REACTIONS OF FURO[2,3-*b*]PYRROLE AND FURO[3,2-*b*]PYRROLE-TYPE ALDEHYDES

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Dedicated to Professor Milan Kratochvíl in honour of his 75 birthday.

The synthesis of methyl 2-formyl-6-(methoxymethyl)furo[2,3-*b*]pyrrole-5-carboxylate (**1d**) is described. The reactions of methyl 2-formylfuro[2,3-*b*]pyrrole-5-carboxylates **1a**–**1d** with malononitrile afforded methyl 2-(2,2-dicyanovinyl)furo[2,3-*b*]pyrrole-5-carboxylates **3a**–**3d**, with methyl cyanoacetate methyl 2-[2-cyano-2-(methoxycarbonyl)vinyl]furo[2,3-*b*]pyrrole-5-carboxylates **4a**–**4d** and with 2-furylacetonitrile methyl 2-[2-cyano-2-(2-furyl)vinyl]-furo[2,3-*b*]pyrrole-5-carboxylates **5a**–**5d**. Compounds **1b**–**1d** and methyl azidoacetate gave the appropriate vinylazides **6b**–**6d**, which were used for preparation of substituted furo[2,3-*b*:4,5-*b*']dipyrroles **7b**–**7d**. Reactivity of furo[2,3-*b*]pyrrole aldehydes **1a**–**1d** and furo[3,2-*b*]pyrrole aldehydes **2a**–**2c** in their reactions with 5,5-dimethylcyclohexane-1,3-dione is compared. The prepared methyl 2-[bis(4,4-dimethyl-2,6-dioxocyclohexyl)-methylfuro[2,3-*b*]pyrrole-5-carboxylates **8a**–**8d** and their isomers **10a**–**10c** cyclized into substituted octahydroxanthenes **9a**–**9d** and **11a**–**11c**, respectively. Methyl 4-benzyl-2-[(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)methyl]furo[3,2-*b*]pyrrole-5-carboxylate (**12**) was prepared using microwave irradiations.

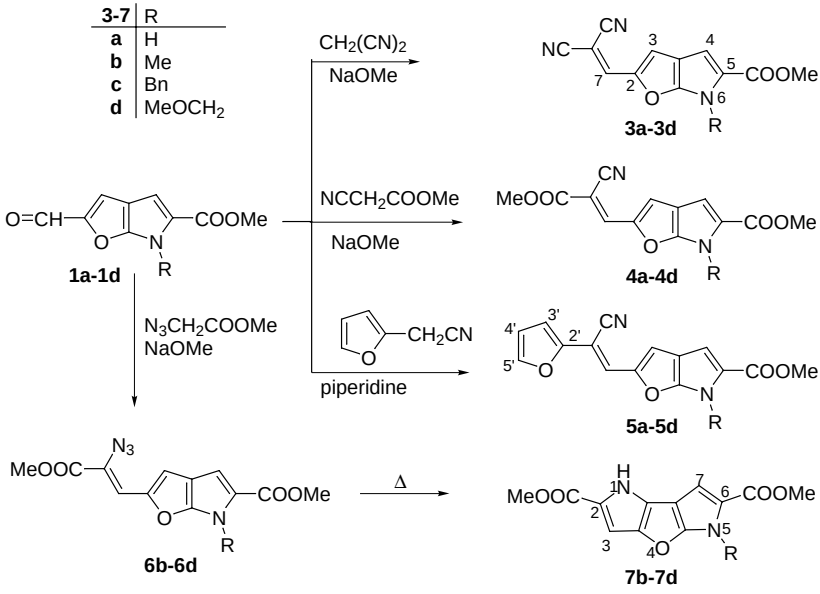
Key words: Furo[2,3-*b*]pyrroles; Furo[3,2-*b*]pyrroles; Furo[2,3-*b*:4,5-*b*']dipyrroles; Octahydroxanthenes.

In continuation of our program aimed at developing efficient syntheses of fused oxygen-nitrogen-containing heterocycles[1–6], we report here on a study of the utilization of substituted furo[2,3-*b*]pyrrole-type aldehydes in the synthesis.

Our previous paper[2] presents the formylation of methyl 6*H*-furo[2,3-*b*]pyrrole-5-carboxylate and its 6-methyl or 6-benzyl derivatives under conditions of the Vilsmeier reaction. This paper presents the formylation of methyl 6-(methoxymethyl)furo[2,3-*b*]pyrrole-5-carboxylate[3]

under the same conditions. In this reaction, analogously to the mentioned cases[2], 2-formylated product **1d** was obtained.

The aim of this study was to synthesize some new condensation products of furo[2,3-*b*]pyrrole-type aldehydes with active methylene compounds (Scheme 1). Additionally, we tried to find favorable reaction conditions in order to increase yields of the condensations.

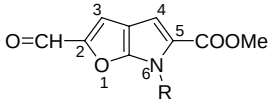


SCHEME 1

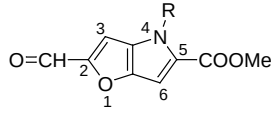
The reactions of methyl 2-formylfuro[2,3-*b*]pyrrole-5-carboxylates **1a**–**1d** with malononitrile afforded methyl 2-(2,2-dicyanovinyl)furo[2,3-*b*]-pyrrole-5-carboxylates **3a**–**3d**, with methyl cyanoacetate methyl 2-[2-cyano-2-(methoxycarbonyl)vinyl]furo[2,3-*b*]pyrrole-5-carboxylates **4a**–**4d** and with 2-furylacetonitrile methyl 2-[2-cyano-2-(2-furyl)vinyl]furo[2,3-*b*]pyrrole-5-carboxylates **5a**–**5d**. All these compounds **3a**–**3d**, **4a**–**4d** and **5a**–**5d** are yellow-orange. Yields of these reactions are comparable with those published in our previous paper[6] presenting condensations of furo- [3,2-*b*]-pyrrole-type aldehydes with the same active methylene compounds. To obtain **5a**–**5d** in the reaction of **1a**–**1d** with 2-furylacetonitrile, we had to use piperidine instead sodium methoxide (due to a lower stability of the final compounds) and to reflux the reaction mixture for 1 h. The cofiguration assignment of the substituents on the double bond for compounds **4c**, **4d**, **5c**

and **5d** has been determined by ^{13}C NMR spectra using the stereospecific coupling constants ^{3}J(CN,H-7) = 13.76 Hz, which confirms that they are the *E*-isomers[7].

Reaction of methyl 2-formyl-6-methylfuro[2,3-*b*]pyrrole-5-carboxylate (**1b**) with methyl azidoacetate in the presence of sodium methoxide was found to proceed smoothly to give **6b**, the thermolysis of which was carried out in boiling toluene leading to dimethyl 5-methyl-1*H*-furo[2,3-*b*:4,5-*b'*]-dipyrrole-2,6-dicarboxylate (**7b**) (Scheme 1). Starting from 6-benzyl (**1c**) and 6-methoxymethyl (**1d**) derivatives, **6c** and **6d** were prepared. The thermolysis of **6b**–**6d** proceeds relatively rapidly until the liberation of nitrogen ceased affording products **7b**–**7d** in moderate yields. The yields of **7b** and **7c** (63 and 73%) are comparable to yields of their [3,2-*b*]-isomers published earlier[5]. The configuration assignment of the substituents on the double bond for compounds **6b**–**6d** was too difficult to prove due to their low stability. Signal of H-3-proton resonance of the compounds **6b**–**6d** is due to anisotropic effect of the azido group[8] shifted downfield. Based upon this fact, we can suppose analogously to our previous paper[9] that the mentioned compounds have *E* arrangement at the double bond and the furo[2,3-*b*]pyrrole–ethylene system is s-cis arranged[10].



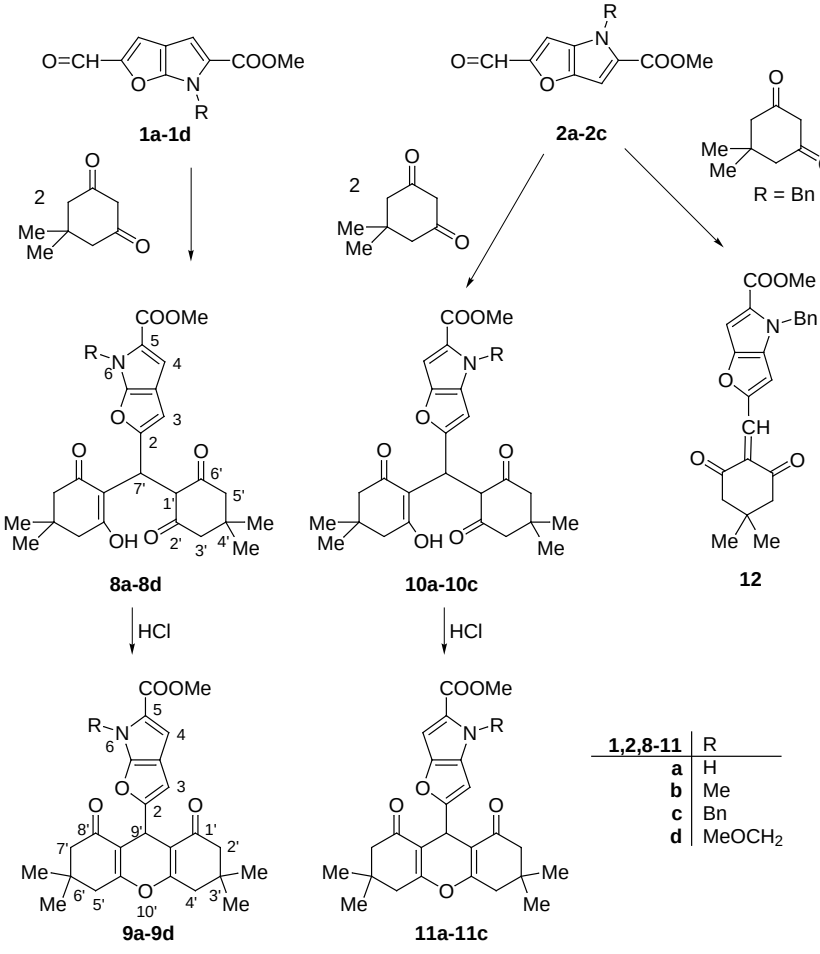
1	R
a	H
b	Me
c	Bn
d	$MeOCH_2$



2	R
a	H
b	Me
c	Bn

We also report on the reaction of aldehydes **1a**–**1d** and **2a**–**2c** with a cyclic active methylene compound, 5,5-dimethylcyclohexane-1,3-dione (dimedone), giving compounds **8a**–**8d** and **10a**–**10c**, respectively, which by subsequent cyclization led to the substituted 1,2,3,4,5,6,7,8-octahydroxanthenes **9a**–**9d** and **11a**–**11c**, respectively (Scheme 2). In ^{1}H NMR spectra of compounds **8** and **10**, we observed a broad signal of OH proton (≈12 ppm) of the enol form, which is stabilized by the other C=O group of the cyclohexane-1,3-dione moiety.

We tried to prepare 1 : 1 condensation products of the mentioned aldehydes with 5,5-dimethylcyclohexane-1,3-dione using methods described earlier[11]. Our effort was unsuccessful in both types of the aldehydes. In all

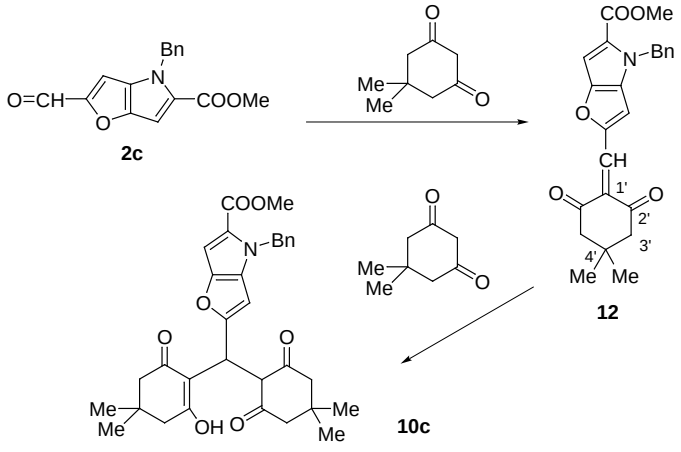


SCHEME 2

cases we isolated xanthene derivatives **9a**–**9d** or **11a**–**11c**. This result can be explained by the fact that reaction of the mentioned aldehydes with dimedone proceeds in two steps with different reaction rates. The first step is based on the aldehyde and dimedone condensation forming the 1 : 1 product, which in the faster second step gives with another molecule of dimedone, *via* Michael addition, the 1 : 2 condensation product (Scheme 3).

We also carried out the reaction under microwave conditions[12,13] using **1a**–**1d** or **2a**–**2c**. We were successful only with methyl 4-benzyl-2-formylfuro[2,3-*b*]pyrrole-5-carboxylate (**2c**) obtaining compound **12** in moderate yield. This surprising result is difficult to explain. We used this compound

for proving the possibility of the proposed mechanism of condensation of title compounds with 5,5-dimethylcyclohexane-1,3-dione. The proposed intermediate **12** with 5,5-dimethylcyclohexane-1,3-dione indeed gave the Michael addition product **10c** (Scheme 3).



SCHEME 3

In conclusion, we can state on the bases of the present synthesis and our previous reaction studies of both fused ring systems, that the 1,4-diheteropentalene system is more stable than its 1,6-positional isomer. In the described experiments we ascertained that if the formyl group occupies the C2 position, the reactivity as well as stability of both systems is comparable. We noticed a remarkable difference in solubility of the two types of aldehydes. Compounds **1a**–**1c** are less soluble than **2a**–**2c**. This observation can be explained by the 1,4-system having a significantly larger calculated dipole moment[2], which may result in the greater solubility. Our main aim to synthesize the 1 : 1 condensation products of the title compounds with 5,5-dimethylcyclohexane-1,3-dione and to compare the results of the classical condensation with those obtained using microwave irradiations was successful only in one case (**2c**). We assume that in this case an optimum ratio between the formation rate of compound **12** and its low solubility was reached.

EXPERIMENTAL

Melting points were determined on a Kofler hot plate apparatus and are uncorrected. Samples for analysis were dried over P_4O_{10} at 60 °C and 30 Pa for 8–10 h. ^{1}H NMR (80 MHz) spectra were recorded on a Tesla BS 587 spectrometer, and ^{13}C NMR (75.43 MHz) spectra on

a Varian VXR-300 in $CDCl_3$. TMS was used as an internal standard; chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. The ^1H and ^{13}C chemical shifts were assigned by comparison with model compounds[14–16] and H,C-COSY was used[11] to correlate carbons with directly bonded protons. IR spectra were taken on a FTIR PU 9802/25 (Philips) spectrometer using KBr technique (0.5 mg in 300 mg KBr, ν in cm^{-1}). UV spectra of methanolic solutions (λ_{max} (log ε); λ_{max} in nm, ε in m^2 mol^{-1}) were recorded on a Specord UV-VIS M-40 (Zeiss, Jena) instrument. Mass spectra were taken on an MS 902-S instrument (AEI, Manchester), with direct inlet, ionizing electron energy 70 eV, trap current 100 μA, and ion sorce temperature 160–180 °C. The reaction progress and purity of all prepared compounds was followed by TLC (SILUFOL UV_{254}, Kavalier, Votice) in the system chloroform–methanol 9 : 1 visualizing spots with UV lamp or iodine vapours. Solvents were purified by published methods.

The following starting compounds were prepared: methyl 6-(methoxymethyl)furo-[2,3-*b*]pyrrole-5-carboxylate[3], methyl 2-formylfuro[2,3-*b*]pyrrole-5-carboxylates **1a**–**1c** (ref.[2]) and methyl 2-formylfuro[3,2-*b*]pyrrole-5-carboxylates **2a**–**2c** (ref.[4]). 5,5-Dimethylcyclohexane-1,3-dione (dimedone) (Aldrich) was used without purification.

Methyl 2-Formyl-6-(methoxymethyl)furo[2,3-*b*]pyrrole-5-carboxylate (**1d**)

A mixture of dimethylformamide (11.7 g, 160 mmol) and phosphorus oxychloride (4.6 g, 30 mmol) was stirred at 0 °C for 20 min. Methyl 6-(methoxymethyl)furo[2,3-*b*]pyrrole-5-carboxylate (2.5 g, 12 mmol) dissolved in dimethylformamide (12 ml) was added at temperature not exceeding 10 °C. The mixture was stirred at 60 °C for 5 h, poured into ice-cold water, neutralized with sodium hydrogencarbonate, allowed to stand overnight and the precipitate was filtered off and crystallized from a hexane–toluene 3 : 1 mixture to give 2.9 g (84%) of **1d**, m.p. 100–103 °C. For $C_{11}H_{11}NO_5$ (237.2) calculated: 55.70% C, 4.67% H, 5.90% N; found: 55.65% C, 4.82% H, 6.15% N. ^1H NMR ($CDCl_3$): 3.37 s, 3 H (CO_2CH_3); 3.88 s, 3 H (OCH_3); 5.82 s, 2 H (CH_2); 7.08 s, 1 H (H-4); 7.38 s, 1 H (H-3); 9.57 s, 1 H (CHO). IR: 1 670 (C=O); 1 709 (C=O).

Methyl 2-(2,2-Dicyanovinyl)-6*H*-furo[2,3-b]pyrrole-5-carboxylate (**3a**)

Methyl 2-formyl-6*H*-furo[2,3-*b*]pyrrole-5-carboxylate (**1a**) (0.6 g, 3 mmol) and malononitrile (0.20 g, 3 mmol) were disolved in a mixture of methanol (20 ml) and toluene (10 ml). A catalytic amount of sodium methoxide was added into the hot mixture. After 5 min fine crystals were filtered off after cooling, washed with cold MeOH and crystallized from MeOH to give 0.60 g (83%) of **3a**, m.p. 273–275 °C. For $C_{12}H_7N_3O_3$ (241.2) calculated: 59.75% C, 2.93% H, 17.42% N; found: 59.81% C, 2.77% H, 17.80% N. ^1H NMR ($(CD_3)_2SO$): 3.76 s, 3 H (CO_2CH_3); 6.88 s, 1 H (H-4); 7.55 s, 1 H (H-3); 8.05 s, 1 H (H-7). IR: 1 692 (C=O); 2 218 (CN); 3 200 (NH).

The following compounds were prepared by this procedure:

Methyl 2-(2,2-dicyanovinyl)-6-methylfuro[2,3-b]pyrrole-5-carboxylate (**3b**). Yield: 80%, m.p. 228–230 °C (MeOH). For $C_{13}H_9N_3O_3$ (255.2) calculated: 61.18% C, 3.55% H, 16.46% N; found: 60.95% C, 3.88% H, 16.39% N. ^1H NMR ($(CD_3)_2SO$): 3.89 s, 3 H (CO_2CH_3); 4.00 s, 3 H ($N\text{-}CH_3$); 6.97 s, 1 H (H-4); 7.34 s, 1 H (H-7); 7.35 s, 1 H (H-3). IR: 1 697 (C=O); 2 224 (CN).

Methyl 6-benzyl-2-(2,2-dicyanovinyl)furo[2,3-b]pyrrole-5-carboxylate (**3c**). Yield: 72%, m.p. 202–205 °C (MeOH–toluene 2 : 1). For $C_{19}H_{13}N_3O_3$ (331.3) calculated: 68.88% C, 3.95% H,

12.68% N; found: 68.67% C, 4.06% H, 12.89% N. ^{1}H NMR ($CDCl_3$): 3.88 s, 3 H (CO_2CH_3); 5.62 s, 2 H (CH_2); 6.98 s, 1 H (H-4); 7.29–7.40 m, 7 H (H_{arom}, H-7, H-3). IR: 1 713 (C=O); 2 220 (CN). UV: 410 (3.59).

Methyl 2-(2,2-dicyanovinyl)-6-methoxymethylfuro[2,3-b]pyrrole-5-carboxylate (**3d**). Yield: 88%, m.p. 166–168 °C (MeOH). For $C_{14}H_{11}N_3O_4$ (285.3) calculated: 58.95% C, 3.89% H, 14.73% N; found: 58.77% C, 3.54% H, 14.75% N. ^{1}H NMR ($CDCl_3$): 3.42 s, 3 H (OCH_3); 3.89 s, 3 H (CO_2CH_3); 5.81 s, 2 H (CH_2); 7.05 s, 1 H (H-4); 7.38 s, 1 H (H-3); 7.41 s, 1 H (H-7). IR: 1 695 (C=O); 2 222 (CN).

Methyl 2-[2-Cyano-2-(methoxycarbonyl)vinyl]-6*H*-furo[2,3-*b*]pyrrole-5-carboxylate (**4a**)

Sodium methoxide (10% methanolic solution, 5 drops) was added to a stirred hot solution of compound **1a** (0.60 g, 3 mmol) and methyl cyanoacetate (0.30 g, 3 mmol) in a mixture of MeOH (20 ml) and toluene (10 ml). The precipitate was filtered off after cooling, washed with cold MeOH and crystallized from MeOH to give 0.49 g (66%) of **4a**, m.p. 268–269 °C. For $C_{13}H_{10}N_2O_5$ (274.2) calculated: 56.94% C, 3.68% H, 10.22% N; found: 56.79% C, 3.35% H, 10.29% N. ^{1}H NMR ($(CD_3)_2SO$): 3.75 s, 6 H (2 × CO_2CH_3); 6.88 s, 1 H (H-4); 7.66 s, 1 H (H-3); 8.03 s, 1 H (H-7); 13.18 s, 1 H (NH). IR: 1 709 (C=O); 2 223 (CN); 3 271 (NH).

The following compounds were prepared by this procedure:

Methyl 2-[2-cyano-2-(methoxycarbonyl)vinyl]-6-methylfuro[2,3-b]pyrrole-5-carboxylate (**4b**). Yield: 77%, m.p. 217–218 °C (MeOH–toluene 2 : 1). For $C_{14}H_{12}N_2O_5$ (288.3) calculated: 58.33% C, 4.20% H, 9.72% N; found: 58.46% C, 4.08% H, 7.81% N. ^{1}H NMR ($CDCl_3$): 3.90 s, 6 H (2 × CO_2CH_3); 4.01 s, 3 H (N-CH_3); 6.95 s, 1 H (H-4); 7.37 s, 1 H (H-3); 7.92 s, 1 H (H-7). IR: 1 706 (C=O); 1 668 (C=O); 2 052 (CN). MS: 289 (20.5), 288 (100), 274 (15.4), 273 (87.2), 257 (23.0), 245 (51.3), 229 (7.2), 228 (7.2), 217 (8.7), 201 (7.7), 158 (15.4), 160 (15.4), 141 (10.3), 120 (5.1), 115 (5.1), 75 (8.2), 66 (6.6), 59 (15.4), 56 (18.4), 50 (15.4).

Methyl 6-benzyl-2-[2-cyano-2-(methoxycarbonyl)vinyl]furo[2,3-b]pyrrole-5-carboxylate (**4c**). Yield: 82%, m.p. 243–245 °C (MeOH–toluene 3 : 1). For $C_{20}H_{16}N_2O_5$ (364.3) calculated: 65.92% C, 4.43% H, 7.69% N; found: 66.02% C, 4.51% H, 7.59% N. ^{1}H NMR ($CDCl_3$): 3.87 s, 3 H (CO_2CH_3); 3.90 s, 3 H (CO_2CH_3); 5.68 s, 2 H (CH_2); 6.97 s, 1 H (H-4); 7.25–7.43 m, 6 H (H_{arom}, H-3); 7.92 s, 1 H (H-7). ^{13}C NMR ($CDCl_3$): 48.62 (NCH_2); 51.70 (CO**C**H_3); 53.17 (CO_2**C**H_3); 94.93 (C-8); 108.40 (C-4); 111.52 (C-3a); 116.41, ^3J(CN,H-7) = 12.9 (CN); 119.07 (C-3); 124.77 (C-5); 128.19, 128.35, 128.83, 136.15 (C-Ph); 139.11 (C-7); 150.07 (C-6a); 156.27 (C-2); 161.59 (C=O); 163.72 (C=O). IR: 1 669 (C=O); 2 214 (CN). UV: 403 (3.30).

Methyl 2-[2-cyano-2-(methoxycarbonyl)vinyl]-6-methoxymethylfuro[2,3-b]pyrrole-5-carboxylate (**4d**). Yield: 72%, m.p. 192–194 °C (MeOH). For $C_{15}H_{14}N_2O_6$ (318.3) calculated: 56.60% C, 4.43% H, 8.80% N; found: 56.48% C, 4.55% H, 8.67% N. ^{1}H NMR ($CDCl_3$): 3.42 s, 3 H (OCH_3); 3.69 s, 6 H (2 × CO_2CH_3); 5.82 s, 2 H (CH_2); 7.04 s, 1 H (H-4); 7.43 s, 1 H (H-3); 7.94 s, 1 H (H-7). ^{13}C NMR ($CDCl_3$): 51.84 (CO_2**C**H_3); 53.22 (CO_2**C**H_3); 57.33 (OCH_3); 75.90 (NCH_2); 95.55 (C-8); 109.33 (C-4); 111.32 (C-3a); 115.79, ^3J(CN,H-7) = 12.8 (CN); 118.55 (C-3); 125.24 (C-5); 139.26 (C-7); 149.97 (C-2); 156.44 (C-6a); 161.28 (C=O); 163.53 (C=O). IR: 1 707 (C=O); 2 216 (CN).

Methyl 2-[2-Cyano-2-(2-furyl)vinyl]-6*H*-furo[2,3-*b*]pyrrole-5-carboxylate (**5a**)

To a hot solution of compound **1a** (0.60 g, 3 mmol) and 2-furylacetonitrile (0.32 g, 3 mmol) in a mixture of MeOH (20 ml) and toluene (10 ml), piperidine (5 drops) was added under stirring and the reaction mixture was refluxed for 1 h. After cooling, fine crystals were fil-

tered off, washed with cold MeOH and crystallized from MeOH to yield 0.61 g (72%) of **5a**, m.p. 239–241 °C. For $C_{15}H_{10}N_2O_4$ (282.2) calculated: 63.82% C, 3.57% H, 9.93% N; found: 63.48% C, 3.75% H, 9.79% N. ^{1}H NMR ($(CD_3)_2SO$): 3.74 s, 3 H (CO_2CH_3); 6.60–6.67 m, 2 H (H-3' and H-4'); 6.81 s, 1 H (H-4); 7.22 s, 1 H (H-3); 7.48 s, 1 H (H-7); 7.76 d, 1 H (H-5'); 12.94 s, 1 H (NH). IR: 1 698 (C=O); 2 220 (CN); 3 251 (NH).

The following compounds were prepared by this procedure:

Methyl 2-[2-cyano-2-(2-furyl)vinyl]-6-methylfuro[2,3-b]pyrrole-5-carboxylate (**5b**). Yield: 82%, m.p. 208–210 °C (MeOH–toluene 2 : 1). For $C_{16}H_{12}N_2O_4$ (296.3) calculated: 64.86% C, 4.08% H, 9.46% N; found: 64.68% C, 3.94% H, 9.64% N. ^{1}H NMR ($CDCl_3$): 3.85 s, 3 H (CO_2CH_3); 4.0 s, 3 H (N-CH_3); 6.38 d, 1 H, *J*(3',4') = 3.4 (H-3'); 6.48 dd, 1 H, *J*(3',4') = 3.4, *J*(4',5') = 1.8 (H-4'); 6.99 s, 1 H (H-4); 7.23 s, 1 H (H-3); 7.26 s, 1 H (H-7); 7.42 d, 1 H, *J*(5',4') = 1.8 (H-5'). IR: 1 693 (C=O); 2 219 (CN).

Methyl 6-benzyl-2-[2-cyano-2-(2-furyl)vinyl]furo[2,3-b]pyrrole-5-carboxylate (**5c**). Yield: 82%, m.p. 200–202 °C (MeOH–toluene 3 : 1). For $C_{22}H_{16}N_2O_4$ (372.4) calculated: 70.96% C, 4.33% H, 7.52% N; found: 71.22% C, 4.15% H, 7.48% N. ^{1}H NMR ($CDCl_3$): 3.84 s, 3 H (CO_2CH_3); 5.68 s, 2 H (CH_2); 6.48 dd, 1 H, *J*(3',4') = 3.4, *J*(4',5') = 1.9 (H-4'); 6.62 d, 1 H, *J*(3',4') = 3.4 (H-3'); 6.96 s, 1 H (H-3); 6.98 s, 1 H (H-4); 7.28 s, 1 H (H-7); 7.30–7.41 m, 5 H (H_{arom}); 7.48 d, 1 H, *J*(5',4') = 1.9 (H-5'). ^{13}C NMR ($CDCl_3$): 48.62 (N-CH_3); 51.40 (CO_2**C**H_3); 96.28 (C-8); 108.00 (C-4); 109.40 (C-3'); 110.58 (C-3a); 111.62 (C-3); 112.46 (C-4'); 116.41, ^3J(CN,H-7) = 13.76 (CN); 122.51 (C-5); 123.66 (C-7); 127.96, 128.23, 128.71, 136.69 (C-Ph); 143.44 (C-5'); 149.29 (C-6a); 151.45 (C-2'); 154.59 (C-2); 161.68 (C=O). IR: 1 699 (C=O); 2 284 (CN). UV: 403 (3.29), 335 (3.02).

Methyl 2-[2-cyano-2-(2-furyl)vinyl]-6-methoxymethylfuro[2,3-b]pyrrole-5-carboxylate (**5d**). Yield: 88%, m.p. 215 °C (toluene–hexane 1 : 5). For $C_{17}H_{14}N_2O_5$ (326.3) calculated: 62.57% C, 4.32% H, 8.59% N; found: 62.58% C, 4.26% H, 8.75% N. ^{1}H NMR ($CDCl_3$): 3.42 s, 3 H (O-CH_3); 3.87 s, 3 H (CO_2CH_3); 5.83 s, 2 H (CH_2); 7.23 s, 1 H (H-7); 6.49 dd, 1 H, *J*(3',4') = 3.4, *J*(4',5') = 1.8 (H-4'); 6.63 d, 1 H, *J*(3',4') = 3.4 (H-3'); 6.99 s, 1 H (H-4); 7.01 s, 1 H (H-3); 7.44 d, 1 H, *J*(5',4') = 1.8 (H-5'). ^{13}C NMR ($CDCl_3$): 51.57 (CO_2**C**H_3); 57.18 (OCH_3); 75.69 (NCH_2); 96.78 (C-8); 109.10 (C-4); 109.63 (C-3'); 110.41 (C-3a); 111.19 (C-3); 112.50 (C-4'); 116.28, ^3J(CN,H-7) = 13.76 (CN); 123.09 (C-5); 123.66 (C-7); 143.58 (C-5'); 149.15 (C-6a); 151.39 (C-2'); 154.76 (C-2); 161.61 (C=O). IR: 1 692 (C=O); 2 220 (CN).

Methyl 2-[2-Azido-2-(2-methoxycarbonyl)vinyl]-6-methylfuro[2,3-*b*]pyrrole-5-carboxylate (**6b**)

A solution of compound **1b** (1.45 g, 7 mmol) and methyl azidoacetate (2.5 g, 20 mmol) in toluene (50 ml) was added at 0 °C during 30 min to methanolic sodium methoxide prepared from sodium (0.7 g, 30 mmol) and dried methanol (50 ml). Stirring was continued for additional 60 min at a temperature not exceeding 5 °C, the reaction mixture was than cooled to –10 °C, a solution of ammonium chloride (0.74 g, 14 mmol) in water (10 ml) was added and the mixture was poured into ice-cold water (250 ml). This mixture was extracted three times with $CHCl_3$ (100 ml). The combined organic solutions were dried with anhydrous sodium sulfate, the residue after evaporation of the solvent under reduced pressure was crysallized from MeOH to give 1.81 g (85%) of **6b**, m.p. 127 °C (dec.). For $C_{13}H_{12}N_4O_5$ (304.3) calculated: 51.32% C, 3.98 % H, 18.41% N; found: 51.36% C, 4.06% H, 18.53% N. ^{1}H NMR ($CDCl_3$): 3.74 s, 6 H (2 × CO_2CH_3); 3.88 s, 3 H (N-CH_3); 6.88 s, 1 H (H-4); 6.95 s, 1 H (H-7); 7.25 s, 1 H (H-3). IR: 1 690 (C=O); 2 220 (N_3).

The following compounds were prepared by this procedure:

Methyl 2-[2-azido-2-(2-methoxycarbonyl)vinyl]-6-benzylfuro[2,3-b]pyrrole-5-carboxylate (**6c**). Yield: 85%, m.p. 135 °C (dec.) (MeOH). For $C_{19}H_{16}N_4O_5$ (380.3) calculated: 60.00% C, 4.24% H, 14.73% N; found: 60.12% C, 4.35% H, 14.64% N. ^{1}H NMR ($CDCl_3$): 3.81 s, 3 H (CO_2CH_3); 3.88 s, 3 H (CO_2CH_3); 5.65 s, 2 H (CH_2); 6.85 s, 1 H (H-4); 6.94 s, 1 H (H-7); 7.26–7.30 m, 6 H (H_{arom}, H-3). IR: 1 717 (C=O); 2 120 (N_3).

Methyl 2-[2-azido-2-(2-methoxycarbonyl)vinyl]-6-methoxymethylfuro[2,3-b]pyrrole-5-carboxylate (**6d**). Yield: 70%, m.p. 104–105 °C (MeOH). For $C_{14}H_{14}N_4O_6$ (334.3) calculated: 50.30% C, 4.22% H, 16.76% N; found: 50.43% C, 4.18% H, 16.62% N. ^{1}H NMR ($CDCl_3$): 3.35 s, 3 H (O-CH_3); 3.86 s, 6 H (2 × CO_2CH_3); 5.79 s, 2 H (CH_2); 6.88 s, 1 H (H-4); 6.98 s, 1 H (H-7); 7.28 s, 1 H (H-3). IR: 1 709 (C=O); 2 124 (N_3).

Dimethyl 5-Methyl-1*H*-furo[2,3-*b*:4,5-*b*']dipyrrole-2,6-dicarboxylate (**7b**)

A stirred solution of compound **6b** (1.52 g, 5 mmol) in toluene (250 ml) was refluxed for 3 h, the solvent was evaporated *in vacuo* and the crude product was crystallized to give 1.38 g (63%) of **7b**, m.p. 245–247 °C (toluene). For $C_{13}H_{12}N_2O_5$ (276.2) calculated: 56.52% C, 4.38% H, 10.14% N; found: 56.42% C, 4.27% H, 9.98% N. ^{1}H NMR (($CD_3)_2SO$): 3.76 s, 3 H (CO_2CH_3); 3.77 s, 3 H (CO_2CH_3); 3.87 s, 3 H (N-CH_3); 6.85 s, 1 H (H-7); 6.86 d, 1 H, *J*(1,3) = 1.5 (H-3); 12.02 s, 1 H (NH). ^{13}C NMR (($CD_3)_2SO$): 31.99 (N-CH_3); 51.09 (CO_2**C**H_3); 51.12 (CO_2**C**H_3); 97.70 (C-3); 99.09 (C-7a); 104.99 (C-7); 118.62 (C-7b); 118.95 (C-6); 123.22 (C-2); 147.69 (C-3a); 156.74 (C-4a); 161.14 (C=O); 161.25 (C=O). IR: 1 697 (C=O); 3 271 (NH).

The following compounds were prepared by this procedure:

Dimethyl 5-benzyl-1H-furo[2,3-b:4,5-b']dipyrrole-2,6-dicarboxylate (**7c**). Yield: 73%, m.p. 266–267 °C (toluene). For $C_{19}H_{16}N_2O_5$ (352.3) calculated: 64.77% C, 4.58% H, 7.59% N; found: 64.57% C, 4.49% H, 7.81% N. ^{1}H NMR (($CD_3)_2SO$): 3.70 s, 6 H (2 × CO_2CH_3); 5.64 s, 2 H (CH_2); 6.82 s, 1 H (H-7); 6.91 s, 1 H (H-3); 7.21–7.24 m, 5 H (H_{arom}); 12.06 s, 1 H (NH). ^{13}C NMR (($CD_3)_2SO$): 47.62 (NCH_2); 51.13 (CO_2**C**H_3); 51.18 (CO_2**C**H_3); 97.76 (C-3); 99.61 (C-7a); 106.90 (C-7); 118.04 (C-7b); 119.19 (C-6); 123.03 (C-2); 126.76, 127.61, 128.68, 137.06 (C-Ph); 147.90 (C-3a); 156.66 (C-4a); 161.05 (C=O); 161.20 (C=O). IR: 1 695 (C=O); 3 271 (NH). UV: 333 (3.33).

Dimethyl 5-(methoxymethyl)-1H-furo[2,3-b:4,5-b']dipyrrole-2,6-dicarboxylate (**7d**). Yield: 82%, m.p. 254–255 °C (toluene). For $C_{14}H_{14}N_2O_6$ (306.3) calculated: 54.90% C, 4.61% H, 9.15% N; found: 54.79% C, 4.52% H, 9.18% N. ^{1}H NMR (($CD_3)_2SO$): 3.26 s, 3 H (CO_2CH_3); 3.18 s, 3 H (CO_2CH_3); 3.72 s, 3 H (CH_3); 5.70 s, 2 H (CH_2); 6.83 s, 1 H (H-7); 6.91 s, 1 H (H-3); 12.23 s, 1 H (NH). ^{13}C NMR (($CD_3)_2SO$): 51.21 (CO_2**C**H_3); 51.33 (CO_2**C**H_3); 56.12 (OCH_3); 74.80 (NCH_2); 97.77 (C-3); 99.50 (C-7a); 106.96 (C-7); 118.64 (C-7b); 119.34 (C-6); 122.94 (C-2); 147.84 (C-3a); 156.92 (C-4a); 160.87 (C-3); 161.27 (C=O). IR: 1 686 (C=O); 3 264 (NH). MS: 306 (96), 301 (18), 276 (16), 275 (18), 274 (20), 244 (50), 230 (80), 216 (24), 215 (10), 201 (8), 199 (18), 198 (50), 129 (12), 88 (10), 59 (8), 53 (10), 45 (100).

Methyl 2-[Bis(4,4-dimethyl-2,6-dioxocyclohexyl)methyl]-6*H*-furo-[2,3-*b*]pyrrole-5-carboxylate (**8a**)

To a methanolic solution (20 ml) of compound **1a** (0.27 g, 1.4 mmol) and 5,5-dimethylcyclohexane-1,3-dione (0.40 g, 2.8 mmol), piperidine (5 drops) was added and the reaction mixture was refluxed for 20 min. After cooling, the precipitate was filtered off, washed with cold MeOH and crystallized from MeOH to yield 0.34 g (53%) of **8a**, m.p. 193–195 °C. For

$C_{25}H_{29}NO_7$ (455.5) calculated: 65.92% C, 6.42% H, 3.08% N; found: 65.78% C, 6.22% H, 3.26% N. ^{1}H NMR ($(CD_3)_2SO$): 0.96 s, 12 H (4 × CH_3); 2.24 s, 8 H (4 × CH_2); 3.67 s, 3 H (CO_2CH_3); 5.88 s, 1 H (H-7'); 5.91 s, 1 H (H-4); 6.56 s, 1 H (H-3); 8.2 bs, 1 H (NH); 12.17 s, 1 H (OH). IR: 1 597 (C=O); 1 686 (C=O); 3 250 (NH).

The following compounds were prepared by this procedure:

Methyl 2-[bis(4,4-dimethyl-2,6-dioxocyclohexyl)methyl]-6-methylfuro[2,3-b]pyrrole-5-carboxylate (**8b**). Yield: 45%, m.p. 186–187 °C (MeOH). For $C_{26}H_{31}NO_7$ (469.5) calculated: 66.51% C, 6.65% H, 2.98% N; found: 66.42% C, 6.32% H, 2.92% N. ^{1}H NMR ($CDCl_3$): 1.10 s, 12 H (4 × CH_3); 2.57 s, 8 H (2 × CH_2); 3.87 s, 3 H (N-CH_3); 3.97 s, 3 H (CO_2CH_3); 5.99 s, 1 H (H-7'); 6.89 s, 1 H (H-4); 7.99 s, 1 H (H-3); 8.91 bs, 1 H (H-1'). IR: 1 705 (C=O).

Methyl 6-benzyl-2-[bis(4,4-dimethyl-2,6-dioxocyclohexyl)methyl]furo[2,3-b]pyrrole-5-carboxylate (**8c**). Yield: 47%, m.p. 129–130 °C (MeOH). For $C_{32}H_{35}NO_7$ (545.6) calculated: 70.44% C, 6.47% H, 2.57% N; found: 70.36% C, 6.32% H, 2.49% N. ^{1}H NMR ($CDCl_3$): 1.05 s, 12 H (4 × CH_3); 2.75 s, 8 H (2 × CH_2); 3.75 s, 3 H (CO_2CH_3); 5.51 bs, 3 H (CH_2, H-7'); 6.06 s, 1 H (H-4); 6.80 s, 1 H (H-3); 7.18–7.54 m, 5 H (H_{arom}); 12.39 bs, 1 H (OH). IR: 1 597 (C=C); 1 699 (C=O).

Methyl 2-[bis(4,4-dimethyl-2,6-dioxocyclohexyl)methyl]-6-(methoxymethyl)furo[2,3-b]pyrrole-5-carboxylate (**8d**). Yield: 85%, m.p. 193–195 °C (MeOH). For $C_{27}H_{33}NO_8$ (499.6) calculated: 64.91% C, 6.66% H, 2.80% N; found: 64.63% C, 6.75% H, 2.64% N. ^{1}H NMR ($CDCl_3$): 1.16 s, 12 H (4 × CH_3); 2.35 s, 8 H (2 × CH_2); 3.25 s, 3 H (O-CH_3); 3.82 s, 3 H (CO_2CH_3); 5.65 m, 3 H (CH_2, H-7'); 6.10 s, 1 H (H-4); 6.91 s, 1 H (H-3); 12.50 bs, 1 H (OH). IR: 1 594 (C=C); 1 698 (C=O).

Methyl 2-(3,3,6,6-Tetramethyl-1(2*H*),8(7*H*)-dioxo-3,4,5,6-tetrahydro-9*H*-xanthen-9-yl)-6*H*-furo[2,3-*b*]pyrrole-5-carboxylate (**9a**)

Compound **8a** (0.14 g, 3 mmol) was dissolved in hot MeOH (15 ml), 5 drops of concentrated hydrochloric acid was added and the reaction mixture was refluxed for 20 min. After cooling, water (5 ml) was added to the reaction mixture and the precipitate was filtered off and than crystallized from MeOH to give 0.10 g (78%) of **9a**, m.p. 164–165 °C. For $C_{25}H_{27}NO_6$ (437.5) calculated: 68.63% C, 6.22% H, 3.20% N; found: 68.69% C, 6.18% H, 3.44% N. ^{1}H NMR ($(CD_3)_2SO$): 1.04 s, 6 H (2 × CH_3); 1.11 s, 6 H (2 × CH_3); 2.27 s, 4 H (2 × CH_2); 2.46 s, 4 H (2 × CH_2); 3.81 s, 3 H (CO_2CH_3); 4.97 s, 1 H (H-9'); 6.33 s, 1 H (H-4); 6.70 d, 1 H (H-3); 8.74 s, 1 H (NH). IR: 1 672 (C=O); 3 263 (NH).

The following compounds were prepared by this procedure:

Methyl 6-methyl-2-(3,3,6,6)-tetramethyl-1(2H),8(7H)-dioxo-3,4,5,6-tetrahydro-9H-xanthen-9-yl)furo[2,3-b]pyrrole-5-carboxylate (**9b**). Yield: 90%, m.p. 185–187 °C (MeOH). For $C_{26}H_{29}NO_6$ (451.5) calculated: 69.16% C, 6.47% H, 3.10% N; found: 69.25% C, 6.31% H, 3.22% N. ^{1}H NMR ($CDCl_3$): 1.03 s, 6 H (2 × CH_3); 1.11 s, 6 H (2 × CH_3); 2.48 s, 4 H (2 × CH_2); 2.56 s, 4 H (2 × CH_2); 3.78 s, 3 H (N-CH_3); 3.88 s, 3 H (CO_2CH_3); 4.98 s, 1 H (H-9'); 6.40 s, 1 H (H-4); 6.61 s, 1 H (H-3). IR: 1 663 (C=O); 1 700 (C=O).

Methyl 6-benzyl-2-(3,3,6,6)-tetramethyl-1(2H),8(7H)-dioxo-3,4,5,6-tetrahydro-9H-xanthen-9-yl)-furo[2,3-b]pyrrole-5-carboxylate (**9c**). Yield: 72%, m.p. 164–165 °C (MeOH). For $C_{32}H_{33}NO_6$ (527.6) calculated: 72.85% C, 6.30% H, 2.65% N; found: 72.61% C, 6.26% H, 2.80% N. ^{1}H NMR ($CDCl_3$): 0.96 s, 6 H (2 × CH_3); 1.16 s, 6 H (2 × CH_3); 2.24 s, 4 H (2 × CH_2); 2.58 s, 4 H (2 × CH_2); 3.74 s, 3 H (CO_2CH_3); 5.35 s, 2 H (CH_2); 4.98 s, 1 H (H-9'); 6.37 s, 1 H (H-4); 6.80 s, 1 H (H-3); 7.19–7.29 m, 5 H (H_{arom}). IR: 1 670 (C=O); 1 699 (C=O). UV: 298 (3.23), 230 (3.34).

Methyl 6-methoxymethyl-2-(3,3,6,6)-tetramethyl-1(2H),8(7H)-dioxo-3,4,5,6-tetrahydro-9H-xanthen-9-yl)furo[2,3-b]pyrrole-5-carboxylate (**9d**). Yield: 82%, m.p. 201–203 °C (MeOH). For $C_{27}H_{31}NO_7$ (481.5) calculated: 67.34% C, 6.49% H, 2.91% N; found: 67.21% C, 6.71% H, 2.85% N. ^{1}H NMR ($CDCl_3$): 1.04 s, 6 H (2 × CH_3); 1.11 s, 6 H (2 × CH_3); 2.26 s, 4 H (2 × CH_2); 2.47 s, 4 H (2 × CH_2); 3.21 s, 3 H (O-CH_3); 3.79 s, 3 H (CO_2CH_3); 4.98 s, 1 H (H-9'); 5.67 s, 2 H (N-CH_2); 6.35 s, 1 H (H-4); 6.84 s, 1 H (H-3). IR: 1 606 (C=C); 1 658 (C=O); 1 703 (C=O).

Reactions of 2-formylfuro[3,2-*b*]pyrrole-5-carboxylates (**2a**–**2c**) with 5,5-dimethylcyclohexane-1,3-dione were carried out under the same conditions described for compounds **1a**–**1d**. By this procedure, the following compounds were prepared:

Methyl 2-[bis(4,4-dimethyl-2,6-dioxocyclohexyl)methyl]-4H-furo[3,2-b]pyrrole-5-carboxylate (**10a**). Yield: 48%, m.p. 142 °C (MeOH). For $C_{25}H_{29}NO_7$ (455.5) calculated: 65.92% C, 6.42% H, 3.08% N; found: 65.84% C, 6.38% H, 3.18% N. ^{1}H NMR ($CDCl_3$): 1.09 s, 12 H (4 × CH_3); 2.35 s, 8 H (2 × CH_2); 3.82 s, 3 H (CO_2CH_3); 5.81 s, 1 H (H-7'); 6.04 s, 1 H (H-1'); 6.59 s, 1 H (H-6); 7.20 s, 1 H (H-3); 8.5 bs, 1 H (NH); 12.12 bs, 1 H (OH). IR: 1 595 (C=C); 1 697 (C=O); 3 250 (NH).

Methyl 2-[bis(4,4-dimethyl-2,6-dioxocyclohexyl)methyl]-4-methylfuro[3,2-b]pyrrole-5-carboxylate (**10b**). Yield: 62%, m.p. 147–150 °C (MeOH). For $C_{26}H_{31}NO_7$ (469.5) calculated: 66.51% C, 6.65% H, 2.98% N; found: 66.75% C, 6.39% H, 2.89% N. ^{1}H NMR ($CDCl_3$): 1.14 s, 12 H (4 × CH_3); 2.36 s, 8 H (2 × CH_2); 3.79 s, 3 H (N-CH_3); 3.91 s, 3 H (CO_2CH_3); 5.53 s, 1 H (H-7'); 6.03 s, 1 H (H-1'); 6.66 s, 1 H (H-6); 7.20 s, 1 H (H-3); 12.26 bs, 1 H (OH). IR: 1 599 (C=C); 1 699 (C=O).

Methyl 4-benzyl-2-[bis(4,4-dimethyl-2,6-dioxocyclohexyl)methyl]furo[3,2-b]pyrrole-5-carboxylate (**10c**). Yield: 53%, m.p. 177 °C (MeOH). For $C_{32}H_{35}NO_7$ (545.6) calculated: 70.44% C, 6.47% H, 2.57% N; found: 70.52% C, 6.38% H, 2.49% N. ^{1}H NMR ($CDCl_3$): 1.09 s, 12 H (4 × CH_3); 2.31 s, 8 H (2 × CH_2); 3.76 s, 3 H (CO_2CH_3); 5.56 bs, 3 H (CH_2, H-7'); 6.10 s, 1 H (H-1'); 6.72 s, 1 H (H-6); 7.19–7.31 m, 6 H (H_{arom}, H-3); 12.21 bs, 1 H (OH). IR: 1 599 (C=C); 1 699 (C=O).

Methyl 2-(3,3,6,6-tetramethyl-1(2H),8(7H)-dioxo-3,4,5,6-tetrahydro-9H-xanthen-9-yl)-4H-furo[3,2-b]pyrrole-5-carboxylate (**11a**). Yield: 91%, m.p. 330 °C (MeOH). For $C_{25}H_{27}NO_6$ (437.5) calculated: 68.63% C, 6.22% H, 3.20% N; found: 68.44% C, 6.18% H, 3.22% N. ^{1}H NMR ($(CD_3)_2SO$): 0.88 s, 6 H (2 × CH_3); 0.98 s, 6 H (2 × CH_3); 2.18 s, 4 H (2 × CH_2); 2.48 s, 4 H (2 × CH_2); 3.68 s, 3 H (CO_2CH_3); 4.67 s, 1 H (H-9'); 6.08 s, 1 H (H-6); 6.56 s, 1 H (H-3); 11.41 s, 1 H (NH). IR: 1 668 (C=O); 1 699 (C=O); 3 364 (NH).

Methyl 4-methyl-2-(3,3,6,6-tetramethyl-1(2H),8(7H)-dioxo-3,4,5,6-tetrahydro-9H-xanthen-9-yl)furo[3,2-b]pyrrole-5-carboxylate (**11b**). Yield: 70%, m.p. 219–220 °C (MeOH). For $C_{26}H_{29}NO_6$ (451.5) calculated: 69.16% C, 6.47% H, 3.10% N; found: 69.47% C, 6.39% H, 2.98% N. ^{1}H NMR ($CDCl_3$): 1.06 s, 6 H (2 × CH_3); 1.11 s, 6 H (2 × CH_3); 2.26 s, 4 H (2 × CH_2); 2.48 s, 4 H (2 × CH_2); 3.78 s, 3 H (N-CH_3); 3.88 s, 3 H (CO_2CH_3); 4.98 s, 1 H (H-9'); 6.40 s, 1 H (H-6); 6.60 s, 1 H (H-3). IR: 1 672 (C=O); 1 703 (C=O). UV: 302 (3.10), 231 (2.96). MS: 452 (24.4), 451 (73.2), 436 (19.5), 330 (24.4), 329 (100), 314 (21.9), 288 (7.3), 273 (24.4), 245 (29.3), 232 (14.6), 225 (9.7), 217 (24.4), 194 (39.0), 186 (5.6), 172 (5.7), 116 (5.7), 83 (17.1), 55 (17.1).

Methyl 4-benzyl-2-(3,3,6,6-tetramethyl-1(2H),8(7H)-dioxo-3,4,5,6-tetrahydro-9H-xanthen-9-yl)furo[3,2-b]pyrrole-5-carboxylate (**11c**). Yield: 86%, m.p. 182–184 °C (MeOH). For $C_{32}H_{33}NO_6$ (527.6) calculated: 72.85% C, 6.30% H, 2.65% N; found: 72.77% C, 6.46% H, 2.72% N. ^{1}H NMR ($CDCl_3$): 1.04 s, 6 H (2 × CH_3); 1.11 s, 6 H (2 × CH_3); 2.26 s, 4 H

(2 × CH_2); 2.74 s, 4 H (2 × CH_2); 3.74 s, 3 H (CO_2CH_3); 4.97 s, 1 H (H-9´); 5.54 s, 2 H (CH_2); 6.18 s, 1 H (H-6); 6.69 s, 1 H (H-3) 7.28–7.17 m, 5 H (H_{arom}). IR: 1 670 (C=O); 1 701 (C=O).

Methyl 4-Benzyl-2-[(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)methyl]furo-[3,2-*b*]pyrrole-5-carboxylate (**12**)

A mixture of **2c** (0.4 g, 1.4 mmol), dimedone (0.2 g, 1.4 mmol), acetic anhydride (1 ml), and a catalytic amount of potassium acetate was stirred in a microwave apparatus (MILESTONE LAVIS 1000) for 10 min. After cooling, the formed crystals were filtered off and crystallized to yield 0.316 g (52%) of **12**, m.p. 186 °C (hexane–toluene 3 : 1). For $C_{24}H_{23}NO_5$ (405.4) calculated: 71.10% C, 5.72% H, 3.45% N; found: 71.22% C, 5.78% H, 3.42% N. ^{1}H NMR ($CDCl_3$): 1.10 s, 6 H (2 × CH_3); 2.58 s, 2 H (CH_2); 2.59 s, 2 H (CH_2); 3.86 s, 3 H (CO_2CH_3); 5.69 s, 2 H (NCH_2); 6.83 s, 1 H (H-6); 7.15–7.33 m, 5 H (H_{arom}); 8.06 s, 1 H (H-3); 8.57 s, 1 H (H-7'). ^{13}C NMR ($CDCl_3$): 28.54 (2 × CH_3); 30.12 (C-4'); 50.74 (NCH_2); 51.85 (CO_2CH_3); 52.21 (CH_2); 53.75 (CH_2); 98.04 (C-3); 111.15 (C-6); 125.55 (C-5); 127.13, 127.85, 128.77, 137.03 (C_{arom}); 130.69 (C-3a); 134.93 (C-1'); 136.09 (C-7'); 151.99, 156.92 (C-2, C-6a); 161.56 (CO_2CH_3); 197.04 (C=O); 197.30 (C=O). IR: 1 549 (C=C); 1 686 (C=O); 1 720 (C=O). UV: 447 (3.39). MS: 405 (41), 346 (6), 318 (5), 314 (10), 282 (14), 204 (6), 92 (18), 88 (10), 59 (8), 53 (10), 50 (15).

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