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ORIGINAL PAPER

Synthesis of novel *N*-aryl-2,5-dihydro-2-iminofuran-3-carboxamides and their chemical transformations

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Abstract Novel *N*-aryl-2,5-dihydro-2-iminofuran-3-carboxamides have been synthesized by condensation of tertiary α-hydroxyketones with *N*-aryl-2-cyanoacetamides**.** The obtained products were transformed to corresponding iminium chlorides, hydrogen sulfates, 2-oxo and 2-(dicyanomethylene) derivatives. All new compounds were characterized by NMR and IR spectral data and elemental analysis.

Keywords Tertiary α-hydroxyketones · 2,5-Dihydrofuran · Cyanoacetamides · Sodium methoxide · Malononitrile

Introduction

2,5-Dihydro-2-oxofuran derivatives are a large family of heterocycles that include synthetically useful compounds, several natural products [1–15], and a number of drugs with diverse biological activities such as antifungal, antibacterial, and anti-inflammatory properties [16–20]. Thus, there has been a continuous interest in the development of efficient and convenient methods for the preparation of these heterocycles and in their applications [11–15, 21–23]. One of the most convenient and common methods of synthesis of functionalized 2,5-dihydro-2-oxofurans is the condensation of α-hydroxyketones with compounds containing active methylene groups (dimethyl malonate, ethyl cyanoacetate, ethyl acetoacetate) in basic conditions [20, 24, 25].

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In this paper, I report the condensation of tertiary α-hydroxyketones with other compounds containing active methylene groups, viz., *N*-aryl-2-cyanoacetamides, in the presence of sodium methoxide affording *N*-aryl-2,5-dihydro-2-iminofuran-3-carboxamides. The reactions reported herein proceed under mild conditions, and the starting materials are readily available.

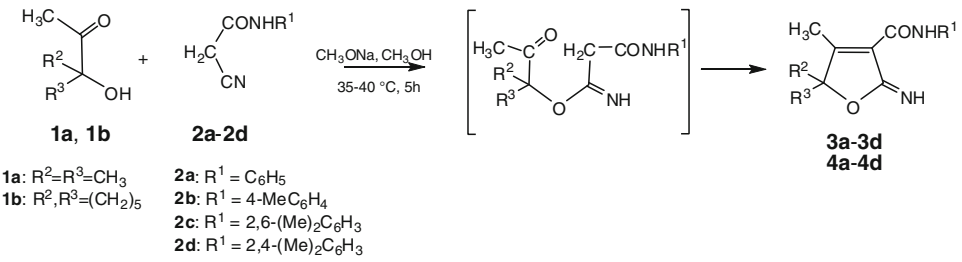
Results and discussion

The condensation of tertiary α-hydroxyketones **1a**, **1b** (1 eq) with *N*-aryl-2-cyanoacetamides **2a**–**2d** (1 eq) in the presence of sodium methoxide (0.1 eq) in dry methanol at 35–40 °C for 5 h afforded *N*-aryl-2,5-dihydro-2-iminofuran-3-carboxamides **3a**–**3d** and *N*-aryl-4-methyl-2-oxo-1-oxaspiro[4.5]dec-3-ene-3-carboxamides **4a**–**4d** in high yields (Scheme 1).

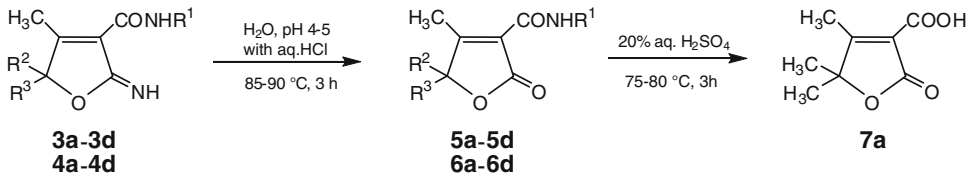
The structures of synthesized compounds **3a**–**3d** and **4a**–**4d** were apparent from IR and NMR spectra and their chemical transformations. The IR, ^{1}H, and ^{13}C NMR spectroscopic data are in agreement with the proposed structures. The IR spectra of compounds **3a**–**3d** and **4a**–**4d** showed bands at $\bar{\nu}$ = 1,630–1,650 (C=N) and 3,240–3,254 cm^{-1} (=N–H). The ^{1}H NMR spectra of compounds **3a**–**3d** and **4a**–**4d** exhibited a singlet identified as C=NH proton (δ = 7.21–7.23 ppm). The ^{13}C NMR spectra of **3a**–**3d** and **4a**–**4d** exhibited 11–13 and 13–15 signals, respectively, in agreement with the proposed structures.

The suggested mechanism for the formation of iminolactones **3a**–**3d** and **4a**–**4d** begins by the addition of the hydroxyl group on the nitrile group followed by a Knoevenagel condensation leading to ring formation according to Scheme 1. It was noticed that the ease of ring formation

Scheme 1



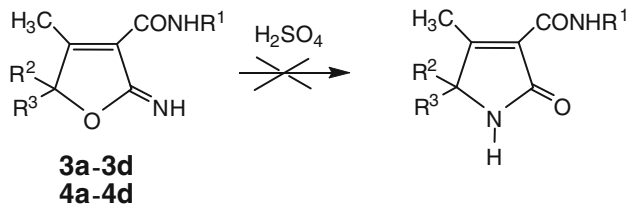
Scheme 2



was due to the presence of a gem-dialkyl producing a Thorpe-Ingold conformational effect [26–28], which states that alkyl substitution on a central methylene causes compression of the internal angle, leading to an easier ring formation. Le Bigot et al. have reported [29, 30] a reaction close to the formation of iminolactones: the formation of iminocoumarin by the condensation of nitrile with salicylaldehyde.

2-Iminolactones **3a–3d** and **4a–4d** are readily hydrolyzed with aqueous hydrochloric acid (at pH 4–5) for 3 h with formation of *N*-aryl-2,5-dihydro-2-oxofuran-3-carboxamides **5a–5d** and **6a–6d** (Scheme 2). Further hydrolysis of the amide group under more rigid conditions (upon heating the reaction mixture in the presence of sulfuric acid) was also carried out in **5a** as one example. That resulted in 2,5-dihydro-4,5,5-trimethyl-2-oxofuran-3-carboxylic acid (**7a**) [31]. The rearrangement of furan derivatives **3a–3d** and **4a–4d** to pyrrole derivatives in concentrated sulfuric acid was not observed (Scheme 3).

The novel 2-iminoderivatives **3a–3d** and **4a–4d** readily form iminium salts (hydrochlorides **8a–8d** and **9a–9d** and hydrogen sulfates **10a–10d**) with mineral acids (both with HCl and H_2SO_4, pH 1–2) (Scheme 4). Iminium hydrochlorides **8a–8d** and **9a–9d** have also been obtained by passing gaseous hydrogen chloride through a benzene solution of 2-iminolactones **3a–3d** and **4a–4d**. Iminium salts **8a–8d**, **9a–9d**, and **10a–10d** are water-soluble compounds and are readily titrated by alkali solution (0.1 N NaOH) and easily transform to 2-iminoderivatives **3a–3d** and **4a–4d** upon treatment with potassium carbonate. Iminium salts **8a–8d**, **9a–9d**, and **10a–10d** are readily hydrolyzed in aqueous solution for 2 h resulting in lactones **5a–5d** and **6a–6d**.



Scheme 3

Further study of chemical transformations of 2-iminolactones **3a–3d** and **4a–4d** showed that, as expected, they were very reactive compounds and readily perform reactions of NH-group substitution. Thus, the reaction with malononitrile readily and in high yields affords condensation products *N*-aryl-2-(dicyanomethylene)-2,5-dihydrofuran-3-carboxamides **11a–11d** and **12a–12d** at the expense of the methylene group of malononitrile (Scheme 5).

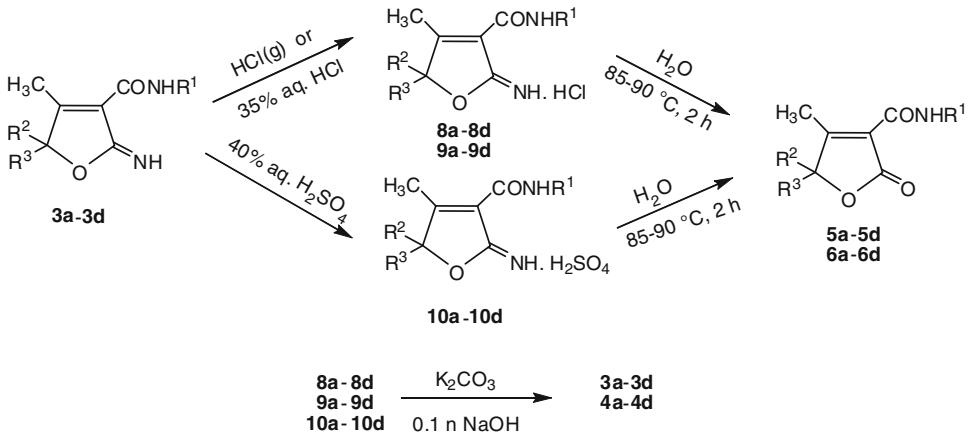
Conclusion

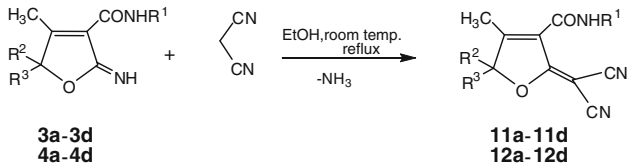
Herein I report synthesis of novel *N*-aryl-2,5-dihydro-2-iminofuran-3-carboxamides **3a–3d** and **4a–4d** via a simple and convenient method by condensation of tertiary α-hydroxyketones with *N*-aryl-2-cyanoacetamides under mild basic conditions. The obtained products were transformed to corresponding iminium chlorides, hydrogen sulfates, 2-oxo and 2-(dicyanomethylene) derivatives. The structures of synthesized compounds **3a–3d** and **4a–4d** were characterized by IR, ^{1}H, and ^{13}C NMR spectral data. The performed chemical reactions of the compounds **3a–3d** and **4a–4d** confirmed that compounds **3a–3d** and **4a–4d** are iminodihydrofurans and not pyrrolinones, which are isomeric to them.

Experimental

All solvents were dried by standard methods. Melting points were measured with an Electrothermal 9100

Scheme 4





Scheme 5

apparatus. Elemental analyses (C, H, and N) were performed using a Heraeus CHN-O-Rapid analyzer, and results agreed with calculated values. IR spectra were recorded on a Specord 751 R spectrometer in Vaseline oil. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-300 VX spectrometer at 300 and 75.46 MHz, respectively. NMR spectra were obtained in DMSO-d_6/CCl_4 1:3 solutions and are reported as parts per million (ppm) downfield from tetramethylsilane as internal standard. The abbreviations used are singlet (s), bs (broad singlet), doublet (d), triplet (t), and multiplet (m). The purity of synthesized compounds was controlled by means of thin-layer chromatography (TLC) on Silufol UV-25 plates, eluent acetone/benzene 1:2, developed by iodine vapors.

The syntheses of compounds **1a**, **1b** were conducted according to known procedures [32] and compounds **2a**–**2d** were prepared by the reaction of ethyl cyanoacetate with arylamines [33].

*General procedure for the preparation of N-aryl-2,5-dihydro-2-iminofuran-3-carboxamides **3a–3d** and **4a–4d***

A mixture of **1a**, **1b** (10 mmol), **2a**–**2d** (10 mmol), and sodium methoxide (1 mmol) in 20 cm^3 dry methanol was heated at 35–40 °C for 5 h. The solvent was removed under reduced pressure. Water was poured into the residue. The solid precipitate obtained was filtered, washed with water, and recrystallized from ethanol.

2,5-Dihydro-2-imino-4,5,5-trimethyl-N-phenylfuran-3-carboxamide (**3a**, $C_{14}H_{16}N_2O_2$)

Prepared from 1.02 g **1a** and 1.6 g 2-cyano-*N*-phenylacetamide (**2a**). White crystals; yield 95%; m.p.: 144–145 °C; $R_f = 0.52$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}300$ (NH), 3,240 (NH), 1,680 (C=O), 1,640 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.42$ (s, 6H, $2CH_3$), 2.35 (s, 3H, CH_3), 7.21 (s, 1H, =NH), 7.34–7.45 (m, 5H, Ar–H), 11.35 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 11.81$, 24.16, 87.64, 118.26, 126.28, 126.89, 127.78, 138.43, 160.41, 166.21, 170.77 ppm.

2,5-Dihydro-2-imino-4,5,5-trimethyl-N-(4-methylphenyl)furan-3-carboxamide (**3b**, $C_{15}H_{18}N_2O_2$)

Prepared from 1.02 g **1a** and 1.74 g 2-cyano-*N*-(4-methylphenyl)acetamide (**2b**). White crystals; yield 93%; m.p.: 139–140 °C; $R_f = 0.54$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}300$ (NH), 3,240 (NH), 1,680 (C=O), 1,640 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.48$ (s, 6H, $2CH_3$), 2.28 (s, 3H, Ar–CH_3), 2.40 (s, 3H, CH_3), 7.21 (s, 1H, =NH), 7.34 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.45 (2H, d, $J = 8.0$ Hz, Ar–H), 9.88 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 11.81$, 22.96, 24.16, 87.64, 118.26, 126.28, 126.89, 127.78, 138.43, 160.41, 166.21, 170.77 ppm.

N-(2,6-Dimethylphenyl)-2,5-dihydro-2-imino-4,5,5-trimethylfuran-3-carboxamide (**3c**, $C_{16}H_{20}N_2O_2$)

Prepared from 1.02 g **1a** and 1.88 g 2-cyano-*N*-(2,6-dimethylphenyl)acetamide (**2c**). White crystals; yield 93%; m.p.: 106–107 °C; $R_f = 0.56$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}300$ (NH), 3,254 (NH), 1,680 (C=O), 1,640 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.44$ (s, 6H, $2CH_3$), 2.23 [s, 6H, Ar–$(CH_3)_2$], 2.42 (s, 3H, CH_3), 7.21 (s, 1H, =NH), 7.34 (s, 3H, Ar–$H_{3,4,5}$), 10.99 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 11.81$, 18.16, 24.16, 87.64, 118.26, 126.27, 126.89, 127.76, 138.43, 160.41, 166.21, 170.77 ppm.

N-(2,4-Dimethylphenyl)-2,5-dihydro-2-imino-4,5,5-trimethylfuran-3-carboxamide (**3d**, $C_{16}H_{20}N_2O_2$)
Prepared from 1.02 g **1a** and 1.88 g 2-cyano-*N*-(2,4-dimethylphenyl)acetamide (**2d**). White crystals; yield 94%; m.p.: 142–143 °C; $R_f = 0.56$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}300$ (NH), 3,250 (NH), 1,680 (C=O), 1,640 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.47$ (s, 6H, $2CH_3$), 2.28 [s, 6H, Ar–$(CH3)_2$], 2.44 (s, 3H, CH_3), 6.91 (d, 1H, $J = 8.0$ Hz, Ar–H_5), 6.93 (s, 1H, Ar–H_3), 7.23 (s, 1H, =NH), 8.01 (d, 1H, $J = 8.0$ Hz, Ar–H_6), 11.38 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 11.81$, 18.16, 22.96, 24.16, 87.64, 118.26, 126.27, 126.89, 127.76, 138.43, 160.41, 166.21, 170.77 ppm.

2-Imino-4-methyl-N-phenyl-1-oxaspiro[4.5]dec-3-ene-3-carboxamide (**4a**, $C_{17}H_{20}N_2O_2$)
Prepared from 1.42 g **1b** and 1.6 g **2a**. White crystals; yield 95%; m.p.: 122–123 °C; $R_f = 0.54$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}400$ (NH), 3,240 (NH), 1,670 (C=O), 1,635 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.27$ (m, 1H), 1.47 (m, 2H), 1.58–1.82 (m, 7H, C_5H_{10}), 2.33 (s, 3H, CH_3), 7.21 (s, 1H, =NH), 7.34–7.45 (m, 5H, Ar–H), 11.35 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 12.08$, 21.22, 23.96, 32.39, 87.64, 118.26, 126.28, 126.89, 127.78, 138.43, 160.41, 166.21, 170.77 ppm.

2-Imino-4-methyl-N-(4-methylphenyl)-1-oxaspiro[4.5]dec-3-ene-3-carboxamide (**4b**, $C_{18}H_{22}N_2O_2$)
Prepared from 1.42 g **1b** and 1.74 g **2b**. White crystals; yield 92%; m.p.: 123–124 °C; $R_f = 0.56$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}400$ (NH), 3,240 (NH), 1,670 (C=O), 1,635 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.27$ (m, 1H), 1.47 (m, 2H), 1.58–1.82 (m, 7H, C_5H_{10}), 2.28 (s, 3H, Ar–CH_3), 2.35 (s, 3H, CH_3), 7.22 (s, 1H, =NH), 7.34 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.45 (d, 2H, $J = 8.0$ Hz, Ar–H), 9.78 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 12.08$, 21.22, 22.96, 23.96, 32.39, 87.64, 118.26, 126.28, 126.89, 127.78, 138.43, 160.41, 166.21, 170.77 ppm.

N-(2,6-Dimethylphenyl)-2-imino-4-methyl-1-oxaspiro-[4.5]dec-3-ene-3-carboxamide (**4c**, $C_{19}H_{24}N_2O_2$)
Prepared from 1.42 g **1b** and 1.88 g **2c**. White crystals; yield 93%; m.p.: 143–144 °C; $R_f = 0.59$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}400$ (NH), 3,240 (NH), 1,670 (C=O), 1,635 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.31$ (m, 1H), 1.57 (m, 2H), 1.63–1.85 (m, 7H, C_5H_{10}), 2.22 [s, 6H, Ar–$(CH3)_2$], 2.40 (3H, s, CH_3), 7.02 (s, 3H, Ar–$H_{3,4,5}$), 7.23 (s, 1H, =NH), 11.02 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 12.08$, 18.16, 21.22, 23.96, 32.39, 87.66, 118.27, 126.29, 126.89, 127.77, 138.44, 160.41, 166.21, 170.77 ppm.

N-(2,4-Dimethylphenyl)-2-imino-4-methyl-1-oxaspiro-[4.5]dec-3-ene-3-carboxamide (**4d**, $C_{19}H_{24}N_2O_2$)
Prepared from 1.42 g **1b** and 1.88 g **2d**. White crystals; yield 94%; m.p.: 160–161 °C; $R_f = 0.59$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}400$ (NH), 3,240 (NH), 1,670 (C=O), 1,635 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.30$ (m, 1H), 1.52 (m, 2H), 1.62–1.84 (m, 7H, C_5H_{10}), 2.28 [s, 6H, Ar–$(CH_3)_2$], 2.43 (s, 3H, CH_3), 6.91 (d, 1H, $J = 8.0$ Hz, Ar–H_5), 6.93 (s, 1H, Ar–H_3), 7.22 (s, 1H, =NH), 8.01 (d, 1H, $J = 8.0$ Hz, Ar–H_6), 11.38 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 12.08$, 18.16, 21.22, 22.96, 23.96, 32.39, 87.64, 118.26, 126.28, 126.89, 127.78, 138.43, 160.41, 166.21, 170.77 ppm.

*General procedure for the preparation of N-aryl-2,5-dihydro-2-oxofuran-3-carboxamides **5a–5d** and **6a–6d***

A mixture of 2-iminoderivative **3a–3d** or **4a–4d** (3 mmol) and 8 cm^3 water in the presence of hydrochloric acid (pH 4–5) was heated at 85–90 °C for 3 h, cooled, extracted with diethyl ether (3×10 cm^3), and the extract was dried with magnesium sulfate. After removal of the solvent, the residue was recrystallized from petroleum ether.

2,5-Dihydro-4,5,5-trimethyl-2-oxo-N-phenylfuran-3-carboxamide (**5a**, $C_{14}H_{15}NO_3$)
White crystals; yield 78%; m.p.: 97–98 °C (ref. [31] 96.5–98 °C).

2,5-Dihydro-4,5,5-trimethyl-N-(4-methylphenyl)-2-oxofuran-3-carboxamide (**5b**, $C_{15}H_{17}NO_3$)
White crystals; yield 78%, m.p.: 91–92 °C; $R_f = 0.53$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}280$ (NH), 1,760 (C=O), 1,680 (C=O), 1,660 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.48$ (s, 6H, $2CH_3$), 2.28 (s, 3H, s, Ar–CH_3), 2.40 (s, 3H, CH_3), 7.34 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.45 (d, 2H, $J = 8.0$ Hz, Ar–H), 9.88 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 11.81$, 22.96, 24.16, 87.62, 118.26, 126.28, 126.89, 127.78, 138.43, 158.40, 161.21, 176.77 ppm.

N-(2,6-Dimethylphenyl)-2,5-dihydro-4,5,5-trimethyl-2-oxofuran-3-carboxamide (**5c**, $C_{16}H_{19}NO_3$)
White crystals; yield 65%; m.p.: 101–102 °C; $R_f = 0.54$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}280$ (NH), 1,760 (C=O), 1,680 (C=O), 1,660 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.44$ (s, 6H, $2CH_3$), 2.23 [s, 6H, Ar–$(CH3)_2$], 2.42 (s, 3H, CH_3), 7.34 (s, 3H, Ar–$H_{3,4,5}$), 10.99 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 11.81$, 18.18, 24.16, 87.64, 118.26, 126.27, 126.89, 127.76, 138.44, 158.42, 162.22, 176.77 ppm.

N-(2,4-Dimethylphenyl)-2,5-dihydro-4,5,5-trimethyl-2-oxofuran-3-carboxamide (**5d**, $C_{16}H_{19}NO_3$)
White crystals; yield 73%; m.p.: 109–110 °C; $R_f = 0.54$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}280$ (NH), 1,760 (C=O), 1,680 (C=O), 1,660 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.47$ (s, 6H, $2CH_3$), 2.28 [s, 6H, Ar–$(CH_3)_2$], 2.44 (s, 3H, CH_3), 6.91 (d, 1H, $J = 8.0$ Hz, Ar–H_5), 6.93 (s, 1H, Ar–H_3), 8.04 (d, 1H, $J = 8.0$ Hz, Ar–H_6), 11.36 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 11.81$, 18.16, 22.96, 24.16, 87.64, 118.26, 126.27, 126.89, 127.76, 138.43, 159.42, 162.20, 176.74 ppm.

4-Methyl-2-oxo-N-phenyl-1-oxaspiro[4.5]dec-3-ene-3-carboxamide (**6a**, $C_{17}H_{19}NO_3$)
White crystals; yield 79%; m.p.: 135–136 °C; $R_f = 0.57$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}280$ (NH), 1,760 (C=O), 1,680 (C=O), 1,660 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.27$ (m, 1H), 1.47 (m, 2H), 1.58–1.82 (m, 7H, C_5H_{10}), 2.35 (s, 3H, CH_3), 7.34–7.45 (m, 5H, Ar–H), 11.35 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 12.08$, 21.22, 23.96, 32.39, 87.64, 118.26, 126.28, 126.89, 127.78, 138.43, 159.42, 162.20, 176.74 ppm.

4-Methyl-N-(4-methylphenyl)-2-oxo-1-oxaspiro[4.5]dec-3-ene-3-carboxamide (**6b**, $C_{18}H_{21}NO_3$)
White crystals; yield 79%; m.p.: 145–147 °C; $R_f = 0.57$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}280$ (NH), 1,760 (C=O), 1,680 (C=O), 1,660 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.26$ (m, 1H), 1.45 (m, 2H), 1.60–1.82 (m, 7H, C_5H_{10}), 2.30 (s, 3H, Ar–CH_3), 2.40 (s, 3H, CH_3), 7.34 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.45 (d, 2H, $J = 8.0$ Hz, Ar–H), 11.35 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 12.08$, 21.22, 22.96, 23.96, 32.39, 87.64, 118.26, 126.28, 126.89, 127.78, 138.43, 159.42, 162.20, 176.74 ppm.

N-(2,6-Dimethylphenyl)-4-methyl-2-oxo-1-oxaspiro-[4.5]dec-3-ene-3-carboxamide (**6c**, $C_{19}H_{23}NO_3$)
White crystals; yield 80%; m.p.: 133–134 °C; $R_f = 0.59$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}280$ (NH), 1,760 (C=O), 1,680 (C=O), 1,660 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.31$ (m, 1H), 1.57 (m, 2H), 1.63–1.85 (m, 7H, C_5H_{10}), 2.22 (s, 6H, Ar–CH_3), 2.40 (s, 3H, CH_3), 7.02 (s, 3H, Ar–$H_{3,4,5}$), 11.02 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 12.08$, 18.16, 21.22, 23.96, 32.39, 87.66, 118.27, 126.29, 126.89, 127.77, 138.44, 158.48, 162.21, 176.76 ppm.

N-(2,4-Dimethylphenyl)-4-methyl-2-oxo-1-oxaspiro-[4.5]dec-3-ene-3-carboxamide (**6d**, $C_{19}H_{23}NO_3$)
White crystals; yield 80%; m.p.: 168–169 °C; $R_f = 0.59$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}280$ (NH), 1,760 (C=O), 1,680 (C=O), 1,660 (C=N), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.30$ (m, 1H), 1.52 (m, 2H), 1.62–1.84 (m, 7H, C_5H_{10}), 2.28 [s, 6H, Ar–$(CH3)_2$], 2.43 (s, 3H, CH_3), 6.91 (d, 1H, $J = 8.0$ Hz, Ar–H_5), 6.93 (s, 1H, Ar–H_3), 8.04 (d, 1H, $J = 8.0$ Hz, Ar–H_6), 11.38 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 12.08$, 18.16, 21.22, 22.96, 23.96, 32.39, 87.64, 118.26, 126.28, 126.89, 127.78, 138.43, 158.44, 162.24, 176.74 ppm.

2,5-Dihydro-4,5,5-trimethyl-2-oxofuran-3-carboxylic acid (**7a**)
A mixture of 0.98 g **5a** (4 mmol) and 14 cm^3 sulfuric acid (20%) was heated at 75–80 °C until the oily layer completely disappeared. The mixture was cooled, extracted with diethyl ether (3×15 cm^3) and dried with magnesium sulfate. Ether was distilled off. Recrystallization from xylol afforded 0.55 g (80%) **7a**. M.p.: 112–113 °C (ref. [31] 112–113 °C).

*General procedure for the preparation of N-aryl-2,5-dihydro-2-iminofuran-3-carboxamide hydrochlorides **8a–8d** and **9a–9d***

Method A: To a solution of 2-iminoderivative **3a–3d** or **4a–4d** (10 mmol) in 15 cm^3 ethanol was added 1 cm^3 hydrochloric acid (35%). The mixture was refluxed at room temperature for 10 min. After ethanol had been partially distilled off, the resulting precipitate was filtered off, washed with diethyl ether, and dried.

Method B: Through a benzene solution of 2-iminoderivative **3a–3d** or **4a–4d** (10 mmol), gaseous hydrogen chloride was passed. The resulting precipitate was filtered off, washed with diethyl ether, and dried.

2,5-Dihydro-2-imino-4,5,5-trimethyl-N-phenylfuran-3-carboxamide hydrochloride (**8a**, $C_{14}H_{16}N_2O{\cdot}HCl$)
White crystals; yield 93% (A), 98% (B); m.p.: 236–239 °C; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 11.42$ (s, 6H, $2CH_3$), 2.35 (s, 3H, CH_3), 7.34–7.45 (m, 5H, Ar–H), 9.22 (s, 1H, NH-Ar), 10.34 (bs, 2H, =NH·HCl) ppm.

2,5-Dihydro-2-imino-4,5,5-trimethyl-N-(4-methylphenyl)furan-3-carboxamide hydrochloride (**8b**, $C_{15}H_{18}N_2O_2{\cdot}HCl$)
White crystals; yield 93% (A), 97% (B); m.p.: 208–212 °C; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.42$ (s, 6H, $2CH_3$), 2.28 (s, 3H, Ar–CH_3), 2.40 (s, 3H, CH_3), 7.34 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.45 (d, 2H, $J = 8.0$ Hz, Ar–H), 9.24 (s, 1H, NH), 10.44 (bs, 2H, =NH·HCl) ppm.

N-(2,6-Dimethylphenyl)-2,5-dihydro-2-imino-4,5,5-trimethylfuran-3-carboxamide (**8c**, $C_{16}H_{20}N_2O_2{\cdot}HCl$)
White crystals; yield 92% (A), 97% (B); m.p.: 229–232 °C; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.45$ (s, 6H, $2CH_3$), 2.23 [s, 6H, Ar–$(CH_3)_2$], 2.42 (s, 3H, CH_3), 7.34 (s, 3H,

Ar–$H_{3,4,5}$), 9.38 (s, 1H, NH), 10.48 (bs, 2H, =NH·HCl) ppm.

N-(2,4-Dimethylphenyl)-2,5-dihydro-2-imino-4,5,5-trimethylfuran-3-carboxamide (**8d**, $C_{16}H_{20}N_2O_2$·HCl)
White crystals; yield 92% (A), 97% (B); m.p.: 222–225 °C; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.45$ (s, 6H, $2CH_3$), 2.28 [s, 6H, Ar–$(CH_3)_2$], 2.44 (s, 3H, CH_3), 6.92 (d, 1H, $J = 8.0$ Hz, Ar–H_5), 6.94 (s, 1H, Ar–H_3), 8.01 (d, 1H, $J = 8.0$ Hz, Ar–H_6), 9.44 (s, 1H, NH), 10.52 (bs, 2H, =NH·HCl) ppm.

2-Imino-4-methyl-N-phenyl-1-oxaspiro[4.5]dec-3-ene-3-carboxamide hydrochloride (**9a**, $C_{17}H_{20}N_2O_2$·HCl)
White crystals; yield 93% (A), 99% (B); m.p.: 181–185 °C; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.27$ (m, 1H), 1.47 (m, 2H), 1.58–1.82 (m, 7H, C_5H_{10}), 2.35 (s, 3H, CH_3), 7.34–7.45 (m, 5H, Ar–H), 9.22 (s, 1H, NH–Ar), 10.34 (bs, 2H, =NH·HCl) ppm.

2-Imino-4-methyl-N-(4-methylphenyl)-1-oxaspiro[4.5]-dec-3-ene-3-carboxamide hydrochloride
(**9b**, $C_{18}H_{22}N_2O_2$·HCl)
White crystals; yield 91% (A), 98% (B); m.p.: 170–174 °C; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.26$ (m, 1H), 1.45 (m, 2H), 1.60–1.82 (m, 7H, C_5H_{10}), 2.30 (s, 3H, Ar–CH_3), 2.40 (s, 3H, CH_3), 7.34 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.45 (d, 2H, $J = 8.0$ Hz, Ar–H), 9.22 (s, 1H, NH), 10.34 (bs, 2H, =NH·HCl) ppm.

N-(2,6-Dimethylphenyl)-2-imino-4-methyl-1-oxaspiro-[4.5]dec-3-ene-3-carboxamide hydrochloride
(**9c**, $C_{19}H_{24}N_2O_2$·HCl)
White crystals; yield 91% (A), 98% (B); m.p.: 195–200 °C; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.31$ (m, 1H), 1.57 (m, 2H), 1.63–1.85 (m, 7H, C_5H_{10}), 2.22 [s, 6H, Ar–$(CH3)_2$], 2.42 (s, 3H, CH_3), 7.02 (s, 3H, Ar–$H_{3,4,5}$), 9.36 (s, 1H, NH), 10.78 (bs, 2H, =NH·HCl) ppm.

N-(2,4-Dimethylphenyl)-2-imino-4-methyl-1-oxaspiro-[4.5]dec-3-ene-3-carboxamide hydrochloride
(**9d**, $C_{19}H_{24}N_2O_2$·HCl)
White crystals; yield 91% (A), 98% (B); m.p.: 175–180 °C; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.30$ (m, 1H), 1.52 (m, 2H), 1.62–1.84 (m, 7H, C_5H_{10}), 2.28 [s, 6H, Ar–$(CH_3)_2$], 2.44 (s, 3H, CH_3), 6.92 (d, 1H, $J = 8.0$ Hz, Ar–H_5), 6.94 (s, 1H, Ar–H_3), 8.01 (d, 1H, $J = 8.0$ Hz, Ar–H_6), 9.38 (s, 1H, NH), 10.86 (bs, 2H, =NH·HCl) ppm.

General procedure for the preparation of N-aryl-2,5-dihydro-2-iminofuran-3-carboxamide hydrogensulfates ***10a–10d***

To a solution of 2-iminoderivative **3a–3d** (2 mmol) in 5 cm^3 ethanol was added 0.6 cm^3 sulfuric acid (40%). The mixture was refluxed at room temperature for 10 min. The formed precipitate was filtered off, washed with ether, and dried.

2,5-Dihydro-2-imino-4,5,5-trimethyl-N-phenylfuran-3-carboxamide hydrogensulfate (**10a**, $C_{14}H_{16}N_2O_2·H_2SO_4$)
White crystals; yield 87%; m.p.: 250–254 °C; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.42$ (s, 6H, $2CH_3$), 2.35 (s, 3H, CH_3), 7.34–7.45 (m, 5H, Ar–H), 9.22 (s, 1H, NH–Ar), 10.34 (bs, 2H, =NH·H_2SO_4) ppm.

2,5-Dihydro-2-imino-4,5,5-trimethyl-N-(4-methylphenyl)-furan-3-carboxamide hydrogensulfate
(**10b**, $C_{15}H_{18}N_2O_2·H_2SO_4$)
White crystals, yield 85%; m.p.: 243–147 °C; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.42$ (s, 6H, $2CH_3$), 2.28 (s, 3H, Ar–CH_3), 2.40 (s, 3H, CH_3), 7.34 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.45 (d, 2H, $J = 8.0$ Hz, Ar–H), 9.24 (s, 1H, NH), 10.44 (bs, 2H, =NH·H_2SO_4) ppm.

N-(2,6-Dimethylphenyl)-2,5-dihydro-2-imino-4,5,5-trimethylfuran-3-carboxamide hydrogensulfate
(**10c**, $C_{16}H_{20}N_2O_2·H_2SO_4$)
White crystals; yield 84% yield; m.p.: 260–262 °C; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.45$ (s, 6H, $2CH_3$), 2.23 [s, 6H, Ar–$(CH_3)_2$], 2.42 (s, 3H, CH_3), 7.34 (s, 3H, Ar–$H_{3,4,5}$), 9.38 (s, 1H, NH), 10.48 (bs, 2H, =NH·H_2SO_4) ppm.

N-(2,4-Dimethylphenyl)-2,5-dihydro-2-imino-4,5,5-trimethylfuran-3-carboxamide hydrogensulfate
(**10d**, $C_{16}H_{20}N_2O_2·H_2SO_4$)
White crystals; yield 85%; m.p.: 252–256 °C; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.45$ (s, 6H, $2CH_3$), 2.28 [s, 6H, Ar–$(CH3)_2$], 2.44 (s, 3H, CH_3), 6.91 (d, 1H, $J = 8.0$ Hz, Ar–H_5), 6.94 (s, 1H, Ar–H_3), 8.01 (d, 1H, $J = 8.0$ Hz, Ar–H_6), 9.42 (s, 1H, NH), 10.52 (bs, 2H, =NH·H_2SO_4) ppm.

General procedure for the hydrolysis of compounds ***8a–8d, 9a–9d,*** *and* ***10a–10d***

A solution of compound **8a–8d**, **9a–9d**, or **10a–10d** (3 mmol) in 5 cm^3 water was heated at 85–90 °C for 2 h. The mixture was cooled and extracted with diethyl ether (3 × 7 cm^3), and the extract was dried with magnesium sulfate. The solvent was distilled off, and the residue was recrystallized from petroleum ether. The products were identical to compounds **3a–3d** and **4a–4d** in melting points.

Reaction of compounds ***8a–8d, 9a–9d,*** *and* ***10a–10d*** *with potassium carbonate*

To an aqueous solution of hydrochloride **8a–8d**, **9a–9d**, or hydrogen sulfate **10a–10d**, a concentrated aqueous solution of potassium carbonate was added (until pH 7–8). The precipitate was filtered off and washed with water to afford

imino derivatives **3a–3d** and **4a–4d**. The combined samples with corresponding iminolactones **3a–3d** and **4a–4d** did not depress the melting points.

General procedure for the preparation of N-aryl-2-(dicyanomethylene)-2,5-dihydrofuran-3-carboxamides ***11a–11d*** *and* ***12a–12d***

A mixture of **3a–3d** or **4a–4d** (5 mmol) and 0.33 g malononitrile (5 mmol) in 10 cm^3 absolute ethanol was refluxed at room temperature until ammonia evolution had ceased. After removal of the solvent, water was poured to the crystalline residue, and the formed precipitate was filtered off, washed with water, and recrystallized from ethanol/water 2:1.

2-(Dicyanomethylene)-2,5-dihydro-4,5,5-trimethyl-N-phenylfuran-3-carboxamide (**11a**, $C_{17}H_{15}N_3O_2$)
White crystals; yield 94%; m.p.: 175–176 °C; $R_f = 0.57$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}240$ (NH), 2,219 (CN), 1,680 (C=O), 1,670 (C=N), 1,635 (C=C), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.42$ (6H, s, $2CH_3$), 2.35 (s, 3H, CH_3), 7.34–7.45 (m, 5H, Ar–H), 11.35 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 11.81$, 24.16, 46.00, 87.64, 115.14, 118.24, 126.26, 126.88, 127.76, 138.44, 160.44, 167.22, 171.77 ppm.

2-(Dicyanomethylene)-2,5-dihydro-4,5,5-trimethyl-N-(4-methylphenyl)furan-3-carboxamide (**11b**, $C_{18}H_{17}N_3O_2$)
White crystals; yield 94%; m.p.: 165–166 °C; $R_f = 0.59$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}240$ (NH), 2,219 (CN), 1,680 (C=O), 1,670 (C=N), 1,635 (C=C), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.44$ (s, 6H, $2CH_3$), 2.28 (s, 3H, Ar–CH_3), 2.40 (s, 3H, CH_3), 7.34 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.45 (d, 2H, $J = 8.0$ Hz, Ar–H), 11.35 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 11.81$, 22.96, 24.14, 46.10, 88.22, 115.15, 118.26, 126.28, 126.89, 127.78, 138.43, 160.41, 166.21, 170.77 ppm.

2-(Dicyanomethylene)-N-(2,6-dimethylphenyl)-2,5-dihydro-4,5,5-trimethylfuran-3-carboxamide
(**11c**, $C_{19}H_{19}N_3O$)
White crystals, yield 93%; m.p.: 189–190 °C; $R_f = 0.61$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}240$ (NH), 2,219 (CN), 1,680 (C=O), 1,670 (C=N), 1,635 (C=C), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.50$ (s, 6H, $2CH_3$), 2.23 [s, 6H, Ar–$(CH3)_2$], 2.42 (s, 3H, CH_3), 7.34 (s, 3H, Ar–$H_{3,4,5}$), 10.99 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 11.81$, 18.16, 24.16, 46.00, 87.66, 115.15, 118.30, 126.25, 126.88, 127.76, 138.43, 160.42, 166.20, 170.76 ppm.

2-(Dicyanomethylene)-N-(2,4-dimethylphenyl)-2,5-dihydro-4,5,5-trimethylfuran-3-carboxamide
(**11d**, $C_{19}H_{19}N_3O_2$)
White crystals; yield 94%; m.p.: 210–212 °C; $R_f = 0.61$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}240$ (NH), 2,219 (CN), 1,680 (C=O), 1,670 (C=N), 1,635 (C=C), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.47$ (s, 6H, $2CH_3$), 2.28 [s, 6H, Ar–$(CH3)_2$], 2.44 (s, 3H, CH_3), 6.91 (d, 1H, $J = 8.0$ Hz, Ar–H_5), 6.94 (s, 1H, Ar–H_3), 8.01 (d, 1H, $J = 8.0$ Hz, Ar–H_6), 11.38 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 11.81$, 18.16, 22.96, 24.16, 46.00, 87.62, 115.15, 118.24, 126.26, 126.87, 127.76, 138.43, 160.41, 166.21, 170.77 ppm.

2-(Dicyanomethylene)-4-methyl-N-phenyl-1-oxaspiro-[4.5]dec-3-ene-3-carboxamide (**12a**, $C_{20}H_{19}N_3O_2$)
White crystals, yield 94%; m.p.: 159–160 °C; $R_f = 0.59$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}240$ (NH), 2,219 (CN), 1,680 (C=O), 1,670 (C=N), 1,635 (C=C), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.27$ (m, 1H), 1.47 (m, 2H), 1.58–1.82 (m, 7H, C_5H_{10}), 2.35 (s, 3H, CH_3), 7.34–7.45 (m, 5H, Ar–H), 11.35 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 12.08$, 21.22, 23.96, 32.39, 46.20, 87.64, 115.15, 118.26, 126.28, 126.89, 127.78, 138.43, 160.41, 166.10, 170.77 ppm.

2-(Dicyanomethylene)-4-methyl-N-(4-methylphenyl)-1-oxaspiro[4.5]dec-3-ene-3-carboxamide
(**12b**, $C_{21}H_{21}N_3O_2$)
White crystals; yield 92%; m.p.: 163–164 °C; $R_f = 0.61$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}240$ (NH), 2,219 (CN), 1,680 (C=O), 1,670 (C=N), 1,635 (C=C), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.26$ (m, 1H), 1.45 (m, 2H), 1.60–1.82 (m, 7H, C_5H_{10}), 2.30 (s, 3H, Ar–CH_3), 2.40 (s, 3H, CH_3), 7.34 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.45 (d, 2H, $J = 8.0$ Hz, Ar–H), 11.35 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 12.08$, 21.22, 22.96, 23.98, 32.38, 46.20, 87.64, 115.15, 118.26, 126.28, 126.89, 127.78, 138.43, 160.44, 167.24, 170.78 ppm.

2-(Dicyanomethylene)-N-(2,6-dimethylphenyl)-4-methyl-1-oxaspiro[4.5]dec-3-ene-3-carboxamide
(**12c**, $C_{22}H_{23}N_3O_2$)
White crystals, yield 93%; m.p.: 164–165 °C; $R_f = 0.65$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}240$ (NH), 2,219 (CN), 1,680 (C=O), 1,670 (C=N), 1,635 (C=C), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^{1}H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.31$ (m, 1H), 1.57 (m, 2H), 1.63–1.85 (m, 7H, C_5H_{10}), 2.22 [s, 6H, Ar–$(CH3)_2$], 2.40 (s, 3H, CH_3), 7.02 (s, 3H, Ar–$H_{3,4,5}$), 11.02 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 12.08$, 18.16, 21.22, 23.96, 32.39, 46.20, 87.66, 115.15, 118.27, 126.29, 126.89, 127.77, 138.44, 160.41, 166.21, 170.77 ppm.

2-(Dicyanomethylene)-N-(2,4-dimethylphenyl)-4-methyl-1-oxaspiro[4.5]dec-3-ene-3-carboxamide
(**12d**, $C_{22}H_{23}N_3O_2$)
White crystals; yield 91%; m.p.: 240–242 °C; $R_f = 0.65$ (acetone/benzene 1:2); IR: $\bar{\nu} = 3{,}240$ (NH), 2,219 (CN), 1,680 (C=O), 1,670 (C=N), 1,635 (C=C), 1,620 (C=C), 1,600–1,500 (Ar) cm^{-1}; ^1H NMR (DMSO-d_6/CCl_4 1:3): $\delta = 1.30$ (m, 1H), 1.52 (m, 2H), 1.62–1.84 (m, 7H, C_5H_{10}), 2.28 [s, 6H, Ar–$(CH_3)_2$], 2.43 (s, 3H, CH_3), 6.91 (d, 1H, $J = 8.0$ Hz, Ar–H_5), 6.94 (s, 1H, Ar–H_3), 8.01 (d, 1H, $J = 8.0$ Hz, Ar–H_6), 11.38 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6/CCl_4 1:3): $\delta = 12.08$, 18.16, 21.22, 22.96, 23.96, 32.36, 46.20, 87.64, 115.15, 118.26, 126.28, 126.89, 127.78, 138.43, 160.41, 166.21, 170.77 ppm.

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