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The title compound **1** reacts with trifluoroacetic anhydride to give the doubly trifluoroacetylated derivative **2** and in addition the coumarin derivative **3**. In refluxing DMF, two moles of **1** react with loss of one molecule of ammonia to afford **4**, which undergoes subsequent *N*-acylation by  $\beta$ -dicarbonyl compounds **9a-f** to yield *N*-acyl derivatives **10a-f**. With dimethyl malonate (**9a**) besides compound **10a**, the cycloacylated compound **11** was also obtained in good yield. Compound **11** is readily hydrolysed and decarboxylated with both acid and alkali to the previously described fused derivative **12**. The latter may be converted into the new thienopyrimidinone derivative by action of aqueous alkali.

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### Introduction.

Aside from its sulfuration at C-1, leading to the corresponding disulfide and its reaction with acetic anhydride to yield the fused pyrimidine **12** [1,2], the reactions of the thienocoumarin derivative **1** (readily accessible in two steps from 2-hydroxyacetophenone, malononitrile and sulfur using diethylamine as catalyst [1,2]), have hitherto not been explored.

As a continuation of our investigations on the reactivity of the title compound **1**, we have reported in a recent paper [3,4] on [4+2]-cycloadditions of compound **1** with some selected dienophiles. Compound **1**, owing to the presence of two nucleophilic groups in the molecule, might also undergo cyclocondensation and/or cycloacylation with appropriate 1,3-dielectrophilic reagents to generate a new heterocyclic component fused to this ring system.

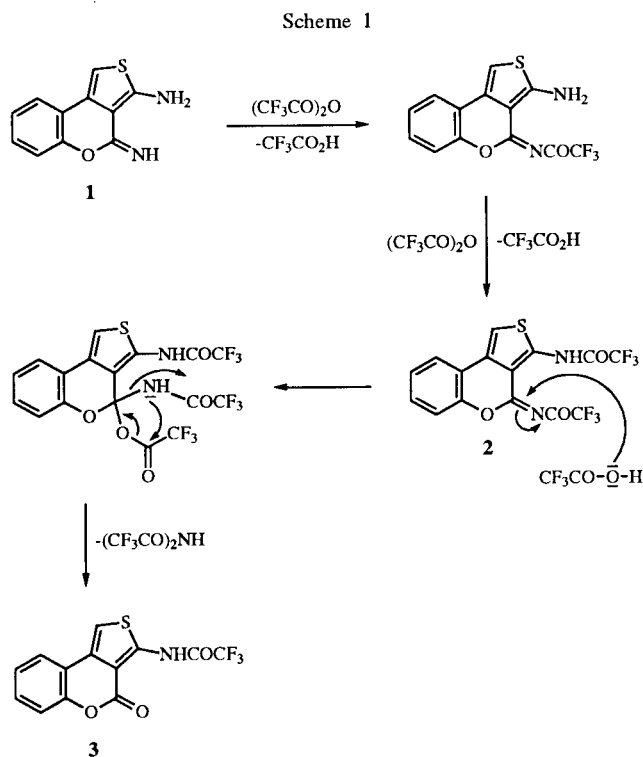
In the present report, we wish to describe the trifluoroacetylation of **1** as well as the reaction of the latter with a variety of 1,3-dicarbonyl compounds ( $\beta$ -ketoesters and  $\beta$ -diesters **9a-f**).

### Results.

In refluxing trifluoroacetic acid, **1** is converted by trifluoroacetic anhydride into the diacyl derivative **2** and the thienocoumarin **3**. The thienocoumarin skeleton is strongly supported by two strong and sharp C=O bands at 1720 and 1700  $\text{cm}^{-1}$  and its fragmentation pattern.

The formation of compound **3** can be explained by the hydrolysis of the imino group in **2** during reaction. Attack on C-4 by trifluoroacetic acid followed by elimination of one mole of *N*-trifluoroacetyl trifluoroacetamide ( $\text{HN}(\text{COCF}_3)_2$ ), is also conceivable.

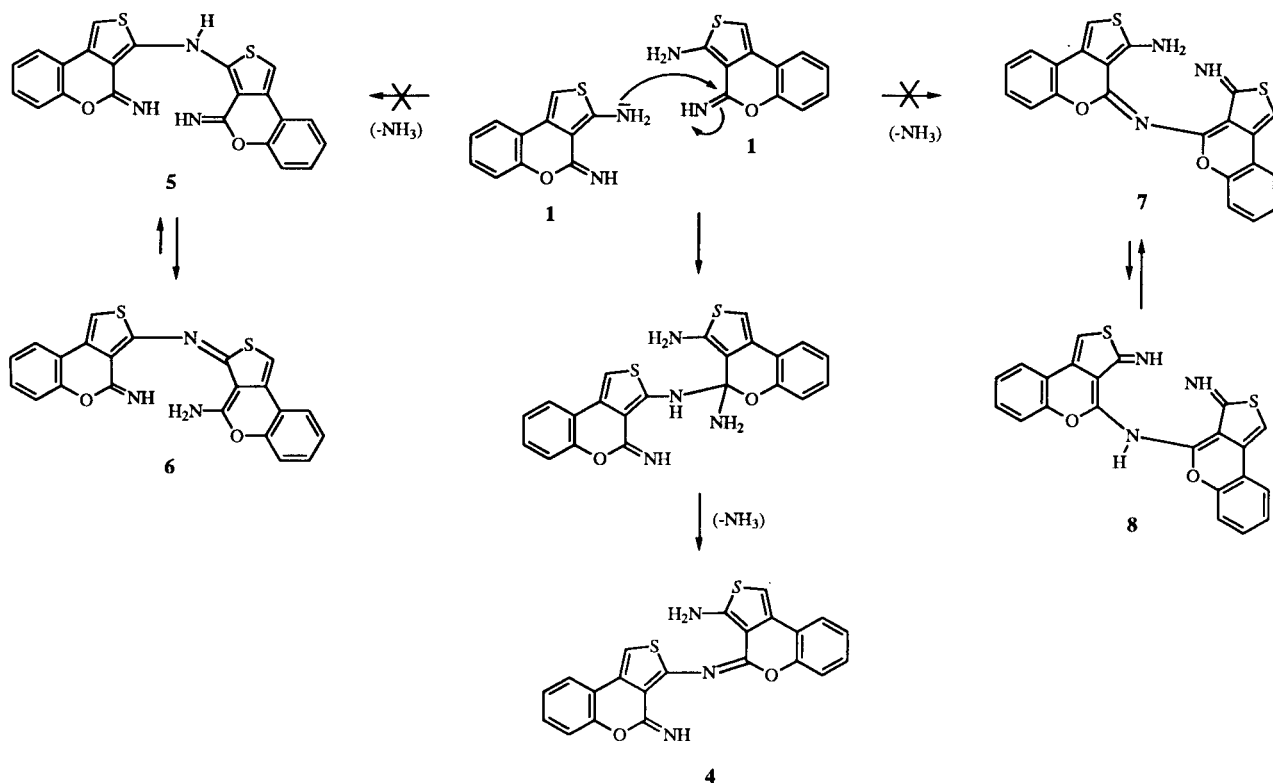
In the course of the reactions of **1** with the  $\beta$ -dicarbonyl reagents **9a-f** either neatly or in boiling DMF ultimately



leading to compounds **10a-f** (Scheme 3), compound **4** was isolated as an intermediate. In fact, in refluxing DMF **1** is converted into the condensation product **4**. Subsequent reactions of **4** with compounds **9a-f** in boiling DMF afforded **10a-f**.

The formation of compound **4** may be rationalized as shown in Scheme 2. Structure **4** which is unsymmetrical, is consistent with the spectral data. Thus, the alternative symmetrical structures **5** and **8** (Scheme 2) were ruled out

Scheme 2



from the available data. Structures **6** and **7**, although unsymmetrical, could also be ruled out for obvious reasons of instability [5,6].

In fact, it is well known that aminothiophenes react with  $\alpha,\beta$ -unsaturated carbonyl compounds with  $-\text{NH}_2$  as the leaving group on the  $\beta$ -carbon, to give aminomethylene derivatives [7]. It has also been reported that 3-aminothiophenes undergo reactions in which the amino group from one molecule attacks the carbon atom bearing the amino group in another. These reactions leading to bis(3-thienyl)amines was first noted by Fisselmann in 1959 [8]. Another example involving this process was reported in 1969 [9]. More recently 3-thiophenamine itself and its 4-methoxy derivative have been shown to give the corresponding bis(3-thienyl)amines on heating [10,11]. Thus the rationale given in Scheme 2 for **4**, involving the elimination of one molecule of ammonia is well supported [7,8,9,10,11].

The formation of compounds **10a-f** probably involves the formation *in situ* of **4** and acylation at  $-\text{NH}_2$  group with loss of a molecule of methanol or ethanol (Scheme 3).

The suggested structures of compounds **10a-f** are in good agreement with their spectral and elemental analysis data.

The reaction of **1** with dimethylmalonate appeared to be a particular case. In fact, when this reaction was run with neat dimethylmalonate, the cycloacylated compound **11**

was obtained in 58% yield (Scheme 4). When run in refluxing DMF, the *N*-acyl derivative **10a** (22%) was formed along with a 27% yield of **11**.

Treatment of **11** with concentrated hydrochloric acid in the presence or absence of stannous dichloride had afforded quantitatively compound **12** [1,2] (Scheme 5). Structure **12** was further confirmed by high resolution  $^1\text{H}$  and  $^{13}\text{C}(^1\text{H})$  nmr and DEPT 135/90 experiments.

Scheme 3

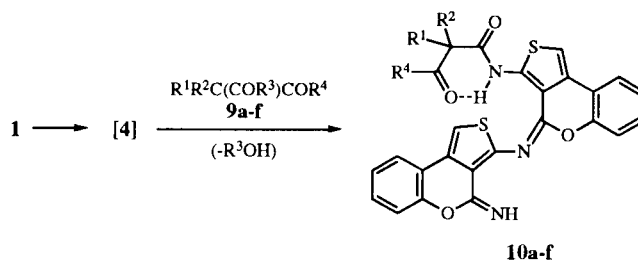
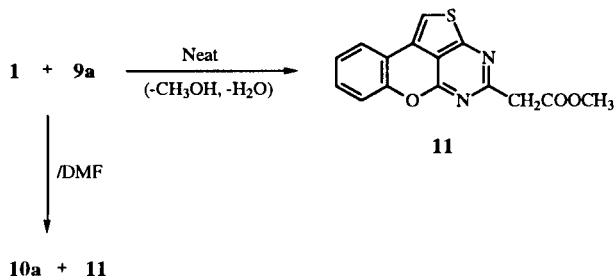


Table 1

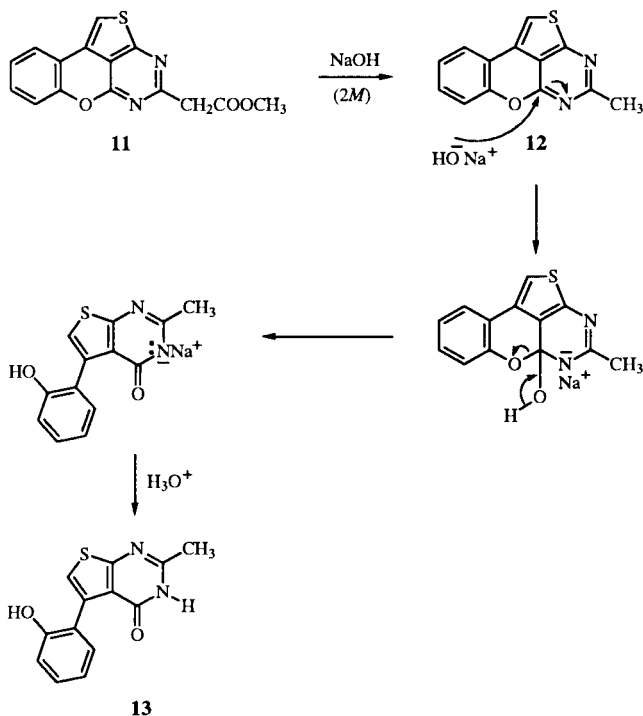
	a	b	c	d	e	f
R <sup>1</sup>	H	H	H	H	H	—
R <sup>2</sup>	H	H	Me	Ph	H	H
R <sup>3</sup>	MeO	EtO	EtO	EtO	EtO	EtO
R <sup>4</sup>	MeO	EtO	EtO	EtO	Me	R <sup>1</sup> , R <sup>4</sup> = -(CH <sub>2</sub> ) <sub>3</sub> -

Scheme 4



On the other hand, treatment of compound **11** with 2*M* aqueous sodium hydroxide at reflux afforded the new thienopyrimidinone **13** in 27% yield. Compound **13** was also prepared in 45% yield from **12** under similar reaction conditions. The formation of **13** might proceed *via* **12** as shown in Scheme 5. This rationale is analogous to the one proposed by Vinot and co-workers [12] to substantiate alkaline hydrolysis of [1]benzopyrano[2,3-*b*]quinoxalin-12-one leading to 3-(*o*-hydroxyphenyl)-1*H*-2-quinoxalinone.

Scheme 5



### Conclusion.

Direct acylation of the title compound **1**, in suitable cases resulting in cyclocondensation to form highly annelated pyrimidines can only be achieved by either applying a large excess of acylating agent, *e.g.* by heating **1** in neat dimethylmalonate, or by using strong acylating conditions, *e.g.* trifluoroacetic anhydride in refluxing trifluoroacetic

acid. Under the latter conditions the acylated 4-imino function acts as a leaving group and is replaced by trifluoroacetoxy preferentially to cyclocondensation.

Under milder conditions, acylation at either NH function (3- $\text{NH}_2$  or 4- $\text{NH}$ ) cannot compete with a ready condensation of two molecules of **1** with formation of **4**. Subsequently analogous condensations starting from **4** may be hampered by decreased accessibility or the remaining nitrogen functions due to steric hindrance. The same bias is effective in the acylation of **4** by the weakly electrophilic  $\beta$ -dicarbonyl compounds **9a-f**.

### EXPERIMENTAL

Elemental and spectroscopic analysis were carried out at the chemistry analytical center of Gerhard-Mercator-Universität-Gesamthochschule Duisburg, Duisburg FRG. All the melting points were determined with a Reichert Thermovar microscope and are uncorrected. The ir and the uv spectra were measured with Perkin-Elmer 283 and 554 spectrophotometers respectively.  $^1\text{H}$  and  $^{13}\text{C}$ ( $^1\text{H}$ )-nmr experiments were performed on a Bruker WM 300 instrument with TMS as internal standard; chemical shifts in  $\delta$  value are given in ppm and coupling constants in brackets are reported in Hz. Electron Impact Mass Spectra (ms) were registered on a Varian Mat 311A instrument at 70 ev, on direct injection. Combustion analysis were performed with CHN + O/S elemental analyser "CARLO ERBA" Model 1106.

#### 3-Amino-4-imino-4*H*-thieno[3,4-*c*][1]benzopyran (**1**).

Compound **1** was prepared according to the procedure described in ref [1,2], yield 7 g (65%), mp  $156^\circ$  (from ethanol) (lit [1,2],  $152^\circ$ , from xylene). The analytical sample was obtained by subliming the recrystallized compound at  $120^\circ$  under 0.2 mbar pressure; ir (potassium bromide):  $\nu_{\text{max}}$  3370, 3280 (=NH,  $\text{NH}_2$ ), 1630, 1610, 1570 ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ ; uv (ethanol):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 200 nm (76,384), 228 (206,538), 267 (236,592), 305 (63,387);  $^1\text{H}$  nmr ( $\text{DMSO}-d_6$ ):  $\delta$  7.87 (broad s, 1H, =NH, deuterium oxide-exchangeable), 7.78-7.75 (dd, 1H, 9-H,  $J = 1.59$ , 7.71 Hz), 7.69 (broad s, 2H,  $\text{-NH}_2$ , deuterium oxide-exchangeable), 7.29-7.23 (ddd, 1H, 7-H,  $J = 1.60$ , 7.04, 8.06 Hz), 7.12-7.07 (ddd, 1H, 8-H,  $J = 1.27$ , 8.15, 14.42 Hz), 7.08-7.05 (dd, 1H, 6-H,  $J = 1.12$ , 8.14), 6.80 (s, 1H, 1-H);  $^{13}\text{C}$ ( $^1\text{H}$ ) nmr ( $\text{DMSO}-d_6$ ):  $\delta$  160.7 (C-4), 155.1 (C-5a), 150.7 (C-3), 129.7 (C-9b), 129.0 (C-7), 123.8 (C-9), 123.5 (C-8), 118.2 (C-9a), 116.3 (C-6), 99.7 (C-3a), 97.1 (C-1); ms:  $m/z$  (%) 216 (100), 215 (40), 199 (6), 76 (2).

*Anal.* Calcd.  $\text{C}_{11}\text{H}_8\text{N}_2\text{OS}$  (216.26): C, 61.09; H, 3.73; N, 12.95; S, 14.83. Found: C, 61.07; H, 3.74; N, 12.97; S, 14.79.

#### Preparation of Compounds **2** and **3**.

A stirred mixture of **1** (2.2 g, 10 mmoles) and trifluoroacetic anhydride (10 ml) in 20 ml of trifluoroacetic acid was heated to reflux for 2 hours. After cooling at room temperature, the resulting resinified precipitate was filtered to afford 1.13 g of a crude material. Recrystallization from acetone gave 0.10 g (2.4%) of **2** which spontaneously crystallized. A second crop of crystals consisting of **3** (0.07 g, 3.2%) was collected from the filtrate after a few days of standing at room temperature.

(4-Trifluoroacetylmino-4*H*-thieno[3,4-*c*][1]benzopyran-3-yl)trifluoroacetamide (**2**).

This compound was obtained as yellow needles, mp 255-257°; ir (potassium bromide):  $\nu_{\max}$  3100 (NH), 1720 (C=O), 1695 (C=O), 1615, 1565, 1520 (C=C)  $\text{cm}^{-1}$ ; uv (THF):  $\lambda_{\max}$  ( $\epsilon$ ) 250 nm (2,328), 292 (1,770), 324 (shoulder, 1,644), 332 (1,702), 376 (799.83); ms:  $m/z$  (%) 408 (65), 339 (100), 214 (2), 199 (2), 186 (2), 69 (13).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_6\text{N}_2\text{O}_3\text{F}_6\text{S}$  (408.28): C, 44.13; H, 1.48; N, 6.86; S, 7.85. Found: C, 44.10; H, 1.50; N, 6.83; S, 7.79.

(4-Oxo-4*H*-thieno[3,4-*c*][1]benzopyran-3-yl)trifluoroacetamide (**3**).

This compound was obtained as white needles, mp 239-241°; ir (potassium bromide):  $\nu_{\max}$  3270 (NH), 3090 (CH), 1720 (C=O), 1680 (C=O), 1610, 1585, 1560, 1535 (C=C)  $\text{cm}^{-1}$ ; uv (THF):  $\lambda_{\max}$  ( $\epsilon$ ) 250 nm (698.23), 290 (282.49), 304 (274.16), 340 (272.27); ms:  $m/z$  (%) 313 (100), 294 (2), 266 (2), 244 (95), 216 (7), 188 (3), 172.1 (4), 76 (4), 69 (12).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_6\text{NO}_3\text{SF}_3$  (313.25): C, 49.84; H, 1.92; N, 4.47. Found: C, 49.89; H, 1.91; N, 4.47.

4-(4-Imino-4*H*-thieno[3,4-*c*][1]benzopyran-3-yl)imino-4*H*-thieno[3,4-*c*][1]benzopyran-3-amine (**4**).

A solution of compound **1** (0.54 g, 2.5 mmoles) in neat diethyl malonate (10 ml) was refluxed with magnetic stirring at 100° for 2 hours during which time a yellow precipitate was formed. Filtration and washing with acetone gave a yellow powder which gradually darkened upon prolonged contact with air. Two recrystallizations from DMSO yielded 0.52 g (50%) of analytical pure **4**, mp >350°; ir (potassium bromide):  $\nu_{\max}$  3410, 3280 (=NH, NH<sub>2</sub>), 1620, 1600, 1575 (C=C/C=N)  $\text{cm}^{-1}$ ; uv (THF):  $\lambda_{\max}$  ( $\epsilon$ ) 252 nm (1,135), 292 (957.19), 322 (741.31), 364 (669.88); <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>):  $\delta$  8.77 (broad s, 1H, =NH, deuterium oxide-exchangeable), 7.96-7.93 (dd, 1H, 9-H, *J* = 6.99, 1.24 Hz), 7.91-7.87 (dd, 1H, 6-H, *J* = 1.13, 10.48 Hz), 7.67 (s, 1H, 1-H), 7.43-7.38 (ddd, 1H, 7-H, *J* = 1.06, 7.38, 8.19 Hz), 7.35 (broad s, 2H, NH<sub>2</sub>, deuterium oxide-exchangeable), 7.31-7.26 (ddd, 1H, 8-H, *J* = 0.99, 7.15, 7.43 Hz), 7.13-7.11 (dd, 1H, 9'-H, *J* = 1.12, 7.39 Hz), 7.10-7.05 (ddd, 1H, 7'-H, *J* = 1.33, 7.62, 8.06 Hz), 6.78-6.74 (ddd, 1H, 8'-H, *J* = 1.01, 7.26, 7.31 Hz), 6.67-6.64 (dd, 1H, 6'-H, *J* = 1.42, 8.00 Hz), 6.19 (s, 1H, 1'-H); <sup>13</sup>C(1H) nmr (DMSO-*d*<sub>6</sub>):  $\delta$  161.2 (C-4), 158.8 (C-4'), 154.7 (C-5a), 152.6 (C-5a'), 152.1 (C-3), 138.8 (C-3'), 136.5 (C-9b), 130.9 (C-7), 129.4 (C-9'), 127.7 (C-7'), 127.1 (C-8), 125.3 (C-3a), 124.7 (C-9), 122.7 (C-3'a), 119.7 (C-9'a), 118.5 (C-9a), 118.2 (C-8'), 114.7 (C-6'), 112.9 (C-1'), 112.1 (C-6), 111.2 (C-9'b), 105.6 (C-1); ms:  $m/z$  (%) 415 (75), 398 (52), 382 (100), 199 (18).

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{13}\text{N}_3\text{O}_2\text{S}_2$  (415.50): C, 63.59; H, 3.15; N, 10.11; S, 15.44. Found: C, 63.53; H, 3.20; N, 9.98; S, 15.32.

General Procedure for Preparation of Compounds **10b-f**.

To a stirred solution of **1** (0.54 g, 2.5 mmoles) in DMF (10 ml) 5 ml of the  $\beta$ -carbonyl compounds **9b-f** ( $\text{R}^1\text{R}^2\text{C}(\text{COR}^3)\text{COR}^4$ ) were added. Stirring was continued under reflux for 6 hours. Cooling at room temperature and standing for several days, caused the formation of a precipitate which was filtered and washed with abundant methanol. Successive recrystallizations of the combined crops from aqueous DMF and glacial acetic acid afforded analytical samples of compounds **10b-f**.

Ethyl 3-[N-[4-(4'-Imino-4'*H*-thieno[3,4-*c*][1]benzopyran-3'-yl)imino-4*H*-thieno[3,4-*c*][1]benzopyran-3-yl]]amido-propanoate (**10b**).

This compound was obtained as a yellow powder (0.30 g, 23%), mp 260-262°; ir (potassium bromide):  $\nu_{\max}$  3440, 3200 (=NH, -NH-), 3080, 2980, 2920 (CH), 1720 (C=O, ester), 1670 (C=O, amide), 1630, 1580, 1535 (C=C/C=N)  $\text{cm}^{-1}$ ; uv (THF):  $\lambda_{\max}$  ( $\epsilon$ ) 250 nm (1,875), 292 (1,849), 324 (1,556), 348 (1,535); <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>):  $\delta$  12.04 (broad s, 1H, =NH, deuterium oxide-exchangeable), 8.90 (broad s, 1H, -NHCO-, deuterium oxide-exchangeable), 7.96-7.93 (dd, 1H, 9-H, *J* = 1.46, 7.59), 7.85 (s, 1H, 1-H), 7.44-7.39 (ddd, 1H, 7-H, *J* = 1.54, 7.61, 7.69 Hz), 7.35-7.32 (dd, 1H, 6-H, *J* = 1.50, 8.86 Hz), 7.33-7.27 (ddd, 1H, 8-H, *J* = 1.59, 7.47, 8.26 Hz), 7.21-7.18 (dd, 1H, 9'-H, *J* = 1.57, 7.46 Hz), 7.12-7.07 (ddd, 1H, 7'-H, *J* = 1.61, 7.63, 7.68 Hz), 6.92 (s, 1H, 1'-H), 6.83-6.78 (ddd, 1H, 8'-H, *J* = 0.80, 7.01, 7.41 Hz), 6.66-6.64 (dd, 1H, 6'-H, *J* = 1.05, 7.90 Hz), 4.23-4.16 (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>, *J* = 7.10 Hz), 3.73 (s, 2H, -COCH<sub>2</sub>CO-), 1.25-1.20 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>, *J* = 7.10 Hz); <sup>13</sup>C(1H) (DMSO-*d*<sub>6</sub>):  $\delta$  168.0 (C=O, ester), 166.9 (C=O, amide), 162.9 (C-4), 161.4 (C-4'), 160.9 (C-5a), 154.2 (C-5'a), 151.6 (C-3), 140.4 (C-3'), 137.0 (C-9b), 130.5 (C-7), 130.1 (C-9'), 128.0 (C-7'), 125.7 (C-7), 125.5 (C-3a), 124.9 (C-9), 123.2 (C-3'a), 121.4 (C-9a), 119.3 (C-9'a), 118.8 (C-8'), 118.7 (C-6), 115.8 (C-1'), 114.9 (C-6' and C-9'b), 113.2 (C-1), 61.0 (-OCH<sub>2</sub>-), 42.0 (-COCH<sub>2</sub>CO-), 14.04 (CH<sub>3</sub>); ms:  $m/z$  (%) 529 (4), 512 (2), 483 (3), 457 (2), 442 (5), 415 (2), 398 (4), 382 (8), 199 (8), 131 (3), 114 (12), 115 (91), 87 (15), 73 (10), 72 (27), 46 (57), 45 (100), 44 (4), 43 (76).

*Anal.* Calcd. for  $\text{C}_{27}\text{H}_{19}\text{N}_3\text{O}_5\text{S}_2$  (529.65): C, 61.23; H, 3.62; N, 7.94; S, 12.11. Found: C, 61.16; H, 3.65; N, 8.02; S, 12.10.

Ethyl 3-[N-[4-(4'-Imino-4'*H*-thieno[3,4-*c*][1]benzopyran-3'-yl)imino-4*H*-thieno[3,4-*c*][1]benzopyran-3-yl]]amido-2-methylpropanoate (**10c**).

This compound was obtained as a green-yellow powder (220 mg, 16%); mp 248-250°; ir (potassium bromide):  $\nu_{\max}$  3400, 3180 (=NH, -NH-), 3080, 2970, 2930 (CH), 1715 (C=O, ester), 1665 (C=O, amide), 1620, 1575, 1535 (C=C/C=N)  $\text{cm}^{-1}$ ; uv (THF):  $\lambda_{\max}$  ( $\epsilon$ ) 248 nm (1,729), 292 (1,517), 322 (1,364), 350 (1,207); <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>):  $\delta$  11.92 (broad s, 1H, =NH, deuterium oxide-exchangeable), 8.90 (broad s, 1H, -CONH-, deuterium oxide-exchangeable), 7.99-7.96 (dd, 1H, 9-H, *J* = 1.57, 7.62 Hz), 7.88 (s, 1H, 1-H), 7.47-7.41 (ddd, 1H, 7-H, *J* = 1.56, 7.59, 7.70 Hz), 7.38-7.34 (dd, 1H, 6-H, *J* = 1.51, 7.77 Hz), 7.35-7.29 (ddd, 1H, 8-H, *J* = 1.51, 7.97, 8.32 Hz), 7.20-7.17 (dd, 1H, 9'-H, *J* = 1.64, 7.47 Hz), 7.12-7.06 (ddd, 1H, 7'-H, *J* = 1.72, 7.68, 7.69 Hz), 6.93 (s, 1H, 1'-H), 6.83-6.78 (ddd, 1H, 8'-H, *J* = 1.41, 7.41, 7.90 Hz), 6.65-6.63 (dd, 1H, 6'-H, *J* = 1.35, 7.21 Hz), 4.20-4.13 (q, 1H, OCH<sub>2</sub>CH<sub>3</sub>, *J* = 6.95 Hz), 3.89-3.82 (q, 1H, -CH(CH<sub>3</sub>)-, *J* = 7.10 Hz), 1.42-1.40 (d, 3H, -(CH<sub>3</sub>)CH-, *J* = 7.11 Hz), 1.19-1.15 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O-, *J* = 7.09 Hz); <sup>13</sup>C(1H) nmr (DMSO-*d*<sub>6</sub>):  $\delta$  170.2 (C=O, ester), 166.9 (C=O, amide), 166.1 (C-4), 161.2 (C-4'), 160.8 (C-5a), 154.2 (C-5'a), 151.6 (C-3), 140.7 (C-3'), 137.1 (C-9b), 130.5 (C-7), 130.0 (C-9'), 127.9 (C-7'), 125.7 (C-8), 125.5 (C-3a), 124.9 (C-9), 123.2 (C-3'a), 121.1 (C-9a), 119.3 (C-9'a), 118.7 (C-6'), 118.5 (C-6), 115.7 (C-1'), 114.8 (C-3'a), 114.7 (C-8'), 113.1 (C-1), 61.0 (-OCH<sub>2</sub>-), 46.4 (-CH(CH<sub>3</sub>)-), 13.9 (CH<sub>3</sub>CH<sub>2</sub>O), 13.7 (-CH(CH<sub>3</sub>)-); ms:  $m/z$  (%) 543 (36), 526 (13), 498 (2), 471 (38), 454 (12), 442 (90), 415 (16), 398 (33), 382 (48), 130 (6), 129 (100), 128 (18), 102 (44), 83 (16), 74 (87), 73 (25), 72 (10), 56 (47), 46 (34), 45 (99), 44 (92), 43 (39).

*Anal.* Calcd. for  $C_{28}H_{21}N_3O_5S_2$  (543.62): C, 61.85; H, 3.90; N, 7.73; S, 11.80. Found: C, 61.99; H, 3.85; N, 7.83; S, 11.84.

Ethyl 3-{*N*-[4-(4'-Imino-4'*H*-thieno[3,4-*c*][1]benzopyran-3'-yl)imino-4*H*-thieno[3,4-*c*][1]benzopyran-3-yl]}amido-2-phenylpropanoate (**10d**).

This compound was obtained as a yellow powder (210 mg, 14%), mp 220-222°; ir (potassium bromide):  $\nu_{\max}$  3420, 3300 (=NH, -NH-), 3080, 3020 (arom CH), 2960, 2910 (alif CH), 1720 (C=O, ester), 1670 (C=O, amide), 1620, 1580, 1530 (C=C/C=N)  $cm^{-1}$ ; uv (THF):  $\lambda_{\max}$  ( $\epsilon$ ) 250 nm (1,778), 290 (1,161), 304 (1,089), 316 (1,035), 346 (843.33); ms: *m/z* (%) 605 (0.3), 533 (0.2), 516 (0.2), 487 (0.3), 442 (5), 388 (15), 315 (57), 236.2 (33), 191 (5), 163 (64), 135 (44), 118 (70), 91 (100), 77 (12), 45 (42), 44 (33), 43 (9).

*Anal.* Calcd. for  $C_{33}H_{23}N_3O_5S_2$  (605.69): C, 65.43; H, 3.84; N, 6.94; S, 10.59. Found: C, 65.47; H, 3.82; N, 7.15; S, 10.67.

3-{*N*-[(4-(4'-Imino-4'*H*-thieno[3,4-*c*][1]benzopyran-3'-yl)imino-4*H*-thieno[3,4-*c*][1]benzopyran-3-yl]}amidoprop-2-one (**10e**).

This compound was obtained as a yellow powder (0.28 g, 22%), mp 248-250°; ir (potassium bromide):  $\nu_{\max}$  3410, 3190 (=NH, -NH-), 3080, 2920 (CH), 1710 (C=O), 1670 (C=O), 1625, 1580, 1535 (C=C/C=N)  $cm^{-1}$ ; uv (THF):  $\lambda_{\max}$  ( $\epsilon$ ) 252 nm (1,927), 293 (1,807), 324 (1,521), 354 (1,510);  $^1H$  nmr (DMSO- $d_6$ ):  $\delta$  11.90 (broad s, 1H, =NH, deuterium oxide-exchangeable), 8.89 (broad s, 1H, -NHCO-, deuterium oxide-exchangeable), 7.97-7.94 (dd, 1H, 9-H,  $J = 1.28, 7.54$  Hz), 7.86 (s, 1H, 1-H), 7.44-7.39 (ddd, 1H, 7-H,  $J = 1.37, 7.25, 7.48$  Hz), 7.37-7.34 (dd, 1H, 6-H,  $J = 1.19, 8.26$  Hz), 7.33-7.28 (ddd, 1H, 8-H,  $J = 1.79, 7.66, 7.80$  Hz), 7.21-7.18 (dd, 1H, 9'-H,  $J = 1.53, 7.43$  Hz), 7.12-7.06 (ddd, 1H, 7'-H,  $J = 1.59, 7.57, 7.70$  Hz), 6.91 (s, 1H, 1'-H), 6.83-6.78 (ddd, 1H, 8'-H,  $J = 1.23, 7.36, 7.62$  Hz), 6.65-6.63 (dd, 1H, 6'-H,  $J = 1.31, 7.99$  Hz), 3.83 (s, 2H, -COCH<sub>2</sub>CO-), 2.25 (s, 3H, -COCH<sub>3</sub>);  $^{13}C$  (1H) nmr (DMSO- $d_6$ ):  $\delta$  208.5 (C=O, ketone), 167.0 (C=O, acetamide), 163.7 (C-4), 161.4 (C-4'), 161.0 (C-5a), 154.1 (C-5'a), 151.7 (C-3), 140.4 (C-3'), 137.0 (C-9b), 130.5 (C-7), 130.1 (C-9'), 128.0 (C-7'), 125.7 (C-8), 125.5 (C-3a), 124.9 (C-9), 123.2 (C-3'a), 121.4 (C-9a), 119.3 (C-9'a), 118.8 (C-8'), 118.6 (C-6), 115.7 (C-1'), 114.9 (C-6' and C-9'b), 113.2 (C-1), 49.9 (CH<sub>2</sub>), 30.71 (CH<sub>3</sub>); ms: *m/z* (%) 499 (5), 442 (4), 415 (51), 414 (3), 398 (44), 382 (90), 199 (15), 101 (6), 84 (100), 69 (86), 57 (10), 44 (40), 43 (65).

*Anal.* Calcd. for  $C_{26}H_{17}N_3O_4S_2$  (499.57): C, 62.51; H, 3.43; N, 8.41; S, 12.84. Found: C, 62.43; H, 3.47; N, 8.30; S, 12.75.

{*N*-[4-(4'-Imino-4'*H*-thieno[3,4-*c*][1]benzopyran-3'-yl)imino-4*H*-thieno[3,4-*c*][1]benzopyran-3-yl]}-2-oxocyclopentanecarboxamide (**10f**).

This compound was obtained as a yellow powder (370 mg, 28%), mp 244-246°; ir (potassium bromide):  $\nu_{\max}$  3420, 3180 (=NH, -NH-), 2960, 2860 (CH), 1730 (C=O, ester), 1670 (C=O, amide), 1620, 1580, 1530 (C=C/C=N)  $cm^{-1}$ ; uv (THF):  $\lambda_{\max}$  ( $\epsilon$ ) 248 nm (1,742), 292 (1,466), 324 (1,213), 348 (1,035); ms: *m/z* (%) 525 (2), 442 (4), 415 (41.95), 414 (2), 398 (41), 382.1 (100), 111 (4), 110 (22), 84 (21), 83 (2), 55 (69), 44 (45), 43 (3).

*Anal.* Calcd. for  $C_{28}H_{19}N_3O_4S_2$  (525.61): C, 63.98; H, 3.65; N, 7.99. Found: C, 63.76; H, 3.65; N, 7.71.

Methyl (6-Oxa-2-thia-3,5-diazaceanthrylen-4-yl)acetate (**11**).

A magnetically stirred solution of **1** (0.54 g, 2.5 mmoles) in 10 ml of neat dimethyl malonate was refluxed at 170° for 6

hours. After cooling to room temperature, the resulted solution was left to stand overnight. This caused the formation of a yellow precipitate. The latter was filtered, washed with methanol and recrystallized from aqueous DMF. An analytical sample of **11** was obtained by sublimation of the recrystallized sample at 180° under 0.2 mbar pressure, yield 0.43 g (52%), mp 200-202°; ir (potassium bromide):  $\nu_{\max}$  3080, 3020, 3000, 2950, 2920, 1720 (C=O, ester), 1620 (C=O, amide), 1580, 1560 (C=C/C=N)  $cm^{-1}$ ; uv (ethanol):  $\lambda_{\max}$  ( $\epsilon$ ) = 248 nm (579.43), 286 (4,217), 322 (604);  $^1H$  nmr (deuteriochloroform):  $\delta$  7.65-7.62 (dd, 1H, 10-H,  $J = 1.30, 7.69$  Hz), 7.37-7.31 (ddd, 1H, 8-H,  $J = 1.60, 6.86, 8.35$  Hz), 7.30-7.27 (ddd, 1H, 9-H,  $J = 1.41, 6.65, 7.98$  Hz), 7.23-7.18 (dd, 1H, 8-H,  $J = 1.73, 14.56$  Hz), 4.04 (s, 2H, -CH<sub>2</sub>COOCH<sub>3</sub>), 3.78 (s, 3H, -CH<sub>2</sub>COOCH<sub>3</sub>), 7.21 (s, 1H, 1-H);  $^{13}C$  (1H) nmr (deuteriochloroform):  $\delta$  169.9 (C=O, ester), 168.4 (C-4), 162.5 (C-5a), 162.4 (C-2a), 152.1 (C-6a), 130.2 (C-8), 125.4 (C-10), 124.1 (C-9), 123.9 (C-10b), 119.5 (C-10c), 118.7 (C-7), 116.3 (C-10a), 111.5 (C-1), 52.4 (-OCH<sub>3</sub>), 45.4 (-CH<sub>2</sub>-); ms: *m/z* (%) 298 (100), 266 (19), 240 (84), 239 (57), 212 (12), 199 (22), 99 (8), 76 (2), 59 (6), 44 (3).

*Anal.* Calcd. for  $C_{15}H_{10}N_2O_3S$  (298.32): C, 60.38; H, 3.39; N, 9.39; S, 10.75. Found: C, 60.42; H, 3.39; N, 9.34; S, 10.60.

#### Preparation of Compounds **10a** and **11**.

To a stirred solution of **1** (0.54 g, 2.5 mmoles) in DMF (5 ml), was added 10 ml of dimethyl malonate. Stirring under reflux at 170° was continued for 6 hours. After cooling to room temperature the reaction mixture was treated with 200 ml of diethyl ether to give a yellow precipitate, which was filtered, washed with abundant methanol and recrystallized successively from aqueous DMF and glacial acetic acid to yield 0.28 g (22%) of analytical sample of **10a**. The above diethyl ether filtrate was left to stand at room temperature for a few days during which another precipitate consisting of **11** was formed. Work up of the latter as above afforded 0.20 g (27%) of pure **11**.

Ethyl 3-{*N*-[4-(4'-Imino-4'*H*-thieno[3,4-*c*][1]benzopyran-3'-yl)imino-4*H*-thieno[3,4-*c*][1]benzopyran-3-yl]}amido-propanoate (**10a**).

This compound was obtained as a white powder, mp 270-272°; ir (potassium bromide):  $\nu_{\max}$  3410, 3210 (=NH, -NH-), 2950, 2920, 2850 (CH), 1725 (C=O, ester), 1670 (C=O, amide), 1625, 1580, 1540, 1510 (C=C/C=N)  $cm^{-1}$ ; uv (THF):  $\lambda_{\max}$  ( $\epsilon$ ) = 254 nm (1,932), 292 (1,754), 322 (1,422), 348 (1,236);  $^1H$  nmr (DMSO- $d_6$ ):  $\delta$  11.98 (broad s, 1H, =NH, deuterium oxide-exchangeable), 8.80 (broad s, 1H, -NHCO-, deuterium oxide-exchangeable), 7.97-7.95 (dd, 1H, 9-H,  $J = 1.12, 6.40$  Hz), 7.87 (s, 1H, 1-H), 7.45-7.40 (ddd, 1H, 7-H,  $J = 1.42, 6.96, 7.31$  Hz), 7.38-7.35 (dd, 1H, 6-H,  $J = 1.23, 7.04$  Hz), 7.34-7.30 (ddd, 1H, 8-H,  $J = 1.03, 6.74, 7.29$  Hz), 7.20-7.17 (dd, 1H, 9'-H,  $J = 1.57, 7.45$  Hz), 7.11-7.06 (ddd, 1H, 7'-H,  $J = 1.64, 6.86, 7.68$  Hz), 6.92 (s, 1H, 1'-H), 6.82-6.78 (ddd, 1H, 8'-H,  $J = 1.54, 6.93, 7.03$  Hz), 6.65-6.62 (dd, 1H, 6'-H,  $J = 1.33, 7.75$  Hz), 3.74 (s, 2H, -CH<sub>2</sub>COOCH<sub>3</sub>), 3.72 (s, 3H, -COOCH<sub>3</sub>);  $^{13}C$  (1H) (DMSO- $d_6$ ):  $\delta$  168.40 (C=O, ester), 167.0 (C=O, amide), 162.8 (C-4), 161.4 (C-4'), 160.9 (C-5a), 154.2 (C-5'a), 151.7 (C-3), 140.34 (C-3'), 137.0 (C-9b), 130.3 (C-7), 129.9 (C-9'), 127.8 (C-7'), 125.7 (C-3a), 125.5 (C-8), 124.7 (C-9), 123.2 (C-3'a), 121.5 (C-9a), 119.3 (C-9'a), 118.6 (C-8'), 118.4 (C-6), 115.6 (C-1'), 114.6 (C-6' and C-9b), 113.0 (C-1), 52.0 (-OCH<sub>3</sub>), 41.6 (-CH<sub>2</sub>-); ms: *m/z* (%) = 515 (2), 457 (3), 443.2 (2), 442 (2), 415 (2), 414 (1), 398

(4), 382 (8), 199 (3), 101 (94), 100 (6), 74 (53), 73 (2), 59 (100), 58 (12), 44 (85), 43 (38).

*Anal.* Calcd. for  $C_{26}H_{17}N_3O_5S_2$  (515.68): C, 60.56; H, 3.33; N, 8.15; S, 12.44. Found: C, 60.58; H, 3.31; N, 8.17; S, 12.24.

#### 4-Methyl-6-oxa-2-thia-3,5-diazaacanthrylene (**12**) [1,2].

A magnetically stirred solution of **11** (0.30 g, 1.0 mmoles) in concentrated hydrochloric acid (10 ml, 37%) was heated at reflux in a water-bath for 3 hours. The precipitate obtained after cooling to room temperature, was filtered and washed with abundant methanol to give a yellow powder which was additionally washed with a saturated aqueous solution of sodium carbonate. Recrystallization from aqueous dimethylformamide or glacial acetic acid gave 0.24 g (100%) of **12** as yellow needles, mp 186-188° (lit [1,2], 180-181° from ligroin); ir (potassium bromide):  $\nu_{\max}$  3060, 3020, 2920, 2840 (CH), 1620, 1580, 1550, 1510 (C=C/C=N)  $cm^{-1}$ ; uv (ethanol):  $\lambda_{\max}$  ( $\epsilon$ ) 252 (529.66), 290 (386.37), 324 (572.80);  $^1H$  nmr (DMSO- $d_6$ /deuteriochloroform):  $\delta$  7.92-7.89 (dd, 1H, 10-H,  $J = 1.46, 7.67$  Hz), 7.74 (s, 1H, 1-H), 7.46-7.42 (dd, 1H, 7-H,  $J = 1.59, 8.38$  Hz), 7.40-7.34 (ddd, 1H, 8-H,  $J = 1.43, 8.28, 8.36$  Hz), 7.32-7.26 (ddd, 1H, 9-H,  $J = 1.53, 7.04, 7.35$  Hz), 2.63 (s, 3H,  $-CH_3$ );  $^{13}C$  ( $^1H$ ) (DMSO- $d_6$ /deuteriochloroform):  $\delta$  166.0 (C-4), 164.2 (C-5a), 159.9 (C-2a), 149.9 (C-6a), 128.2 (C-9), 123.5 (C-10), 122.8 (C-8), 121.4 (C-10b), 117.7 (C-10c), 116.5 (C-7), 113.4 (C-10a), 110.3 (C-1), 37.9 (CH<sub>3</sub>); ms:  $m/z$  (%) 242 (7), 241 (17), 240 (100), 239 (2), 199 (32), 76 (2).

*Anal.* Calcd. for  $C_{13}H_8N_2OS$  (240.29): C, 64.97; H, 3.36; N, 11.66; S, 13.35. Found: C, 64.98; H, 3.43; N, 11.66; S, 13.33.

#### 2-Methyl-5-(2-hydroxyphenyl)-3,4-dihydrothieno[3,2-*e*]pyrimidin-4-one (**13**).

A stirred suspension of compound **11** (0.30 g, 1.0 mmoles) in a 2 M sodium hydroxide aqueous solution was refluxed in a water-bath up to complete dissolution. Stirring and refluxing were pursued until reappearance of another precipitate (1.5 hours). The suspension was allowed to cool and then left to stand at room temperature overnight. The precipitate was filtered, air-dried and recrystallized from water to afford 0.07 g (27%) of analytical sample of **13** as a yellow powder, mp 267-268°; ir (potassium bromide):  $\nu_{\max}$  3540 (OH), 3320, 3230 (NH), 3100, 3090, 3040, 2920, 2850, 2760 (CH), 1670 (C=O), 1635, 1590, 1570 (C=C/C=N)  $cm^{-1}$ ; uv (ethanol):  $\lambda_{\max}$  ( $\epsilon$ ) 250 nm (2,032), 286 (1,419), 306 (1,528);  $^1H$  nmr (DMSO- $d_6$ ):  $\delta$  12.19 (broad s, 1H,  $-OH$ , deuterium oxide-exchangeable), 9.29 (broad s, 1H,  $-NH-$ , deuterium oxide-exchangeable), 7.20 (s, 1H, 6-H), 7.16-7.14 (dd, 1H, 3'-H,  $J = 1.35, 6.06$  Hz), 7.15-7.11 (ddd, 1H, 5'-H,  $J = 1.62,$

6.32, 8.95 Hz), 6.85-6.82 (dd, 1H, 6'-H,  $J = 1.08, 8.58$  Hz), 6.80-6.74 (ddd, 1H, 4'-H,  $J = 1.09, 7.41, 8.17$ ), 2.34 (s, 3H,  $-CH_3$ );  $^{13}C$  ( $^1H$ ) nmr (DMSO- $d_6$ ):  $\delta$  165.0 (C=O, amide), 157.9 (C-4), 155.2 (C-2'), 155.0 (C-7a), 134.7 (C-4a), 131.0 (C-6'), 128.6 (C-4'), 123.5 (C-1'), 120.4 (C-5), 119.5 (C-5'), 118.2 (C-3'), 115.3 (C-6), 20.8 ( $-CH_3$ ); ms:  $m/z$  (%) 258 (100), 241 (26), 230 (8), 217 (25), 189 (3), 174 (6), 43 (47).

*Anal.* Calcd. for  $C_{13}H_{10}N_2O_2S$  (258.30): C, 60.45; H, 3.90; N, 10.85; S, 12.41. Found: C, 60.72; H, 3.92; N, 10.84; S, 12.46.

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