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Synthesis of 1-Substituted 2-Azaspiro[4.5]deca-6,9-dien-8-ones and 2-Azaspiro[4.5]deca-1,6,9-trien-8-ones by Condensation of 2,6-Dimethylphenol with Isobutyraldehyde and Nitriles

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Abstract—1-Substituted 3,3,7,9-tetramethyl-2-azaspiro[4.5]deca-6,9-dien-8-ones and 3,3,7,9-tetramethyl-2-azaspiro[4.5]deca-1,6,9-trien-8-ones were synthesized by three-component condensation of 2,6-dimethylphenol with isobutyraldehyde and nitriles in concentrated sulfuric acid.

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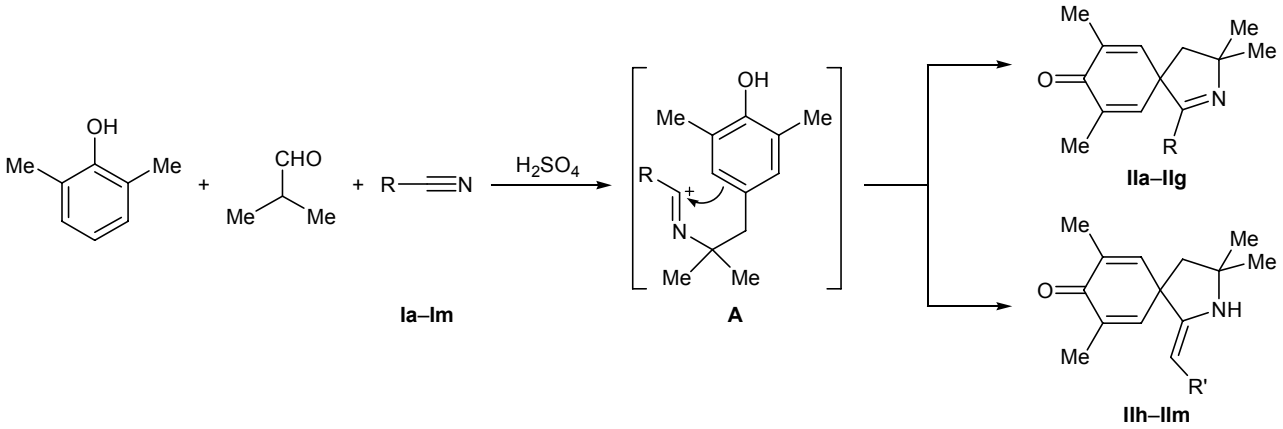
Compounds having a 2-azaspiro[4.5]decane skeleton rarely occur in nature. Examples of such structures are annosqualine isolated from the Stems of *Annona squamosa* [1], spirostaphylotrichins produced by *Staphylotrichum coccosporum* [2–4], triticones (spirocyclic lactams from the fungal plant pathogen *Drechslera tritici-repentis* [5]), and spiro-arogenate (a spiro-γ-lactam produced by *Neurospora crassa* from prephenic acid [6, 7]). Some 2-azaspiro[4.5]decanes attract certain interest from the viewpoints of medicinal and synthetic organic chemistry. Some synthetic analogs of natural 2-azaspirane derivatives showed high immunosupressive activity [8]. Kazmierski et al. [9] proposed novel HIV-1 protease inhibitors on the basis of a spirocyclic pyrrolidone. It was also found that 2-azaspiranes are formed as intermediate products in the Bischler–Napieralski [10, 11] or Ritter [12] syntheses of isoquinolines and phenanthridines.

Several synthetic approaches to 2-azaspiro[4.5]-decane derivatives have been reported. Some procedures imply building of 2-azaspiro[4.5]decane skeleton from cyclohexanone or cyclohexene fragments. 2-Azaspiranes can be synthesized according to Buchwald–Hartwig via intramolecular cyclization of the corresponding cyclohexanone derivatives [13] and by radical cyclization of *N*,*N*-diallyl-2-oxocyclohexanecarboxamides in the presence of $Mn(OAc)_3$ [14] or of 2-bromo-substituted diene amides, e.g., *N*-benzyl-2-bromo-*N*-[1-(cyclohex-1-en-1-yl)vinyl]propanamide, in the presence of $CuBr–(C_5H_5N)_3N$ [15]. A group of methods for the preparation of 2-azaspirane systems is based on dearomatization of arenes with simultaneous construction of pyrrolidinone fragment. Acid-catalyzed intramolecular *ipso*-cyclization of electron-rich aromatic diazoacetamides [16] or thionium ions generated by reaction of *N*-benzylglyoxamides with thiols [17] leads to the formation of spirocyclic lactams. 2-Azaspiranes can also be obtained by oxidative radical *ipso*-cyclization of *N*-[*p*-methoxy(hydroxy)benzyl]acetamides [18] and substituted *N*-benzyltrichloroacetamides [19]. Pigge et al. [20–24] developed a procedure for the synthesis of 2-azaspiranes via aromatic nucleophilic substitution in the presence of (η^6-arene)$RuCp^+$ complexes. Another possible way to 2-azaspiranes is based on the reaction of tricarbonyl (η^5-1-alkyl-4-methoxycyclohexadienylium)iron with difunctional nucleophiles [25]. Intramolecular ene-type [6+2]-cyclization of $Fe(CO)_3$–(cyclohexa-1,3-diene) complexes having a pendant double bond was reported to afford spirocyclic systems [26–28]. 2-Azaspiro[4.5]-deca-6,9-diene-3,8-diones were synthesized by tandem Ugi reaction and intramolecular Michael 5-*exo*-addition [29].

Scheme 1.



I, R = MeS (**a**), Ph (**b**), 3,4-$(MeO)_2C_6H_3$ (**c**), pyridin-2-yl (**d**), $PhCH_2$ (**e**), 3,4-$(MeO)_2C_6H_3CH_2$ (**f**), Me (**g**), pyridin-2-ylmethyl (**h**), $MeOCOCH_2$ (**i**), $EtOCOCH_2$ (**j**), H_2NCOCH_2 (**k**), 1*H*-benzimidazol-2-ylmethyl (**l**), 1,3-benzothiazol-2-ylmethyl (**m**); **II**, R′ = MeS (**a**), Ph (**b**), 3,4-$(MeO)_2C_6H_3$ (**c**), pyridin-2-yl (**d**, **h**), $PhCH_2$ (**e**), 3,4-$(OMe)_2C_6H_3CH_2$ (**f**), Me (**g**), MeOCO (**i**), EtOCO (**j**), H_2NCO (**k**), 1*H*-benzimidazol-2-yl (**l**), 1,3-benzothiazol-2-yl (**m**).

However, most of the above syntheses of 2-azaspiro[4.5]decane systems include a number of steps; therefore, development of simpler and more general procedures for the preparation of such compounds is an important problem.

We previously proposed a procedure for the synthesis of 2-azaspiro[4.5]deca-6,9-dien-8-ones and 2-azaspiro[4.5]deca-1,6,9-trien-8-ones on the basis of three-component condensation of anisole [30] or substituted anisoles [31–34] with an α-branched aldehyde and a nitrile under acid catalysis. In continuation of these studies in the present work we examined three-component condensation of isobutyraldehyde with phenols and nitriles, catalyzed by concentrated sulfuric acid. Clearly, the use of phenol instead of anisoles as aromatic component should ensure higher reactivity in electrophilic substitution and is attractive from the viewpoint of accessibility of initial reactants.

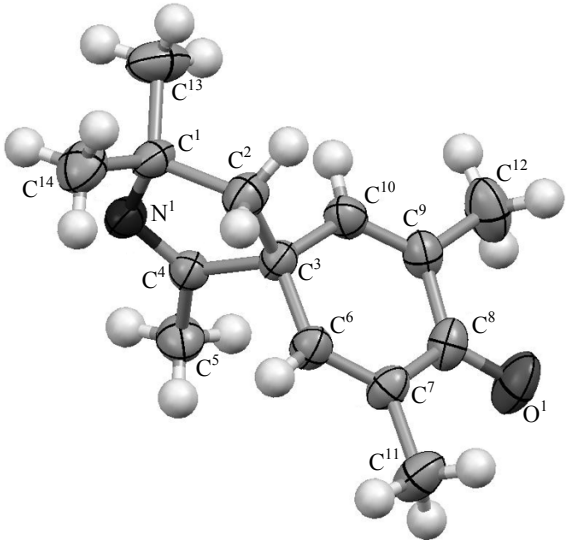
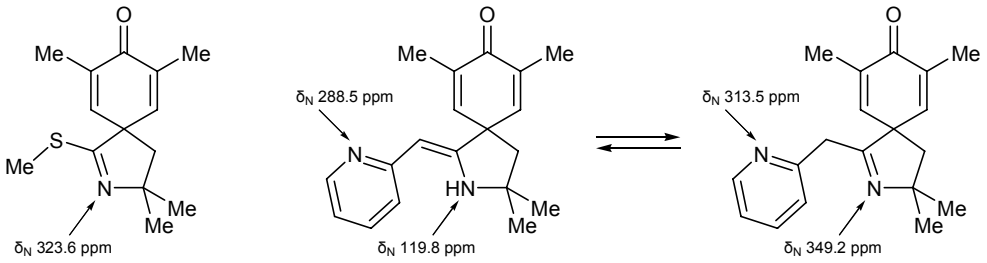


Fig. 1. Structure of the molecule of 1,3,3,7,9-pentamethyl-2-azaspiro[4.5]deca-1,6,9-trien-8-one (**IIg**) according to the X-ray diffraction data.

Reactions of isobutyraldehyde with nitriles and such hydroxy aromatics as phenol, 2-methylphenol, or 4-methylphenol resulted in the formation of tarry mixtures which were difficult to separate, and we failed to isolate spirane systems. Obviously, the reason is a number of side processes, such as acid-catalyzed polymerization of phenol and aldehyde [35] and Baeyer reaction with formation of diarylmethane derivatives [35–37]. To exclude the possibility for *ortho* attack on phenol molecule by aldehyde and suppress side reactions we used 2,6-dimethylphenol as aromatic component in the three-component condensation.

We found that 2,6-dimethylphenol reacts with isobutyraldehyde and nitriles **Ia**–**Im** in 92% sulfuric acid to give 2-azaspiro[4.5]deca-6,9-dien-8-ones **IIa**–**IIg** and 2-azaspiro[4.5]deca-1,6,9-trien-8-ones **IIh**–**IIm** (Scheme 1). Compounds **IIa**–**IIm** displayed in the ^1H NMR spectra singlets from geminal methyl groups on C^3 (δ 1.37–1.49 ppm), methyl groups on C^7 and C^9 (δ 1.76–1.94 ppm), methylene protons on C^4 (δ 2.00–2.20 ppm), and olefinic protons on C^6 and C^{10} (δ 6.23–6.93 ppm). The structure of **IIg** was proved by X-ray analysis (Fig. 1). In the spectra of **IIi**–**IIm** we observed a singlet at δ 3.91–4.69 ppm from vinylic proton and a broadened singlet at δ 8.26–8.90 ppm from the NH proton, which indicated their enamine structure.

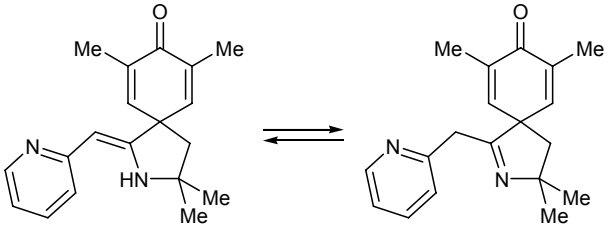


IIa **IIh**

Fig. 2. ^{15}N chemical shifts of model 3,3,7,9-tetramethyl-1-methylsulfanyl-2-azaspiro[4.5]deca-1,6,9-trien-8-one (**IIa**) and 3,3,7,9-tetramethyl-1-(pyridin-2-ylmethylidene)-2-azaspiro[4.5]deca-6,9-dien-8-one (**IIh**).

According to the ^{1}H NMR data, compound **IIh** in $CDCl_3$ exists as a mixture of enamino and imino tautomers at a ratio of 4:1 (Scheme 2). The ^{1}H NMR spectrum contained two sets of signals from the methyl groups on C^3 (δ 1.49 and 1.44 ppm), C^7-CH_3 and C^9-CH_3 (δ 1.93 and 1.78 ppm), and C^4H_2 (δ 2.13 and 2.04 ppm) and two sets of signals from protons in the pyridine ring. Enamino tautomer **A** gave rise to a singlet at δ 4.70 ppm from the C^1=CH proton and a broadened singlet at δ 8.86 ppm from the NH group. Tautomer **B** was characterized by a singlet at δ 3.61 ppm due to protons in the C^1-CH_2 group.

Scheme 2.



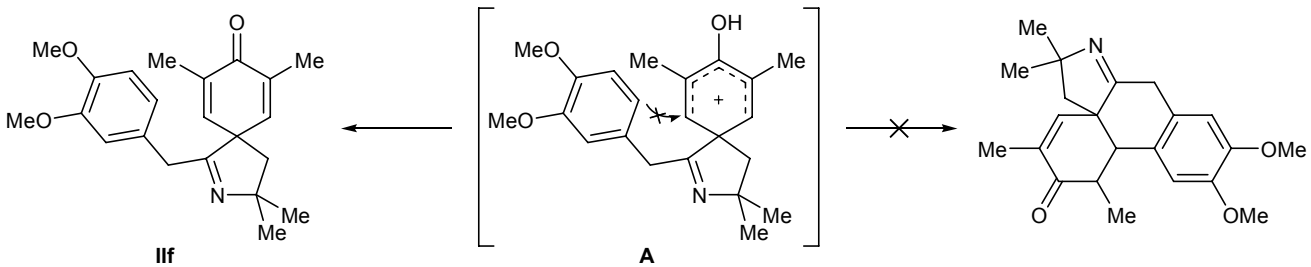
A **IIh** **B**

In the condensation with 3,4-dimethoxyphenylacetonitrile (**If**) as nitrile component we succeeded in isolating for the first time spirane **IIf**. We previously showed [38] that three-component reaction of anisole or *p*-methylanisole with isobutyraldehyde and 3,4-dimethoxyphenylacetonitrile leads to the formation of neospiroenone systems as a result of attack by electron-rich phenyl fragment on intermediate spiro-σ-complex. The formation of compound **IIf** in the three-component condensation with 2,6-dimethylphenol may be rationalized in terms of both reduced positive charge on σ-complex **A** due to effect of the phenolic hydroxy group and stabilization of σ-complex **A** via abstraction of proton from the phenolic hydroxy group, which prevents subsequent cyclization to neospirodienone system (Scheme 3).

As in the reaction with anisole [39], we failed to isolate spirane system in the three-component condensation with chloroacetonitrile due to fast dienone–phenol rearrangement, leading to the formation of only amide **III** as formal classical Ritter reaction product. The corresponding spirane was detected only by GC–MS analysis of the reaction mixture immediately after the reaction was complete (Scheme 4).

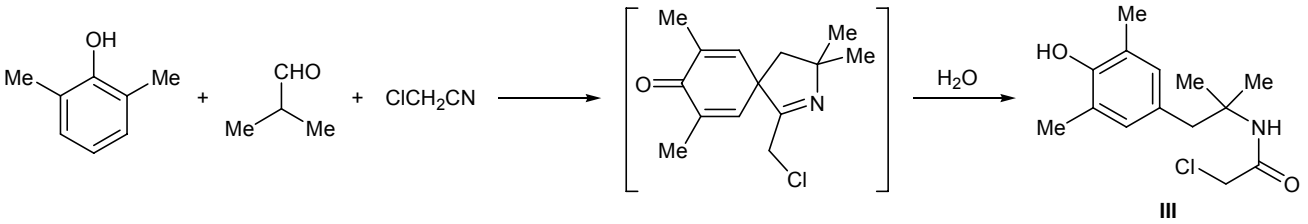
The reaction with malononitrile as nitrile component gave compound **IV** as a result of condensation involving both cyano groups (Scheme 5). The structure of compound **IV** was confirmed by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy, including two-dimensional ^{1}H–^{13}C HSQC and HMBC and ^{1}H–^{15}N HMBC techniques. The ^{1}H and ^{13}C NMR spectra contained only one set of signals corresponding to "symmetric" structure **IV**. The intensity of the methyl protons signals at δ 1.42 (3-CH_3) and 1.85 ppm (7-CH_3, 9-CH_3) was equivalent to 12 protons, and the singlet at δ 2.02 ppm (methylene protons) had an intensity of 4H with respect to the CH

Scheme 3.



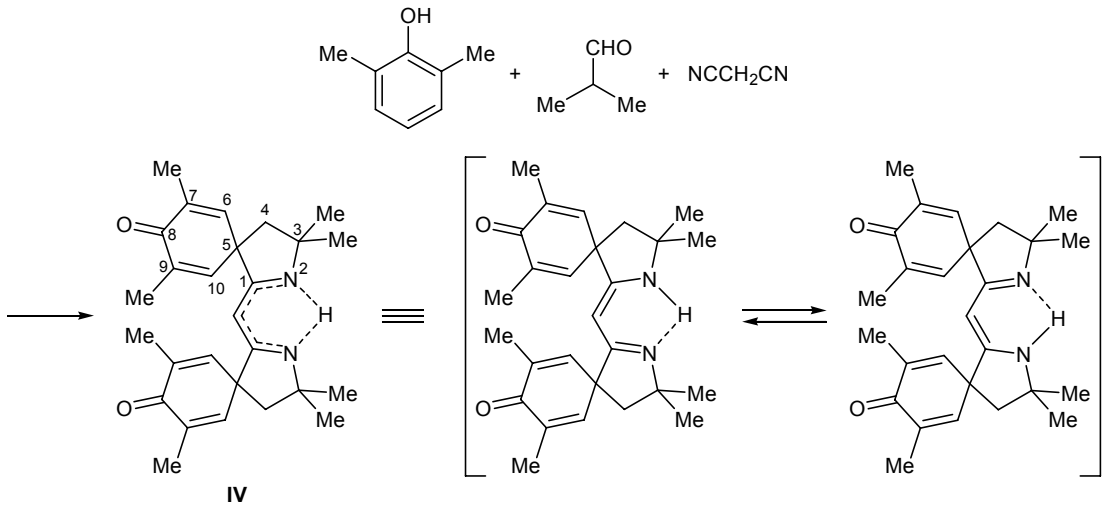
IIf **A**

Scheme 4.



III

Scheme 5.



IV

signal at δ 3.80 ppm. The NH signal in the spectrum recorded from a solution of **IV** in $CDCl_3$ appeared in the δ range from 2 to 6 ppm; it was so broadened that it was difficult to distinguish it from the baseline. Compound **IV** in DMSO-d_6 displayed a broadened signal centered at δ ~9 ppm with a width of ~200 Hz. The chemical shift of the CH carbon atom (δ_C 78.87 ppm) indicates its average hybridization between sp^2 and sp^3. The ^1H–^{15}N HMBC spectrum contained only one signal from nitrogen atom coupled through three bonds with the CH proton and protons in the C^4H_2 and $C^3(CH_3)_2$ groups. The chemical shift of the nitrogen (δ_N 220.2 ppm) can also be interpreted as an average value between enamine and imine nitrogen atoms. This is confirmed by the ^{15}N chemical shifts measured for structurally related compounds **IIa** and **IIh** (Fig. 2).

Thus the above spectral data indicate that compound **IV** in solution exists as symmetric structure with delocalized electron density (fast interconversion of one enaminoazomethine tautomer into another).

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on Varian Mercury Plus (300.06 and 75.46 MHz, HMDS) and Bruker Avance-500 spectrometers (500.13 and 125.76 MHz, respectively; TMS as internal reference). The ^{15}N NMR spectra were measured on a Bruker Avance-500 spectrometer at 50.7 MHz using liquid ammonia as external reference. The mass spectra were obtained on an Agilent Technologies 6890N/5975B GC–MS system [HP-5ms column, 30 m×0.25 mm, film thickness 0.25 μm; carrier gas helium; electron impact, 70 eV; ion source temperature 200°C] and on a Varian MAT 311A spectrometer (electron impact, 70 eV). The elemental compositions were determined on a Leco CHNS-932 analyzer. The IR spectra were recorded on a Bruker IFS-66 spectrometer with Fourier transform from samples dispersed in mineral oil. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates; spots were visualized by treatment with a 0.5% solution of tetrachloro-1,4-benzoquinone in toluene. Silica gel (0.06–0.20 mm, 70–230 mesh; Lancaster) was used for preparative column chromatography. The melting points were measured on a PTP melting point apparatus and are uncorrected.

X-Ray analysis of compoun IIg. Single crystals of **IIg** were obtained by crystallization from ethyl acetate. The X-ray diffraction data were acquired at 295(2) K on an Xcalibur-3 diffractometer equipped with a CCD

detector (MoK_α irradiation, graphite monochromator, ω-scanning). The structure was solved by the direct method using SHELXS-97 and was refined in anisotropic approximation (isotropic for hydrogen atoms) using SHELXL-97. The crystallographic data and parameters of X-ray diffraction experiment are given in table.

Compounds IIa–IIj, III, and IV (*general procedure*). A mixture of 5 mmol of 2,6-dimethylphenol, 5 mmol of isobutyraldehyde, and 5 mmol of nitrile **Ia**–**Ih** in 1 ml of methylene chloride was added dropwise under stirring to 6 ml of 92% sulfuric acid cooled with ice water. The mixture was stirred for 20 min at room temperature, poured into a mixture of ice and 25 ml of aqueous ammonia, and extracted with methylene chloride (3×25 ml). The combined extracts were dried over $MgSO_4$, the solvent was distilled off, and the residue was crystallized from appropriate solvent or purified by chromatography.

3,3,7,9-Tetramethyl-1-methylsulfanyl-2-azaspiro-[4.5]deca-1,6,9-trien-8-one (IIa). Yield 0.43 g (35%), mp 95.5–97.5°C (from hexane–ethyl acetate). IR spectrum, ν, cm^{-1}: 1665, 1637, 1588. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 s (6H, 3-CH_3), 1.92 s (6H, 7-CH_3, 9-CH_3), 2.15 s (2H, CH_2), 2.36 s (3H, SMe), 6.50 (2H, 6-H, 10-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.89 (SMe), 16.06 (7-CH_3, 9-CH_3), 31.01 (3-CH_3), 48.97 (C^4), 61.78 and 74.06 (C^3, C^5), 134.93 (C^7, C^9), 144.81 (C^6, C^{10}), 168.32 (C^1), 186.15 (C^8). ^{15}N NMR spectrum ($CDCl_3$): δ_N 323.6 ppm. Mass spectrum, *m*/*z* (I_{rel}, %): 249 (0.6) $[M]^+$, 234 (4.7) $[M - Me]^+$, 176 (100) $[M - MeSCN]^+$, 161 (66.6) $[M - MeSCN - Me]^+$, 146 (3.4), 134 (16.5), 121 (36), 106 (3.1), 91 (16.6), 65 (5.2), 41 (8.1). Found, %: C 67.25; H 7.80; N 5.74; S 12.93. $C_{14}H_{19}NOS$. Calculated, %: C 67.47; H 7.63; N 5.62; S 12.90.

3,3,7,9-Tetramethyl-1-phenyl-2-azaspiro[4.5]-deca-1,6,9-trien-8-one (IIb). Yield 0.80 g (57%), mp 125–127°C (from hexane–ethyl acetate). IR spectrum, ν, cm^{-1}: 3055, 1661, 1623, 1606, 1574, 1540. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.49 s (6H, 3-CH_3), 1.94 s (6H, 7-CH_3, 9-CH_3), 2.19 s (2H, CH_2), 6.75 s (2H, 6-H, 10-H), 7.30 m (3H, Ph), 7.63 m (2H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.15 (7-CH_3, 9-CH_3), 30.66 (3-CH_3), 49.63 (C^4), 60.85, 72.18 (C^3, C^5), 127.53, 128.16, 130.36 (Ph), 133.74, 134.43 (Ph, C^7, C^9), 146.90 (C^6, C^{10}), 166.46 (C^1), 186.26 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 279 (0.2) $[M]^+$, 176 (100) $[M - PhCN]^+$, 161 (64.8) $[M - PhCN - Me]^+$, 145 (5.3), 134 (13.0), 121 (28.7), 103 (27.5), 91.1 (14), 77 (11.2), 65 (3.4), 51 (3.9), 41 (4.2). Found, %: C 81.42; H 7.44; N 5.04. $C_{19}H_{21}NO$. Calculated, %: C 81.68; H 7.58; N 5.01.

Crystallographic data for 1,3,3,7,9-pentamethyl-2-azaspiro-[4.5]deca-1,6,9-trien-8-one (**IIg**) and parameters of X-ray diffraction experiment

Parameter	Value
Formula	$C_{14}H_{19}NO$
Molecular weight	217.31
Crystal system	Monoclinic
Space group	*C*2/*c*
a, Å	11.5115(10)
b, Å	11.1898(10)
c, Å	20.184(3)
α, deg	90.00
β, deg	94.537(9)
γ, deg	90.00
V , $Å^3$	2591.8(5)
Z	8
d_{calc}, g/cm^{-3}	1.114
μ, mm^{-1}	0.069
Scan range, deg	2.79–26.36
Total number of reflections	4450
Number of independent reflections	2561
Number of refined parameters	150
R_{int}	0.0331
R, %	4.35
R_1 for reflections with $I > 2(I)$	0.0435
wR_2	0.0898
R_1 for all reflections	0.1170
wR_2	0.0990

1-(3,4-Dimethoxyphenyl)-3,3,7,9-tetramethyl-2-azaspiro[4.5]deca-1,6,9-trien-8-one (IIc). Yield 0.98 g (58%), mp 118–120°C (from propan-2-ol). IR spectrum, ν, cm^{-1}: 3000, 1662, 1633, 1603, 1578, 1514. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.48 s (6H, 3-CH_3), 1.94 s (6H, 7-CH_3, 9-CH_3), 2.18 s (2H, CH_2), 3.79 s (3H, OMe), 3.86 s (3H, OMe), 6.71 d (1H, 5′-H, ^3J = 8.6 Hz), 6.78 s (2H, 6-H, 10-H), 7.19 d.d (1H, 6′-H, ^3J = 8.6, ^4J = 1.9 Hz), 7.34 d (1H, 2′-H, ^4J = 1.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.03 (7-CH_3, 9-CH_3), 30.66 (3- CH_3), 49.56 (C^4), 55.49 (OMe), 55.60 (OMe), 60.69 and 71.88 (C^3, C^5), 110.07 and 110.22 ($C^{2'}$, $C^{5'}$), 120.76 ($C^{6'}$), 126.41 ($C^{1'}$), 134.02 (C^7, C^9); 147.43, 148.23, 150.71 (C^6, C^{10}, $C^{3'}$, $C^{4'}$), 165.25 (C^1), 186.14 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %):

339 (1.7) $[M]^+$, 205 (1.0), 176 (100) $[M - (MeO)_2C_6H_3CN]^+$, 161 (58.6) $[M - (MeO)_2C_6H_3CN - Me]^+$, 148 (11.9), 134 (8.4), 121 (19.5), 105 (8.1), 91 (12.6), 77 (10.7), 65 (7.3), 51 (2.7), 41 (3.9). Found, %: C 73.92; H 7.32; N 4.13. $C_{21}H_{25}NO_3$. Calculated, %: C 74.31; H 7.42; N 4.13.

3,3,7,9-Tetramethyl-1-(pyridin-2-yl)-2-azaspiro-[4.5]deca-1,6,9-trien-8-one (IId). Yield 0.50 g (36%), mp 136–137°C (from hexane–ethyl acetate). IR spectrum, ν, cm^{-1}: 3059, 3009, 1667, 1633, 1611, 1581, 1534. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.52 s (6H, 3-CH_3), 1.91 s (6H, 7-CH_3, 9-CH_3), 2.19 s (2H, CH_2), 6.68 s (2H, 6-H, 10-H), 7.21 d.d.d (1H, 5′-H, ^3J = 7.7, 4.8, ^4J = 0.9 Hz), 7.61 t.d (1H, 4′-H, ^3J = 7.7, ^4J = 1.8 Hz), 7.76 br.d (1H, 3′-H, ^3J = 7.0 Hz), 8.45 br.d (1H, 6′-H, ^3J = 4.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 16.15 and 16.03 (7-CH_3, 9-CH_3), 30.64 (3-CH_3), 48.92 (C^4), 60.50 and 72.98 (C^3, C^5), 122.47 and 124.48 ($C^{3'}$, $C^{5'}$), 134.04 (C^7, C^9), 135.91 ($C^{4'}$), 146.17 (C^6, C^{10}), 149.18 ($C^{2'}$), 167.34 (C^1), 186.83 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 280 (15.1) $[M]^+$, 237 (1.2), 197 (1.5), 176 (100) $[M - C_5H_4NCN]^+$, 161 (76.3) $[M - C_5H_4NCN - Me]^+$, 146 (4.5), 134 (17.1), 121 (36.4), 105 (30.2), 91 (18.1), 77 (14.4), 65 (4.4), 51 (6.3), 41 (6.1). Found, %: C 76.89; H 7.01; N 9.93. $C_{14}H_{19}NO$. Calculated, %: C 77.11; H 7.19; N 9.99.

1-Benzyl-3,3,7,9-tetramethyl-2-azaspiro[4.5]-deca-1,6,9-trien-8-one (IIe). Yield 0.56 g (38%), mp 95–106°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3032, 1665, 1647, 1626. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.43 s (6H, 3-CH_3), 1.76 s (6H, 7-CH_3, 9-CH_3), 2.00 s (2H, CH_2), 3.37 s (2H, CH_2), 6.23 s (2H, 6-H, 10-H), 7.16 m (5H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.82 (7-CH_3, 9-CH_3), 30.63 (3-CH_3), 36.61 (CH_2), 47.50 (C^4), 62.43 and 73.35 (C^3, C^5); 126.40, 128.10, 128.75 (Ph); 134.90, 136.44 (C^7, C^9, Ph); 145.11 (C^6, C^{10}), 168.91 (C^1), 186.06 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 293 (0.2) $[M]^+$, 176 (100) $[M - PhCH_2CN]^+$, 161 (64) $[M - PhCN - Me]^+$, 146 (4.2), 134 (13.9), 121 (31.8), 117 (28.3), 105 (9), 91 (31.3), 77 (8.4), 65 (7.1), 51 (4.4), 41 (5.4). Found, %: C 81.67; H 7.74; N 4.79. $C_{20}H_{23}NO$. Calculated, %: C 81.87; H 7.90; N 4.77.

1-(3,4-Dimethoxybenzyl)-3,3,7,9-tetramethyl-2-azaspiro[4.5]deca-1,6,9-trien-8-one (IIf). Yield 1.13 g (64%), mp 106–112°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3001, 1664, 1634, 1591, 1514. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.43 (6H, 3-CH_3), 1.78 s (6H, 7-CH_3, 9-CH_3), 2.00 s (2H, CH_2), 3.30 s (2H, CH_2), 3.81 s (3H, OMe), 3.83 s (3H, OMe), 6.24 s (2H, 6-H, 10-H), 6.57 d.d (1H, 6′-H, ^3J = 8.3, ^4J = 1.9 Hz), 6.69 d (1H, 2′-H, ^4J = 1.9 Hz), 6.72 d (1H, 5′-H, ^3J = 8.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.69 (7-CH_3, 9-CH_3), 30.66 (3-CH_3), 36.18 (CH_2), 47.94 (C^4), 55.71 (OMe), 55.91 (OMe), 62.61 and 73.36 (C^3, C^5); 111.68, 112.47, 121.39 ($C^{2'}$, $C^{5'}$, $C^{6'}$); 129.32 ($C^{1'}$), 134.96 (C^7, C^9), 144.98 (C^6, C^{10}), 147.94 and 149.07 ($C^{3'}$, $C^{4'}$), 169.16 (C^1), 185.96 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 353 (1.1) $[M]^+$, 177 (100) $[M - (MeO)_2C_6H_3CH_2CN + H]^+$, 161 (49.1) $[M - (MeO)_2C_6H_3CH_2CN - Me]^+$, 146 (10.3), 135 (14.6), 121 (14.3), 107 (19.2), 91 (15.9), 77 (10), 65 (6.4), 51 (4.3), 41 (2.6). Found, %: C 74.35; H 7.60; N 3.95. $C_{22}H_{27}NO_3$. Calculated, %: C 74.76; H 7.70; N 3.96.

1,3,3,7,9-Pentamethyl-2-azaspiro[4.5]deca-1,6,9-trien-8-one (IIg) was synthesized from 5 mmol of 2,6-dimethylphenol, 5 mmol of isobutyraldehyde, and 15 mmol of acetonitrile. Yield 0.47 g (43%), mp 95–97°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 1644, 1630, 1543. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 s (6H, 3-CH_3), 1.72 s (3H, 1-CH_3), 1.93 s (6H, 7-CH_3, 9-CH_3), 2.06 s (2H, CH_2), 6.47 s (2H, 6-H, 10-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.18 and 15.74 (1-CH_3, 7-CH_3, 9-CH_3), 30.48 (3-CH_3), 47.13 (C^4), 62.34 and 73.12 (C^3, C^5), 135.03 (C^7, C^9), 144.94 (C^6, C^{10}), 167.36 (C^1), 185.81 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 217 (0.4) $[M]^+$, 202 (2.1) $[M - Me]^+$, 176 (100) $[M - MeCN]^+$, 161 (85) $[M - MeCN - Me]^+$, 147 (5.7), 134 (21.2), 121 (45.3), 105 (11.7), 91 (22.7), 77 (10), 65 (6.2), 41 (13.2). Found, %: C 77.39; H 8.54; N 6.46. $C_{14}H_{19}NO$. Calculated, %: C 77.38; H 8.81; N 6.45.

3,3,7,9-Tetramethyl-1-(pyridin-2-ylmethylidene)-2-azaspiro[4.5]deca-6,9-dien-8-one (IIh). Yield 0.40 g (27%), mp 166–167.5°C (from propan-2-ol). IR spectrum, ν, cm^{-1}: 3283, 3023, 1663, 1624, 1587, 1537. ^1H NMR spectrum ($CDCl_3$), δ, ppm: tautomer **A**: 1.49 s (6H, 3-CH_3), 1.93 s (6H, 7-CH_3, 9-CH_3), 2.13 s (2H, CH_2), 4.70 s (1H, =CH), 6.72 s (2H, 6-H, 10-H), 6.74 d.d.d (1H, 5′-H, ^3J = 7.7, 5.3, ^4J = 1.0 Hz), 6.74 d.m (1H, 3′-H, ^3J = 7.7 Hz), 7.39 t.d (1H, 4′-H, ^3J = 7.7, ^4J = 1.6 Hz), 8.37 d.d (1H, 6′-H, ^3J = 5.3, ^4J = 1.6 Hz), 8.86 br.s (1H, NH); tautomer **B**: 1.44 s (6H, 3-CH_3), 1.78 s (6H, 7-CH_3, 9-CH_3), 2.04 s (2H, 4-H), 3.61 s (2H, CH_2), 6.33 s (2H, 6-H, 10-H), 7.08 d.d.d (1H, 5′-H, ^3J = 7.7, 5.0, ^4J = 1.0 Hz), 7.14 d.m (1H, 3′-H, ^3J = 7.7 Hz), 7.57 t.d (1H, 4′-H, ^3J = 7.7, ^4J = 1.8 Hz), 8.47 d.d (1H, 6′-H, ^3J = 5.0, ^4J = 1.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: tautomer **A**: 16.10 (7-CH_3, 9-CH_3), 31.62 (3-CH_3), 47.22 (C^4), 52.90 and 60.18 (C^3, C^5), 87.68 (CH=), 116.35 and

120.71 ($C^{3'}$, $C^{5'}$), 132.77 (C^7, C^9), 135.36 ($C^{4'}$); 147.33, 147.67, 151.89 (C^6, C^{10}, $C^{2'}$, $C^{6'}$); 159.65 (C^1), 187.15 (C^8). ^{15}N NMR spectrum ($CDCl_3$), δ_N, ppm: **A**: 119.8 (N^2), 288.5 ($N^{1'}$); **B**: 349.2 (N^2), 313.5 ($N^{1'}$). Mass spectrum, *m*/*z* (I_{rel}, %): 294 (9.3) $[M]^+$, 176 (100) $[M - NHCH{=}CHC_5H_4N]^+$, 161 (76.3), 146 (8.2), 135 (15.9), 119 (59.1), 105 (11.4), 91 (26.6), 78 (23.8), 65 (10.5), 51 (9.2), 41 (7.7). Found, %: C 81.67; H 7.74; N 4.79. $C_{20}H_{23}NO$. Calculated, %: C 81.87; H 7.90; N 4.77.

Methyl 2-(3,3,7,9-tetramethyl-8-oxo-2-azaspiro-[4.5]deca-6,9-dien-1-ylidene)acetate (IIi). Yield 0.72 g (52%), mp 155–156°C (from ethanol). IR spectrum, ν, cm^{-1}: 3360, 3256, 1661, 1633, 1602. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.41 s (6H, 3-CH_3), 1.81 s (6H, 7-CH_3, 9-CH_3), 2.11 s (2H, CH_2), 3.47 s (3H, OCH_3), 3.91 s (1H, =CH), 6.79 s (2H, 6-H, 10-H), 8.26 br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 15.60 (7-CH_3, 9-CH_3), 30.36 (3-CH_3), 45.56 (C^4), 49.60 (OCH_3), 52.78 and 61.66 (C^3, C^5), 75.30 (=CH), 132.63 (C^7, C^9), 146.36 (C^6, C^{10}), 162.34 (C^1), 169.11 (C=O), 185.78 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 275 (87.5) $[M]^+$, 260 (24.9) $[M - Me]^+$, 243 (26.6), 228 (56.9), 216 (57.1) $[M - COOMe]^+$, 200 (22.4), 188 (20.2), 176 (91.3) $[M - NHCH{=}CHCOOMe]^+$, 161 (100) $[M - NHCH{=}CHCOOMe - Me]^+$, 148 (9.1), 134 (23.5), 121 (47.5), 105 (14.4), 91 (27.7), 77 (13), 68 (13.3), 55 (10.8). Found, %: C 69.47; H 7.57; N 5.05. $C_{16}H_{21}NO_3$. Calculated, %: C 69.79; H 7.69; N 5.09.

Ethyl 2-(3,3,7,9-tetramethyl-8-oxo-2-azaspiro-[4.5]deca-6,9-dien-1-ylidene)acetate (IIj). Yield 0.82 g (57%), mp 157–158.5°C (from ethanol). IR spectrum, ν, cm^{-1}: 3364, 3246 w, 1663, 1631, 1602. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.11 t (3H, CH_2CH_3, ^3J = 7.1 Hz), 1.41 s (6H, 3-CH_3), 1.81 s (6H, 7-CH_3, 9-CH_3), 2.11 s (2H, CH_2), 3.90 s (1H, =CH), 3.98 q (2H, OCH_2, ^3J = 7.1 Hz), 6.79 s (2H, 6-H, 10-H), 8.26 br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 14.58 (CH_2CH_3), 15.59 (7-CH_3, 9-CH_3), 30.39 (3-CH_3), 45.56 (C^4), 57.78 (OCH_2), 52.76 (C^5), 61.63 (C^3, C^5), 75.56 (=CH), 132.60 (C^7, C^9), 146.37 (C^6, C^{10}), 162.33 (C^1), 168.83 (C=O), 185.78 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 289 (59.5) $[M]^+$, 274 (14.6) $[M - Me]^+$, 244 (21.9) $[M - OEt]^+$, 228 (40.2), 216 (43.5) $[M - COOEt]^+$, 200 (15.9), 188 (13.4), 176 (100) $[M - NHCH{=}CHCOOEt]^+$, 161 (87.6) $[M - NHCH{=}CHCOOEt - Me]^+$, 148 (8.2), 134 (20.9), 121 (42.8), 114 (16.5), 105 (13.2), 91 (23), 86 (14.6), 77 (10.3), 55 (10). Found, %: C 70.30; H 7.83; N 4.79. $C_{17}H_{23}NO_3$. Calculated, %: C 70.56; H 8.01; N 4.84.

2-Chloro-*N*-[1-(4-hydroxy-3,5-dimethylphenyl)-2-methylpropan-2-yl]acetamide (III). Yield 0.47 g (35%), mp 125–126°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3385, 3291, 2995, 1659, 1598, 1536. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 s [6H, $C(CH_3)_2$], 2.22 s (6H, 3′-CH_3, 5′-CH_3), 2.83 s (2H, CH_2), 3.93 s (2H, CH_2Cl), 4.64 br.s (1H, OH), 6.31 br.s (1H, NH), 6.74 s (2H, 2′-H, 6′-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.94 (3′CH_3, 5′-CH_3), 26.56 [$C(CH_3)_2$], 42.98 and 44.98 (CH_2Cl, CH_2); 54.11 [$C(CH_3)_2$], 122.97 and 128.35 ($C^{1'}$, $C^{3'}$, $C^{5'}$), 130.48 ($C^{2'}$, $C^{6'}$), 151.10 ($C^{4'}$), 165.22 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 269 (2) $[M]^+$, 176 (57) $[M - NH(CO)CH_2Cl - H]^+$, 161 (11), 147 (6), 134 (100), 121 (6), 115 (4), 105 (4), 91 (14), 77 (8), 58 (94), 42 (4). Found, %: C 62.25; H 7.53; N 5.14. $C_{14}H_{20}ClNO_2$. Calculated, %: C 62.33; H 7.47; N 5.19.

3,3,7,9-Tetramethyl-1-[(3,3,7,9-tetramethyl-8-oxo-2-azaspiro[4.5]deca-1,6,9-trien-1-yl)methylidene]-2-azaspiro[4.5]deca-6,9-dien-8-one (IV) was synthesized from 5 mmol of 2,6-dimethylphenol, 5 mmol of isobutyraldehyde, and 2.5 mmol of malononitrile. Yield 0.26 g (22%), mp 221–224°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 1664, 1634, 1600, 1536. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 1.42 s (12H, 3-CH_3, 3′-CH_3), 1.85 s (12H, 7-CH_3, 7′-CH_3, 9-CH_3, 9′-CH_3), 2.02 s (4H, 4-H, 4′-H), 3.80 s (1H, CH), 6.53 s (4H, 6-H, 6′-H, 10-H, 10′-H); in DMSO-d_6: 1.37 s (12H, 3-CH_3), 3′-CH_3), 1.72 s (12H, 7-CH_3, 7′-CH_3, 9-CH_3, 9′-CH_3), 2.02 s (4H, 4-H, 4′-H), 3.58 s (1H, CH), 6.72 s (4H, 6-H, 6′-H, 10-H, 10′-H), 8.95 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.07 (7-CH_3, 7′-CH_3, 9-CH_3, 9′-CH_3), 31.75 (3-CH_3, 3′-CH_3), 47.89 (C^4, $C^{4'}$), 56.93 (C^3, $C^{3'}$), 66.26 (C^5, $C^{5'}$), 78.87 (CH), 133.63 (C^7, $C^{7'}$), 146.51 (C^6, $C^{6'}$), 162.12 (C^1, $C^{1'}$), 186.73 (C^8, $C^{8'}$). ^{15}N NMR spectrum ($CDCl_3$): δ_N 220.2 ppm (N^2, $N^{2'}$). Mass spectrum, *m*/*z* (I_{rel}, %): 418 (6.8) $[M]^+$, 243 (66.3), 227 (12), 212 (2.3), 176 (100), 161 (33), 146 (3.8), 135 (17.7), 121 (13.9), 105 (6.1), 91 (9.1), 77 (4.4), 77 (4.4), 55 (9). Found, %: C 77.06; H 8.11; N 6.63. $C_{27}H_{34}N_2O_2$. Calculated, %: C 77.48; H 8.19; N 6.69.

Compounds IIk–IIm (*general procedure*). Nitrile **Ik–Im**, 5 mmol, was dissolved in 6 ml of 92% sulfuric acid, a mixture of 5 mmol of 2,6-dimethylphenol and 5 mmol of isobutyraldehyde in 1 ml of methylene chloride was added, the mixture was stirred for 20 min at room temperature and poured into a mixture of ice and 25 ml of aqueous ammonia. The precipitate was filtered off, washed with methylene chloride, dried, and recrystallized from DMSO to isolate compounds

IIk and **III**; to isolate compound **IIm**, the mixture was extracted with methylene chloride (3×25 ml), the combined extracts were dried over $MgSO_4$, the solvent was distilled off, and the residue was purified by chromatography using chloroform–acetone (25:1) as eluent.

2-(3,3,7,9-Tetramethyl-8-oxo-2-azaspiro[4.5]-deca-6,9-dien-1-ylidene)acetamide (IIk). Yield 0.63 g (48%), mp 178–179°C. IR spectrum, ν, cm^{-1}: 3429, 3311, 3280, 3186, 1673, 1654, 1625, 1562. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.37 s (6H, 3-CH_3), 1.80 s (6H, 7-CH_3, 9-CH_3), 2.05 s (2H, CH_2), 4.10 s (1H, =CH), 6.15 br.s (2H, NH_2), 6.79 s (2H, 6-H, 10-H), 8.37 br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 15.70 (7-CH_3, 9-CH_3), 30.78 (3-CH_3), 45.82 (C^4), 52.46 and 60.45 (C^3, C^5), 79.92 (CH=), 131.96 (C^7, C^9), 147.44 (C^6, C^{10}), 158.54 (C^1), 171.52 (C=O), 186.09 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 260 (23.5) $[M]^+$, 245 (2.6) $[M - Me]^+$, 228 (10), 216 (5) $[M - CONH_2]^+$, 200 (4.8), 176 (100) [*M* – NHCH=CHCONH$_2$], 161 (82.2), 146 (5.9), 134 (19.6), 121 (37.6), 105 (11.3), 91 (21.8), 85 (19.8), 77 (10.1), 55 (8.5). Found, %: C 69.30; H 7.73; N 10.76. $C_{15}H_{20}N_2O_2$. Calculated, %: C 69.20; H 7.74; N 10.76.

1-(1*H*-Benzimidazol-2-ylmethylidene)-3,3,7,9-tetramethyl-2-azaspiro[4.5]deca-6,9-dien-8-one (III). Yield 0.51 g (31%), mp 234.5°C (decomp.). IR spectrum, ν, cm^{-1}: 3296, 3171, 3020, 1660, 1622, 1530. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.48 s (6H, 3-CH_3), 1.84 s (6H, 7-CH_3, 9-CH_3), 2.20 s (2H, CH_2), 4.57 s (1H, =CH), 6.93 s (2H, 6-H, 10-H), 7.00 m (2H, H_{arom}), 7.21 br.d (1H, H_{arom}, ^3J = 6.9 Hz), 7.43 br.d (1H, H_{arom}, ^3J = 6.6 Hz), 8.47 br.s and 11.49 br.s (1H each, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 15.69 (7-CH_3, 9-CH_3), 31.12 (3-CH_3), 46.54 (C^4), 52.30 and 60.49 (C^3, C^5), 75.44 (CH=), 113.22 ($C^{4'}$, $C^{7'}$), 120.52 and 121.60 ($C^{5'}$, $C^{6'}$), 131.97 and 133.73 ($C^{4a'}$, C^7, $C^{7'}$, C^9), 144.63 and 147.43 (C^6, C^{10}, $C^{2'}$), 161.81 (C^1), 186.12 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 333 (14.9) $[M]^+$, 318 (2.9) $[M - Me]^+$, 176 (39) $[M - NHCH=CHC_7H_6N_2]^+$, 158 (100), 146 (2.5), 131 (11.4), 121 (13.4), 105 (5.7), 91 (9.3), 77 (5.5), 55 (4.9). Found, %: C 75.63; H 7.39; N 12.60. $C_{21}H_{23}N_3O$. Calculated, %: C 75.65; H 6.95; N 12.60.

1-(1,3-Benzothiazol-2-ylmethylidene)-3,3,7,9-tetramethyl-2-azaspiro[4.5]deca-6,9-dien-8-one (IIm). Yield 0.47 g (27%), mp 178–179°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3260, 1662, 1625, 1598. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.53 s (6H, 3-CH_3), 1.93 s (6H, 7-CH_3, 9-CH_3), 2.19 s (2H, CH_2), 4.92 s (1H, =CH), 6.68 s (2H, 6-H, 10-H), 7.15 br.t (1H, H_{arom}, ^3J = 7.9 Hz), 7.32 br.t (1H, H_{arom}, ^3J = 7.9 Hz), 7.67 d.d (1H, H_{arom}, ^3J = 7.9, ^4J = 0.9 Hz), 7.76 d.d (1H, H_{arom}, ^3J = 7.9, ^4J = 0.9 Hz), 8.90 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.03 (7-CH_3, 9-CH_3), 31.28 (3-CH_3), 47.27 (C^4), 52.48 and 60.92 (C^3, C^5), 82.17 (CH=); 120.04, 120.86, 122.58, 125.37 ($C^{4'}$, $C^{5'}$, $C^{6'}$, $C^{7'}$); 132.51 and 133.43 ($C^{7a'}$, C^7, C^9), 145.78 (C^6, C^{10}), 154.07 and 154.53 ($C^{2'}$, $C^{3a'}$), 167.83 (C^1), 186.50 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 350 (34.4) $[M]^+$, 335 (2.8) $[M - Me]^+$, 201 (2.9), 176 (100) $[M - NHCH=CHC_7H_5NS]^+$, 161 (37.5), 149 (22.7), 135 (13.2), 121 (18.9), 108 (8.3), 91 (11.8), 77 (6.7), 55 (8.6). Found, %: C 71.15; H 6.54; N 8.08; S 9.04. $C_{21}H_{22}N_2OS$. Calculated, %: C 71.97; H 6.33; N 7.99; S 9.15.

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