83–2.11 (*m*, 2 H); 2.49–2.70 (*m*, 2 H); 3.09–3.33 (*m*, 2 H); 6.49 (*d*, *J* = 7.8, 1 H); 6.79–6.82 (*m*, 2 H); 6.86 (*t*, *J* = 7.4, 1 H); 6.97 (*d*, *J* = 8.9, 1 H); 7.06 (*d*, *J* = 7.4, 1 H); 7.12 (*dd*, *J* = 3.0, 4.8, 1 H); 7.16 (*td*, *J* = 7.4, 1.1, 1 H); 7.38 (*td*, *J* = 7.5, 1.1, 1 H); 7.57 (*td*, *J* = 8.4, 1.2, 1 H); 7.64 (*d*, *J* = 8.9, 1 H); 7.72 (*s*, 1 H); 7.73 (*d*, *J* = 7.8, 1 H); 8.55 (*d*, *J* = 8.4, 1 H); selective irradiation at 420.73 Hz→simplification at 2.49–2.70 and 3.09–3.33: *AB*-type spectra at 2.73 (J_{AB} = 14.8, $\Delta\nu$ = 9.9) and 3.33 (J_{AB} = 15.1, $\Delta\nu$ = 9.6). ^{13}C-NMR (62.5 MHz): 20.93 (Me); 25.56 (Me); 27.92 (CH_2); 29.51 (CH_2); 44.01 (CH_2N); 52.15 (C); 98.93 (C); 106.81 (CH); 116.92 (CH); 119.54 (CH); 120.21 (CH); 121.58 (CH); 121.68 (CH); 122.70 (C); 124.22 (CH); 125.49 (CH); 127.17 (CH); 127.83 (CH); 127.95 (2 CH); 129.31 (C); 130.30 (CH); 130.90 (C); 135.69 (C); 141.67 (C); 143.98 (C); 146.95 (C); 151.11 (CH). Anal. calc. for $C_{28}H_{26}N_2OS$: C 76.68, H 5.97, N 6.37, S 7.3; found: C 76.68, H 6.00, N 6.32, S 7.3.

*1,3,3-Trimethylspiro[1*H*-indole-2(3*H*),3′-[3*H*]naphth[2,1-b][1,4]oxazine]-9′-yl Thiophene-3-carboxylate* (**15**). After 5 days, yield 71%. M.p. 220–221°. IR (KBr): 3110, 1734, 1244, 1180, 740, 695. ^{1}H-NMR (250 MHz): 1.35 (*s*, 6 H); 2.76 (*s*, 3 H); 6.58 (*d*, *J* = 7.7, 1 H); 6.90 (*t*, *J* = 7.1, 1 H); 6.99 (*d*, *J* = 8.9, 1 H); 7.08 (*d*, *J* = 7.4, 1 H); 7.22 (*td*, *J* = 7.7, 1.2, 1 H); 7.25 (*dd*, *J* = 8.9, 2.2, 1 H); 7.39 (*dd*, *J* = 5.1, 3.0, 1 H); 7.67 (*d*, *J* = 8.9, 1 H); 7.70 (*dd*, *J* = 5.1, 1.0, 1 H); 7.71 (*s*, 1 H); 7.79 (*d*, *J* = 8.9, 1 H); 8.34–8.36 (*m*, 2 H). ^{13}C-NMR (62.5 MHz): 20.74 (Me); 25.38 (Me); 29.61 (MeN); 51.84 (C); 98.75 (C); 107.13 (CH); 113.10 (CH); 116.62 (CH); 119.40 (CH); 119.87 (CH); 121.47 (CH); 122.90 (C); 126.37 (CH); 127.28 (C); 128.01 (CH); 128.26 (CH); 129.36 (CH); 130.00 (CH); 131.79

(C); 132.93 (C); 134.06 (CH); 135.79 (C); 144.75 (C); 147.53 (C); 149.73 (C); 150.79 (CH); 161.26 (COO). Anal. calc. for $C_{27}H_{22}N_2O_3S$: C 71.34, H 4.87, N 6.16, S 7.0; found: C 71.15, H 4.93, N 6.16, S 7.1.

*1,3,3-Trimethylspiro[1*H*-indole-2(3*H*),3'-[3*H*]naphth[2,1-*b*][1,4]oxazine]-9'-yl Thiophene-3-acetate* (**16**). After 5 days, yield 73%. M.p. 118–119°. IR (KBr): 3100, 1759, 1251, 1120, 835, 744. ^{1}H-NMR (250 MHz): 1.33 (*s*, 6 H); 2.75 (*s*, 3 H); 3.96 (*s*, 2 H); 6.57 (*d*, *J* = 7.7, 1 H); 6.89 (*td*, *J* = 7.4, 0.7, 1 H); 6.98 (*d*, *J* = 8.8, 1 H); 7.08 (*d*, *J* = 7.5, 1 H); 7.11 (*dd*, *J* = 8.7, 2.3, 1 H); 7.18 (*dd*, *J* = 4.9, 1.3, 1 H); 7.20 (*dd*, *J* = 7.7, 1.2, 1 H); 7.29–7.30 (*m*, 1 H); 7.35 (*dd*, *J* = 4.9, 3.0, 1 H); 7.64 (*d*, *J* = 8.9, 1 H); 7.70 (*s*, 1 H); 7.74 (*d*, *J* = 8.8, 1 H); 8.22 (*d*, *J* = 2.3, 1 H). ^{13}C-NMR (62.5 MHz): 20.70 (Me); 25.36 (Me); 29.58 (MeN); 35.95 (CH_2); 51.83 (C); 98.74 (C); 107.12 (CH); 112.87 (CH); 116.64 (CH); 119.14 (CH); 119.87 (CH); 121.46 (CH); 122.82 (C); 123.25 (CH); 125.97 (CH); 127.25 (C); 128.00 (CH); 128.48 (CH); 129.36 (CH); 129.98 (CH); 131.68 (C); 132.89 (C); 135.75 (C); 144.75 (C); 147.50 (C); 149.67 (C); 150.82 (CH); 169.72 (COO). Anal. calc. for $C_{28}H_{24}N_2O_3S$: C 71.77, H 5.16, N 5.97, S 6.8; found: C 71.76, H 5.16, N 5.80, S 6.7.

*1,3,3-Trimethylspiro[1*H*-indole-2(3*H*),3'-[3*H*]naphth[2,1-*b*][1,4]oxazine]-9'-yl 3-(Thien-3-yl)prop-2-enoate* (**17**). After 5 days, yield 75%. M.p. 170–171°. IR (KBr): 3097, 1728, 1252, 1192, 785, 744. ^{1}H-NMR (250 MHz): 1.35 (*s*, 6 H); 2.76 (*s*, 3 H); 6.51 (*d*, *J* = 15.8, 1 H); 6.58 (*d*, *J* = 7.7, 1 H); 6.90 (*t*, *J* = 7.2, 1 H); 6.99 (*d*, *J* = 8.9, 1 H); 7.09 (*d*, *J* = 7.2, 1 H); 7.21 (*dd*, *J* = 8.8, 2.0, 1 H); 7.24 (*d*, *J* = 7.4, 1 H); 7.39 (*d*, *J* = 2.0, 2 H); 7.59 (*t*, *J* = 2.0, 1 H); 7.66 (*d*, *J* = 8.9, 1 H); 7.71 (*s*, 1 H); 7.78 (*d*, *J* = 8.8, 1 H); 7.91 (*d*, *J* = 15.8, 1 H); 8.31 (*d*, *J* = 2.3, 1 H). ^{13}C-NMR (62.5 MHz): 20.72 (Me); 25.36 (Me); 29.60 (MeN); 51.81 (C); 98,71 (C); 107.11 (CH); 113.01 (CH); 116.52 (CH); 116.88 (CH); 119.42 (CH); 119.86 (CH); 121.46 (CH); 122.87 (C); 125.18 (CH); 127.16 (CH); 127.22 (C); 128.00 (CH); 128.91 (CH); 129.32 (CH); 129.98 (CH); 131.78 (C); 135.78 (C); 137.38 (C); 139.98 (CH); 144.70 (C); 147.52 (C); 149.84 (C); 150.73 (CH); 165.84 (COO). Anal. calc. for $C_{29}H_{24}N_2O_3S$: C 72.47, H 5.03, N 5.82, S 6.6; found: C 72.01, H 5.30, N 5.57, S 6.3.

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