

# Preparation of 2-substituted furo[3,2-*b*]pyrroles and their reactions with dimethyl butynedioate

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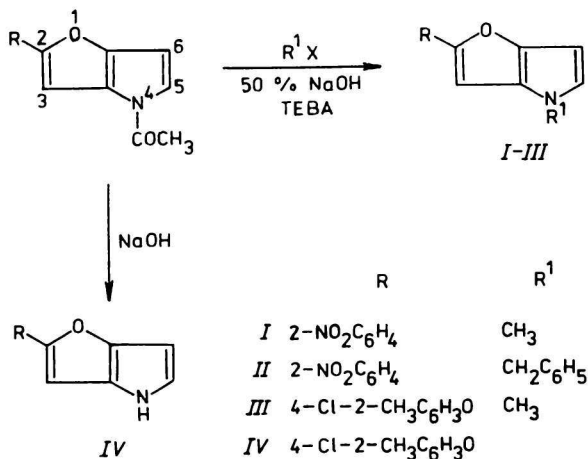
The synthesis of 2-(2-nitrophenyl)-, 2-(4-chloro-2-methylphenoxy)furo[3,2-*b*]pyrroles, and their *N*-substituted derivatives, as well as the preparation of 1,2-dihydropyrrolo[2',3':4,5]furo[3,2-*b*]indole is described. Reactions of prepared compounds with dimethyl butynedioate were investigated. It was found that the reaction course is influenced by substituents attached to the furo[3,2-*b*]pyrrole system. Products of [4 + 2] cycloaddition as well as products of Michael addition were obtained.

Описан синтез 2-(2-нитрофенил)-, 2-(4-хлор-2-метилфенокси)фуоро[3,2-*b*]пирролов и их *N*-замещенных производных и также синтез 1,2-дигидропирроло[2',3':4,5]фуоро[3,2-*b*]индола. Приводятся результаты исследования их реакций с диметилбутиндиоатом. В зависимости от заместителей присутствующих на фуоро[3,2-*b*]пиррольной системе были получены продукты [4 + 2] циклоприсоединения и присоединения Михаэля.

Our preceding papers [1—3] presented the results of the addition and cycloaddition reactions for furo[3,2-*b*]pyrrole derivatives. We described the 1,3-dipolar cycloadditions of two furo[3,2-*b*]pyrrole derivatives with *C*-benzoyl-*N*-phenylnitron and *N,N*-diphenylnitron which proceeded regiospecifically in positions 2 and 3 of the furan ring [1]. In another paper [2] we have published the results of the study on the reaction of 2-aryl-4*H*-furo[3,2-*b*]pyrroles and their *N*-substituted derivatives with dimethyl butynedioate. Depending on the substituent in position 4 of the furo[3,2-*b*]pyrrole system the reaction afforded products of Michael addition or [4 + 2] cycloaddition with subsequent transformation of the pyrrole ring leading to substituted benzo[*b*]furan derivatives. Our further investigations have shown that with furo[3,2-*b*]pyrrole derivatives containing no substituent in position 2, the cycloaddition reaction proceeds on the furan ring and leads to the transformation of furo[3,2-*b*]pyrroles into substituted indoles. Using ethyl propynoate as the unsymmetrically substituted dienophile the regiospecificity of [4 + 2] cycloaddition reactions taking place on the furan part of the furo[3,2-*b*]pyrrole system has been found out [3].

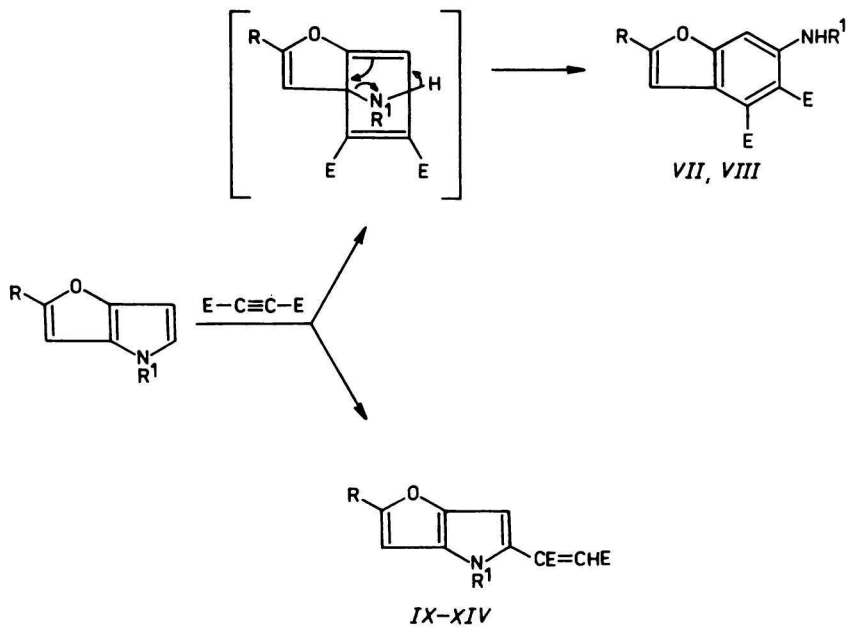
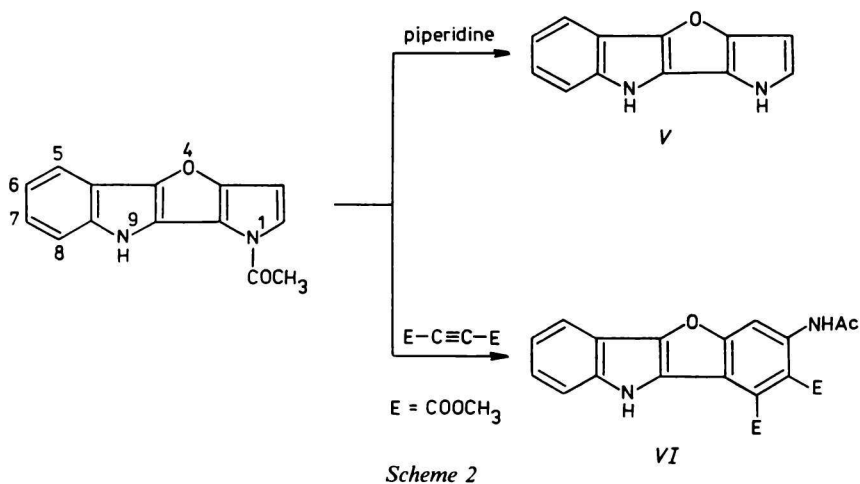
In this work we were interested in the study of the reactions of 2-substituted furo[3,2-*b*]pyrroles and 1-acetylpyrrolo[2',3':4,5]furo[3,2-*b*]indole with dimethyl butynedioate.

The starting 4-acetyl-2-(2-nitrophenyl)furo[3,2-*b*]pyrrole was prepared by acetylation of a corresponding acid [4, 5], 4-acetyl-2-(4-chloro-2-methylphenoxy)furo[3,2-*b*]pyrrole was obtained analogously [6]. From the mentioned acetyl derivatives and corresponding halo derivatives in the conditions of interphase transfer catalysis *N*-methylated and *N*-benzylated derivatives *I*—*III* were prepared (Scheme 1). The course of this reaction is inherent in the hydrolysis of corresponding *N*-acetylated furo[3,2-*b*]pyrrole and the formed furo[3,2-*b*]pyrrole derivative is substituted in the position 4. The compound *IV* was obtained by hydrolysis of corresponding 4-acetyl derivative with sodium hydroxide. Pyrrolo[2',3':4,5]furo[3,2-*b*]indole (*V*) was obtained in an excellent yield by the reflux of its 1-acetyl derivative in toluene in the presence of piperidine.



Scheme 1

1-Acetylpyrrolo[2',3':4,5]furo[3,2-*b*]indole reacts with dimethyl butynedioate in  $\alpha$ -positions of the pyrrole ring giving [4 + 2] cycloadduct, which due to the low stability could not be isolated and which by the subsequent 1,5-sigmatropic rearrangement gave the isolated dimethyl 3-acetylaminobenzo[*b*]furo[3,2-*b*]indole-1,2-dicarboxylate (*VI*) (Scheme 2). During the study of the reactions of compounds *I*—*IV* and their *N*-acetyl derivatives we found out that the substituents attached at position 4 expressively influenced their course, which is supported by the structure of isolated products *VII*—*XIV* (Scheme 3). Unsubstituted derivative as well as *N*-benzyl and *N*-methyl derivatives with



|      | R  | R <sup>1</sup>     |      | R  | R <sup>1</sup>                                |
|------|--|--------------------|------|--|---|
| VII  | 4-Cl-2-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> O | CH <sub>3</sub> CO | XI   | 2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>        | H   |
| VIII | 2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>        | CH <sub>3</sub> CO | XII  | 2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>        | CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> |
| IX   | 2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>        | CH <sub>3</sub> CO | XIII | 4-Cl-2-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> O | CH <sub>3</sub>                               |
| X    | 2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>        | CH <sub>3</sub>    | XIV  | 4-Cl-2-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> O | H   |

Scheme 3

dimethyl butynedioate afforded only the products of Michael addition taking place at C-5 furo[3,2-*b*]pyrrole system giving rise to compounds *X—XIV*, which is in good agreement with the results obtained during the study of 2-phenyl- and 2-(4-methylphenyl)-4*H*-furo[3,2-*b*]pyrroles as well as their *N*-methylated derivatives [2].

In case of the reaction of 4-acetyl-2-(4-chloro-2-methylphenoxy)furo[3,2-*b*]pyrrole we assumed that mesomeric conjugation of the acetyl group with  $\pi$ -electron system of the skeleton leads to partial localization of the lone electron pair at the nitrogen atom enhancing the diene character of its pyrrole part. This assumption has been confirmed by isolation of dimethyl 6-(acetylamino)-2-(4-chloro-2-methylphenoxy)benzo[*b*]furan-4,5-dicarboxylate (*VII*). Structure of *VII* was confirmed analogously as that of 2-phenyl and 4-methylphenyl derivatives described in our paper [2].

The reaction of 4-acetyl-2-(2-nitrophenyl)furo[3,2-*b*]pyrrole with dimethyl butynedioate after 10 d of the reflux in acetonitrile afforded dimethyl 6-(acetylamino)-2-(2-nitrophenyl)benzo[*b*]furan-4,5-dicarboxylate (*VIII*) and dimethyl 4-acetyl-2-(2-nitrophenyl)furo[3,2-*b*]pyrrol-5-ylbutenedioate (*IX*).

The structure of the synthesized compounds was confirmed by <sup>1</sup>H NMR spectra. The rise of the compounds *I—V* from the corresponding *N*-acetyl derivatives was proved by a disappearance of acetyl group proton signals (*I, III*) and by a presence of methyl (*I, III*) and benzyl group (*II*) proton signals. Long-range coupling constant between H-3 and H-6 protons of furo[3,2-*b*]pyrrole system in compounds *I—IV* and in Michael type adducts *IX—XIV* was found to be 0.7—1.0 Hz.

The addition of dimethyl butynedioate in the position 5 of furo[3,2-*b*]pyrrole skeleton is proved by the absence of the H-5 proton signal of furo[3,2-*b*]pyrrole system and by the presence of proton double bond signal ( $\delta = 5.96—6.13$  ppm).

<sup>1</sup>H NMR spectra of substituted benzo[*b*]furan derivatives *VII, VIII* and their condensed analogue *VI* show H-4 and H-7 proton signals in the region of  $\delta = 7.80—8.00$  ppm. H-3 and H-7 signals are insignificantly split due to a long-range interaction  $J_{3,7} = 0.8—1.0$  Hz.

Compounds containing nitro group attached to benzene ring displayed in the IR spectrum the absorption bands of the vibrations  $\nu_{as}(\text{NO}_2)$  at  $\tilde{\nu} = 1525—1535$  cm<sup>-1</sup> and  $\nu_s(\text{NO}_2)$  at  $\tilde{\nu} = 1360—1375$  cm<sup>-1</sup>. The  $\nu(\text{CO})$  in synthesized compounds lie at  $\tilde{\nu} = 1685—1728$  cm<sup>-1</sup>.

Electronic spectra of the described compounds contained a few typical bands of polycondensed aromatic systems — the intense band at  $\lambda = 324—420$  nm and the weak band at  $\lambda = 228—270$  nm. Relatively high values  $\lambda_{\text{max}}$  were found, as expected, with compounds having the longer conjugated system.

## Experimental

The IR spectra were measured on a Specord 71 IR (Zeiss, Jena) spectrophotometer using KBr technique (1 mg/300 mg KBr). The electronic spectra were measured with a Specord UV VIS (Zeiss, Jena) spectrophotometer. Measuring range 200—800 nm, concentration of the measured compounds in methanol  $1 \times 10^{-4}$  mol dm<sup>-3</sup> at room temperature. The <sup>1</sup>H NMR spectra of compounds prepared were recorded with Tesla BS 487 C apparatus operating at 80 MHz in hexadeuterodimethyl sulfoxide, deuteriochloroform, and hexadeuteroacetone, the internal references being hexamethyldisiloxane and tetramethylsilane.

The following starting compounds were prepared: 4-acetyl-2-(4-chloro-2-methylphenoxy)furo[3,2-*b*]pyrrole according to [6], 4-acetyl-2-(2-nitrophenyl)furo[3,2-*b*]pyrrole and 1-acetylpyrrolo[2',3':4,5]furo[3,2-*b*]indole according to [4], 2-(2-nitrophenyl)-4*H*-furo[3,2-*b*]pyrrole according to [7].

### *4-Methyl-2-(2-nitrophenyl)furo[3,2-*b*]pyrrole (I)*

To the solution of 4-acetyl-2-(2-nitrophenyl)furo[3,2-*b*]pyrrole (2.70 g; 10 mmol) in benzene (60 cm<sup>3</sup>) sodium hydroxide (30 cm<sup>3</sup>, 50%), benzyltrimethylammonium chloride (0.44 g), and methyl iodide (1.56 g; 11 mmol) were added. The reaction mixture was stirred at 60—70°C for 4 h, cooled, the organic layer separated and aqueous one extracted with ether. The combined extracts were washed with water, dried with Na<sub>2</sub>SO<sub>4</sub> and solvents were removed under diminished pressure. Yield = 1.9 g (78%), m.p. = 88—90°C (petroleum ether). For C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub> (*M<sub>r</sub>* = 242.2) *w<sub>i</sub>*(calc.): 64.47% C, 4.16% H, 11.57% N; *w<sub>i</sub>*(found): 64.41% C, 4.13% H, 11.46% N. <sup>1</sup>H NMR spectrum (hexadeuteroacetone), δ/ppm: 7.31—7.88 (4H, m, H<sub>arom</sub>), 6.93 (1H, d, H-3), 6.78 (1H, d, H-5), 5.94 (1H, dd, H-6), 3.60 (3H, s, N—CH<sub>3</sub>), *J*<sub>5,6</sub> = 3 Hz, *J*<sub>3,6</sub> = 1 Hz. IR spectrum (KBr),  $\tilde{\nu}$ /cm<sup>-1</sup>: 1535 (*v*<sub>as</sub>(NO<sub>2</sub>)), 1360 (*v*<sub>s</sub>(NO<sub>2</sub>)). UV spectrum (methanol), λ<sub>max</sub>/nm (log {ε}): 330 (3.88).

*4-Benzyl-2-(2-nitrophenyl)furo[3,2-*b*]pyrrole (II)* was prepared similarly. Yield = 63%, m.p. = 76—77°C (ethanol). For C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub> (*M<sub>r</sub>* = 318.3) *w<sub>i</sub>*(calc.): 71.70% C, 4.43% H, 8.80% N; *w<sub>i</sub>*(found): 71.58% C, 4.39% H, 8.82% N. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>), δ/ppm: 7.34—7.80 (4H, m, H<sub>arom</sub>), 7.25 (5H, s, H<sub>arom</sub>), 7.04 (1H, d, H-5), 6.98 (1H, d, H-3), 6.07 (1H, dd, H-6), 5.16 (1H, s, N—CH<sub>2</sub>), *J*<sub>5,6</sub> = 3.0 Hz, *J*<sub>3,6</sub> = 0.8 Hz. IR spectrum (KBr),  $\tilde{\nu}$ /cm<sup>-1</sup>: 1525 (*v*<sub>as</sub>(NO<sub>2</sub>)), 1360 (*v*<sub>s</sub>(NO<sub>2</sub>)). UV spectrum (methanol), λ<sub>max</sub>/nm (log {ε}): 266 (2.41), 370 (2.85).

*2-(4-Chloro-2-methylphenoxy)-4-methylfuro[3,2-*b*]pyrrole (III)* was prepared analogically. Yield = 65%, m.p. = 77—79°C (methanol). For C<sub>14</sub>H<sub>12</sub>ClNO<sub>2</sub> (*M<sub>r</sub>* = 261.7) *w<sub>i</sub>*(calc.): 64.26% C, 4.62% H, 5.35% N, 13.55% Cl; *w<sub>i</sub>*(found): 64.09% C, 4.51% H, 5.50% N, 13.56% Cl. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>), δ/ppm: 6.76—7.57 (3H, m, H<sub>arom</sub>), 6.95 (1H, d, H-5), 6.19 (1H, d, H-3), 5.56 (1H, dd, H-6), 3.56 (3H, s, N—CH<sub>3</sub>), 2.26 (3H, s, CH<sub>3</sub><sub>arom</sub>), *J*<sub>5,6</sub> = 4.0 Hz, *J*<sub>3,6</sub> = 0.7 Hz. UV spectrum (methanol), λ<sub>max</sub>/nm (log {ε}): 278 (2.67).

*2-(4-Chloro-2-methylphenoxy)-4H-furo[3,2-b]pyrrole (IV)*

The mixture of 4-acetyl-2-(4-chloro-2-methylphenoxy)furo[3,2-b]pyrrole (0.81 g; 3 mmol) and sodium hydroxide (20 cm<sup>3</sup>, 5%) in ethanol (100 cm<sup>3</sup>) was refluxed for 1 h and then poured onto ice (500 g). The separated precipitate was filtered off and crystallized. Yield = 0.71 g (96%), m.p. = 57–59 °C (hexane). For C<sub>13</sub>H<sub>10</sub>ClNO<sub>2</sub> (*M<sub>r</sub>* = 247.7) *w<sub>i</sub>*(calc.): 63.04% C, 4.07% H, 5.66% N, 14.31% Cl; *w<sub>i</sub>*(found): 63.16% C, 4.13% H, 5.41% N, 14.02% Cl. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ/ppm: 10.64 (1H, m, NH), 6.75–7.33 (3H, m, H<sub>arom</sub>), 6.65 (1H, m, H-5), 6.03 (1H, d, H-3), 5.94 (1H, m, H-6), 2.25 (3H, s, CH<sub>3</sub>), *J*<sub>3,6</sub> = 1.0 Hz, *J*<sub>5,6</sub> = 3.0 Hz, *J*<sub>4,6</sub> = 1.4 Hz, *J*<sub>4,5</sub> = 2.8 Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 3450 (ν(NH)). UV spectrum (methanol), λ<sub>max</sub>/nm (log {ε}): 270 (2.63).

*1,9-Dihydropyrrolo[2',3':4,5]furo[3,2-b]indole (V)*

The mixture of 1-acetylpyrrolo[2',3':4,5]furo[3,2-b]indole (2.38 g; 10 mmol) and piperidine (0.93 g; 11 mmol) was refluxed in toluene (50 cm<sup>3</sup>) for 2 h. After cooling the mixture was washed with diluted hydrochloric acid (φ = 1:1), then with water to pH = 7. The organic layer was dried with anhydrous sodium sulfate and the solvent was distilled off *in vacuo*. Yield = 1.59 g (81%), m.p. = 144–146 °C (hexane). For C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O (*M<sub>r</sub>* = 196.2) *w<sub>i</sub>*(calc.): 73.46% C, 4.11% H, 14.28% N; *w<sub>i</sub>*(found): 73.51% C, 4.16% H, 14.12% N. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ/ppm: 7.63–7.79 and 7.12–7.24 (4H, m, H<sub>arom</sub>), 7.25 (1H, d, H-2), 6.31 (1H, d, H-3), *J*<sub>2,3</sub> = 3.6 Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 3420 (ν(NH)). UV spectrum (methanol), λ<sub>max</sub>/nm (log {ε}): 263 (2.81), 326 (3.02).

*Dimethyl 3-acetylaminobenzo[b]furo[3,2-b]indole-1,2-dicarboxylate (VI)*

A mixture of 1-acetylpyrrolo[2',3':4,5]furo[3,2-b]indole (1 g; 4.2 mmol) and dimethyl butynedioate (0.54 g; 3.8 mmol) was refluxed in acetonitrile (10 cm<sup>3</sup>) for 6 h. After cooling the precipitate was filtered off. Yield = 1.0 g (63%), m.p. = 220–221 °C (ethanol). For C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub> (*M<sub>r</sub>* = 380.4) *w<sub>i</sub>*(calc.): 63.15% C, 4.24% H, 7.37% N; *w<sub>i</sub>*(found): 63.05% C, 4.11% H, 7.23% N. <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>), δ/ppm: 10.84 (1H, s, NHCOCH<sub>3</sub>), 9.63 (1H, s, NH), 8.00 (1H, s, H-4), 7.01–7.78 (4H, m, H<sub>arom</sub>), 3.98 (3H, s, OCH<sub>3</sub>), 3.78 (3H, s, OCH<sub>3</sub>), 1.95 (3H, s, COCH<sub>3</sub>). IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 3380 (ν(NH)), 1719 (ν(C=O)), 1680 (ν(C=O)). UV spectrum (methanol), λ<sub>max</sub>/nm (log {ε}): 228 (3.04), 307 (3.10), 370 (3.18).

*Dimethyl 6-(acetylamino)-2-(4-chloro-2-methylphenoxy)benzo[b]furan-4,5-dicarboxylate (VII)* was obtained similarly from 4-acetyl-2-(4-chloro-2-methylphenoxy)furo[3,2-b]pyrrole by reflux for 5 h. Yield = 0.63 g (42%), m.p. = 149–150 °C (methanol). For C<sub>21</sub>H<sub>18</sub>ClNO<sub>7</sub> (*M<sub>r</sub>* = 431.8) *w<sub>i</sub>*(calc.): 58.41% C, 4.20% H, 3.25% N, 8.21% Cl; *w<sub>i</sub>*(found): 58.32% C, 4.08% H, 3.52% N, 7.95% Cl. <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>), δ/ppm: 7.80 (1H, d, H-7), 7.23–7.43 (3H, m, H<sub>arom</sub>), 5.90 (1H, d, H-3), 3.73 (3H, s,

OCH<sub>3</sub>), 3.70 (3H, s, OCH<sub>3</sub>), 2.17 (3H, s, COCH<sub>3</sub>), 1.92 (3H, s, CH<sub>3</sub><sub>arom</sub>),  $J_{3,7} = 0.8$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1720 ( $\nu(\text{C}=\text{O})$ ), 1698 ( $\nu(\text{C}=\text{O})$ ). UV spectrum (methanol),  $\lambda_{\text{max}}/\text{nm}$  (log  $\{\epsilon\}$ ): 236 (2.93), 273 (3.08), 328 (3.15).

*Dimethyl 6-(acetylamino)-2-(2-nitrophenyl)benzo[b]furan-4,5-dicarboxylate (VIII)* and *dimethyl 4-acetyl-2-(2-nitrophenyl)furo[3,2-*b*]pyrrol-5-ylbutenedioate (IX)* were obtained from 4-acetyl-2-(2-nitrophenyl)furo[3,2-*b*]pyrrole after 10 d reflux after chromatography (silica gel, eluent benzene—acetone ( $\phi_r = 20:1$ )). Yield of *VIII* = 33 %, m.p. = 164—165 °C (ethanol). For C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub> ( $M_r = 412.5$ )  $w_i(\text{calc.})$ : 58.24 % C, 3.90 % H, 6.97 % N;  $w_i(\text{found})$ : 58.20 % C, 3.79 % H, 6.74 % N. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta/\text{ppm}$ : 9.65 (1H, s, NH), 7.62—8.05 (4H, m, H<sub>arom</sub>), 7.93 (1H, d, H-7), 7.55 (1H, d, H-3), 3.85 (3H, s, OCH<sub>3</sub>), 3.76 (3H, s, OCH<sub>3</sub>), 1.96 (3H, s, COCH<sub>3</sub>),  $J_{3,7} = 1.0$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1720 ( $\nu(\text{CO})$ ), 1700 ( $\nu(\text{CO})$ ), 1535 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1370 ( $\nu_{\text{s}}(\text{NO}_2)$ ). UV spectrum (methanol),  $\lambda_{\text{max}}/\text{nm}$  (log  $\{\epsilon\}$ ): 243 (2.98), 337 (3.08). Yield of *IX* = 20 %, m.p. = 129—130 °C (methanol). For C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub> ( $M_r = 412.5$ )  $w_i(\text{calc.})$ : 58.24 % C, 3.90 % H, 6.79 % N;  $w_i(\text{found})$ : 58.18 % C, 3.82 % H, 6.68 % N. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta/\text{ppm}$ : 7.45—7.93 (4H, m, H<sub>arom</sub>), 7.46 (1H, d, H-3), 6.75 (1H, s, =C—H), 6.60 (1H, d, H-6), 3.59 (3H, s, OCH<sub>3</sub>), 3.51 (3H, s, OCH<sub>3</sub>), 2.57 (3H, s, COCH<sub>3</sub>),  $J_{3,6} = 0.8$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 3380 ( $\nu(\text{NH})$ ), 1720 ( $\nu(\text{C}=\text{O})$ ), 1694 ( $\nu(\text{C}=\text{O})$ ), 1535 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1370 ( $\nu_{\text{s}}(\text{NO}_2)$ ). UV spectrum (methanol),  $\lambda_{\text{max}}/\text{nm}$  (log  $\{\epsilon\}$ ): 240 (2.94), 336 (3.02).

*Dimethyl 4-methyl-2-(2-nitrophenyl)furo[3,2-*b*]pyrrol-5-ylbutenedioate (X)* was obtained analogously from *I*. Yield = 31 %, m.p. = 152—153 °C (benzene). For C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>7</sub> ( $M_r = 384.3$ )  $w_i(\text{calc.})$ : 59.38 % C, 4.20 % H, 7.29 % N;  $w_i(\text{found})$ : 59.31 % C, 4.13 % H, 7.18 % N. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta/\text{ppm}$ : 7.26—7.82 (4H, m, H<sub>arom</sub>), 6.66 (1H, d, H-3), 6.30 (1H, d, H-6), 6.01 (1H, s, =C—H), 3.94 (3H, s, OCH<sub>3</sub>), 3.75 (3H, s, N—CH<sub>3</sub>), 3.75 (3H, s, OCH<sub>3</sub>),  $J_{3,6} = 0.8$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1710 ( $\nu(\text{C}=\text{O})$ ), 1690 ( $\nu(\text{C}=\text{O})$ ), 1535 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1360 ( $\nu_{\text{s}}(\text{NO}_2)$ ). UV spectrum (methanol),  $\lambda_{\text{max}}/\text{nm}$  (log  $\{\epsilon\}$ ): 240 (2.89), 324 (3.02).

*Dimethyl 2-(2-nitrophenyl)-4H-furo[3,2-*b*]pyrrol-5-ylbutenedioate (XI)* was obtained from 2-(2-nitrophenyl)-4H-furo[3,2-*b*]pyrrole. Yield = 31 %, m.p. = 170—171 °C (ethanol). For C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>7</sub> ( $M_r = 370.3$ )  $w_i(\text{calc.})$ : 58.38 % C, 3.81 % H, 7.57 % N;  $w_i(\text{found})$ : 58.24 % C, 3.75 % H, 7.46 % N. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta/\text{ppm}$ : 11.8 (1H, s, NH), 7.43—7.86 (4H, m, H<sub>arom</sub>), 7.06 (1H, d, H-3), 6.49 (1H, d, H-6), 6.04 (1H, s, =C—H), 3.74 (3H, s, OCH<sub>3</sub>), 3.65 (3H, s, OCH<sub>3</sub>),  $J_{3,6} = 0.8$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1705 ( $\nu(\text{C}=\text{O})$ ), 1675 ( $\nu(\text{C}=\text{O})$ ), 1530 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1360 ( $\nu_{\text{s}}(\text{NO}_2)$ ). UV spectrum (methanol),  $\lambda_{\text{max}}/\text{nm}$  (log  $\{\epsilon\}$ ): 238 (2.93), 324 (3.04).

*Dimethyl 4-benzyl-2-(2-nitrophenyl)furo[3,2-*b*]pyrrol-5-ylbutenedioate (XII)* was obtained from *II*. Yield = 56 %, m.p. = 102—103 °C (ethanol). For C<sub>25</sub>H<sub>20</sub>N<sub>2</sub>O<sub>7</sub> ( $M_r = 460.4$ )  $w_i(\text{calc.})$ : 65.22 % C, 4.38 % H, 6.09 % N;  $w_i(\text{found})$ : 65.17 % C, 4.32 % H, 5.99 % N. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta/\text{ppm}$ : 7.23—7.71 (4H, m, H<sub>arom</sub>), 7.22 (5H, s, H<sub>arom</sub>), 7.03 (1H, d, H-3), 6.80 (1H, d, H-6), 6.13 (1H, s, =C—H), 4.99 (1H, s, N—CH<sub>2</sub>), 3.64 (3H, s, OCH<sub>3</sub>), 3.55 (3H, s, OCH<sub>3</sub>),  $J_{3,6} = 0.7$  Hz. IR spectrum (KBr),

$\tilde{\nu}/\text{cm}^{-1}$ : 1730 ( $\nu(\text{C}=\text{O})$ ), 1695 ( $\nu(\text{C}=\text{O})$ ), 1530 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1365 ( $\nu_{\text{s}}(\text{NO}_2)$ ). UV spectrum (methanol),  $\lambda_{\text{max}}/\text{nm}$  ( $\log \{\epsilon\}$ ): 270 (3.18), 420 (3.23).

*Dimethyl 2-(4-chloro-2-methylphenoxy)-4-methylfuro[3,2-b]pyrrol-5-ylbutenedioate (XIII)* was obtained from *III* analogously. Yield = 38 %, m.p. = 152–154 °C (benzene). For  $\text{C}_{20}\text{H}_{18}\text{ClNO}_6$  ( $M_r = 403.8$ )  $w_i(\text{calc.})$ : 59.49 % C, 4.49 % H, 3.47 % N, 8.78 % Cl;  $w_i(\text{found})$ : 59.54 % C, 4.40 % H, 3.34 % N, 8.66 % Cl.  $^1\text{H}$  NMR spectrum ( $\text{DMSO-d}_6$ ),  $\delta/\text{ppm}$ : 6.83–7.38 (3H, m,  $\text{H}_{\text{arom}}$ ), 6.11 (1H, d, H-3), 5.96 (1H, s,  $=\text{C}-\text{H}$ ), 5.68 (1H, d, H-6), 3.79 (3H, s,  $\text{OCH}_3$ ), 3.73 (3H, s,  $\text{OCH}_3$ ), 3.61 (3H, s,  $\text{N}-\text{CH}_3$ ), 2.28 (3H, s,  $\text{CH}_{3\text{arom}}$ ),  $J_{3,6} = 0.8$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1720 ( $\nu(\text{C}=\text{O})$ ), 1690 ( $\nu(\text{C}=\text{O})$ ).

*Dimethyl 2-(4-chloro-2-methylphenoxy)-4H-furo[3,2-b]pyrrol-5-ylbutenedioate (XIV)* was prepared from *IV*. Yield = 34 %, m.p. = 131–132 °C (hexane). For  $\text{C}_{19}\text{H}_{16}\text{ClNO}_6$  ( $M_r = 389.8$ )  $w_i(\text{calc.})$ : 58.56 % C, 4.14 % H, 3.59 % N, 9.09 % Cl;  $w_i(\text{found})$ : 58.48 % C, 4.03 % H, 3.38 % N, 8.97 % Cl.  $^1\text{H}$  NMR spectrum ( $\text{DMSO-d}_6$ ),  $\delta/\text{ppm}$ : 6.87–7.43 (3H, m,  $\text{H}_{\text{arom}}$ ), 6.14 (1H, d, H-3), 5.98 (1H, s,  $=\text{C}-\text{H}$ ), 5.85 (1H, d, H-6), 3.93 (3H, s,  $\text{OCH}_3$ ), 3.82 (3H, s,  $\text{OCH}_3$ ), 2.26 (3H, s,  $\text{CH}_{3\text{arom}}$ ),  $J_{3,6} = 0.8$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1728 ( $\nu(\text{C}=\text{O})$ ), 1695 ( $\nu(\text{C}=\text{O})$ ).

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