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Dedicated to Professor Milan Kratochvíl on the occasion of his 75<sup>th</sup> birthday

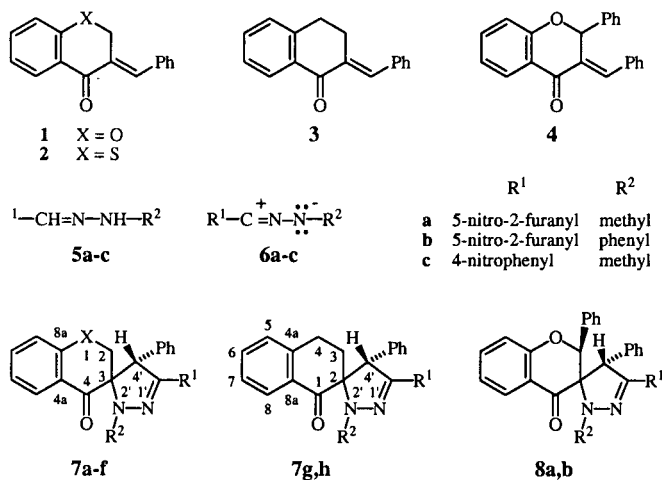
The regio- and stereoselective synthesis of spiropyrazolines **7** and **8** *via* 1,3-dipolar cycloaddition of *C*-2-(5-nitrofuryl)-*N*-methylnitrilimine, *C*-2-(5-nitrofuryl)-*N*-phenylnitrilimine and *C*-4-nitrophenyl-*N*-methylnitrilimine to (*E*)-3-benzylidenechromanone (**1**), -1-thiochromanone **2**, -1-tetralone **3** and (*E*)-3-benzylidene-flavanone (**4**) is reported. The relative configuration and conformations of the spiropyrazolines were elucidated by various nmr methods.

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1,3-Dipolar cycloadditions offer a convenient one-step route for the construction of a variety of different five-membered heterocycles. The scope of the synthesis of 2-pyrazolines and pyrazoles from very reactive dipoles as nitrilimines and a wide range of different multiple bonds was thoroughly explored [1]. The interesting biological activities of various dihydropyrazoles substituted with fused ring system [2-5] focused great attention on this skeleton and prompted us to extend our studies to the synthesis of new spirodihydropyrazoles by 1,3-dipolar cycloaddition of suitable dipoles on different exocyclic carbon-carbon double bonds. Recently we reported on the synthesis and stereochemical investigations of various dihydropyrazoles substituted with fused ring systems [6]. The spiropyrazolines prepared by 1,3-dipolar cycloaddition of diazomethane and exocyclic  $\alpha,\beta$ -enones were studied in detail [7-9]. With the goal of developing a simple route to spiropyrazolines *via* a 1,3-dipolar cycloaddition, we have chosen some heterocyclic compounds possessing an exocyclic double bond as the dipolarophiles for nitrilimine cycloadditions.

We describe here preparation of some new spiropyrazolines *via* 1,3-dipolar cycloaddition of *C*-2-(5-nitrofuryl)-*N*-methyl, phenylnitrilimines and *C*-(4-nitrophenyl)-*N*-methyl nitrilimine with (*E*)-3-benzylidenechromanone (**1**), -1-thiochromanone (**2**), (*E*)-2-benzylidene-1-tetralone (**3**) and (*E*)-3-benzylidene-flavanone (**4**), respectively. Our preliminary results in the cycloaddition of *C*-2-(5-nitrofuryl)-*N*-methylnitrilimine to **1-4** have been subject of a recent communication [10].

1,3-Dipolar cycloaddition reactions of nitrilimines **6a-c** to dipolarophiles **1-4** were performed by *in situ* techniques. The most common method using hydrazoneyl halides as precursors for the generation of nitrilimines could not be used [11] and we applied a very simple and elegant method first published by Hassner to prepare diphenyl nitrilimine [12]. This method is based on the treatment of chloramine T trihydrate (*N*-chloro-*N*-sodio-4-methylbenzen-



Compound	X	R <sup>1</sup>	R <sup>2</sup>
7a	O	5-nitro-2-furanyl	methyl
7b	O	4-nitrophenyl	methyl
7c	S	5-nitro-2-furanyl	methyl
7d	S	4-nitrophenyl	methyl
7e	O	5-nitro-2-furanyl	phenyl
7f	S	5-nitro-2-furanyl	phenyl
7g	CH <sub>2</sub>	5-nitro-2-furanyl	methyl
7h	CH <sub>2</sub>	4-nitrophenyl	methyl
8a	-	5-nitro-2-furanyl	methyl
8b	-	4-nitrophenyl	methyl

sulfoamide) on an appropriate aldehyde hydrazone. This method turned out to be the most versatile and perfectly suited also for application on furan derivatives [13,14].

Typically, the cycloaddition was carried out by heating an equimolecular mixture of hydrazone **5a-c** and the (*E*)-benzylidene derivative **1-4** with a small excess of chloramine T in methanol under reflux. The course of the reaction was monitored by thin layer chromatography and cycloaddition

was completed in some cases within a few minutes. Each heterocyclic dipolarophile reaction proceeds smoothly in highly regio- and face selective manner. There are four possible products of the nitrilimine cycloaddition with **1-3**, two regioisomeric pairs resulting from *anti* and *syn* face attack related to methylene group in the dipolarophile. Only adducts **7a-h**, in which the nitrogen atom has become attached to the spiro carbon were formed. It has been found that cycloadditions of *C*-aryl- and *C*-heteroaryl-*N*-methyl, or -*N*-phenyl nitrilimines to the exocyclic double bond of **1-3** proceeded with complete regio- and diastereoselectivity affording exclusively in one step, *trans*-spiropyrazolines **7** with respect to the position of the carbonyl and the phenyl groups (Scheme 1). Spiropyrazolines **7a-h** are formed by attack of the carbon atom of the nitrilimine at the CH terminus of the exocyclic double bond, similarly to the previously investigated cycloaddition of diazomethane to dipolarophiles **1-3** [7,8,15]. None of three other possible adducts were detected in the crude reaction mixture by nmr spectroscopy.

The cycloadditions of nitrilimines **6a,b** to (*E*)-3-benzylidene-flavanone (**4**) afforded exclusively the *anti* spiropyrazolines **8a,b** despite the appearance of a further centre of chirality at C-2. In every case of the nitrilimine cycloaddition to **4**, the steric interaction with the axial phenyl group directs the attack of the 1,3-dipole to the opposite side. The observed high stereoselectivity of nitrilimine to **4** is fully in accord with the previously described stereochemical outcome of the cycloaddition of diazomethane [8,15,16], nitrile oxides [10] and nitrones [10]. We have found, that conformational behaviour of the starting (*E*)-3-benzylidene-flavanone is a decisive factor in the high stereoselectivity, the attack of the 1,3-dipole proceeds from the sterically less hindered side, *i.e.* opposite to the C-2 phenyl group. The corresponding *syn* diastereomers as well as regioisomeric diastereoisomers have not been detected in the crude reaction mixture by nmr spectroscopy.

The structure of the spiropyrazolines **7** and **8** prepared were unambiguously elucidated by their  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectral data. For the determination of the relative configuration and stereostructure of the prepared spiropyrazolines **7a-h** and **8a,b** some special measurements and nmr techniques were used. The regioselectivity is deduced from the  $^{15}\text{N}$  chemical shifts. A new alternative method based on  $^{15}\text{N}$  chemical shifts allowing the safe differentiation between the *a priori* possible two regioisomers resulting from cycloaddition reactions was used [17]. The relative configuration and conformational behaviour of the above-mentioned spiropyrazolines are subject of a special study [17].

## EXPERIMENTAL

The melting points were determined with a Kofler hot-stage apparatus, the ir spectra were taken with Philips analytical PU 9800 FTIR spectrometer potassium bromide pellets, the  $^1\text{H}$  and  $^{13}\text{C}$  nmr

spectra of deuteriochloroform solutions containing tetramethyl silane as the internal standard were measured with Varian VXR 300 and Bruker DRX-500 instruments. All reagents were purified and dried prior to use. Analyses (tlc) were carried out with UV<sub>254</sub> silica gel 60 (0.040-0.063 mm Merck). All new compounds were identified by their  $^1\text{H}$  and  $^{13}\text{C}$  and ir spectra, respectively.

### General Procedure for the Preparation of Spiropyrazolines **7** and **8**.

The reaction mixture of 1.0 mmole *N*-substituted hydrazone **5a-c**, 1.0 mmole of dipolarophile (**1-4**) and 1.1-1.2 mmoles of Chloramine T in methanol (30 ml) was stirred under reflux and the progress of the reaction was monitored by tlc. The solvent was removed under reduced pressure and the residue was flash chromatographed on silica gel column using isohexane/ethyl acetate mixture (5:1) eluent.

#### 2',4'-Dihydro-2'-methyl-5'-(5-nitro-2-furanyl)-4'-phenylspiro[2H-1-benzopyran-3(4H),3'-[3H]pyrazol]-4-one (**7a**).

This compound was isolated as orange crystals in 91% yield, mp 249-250°; ir:  $\nu$  1686 (C=O), 1591, 1479 (C=C), 1541 (NO<sub>2</sub>as), 1354 (NO<sub>2</sub>s), 1302 (C-O-C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  3.18 (s, 3H, N-CH<sub>3</sub>), 4.10 (d, 1H, H-2<sub>eq</sub>, J = 12.0 Hz), 4.30 (d, 1H, H-2<sub>ax</sub>), 4.80 (s, 1H, H-4'), 6.43 (d, 1H, H-furan, J = 3.6 Hz), 6.95 (d, 1H, H-8, J = 8.1 Hz), 7.12 (dd, 1H, H-6, J = 7.8 Hz), 7.19 (d, 1H, H-furan), 7.18-7.35 (m, 5H, H-Ar), 7.55 (ddd, 1H, H-7, J = 7.8 Hz, J = 1.5 Hz), 7.98 (dd, 1H, H-5, J = 7.8 Hz, J = 1.5 Hz);  $^{13}\text{C}$  nmr:  $\delta$  37.5 (N-CH<sub>3</sub>), 57.6 (C-4'), 69.9 (C-2), 73.9 (C-3), 110.4, 113.3 (C-3, C-4 furan), 118.0 (C-8), 119.3 (C-4a), 122.5 (C-6), 133.2, 129.2, 129.2, 128.8 (C-Ar), 128.2 (C-5), 139.2 (C-5'), 150.2 (C-2 furan), 151.6 (C-5 furan), 161.0 (C-8a), 189.1 (C-4).

Anal. Calcd. for C<sub>22</sub>H<sub>17</sub>N<sub>3</sub>O<sub>5</sub>: C, 65.50; H, 4.25; N, 10.42. Found: C, 65.30; H, 3.94; N, 10.19.

#### 2',4'-Dihydro-2'-methyl-5'-(4-nitrophenyl)-4'-phenylspiro[2H-1-benzopyran-3(4H),3'-[3H]pyrazol]-4-one (**7b**).

This compound was isolated as pale yellow crystals in 85% yield, mp 275-276°; ir:  $\nu$  1699 (C=O), 1601 (C=N), 1512, 1462 (C=C), 1545 (NO<sub>2</sub>as), 1338 (NO<sub>2</sub>s), 1298 (C-O-C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  3.17 (s, 3H, N-CH<sub>3</sub>), 4.09 (d, 1H, H-2<sub>eq</sub>, J = 11.4 Hz), 4.28 (d, 1H, H-2<sub>ax</sub>), 4.79 (s, 1H, H-4'), 6.97 (d, H-8, J = 8.1 Hz), 7.11 (dd, 1H, H-6, J = 8.1 Hz), 7.33 (m, 5H, H-Ar), 7.55 (ddd, 1H, H-7, J = 8.1 Hz, J = 1.5 Hz), 7.71 (d, 2H, H-Ar, J = 9.0 Hz), 7.98 (dd, 1H, H-5, J = 8.1 Hz, J = 1.5 Hz), 8.04 (d, 2H, H-Ar);  $^{13}\text{C}$  nmr:  $\delta$  37.4 (N-CH<sub>3</sub>), 57.7 (C-4'), 70.0 (C-2), 74.0 (C-3), 117.9 (C-8), 119.1 (C-4a), 122.3 (C-6), 126.3, 123.7, 146.8 (C-Ar), 128.2 (C-5), 137.7 (C-7), 150.0 (C-5'), 160.9 (C-8a), 189.8 (C-4).

Anal. Calcd. for C<sub>24</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>: C, 69.72; H, 4.63; N, 10.16. Found: C, 70.09; H, 4.52; N, 10.35.

#### 2',4'-Dihydro-2'-methyl-5'-(5-nitro-2-furanyl)-4'-phenylspiro[2H-1-benzothiopyran-3(4H),3'-[3H]pyrazol]-4-one (**7c**).

This substance was obtained as orange needles in 71% yield, mp 226-227°; ir:  $\nu$  674 (C=O), 1587 (C=N), 1560, 1479 (C=C), 1541 (NO<sub>2</sub>as), 1354 (NO<sub>2</sub>s), 1300 (C-O-C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr: (2.87 (d, 1H, H-2<sub>eq</sub>, J = 13.5 Hz), 3.24 (s, 3H, N-CH<sub>3</sub>), 3.61 (d, 1H, H-2<sub>ax</sub>), 4.65 (s, 1H, H-4'), 6.50 (d, 1H, H-furan, J = 3.9 Hz), 7.18 (d, 1H, H-furan), 7.21 (d, 1H, H-8, J = 7.5 Hz), 7.24 (dd, 1H, H-6, J = 7.5 Hz), 7.44 (ddd, 1H, H-7, J = 7.5 Hz, J = 1.5 Hz), 8.17 (dd, 1H, H-5, J = 7.5 Hz, J = 1.5 Hz);  $^{13}\text{C}$  nmr:  $\delta$  29.9 (C-2), 36.4 (N-CH<sub>3</sub>), 58.0 (C-4'), 76.4 (C-3), 109.9, 113.8 (C-3,

C-4 furan), 125.5 (C-6), 127.0 (C-8), 128.9 (C-4a), 134.0, 128.7, 128.7, 128.7 (C-Ar), 131.1 (C-5), 134.2 (C-7), 139.2 (C-5'), 141.1 (C-8a), 150.5 (C-2 furan), 151.3 (C-5 furan), 189.3 (C-4).

*Anal.* Calcd. for  $C_{22}H_{17}N_3O_4S$ : C, 63.00; H, 4.09; N, 10.02; S, 7.64. Found: C, 62.74; H, 4.02; N, 9.92; S, 7.73.

2',4'-Dihydro-2'-methyl-5'-(4-nitrophenyl)-4'-phenylspiro[2H]-1-benzothiopyran-3(4H),3'-[3H]-pyrazol]-4-one (7d).

This compound was isolated as yellow crystals in 74% yield, mp 223-224°; ir:  $\nu$  1694 (C=O), 1511, 1464 (C=C), 1339 (NO<sub>2</sub>as), 1294 (C-O-C)  $cm^{-1}$ ; <sup>1</sup>H nmr:  $\delta$  2.83 (d, 1H, H-2<sub>eq</sub>, J = 13.5 Hz), 3.23 (s, 3H, N-CH<sub>3</sub>), 3.55 (d, 1H, H-2<sub>ax</sub>), 4.68 (s, 1H, H-4'), 7.20 (d, 1H, H-8, J = 6.9 Hz), 7.24 (dd, 1H, H-6, J = 7.5 Hz), 7.30 (m, 5H, H-Ar), 7.43 (ddd, 1H, H-7, J = 6.9 Hz, J = 1.5 Hz), 7.58 (d, 2H, H-Ar, J = 9.0 Hz), 8.00 (d, 2H, H-Ar), 8.14 (dd, 1H, H-5, J = 7.8 Hz, J = 1.5 Hz); <sup>13</sup>C nmr:  $\delta$  30.4 (C-2), 36.5 (N-CH<sub>3</sub>), 58.6 (C-4'), 76.3 (C-3), 125.8 (C-6), 130.8 (C-5), 138.0, 125.9, 123.6, 146.6 (C-Ar), 126.9 (C-8), 129.2 (C-4a), 150.1 (C-5'), 134.0 (C-7), 141.1 (C-8a), 190.1 (C-4).

*Anal.* Calcd. for  $C_{24}H_{19}N_3O_5S$ : C, 67.12; H, 4.46; N, 9.78; S, 7.47. Found: C, 67.25; H, 4.22; N, 10.11; S, 7.80.

2',4'-Dihydro-5'-(5-nitro-2-furanyl)-2'-phenyl-4'-phenylspiro[2H-benzopyran-3(4H),3'-[3H]pyrazol]-4-one (7e).

This substance was prepared as pale yellow plates in 52% yield, mp 235-236°; ir:  $\nu$  1699 (C=O), 1604 (C=N), 1597, 1466 (C=C), 1549 (NO<sub>2</sub>as), 1356 (NO<sub>2</sub>s), 1296 (C-O-C)  $cm^{-1}$ ; <sup>1</sup>H nmr:  $\delta$  4.30 (d, 1H, H-2<sub>eq</sub>, J = 12.0 Hz), 4.84 (d, 1H, H-2<sub>ax</sub>), 4.86 (s, 1H, H-4'), 6.57 (d, 1H, H-furan, J = 3.9 Hz), 7.21 (d, 1H, H-furan), 6.87 (d, 1H, H-8, J = 8.4 Hz), 7.05 (m, 1H, H-Ar), 7.20-7.40 (m, 9H, H-Ar), 7.11 (dd, 1H, H-6, J = 8.1 Hz), 7.53 (ddd, 1H, H-7, J = 8.1 Hz, J = 1.5 Hz), 7.98 (dd, 1H, H-5, J = 8.1 Hz, J = 1.5 Hz); <sup>13</sup>C nmr:  $\delta$  59.2 (C-4'), 67.9 (C-2), 74.6 (C-3), 111.1, 113.5 (C-3, C-4 furan), 117.9 (C-8), 122.4 (C-6), 120.3, 123.9, 128.3, 128.9, 129.0, 129.1, 133.1, 141.8 (C-Ar), 128.6 (C-5), 137.2 (C-7), 139.6 (C-5'), 149.9 (C-2 furan), 151.5 (C-5 furan), 160.7 (C-8a), 188.2 (C-4).

*Anal.* Calcd. for  $C_{27}H_{19}N_3O_5$ : C, 69.67; H, 4.11; N, 9.03. Found: C, 69.43; H, 4.28; N, 8.89.

2',4'-Dihydro-5'-(5-nitro-2-furanyl)-2'-phenyl-4'-phenylspiro[2H-1-benzothiopyran-3(4H),3'-[3H]pyrazol]-4-one (7f).

This compound was obtained as orange crystals in 54% yield, mp 257-258°; ir:  $\nu$  1682 (C=O), 1591 (C=N), 1552, 1491 (C=C), 1523 (NO<sub>2</sub>as), 1338 (NO<sub>2</sub>s)  $cm^{-1}$ ; <sup>1</sup>H nmr:  $\delta$  2.95 (d, 1H, H-2<sub>eq</sub>, J = 13.5 Hz), 4.29 (d, 1H, H-2<sub>ax</sub>), 4.84 (s, 1H, H-4'), 6.66 (d, 1H, H-furan, J = 3.9 Hz), 7.21 (d, 1H, H-furan), 7.06 (dd, 1H, H-6, J = 6.9 Hz), 7.24-7.35 (m, 11H, H-Ar), 7.46 (dd, 1H, H-7, J = 7.5 Hz), 8.18 (d, 1H, H-5, J = 6.8 Hz); <sup>13</sup>C nmr:  $\delta$  29.9 (C-2), 59.4 (C-4'), 76.5 (C-3), 110.7, 113.9 (C-3, C-4 furan), 119.9 (C-8), 125.7 (C-6), 141.0, 123.5, 128.7, 123.5 (C-Ar), 128.2 (C-4a), 131.5 (C-5), 134.5 (C-7), 139.9 (C-5'), 141.6 (C-8a), 150.3 (C-2 furan), 151.3 (C-5 furan), 188.6 (C-4).

*Anal.* Calcd. for  $C_{27}H_{19}N_3O_4S$ : C, 67.35; H, 3.98; N, 8.73; S, 6.66. Found: C, 67.46; H, 4.10; N, 8.64; S, 6.78.

2',3,4,4'-Tetrahydro-2'-methyl-5'-(5-nitro-2-furanyl)-4'-phenylspiro[naphthalene-2(1H),3'-[3H]pyrazol]-1-one (7g).

This substance was prepared as yellow needles in 75% yield, mp 228-229°; ir:  $\nu$  1686 (C=O), 1601 (C=N), 1581, 1491 (C=C), 1545 (NO<sub>2</sub>as), 1358 (NO<sub>2</sub>s)  $cm^{-1}$ ; <sup>1</sup>H nmr:  $\delta$  2.14 (m, 1H,

H-3<sub>eq</sub>), 2.37 (m, 1H, H-3<sub>ax</sub>), 2.70 (m, 1H, H-4<sub>eq</sub>), 2.90 (m, 1H, H-4<sub>ax</sub>), 3.22 (s, 3H, N-CH<sub>3</sub>), 4.46 (s, 1H, H-4'), 6.49 (d, 1H, H-furan, J = 3.9 Hz), 7.17 (d, 1H, H-furan), 7.20 (d, 1H, H-5, J = 7.9 Hz), 7.26-7.34 (m, 5H, H-Ar), 7.38 (dd, 1H, H-7, J = 7.5 Hz), 7.55 (dd, 1H, H-6, J = 7.5 Hz), 8.12 (d, 1H, H-8, J = 7.8 Hz); <sup>13</sup>C nmr:  $\delta$  26.0 (C-4), 26.7 (C-3), 35.8 (N-CH<sub>3</sub>), 57.1 (C-4'), 77.8 (C-2), 109.3, 114.0 (C-3, C-4 furan), 127.3 (C-7), 128.7 (C-5), 129.1 (C-8), 129.9 (C-8a), 134.4 (C-6), 128.5, 129.0, 129.2, 134.9 (C-Ar), 138.2 (C-5'), 148.2 (C-4a), 151.1 (C-2 furan), 151.2 (C-5 furan), 192.7 (C-1).

*Anal.* Calcd. for  $C_{23}H_{19}N_3O_4$ : C, 68.82; H, 4.47; N, 10.47. Found: C, 68.70; H, 4.56; N, 10.35.

2',3,4,4'-Tetrahydro-2'-methyl-5'-(4-nitrophenyl)-4'-phenylspiro[naphthalene-2(1H),3'-[3H]pyrazol]-1-one (7h).

This compound was obtained as red crystals in 70% yield, mp 239-240°; ir:  $\nu$  1695 (C=O), 1597 (C=N), 1508, 1454 (C=C), 1537 (NO<sub>2</sub>as), 1334 (NO<sub>2</sub>s)  $cm^{-1}$ ; <sup>1</sup>H nmr:  $\delta$  2.06 (ddd, 1H, H-3<sub>eq</sub>, J = 4.7 Hz, J = 13.7 Hz, J = 2.8 Hz), 2.34 (ddd, 1H, H-3<sub>ax</sub>, J = 5.2 Hz, J = 13.6 Hz), 2.70 (ddd, 1H, H-4<sub>eq</sub>, J = 4.2 Hz, J = 13.3 Hz, J = 2.5 Hz), 2.97 (ddd, 1H, H-4<sub>ax</sub>, J = 4.7 Hz, J = 13.4 Hz), 3.20 (s, 3H, N-CH<sub>3</sub>), 4.48 (s, 1H, H-4'), 7.21 (d, 1H, H-5, J = 7.2 Hz), 7.25-7.34 (m, 6H, H-Ar), 7.52 (dd, 1H, H-6, J = 7.2 Hz), 7.55 (d, 2H, H-Ar, J = 9.0 Hz), 7.96 (d, 2H, H-Ar), 8.08 (d, 1H, H-8, J = 7.5 Hz); <sup>13</sup>C nmr:  $\delta$  26.0 (C-4), 27.1 (C-3), 35.9 (N-CH<sub>3</sub>), 57.7 (C-4'), 77.8 (C-2), 127.1 (C-7), 128.7 (C-5), 129.0 (C-8), 134.3 (C-6), 145.5, 123.6, 127.1, 135.0 (C-Ar), 130.1 (C-8a), 138.6 (C-5'), 146.2 (C-4a), 193.4 (C-1).

*Anal.* Calcd. for  $C_{25}H_{21}N_3O_5$ : C, 72.98; H, 5.14; N, 10.21. Found: C, 73.15; H, 5.23; N, 10.14.

2',4'-Dihydro-2'-methyl-5'-(5-nitro-2-furanyl)-2,4'-diphenylspiro[2H-1-benzopyran-3(4H),3'-[3H]pyrazol]-4-one (8a).

This substance was isolated as yellow crystals in 78% yield, mp 253-254°; ir:  $\nu$  1686 (C=O), 1603 (C=N), 1512, 1487 (C=C), 1549 (NO<sub>2</sub>as), 1352 (NO<sub>2</sub>s), 1298 (C-O-C)  $cm^{-1}$ ; <sup>1</sup>H nmr:  $\delta$  3.32 (s, 3H, N-CH<sub>3</sub>), 4.86 (s, 1H, H-4'), 5.49 (s, 1H, H-2), 6.46 (d, 1H, H-furan, J = 3.9 Hz), 7.15 (d, 1H, H-furan), 6.76 (d, 2H, H-Ar, J = 7.5 Hz), 6.83 (d, 1H, H-8, J = 7.6 Hz), 7.03 (dd, 2H, H-Ar, J = 7.5 Hz), 7.09 (dd, 1H, H-6, J = 7.8 Hz), 6.95-7.20 (m, 6H, H-Ar), 7.48 (dd, 1H, H-7, J = 7.8 Hz), 8.02 (d, 1H, H-5, J = 7.8 Hz); <sup>13</sup>C nmr:  $\delta$  38.4 (N-CH<sub>3</sub>), 56.4 (C-4'), 75.1 (C-3), 84.7 (C-2), 110.9, 113.4 (C-3, C-4 furan), 118.8 (C-4a), 118.8 (C-8), 122.4 (C-6), 126.7 (C-5), 133.3, 128.4, 128.4, 128.8, 136.1, 127.8, 128.4, 127.8 (C-Ar), 137.4 (C-7), 139.0 (C-5'), 149.6 (C-2 furan), 151.6 (C-5 furan), 158.7 (C-8a), 189.7 (C-4).

*Anal.* Calcd. for  $C_{28}H_{21}N_3O_5$ : C, 70.14; H, 4.41; N, 8.76. Found: C, 70.08; H, 4.32; N, 8.90.

2',4'-Dihydro-2'-methyl-5'-(4-nitrophenyl)-2,4'-diphenylspiro[2H-1-benzopyran-3(4H),3'-[3H]pyrazol]-4-one (8b).

This compound was prepared as yellow needles in 71% yield, mp 189-191°; ir:  $\nu$  1682 (C=O), 1603 (C=N), 1514, 1473 (C=C), 1568 (NO<sub>2</sub>as), 1338 (NO<sub>2</sub>s), 1300 (C-O-C)  $cm^{-1}$ ; <sup>1</sup>H nmr:  $\delta$  3.31 (s, 3H, N-CH<sub>3</sub>), 4.88 (s, 1H, H-4'), 5.45 (s, 1H, H-2), 6.80 (d, 2H, H-Ar, J = 7.2 Hz), 6.82 (d, 1H, H-8, J = 8.9 Hz), 7.05 (m, 3H, H-Ar), 7.08 (dd, 1H, H-6, J = 9.0 Hz), 7.18 (dd, 1H, H-Ar, J = 7.5 Hz), 7.46 (ddd, 1H, H-7, J = 7.8 Hz, J = 1.5 Hz), 7.62 (d, 2H, H-Ar, J = 8.7 Hz), 8.01 (dd, 1H, H-5, J = 7.5 Hz, J = 1.5 Hz), 8.02 (d, 2H, H-Ar); <sup>13</sup>C nmr:  $\delta$  38.5 (N-CH<sub>3</sub>), 56.7 (C-4'), 77.0 (C-3), 84.3 (C-2), 118.0 (C-4a), 118.8 (C-8), 122.2 (C-6),

127.0 (C-5), 123.6, 127.6, 127.8, 128.1, 128.2, 128.3, 128.4, 128.9, 133.3, 136.2, 137.4, 146.9 (C-Ar), 137.2 (C-7), 151.0 (C-5'), 158.7 (C-8a), 190.4 (C-4).

Anal. Calcd. for  $C_{30}H_{23}N_3O_4$  : C, 73.61; H, 4.74; N, 8.58. Found: C, 73.49; H, 4.62; N, 8.73.

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