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Aminonitrone-*N*-hydroxyaminoimine tautomeric equilibrium in the series of 1-hydroxy-2-imidazolines

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Abstract

A series of 2-substituted 1-hydroxy-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazoles have been synthesized. Various effects on the state of the aminonitrone-*N*-hydroxyaminoimine tautomeric equilibrium, including solvent effects and substituent effect in the 2 position of heterocycle, have been studied.
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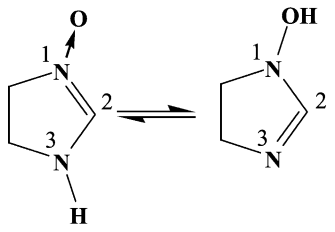
Keywords: Tautomerism; Ab initio calculations; 2-Imidazoline; 4,5-Dihydro-1H-imidazole; Nitrone

1. Introduction

The 1,3-dipolar cycloaddition reaction is a powerful tool for the design of heterocyclic structures. This is a useful approach to syntheses of complex structures with adjusted geometry in view of the high regio- and stereo-selectivity of this reaction. Further transformations of the initially formed cycloadducts make this strategy highly versatile [1]. Nitrones are typical examples of 1,3-dipoles easily participating in cycloaddition reactions. 1,3-Cycloaddition reaction is well studied for nitrones in the series of 2,5-dihydro-1H-imidazole-3-oxides and are still being investigated [2]. Data on cycloadditions of 4,5-dihydro-1H-imidazoles are scarce [3,4]; there is only one instance of the involvement of 4,5-dihydro-1H-imidazole with a nitrone group in the heterocycle as a dipole into cycloaddition reaction [5] No data are available on participation of 4,5-dihydro-1H-imidazole-3-oxide without substituents at the second nitrogen atom in this reaction.

The distinguishing feature of 4,5-dihydro-1H-imidazole-3-oxide with an unsubstituted nitrogen atom is the possibility of existence in two tautomeric forms: aminonitrone (**A**) and *N*-hydroxyaminoimino (**B**) [6].



A **B**

Of these two forms, only **A** can act as a 1,3-dipole; in its reactions with dipolarophiles, form **B** can only act as a nucleophile. Therefore, reactions of compounds of this type with activated alkenes or alkynes as dipolarophiles will probably occur as nucleophilic additions or cycloadditions. Since cycloadditions are generally considered to be concerted processes, the reaction kinetics must depend on the content of the nitrone form; however, no data are available in the literature concerning the state of the **A** ⇄ **B** tautomeric equilibrium. According to the data published in ref.[6], the major form of imidazoline **1d** in ethanolic solutions is aminonitrone. Imidazoline **1c** exists in chloroform

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solutions mainly in *N*-hydroxyaminoimino form [7]. Thus, the available data preclude any conclusions about the composition of the tautomeric mixture, affecting the reactions of 4,5-dihydro-1H-imidazole-3-oxide derivatives with dipolarophiles. The aim of the present work, therefore, is investigation of the influence of the structure and nature of the solvent on the state of the **A** ⇄ **B** tautomeric equilibrium.

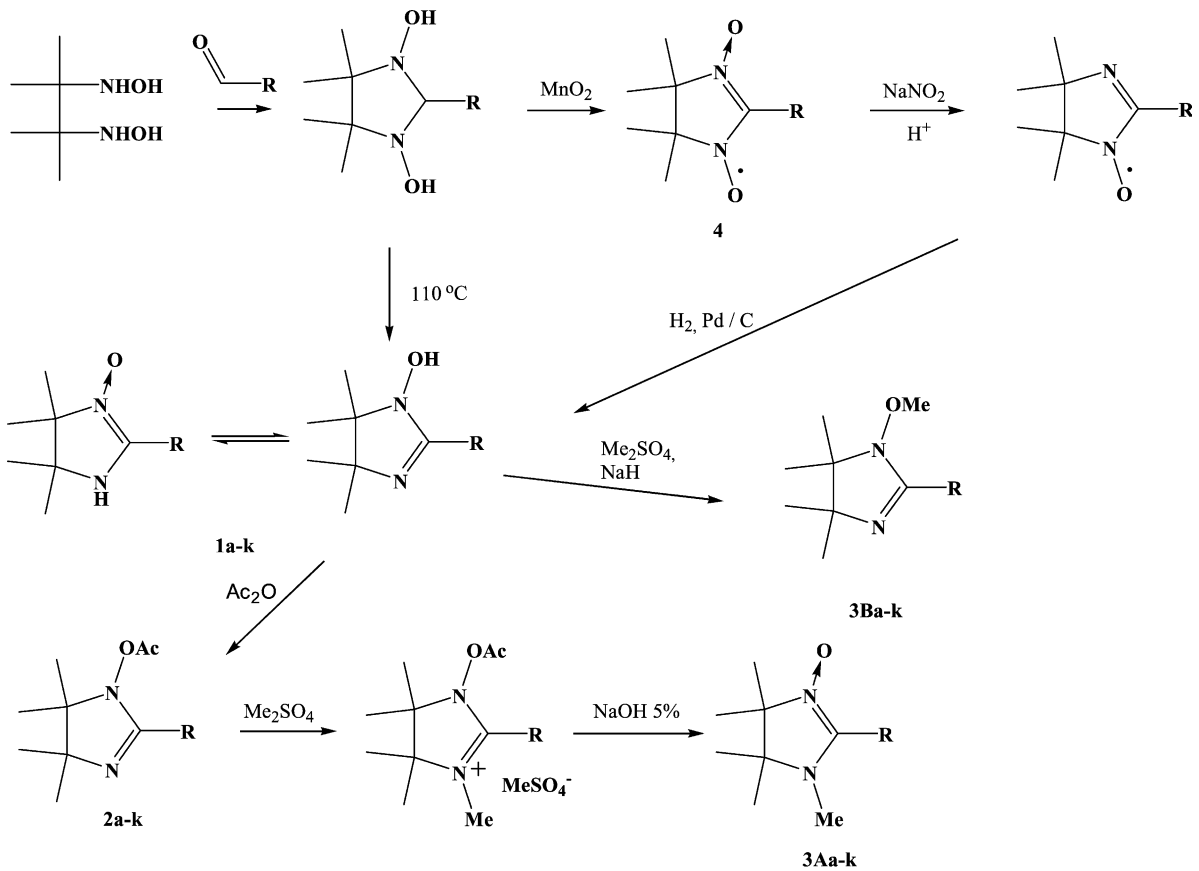
2. Results and discussion

Aminonitrone-*N*-hydroxyaminoimine tautomerism is considered to be an acid-base equilibrium with the ratio between the forms dictated by the ratio of their acidity constants. The state of the [**A**] ⇄ [**B**] tautomeric equilibrium depends on the balance between the stabilizing and destabilizing factors.

The ratio between the tautomeric forms was determined by ^{13}C NMR. In this case, as well as in most acid–base equilibria, proton transfer from one form to another is fast on the NMR time scale, precluding NMR observation of each form separately and direct determination of the ratio between the forms. At temperatures lowered to −90 °C, one can only observe the broadening of the signals of the methyl protons, which may result from the retardation of the imidazoline heterocycle inversion.

The ratio between the tautomeric forms was determined using the position of the metathetical signal relative to the respective signals of 'fixed tautomers' **3Aa–k** and **3Ba–k** in the ^{13}C NMR spectra; $\mathbf{1B} = \mathbf{1A} = \Delta\delta_1/\Delta\delta_2$. The C-2 atom was shown to be most sensitive to tautomeric transformations ($\Delta\delta$ is maximal). Synthesis of 'models' **3B** and **3A** is shown in Scheme 1.

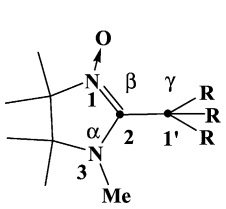
Replacement of the proton at N-1 to the methyl group or of the hydroxy group to the methoxy group can obviously lead to noticeable changes in the positions of the signals of the nearest atoms (1–4 bonds). These changes must be taken into account in determining the ratio between the tautomeric forms (β-, γ- and δ-effects of substituent). Using the chemical shifts of C-1′ for this purpose seems to be justified despite their lower sensitivity to tautomeric transformations, because the substituent introduced at that atom into the model



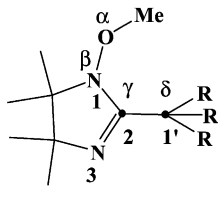
R = CF_3 (a), H (b), CH_3(c), Ph (d), *p*-NO_2-C_6H_4 (e), p-$CH_3OC_6H_4$ (f), 2,4-$(CH_3)_2C_6H_3$ (g), 2,4,6-$(CH_3)_3C_6H_2$ (h) 4-Br-2-HOC_6H_3 (i), 3-OH-2-pyridyl (j), 2-Ph-vinyl (k)

Scheme 1.

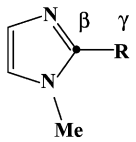
molecule usually has minor effect compared to the substitutent at C-2.



3A(a-k)



3B(a-k)



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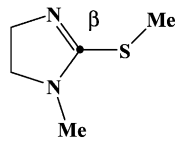

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The β- and γ-effects of the methyl group for the series of *N*-methyl-substituted 4,4,5,5-tetramethyl-2-imidazoline-1-oxides **3Aa–k** were evaluated from literature data for structurally related compounds **5** and **6** (Table 1).

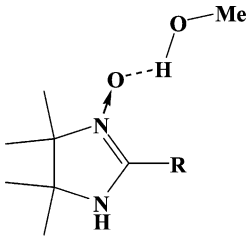
Based on the values of the γ-effect of the methyl group in molecule **5** (Table 1), the γ-effect of the methyl group in 2-substituted 1-methoxy-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazoles **3B** is expected to be 0–1.0 ppm. Replacement of the methyl group by acyl in **2b–e,g** changes the chemical shift of C-2 by only 0.5–1.0 ppm. Moreover, replacement of hydrogen at nitrogen atom to the methyl group of imidazoline **1a**, which in chloroform solutions exists almost entirely in *N*-hydroxyaminoimino form **B** (see below), shifts the signal of C-2 (γ-position) in the ^{13}C NMR spectrum by -0.81 ppm, in which case the δ-effect is shown to be insignificant.

Based on the values of the β- and γ-effect (for **3Ac**, $\beta = 1.1$ ppm, $\gamma = -1.6$ ppm; for **3Bc**, $\gamma = 0.5$ ppm and $\delta = 0.0$ ppm), we determined the composition of the **1Ac** **1Bc** tautomeric mixture using ^{13}C NMR spectra. The C-2 and C-1′ chemical shifts of **1c** along with those of models **3AC** and **3BC** and the tautomer ratio are summarized in Table 2 for different solvents. The tautomer ratios obtained from the C-2 chemical shifts seem to be more reliable than those obtained from the C-1′ chemical shifts due to the correct calculation of methyl group effects and the higher sensitivity of the former to tautomeric transformations.

Table 1
β and γ effects of the methyl group for **5** and **6** based on literature data [9–12]

	5			**6**
	R = H	R = Me	R = Ph	
β	2.8	0.2	0.5	1.1
γ	–	−2.4	0.1	–

The solvent has a pronounced effect on the composition of the tautomeric mixture (Table 2). According to calculations, nitrone form **A** is more polar than *N*-hydroxyaminoimino form **B** (HF/6-31G(d,p), μ(**1Ac**) = 5.43 D, μ(**1Bc**) = 2.35 D); hence, polar solvents stabilize form **A** more effectively than form **B**. Thus, the content of nitrone form **1Ac** grows noticeably with solvent inductivity in the order $CCl_4 < CDCl_3 < CD_2Cl_2$. To evaluate the solvent effect, specific solvation effects must be taken into account along with solvent inductivity. Thus, protic solvents such as methanol are capable of forming hydrogen bonds, which are more important for the nitrone form (structure **7**). Aprotic solvents (DMSO) form solvates of type **8**, stabilizing *N*-hydroxyaminoimino form **B**.



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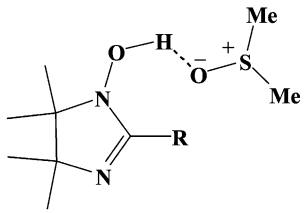

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Thus, in the case of methanol as a solvent, nitrone form **A** is stabilized by both high inductivity and hydrogen bonding. In DMSO, these are counter-effects. This leads to an anomalously high content of form **1Bc** in DMSO-d_6 and immeasurably low content in CD_3OD (Table 2).

Intramolecular hydrogen bonding is even more essential to the **A** : **B** ratio than intermolecular hydrogen bonding. Thus, in contrast to **1b** and **1c**, imidazolines **1i** and **1j** exist in nitrone form **A** even in crystals due to intramolecular hydrogen bonding between the aromatic hydroxyl group and the nitrone oxygen atom [8].

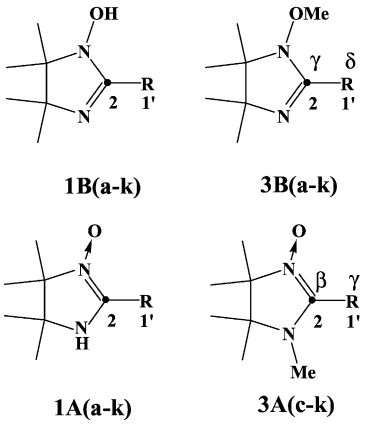
Since in some solvents imidazoline **1c** exists in only one tautomeric form, the β-, γ-, and δ-effects may be evaluated more accuratelyfor each substituent R. Thus, the difference between the C-2 and C-1′ chemical shifts of imidazoline **1c** in *N*-hydroxyaminoimino form **B** (in CCl_4 as a solvent) and the corresponding methoxy derivative **3Bc** actually equals the values of the γ- and δ-effects of the methyl group attached to the oxygen atom. In methanol, **1c** exists in nitrone form, permitting one to calculate the effect of the methyl group attached to nitrogen atom. This assumption gives β(**3Ac**) = 0.2 ppm, γ(**3Ac**) = −1.6 ppm, γ(**3Bc**) = 1.0 ppm, and δ(**3Bc**) = 0.2 ppm. For **1a**,

Table 2
^{13}C NMR chemical shifts of C_2 and $C_{1'}$ atoms in compounds **3Ac**, **3Bc**, and **1c** in different solvents

	ε[a]	C_2				$C_{1'}$			
		3Ac	**1c**	**3Bc**	**B/A**	**3Ac**	**1c**	**3Bc**	**B/A**
CCl_4	2.23	149.37	165.14	164.11	$\gg 10$	9.69	13.49	13.28	$\gg 10$
$CDCl_3$	4.70	146.35	159.27	163.48	2.97 (2.50)	8.74	12.52	13.11	3.64 (2.74)
CD_2Cl_2	8.9	154.50	157.67	163.84	0.64 (0.47)	9.78	12.15	13.49	0.58 (0.50)
CH_3OD	32.6	153.08	152.88	166.26	$\ll 0.1$	8.30	9.89	12.70	$\ll 0.1$
DMSO-d_6	49	151.63	161.68	162.91	6.45 (4.54)	9.12	13.07	13.47	5.88 (3.87)

The values in parentheses calculated using the corrected values of β, γ and δ effects.
[a] Dielectric constants for non-deuterated solvents.

similar calculations give γ(**3Ba**) = 0.81 ppm and δ(**3Ba**) = 0.15 ppm.



1B(a-k) **3B(a-k)**

1A(a-k) **3A(c-k)**

This refinement of the β-, γ-, and δ-effects does not markedly change the calculated ratio of forms, but improves the correlation between the data obtained for the C-2 and C-1′ atoms (Table 2).

The nature of the substituent in the 2 position of the imidazoline heterocycle markedly influences the state of the tautomeric equilibrium. Interaction of the substituent with the π-system changes the acid-base properties of both heteroatomic fragments. Substituent effects on the tautomeric equilibrium were investigated in chloroform (Table 3), because this solvent is not involved in specific interactions with molecule **1**. To calculate the ratio between forms **B** and **A**, we used the averaged values of effects: $\beta = 1.1$ ppm and $\gamma = 0.1$ ppm for **3A** (for **3Ac**, $\gamma = -1.6$ ppm); $\gamma = 0.5$ ppm and $\delta = 0.0$ ppm for **3B**. The accuracy of these estimations is only important if the difference in the concentrations of forms very large.

The form concentrations obtained from the C-2 and C-1′ chemical shifts are in good agreement with each other (Fig. 1). For 2-aryl-substituted compound **1** (R = Ph, *p*-NO_2-Ph, etc.), where **B** : **A** < 1, the inverse proportion, **A** : **B**, is more appropriate.

The substituent effect at the C-2 atom of imidazoline seems to be the result of the action of several factors (inductive or mesomeric effects, polarity, etc.). One of possible reasons for the shift of the tautomeric equilibrium is unequal modification of the acidity constants of the tautomeric forms. The degree of stabilization must be proportional to changes in electron density on the atoms bearing the acid proton (N-3 and O). Increased electron density results in increased X–H bond order, stabilizing the structures. Decreased electron density acts oppositely. The inductive effect is known to decrease noticeably on the distance. The distances between the N- and O-acidic centers and the **R** substituent differ in tautomers **B** and **A**: three and two bonds, respectively. The ability of a bond to transmit polarization effect increases with bond order, changing oppositely with the length of the bond. Typical

Table 3
^{13}C NMR chemical shifts of C_2 and $C_{1'}$ atoms (chloroform) of **3A**, **3B**, and **1** and the **B**:**A** ratio

R	C_2				$C_{1'}$			
	3A	**1**	**3B**	**B**:**A**	**3A**	**1**	**3B**	**B**:**A**
a	136.5[a]	155.6	154.79	$\gg 10$	111.2[a]	117.44	117.29	$\gg 10$
b	138[a]	153.34	156.32	4.72	–	–	–	–
c	146.35	159.27	163.84	2.97	8.736	12.515	13.114	3.64
d	145.79	147.67	164.95	0.17	125.49	126.38	131.299	0.20
e	145.05	148.05	163.14	0.26	131.33	132.69	137.55	0.30
f	147.05	144	164.96[b]	<0.1	117.18	118.18	122.72	0.18
g	147.35	155.05	165.38	0.81	122.25	125.49	128.31	1.18
h	148	152	165.06[b]	0.38	121.7	123.88	127.73	0.59
k	142.82	145.89	162.07[b]	0.25	109.16	110.77	115.59	0.35

[a] Calculated from the experimental values of substituent α-effects ($\alpha_H = 0$ ppm, $\alpha_{CF3} \approx -1.5$ ppm).
[b] NMR of acyl-substituted derivatives **2f**, **h**, **k**. The difference between the γ-effects was taken into account ($\Delta\gamma \approx 1.0$ ppm).

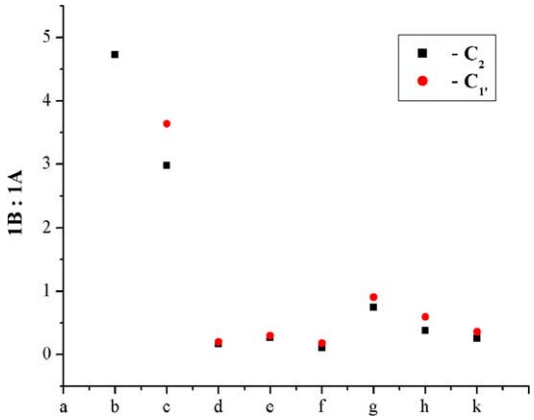


Fig. 1. The values of **1B(b-k)**: **1A(b-k)** and C_2 (C_1) correlation.

bond lengths reported in the literature are C–N 1.514 (Å), C=N 1.281 (Å), [13] N–O 1.460 (Å), [14] and N=O 1.197 (Å) [15]. On the other hand, according to X-ray analysis data and quantum-mechanical calculations (Table 4), N_1–C_2 and N_1–O in **2** and C_2–N_3 in **1A** are very nearly single bonds. Hence, the inductive effect of substituent R is greater on nitrogen compared to oxygen, and the substituent with a negative (−I) inductive effect, will destabilize the nitrone form more effectively compared to the *N*-hydroxyaminoimino form. Substituents with a positive (+I) inductive effect will stabilize nitrone form **A**. Thus, the content of the nitrone form changes as follows: $CH_3 > H > CF_3$ (Table 3).

The substituent attached to an sp^2-hybridized carbon displays a −I effect. At the same time, it can have a strong mesomeric effect. The larger the overlap integral, the higher the efficiency of the transmission. According to X-ray analysis data and quantum-mechanical calculations (Table 4), the bond order for N_1–C_2 in form **B** and C_2–N_3 in form **A** is higher than single, leading to an overlap

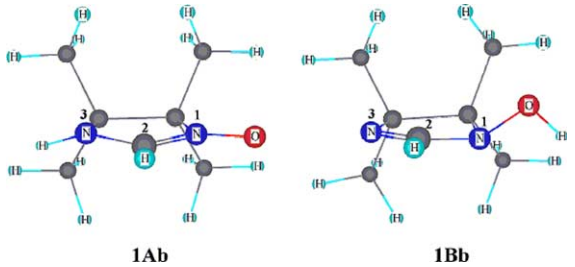


Fig. 2. The spatial structure of **1Ab** (ab initio calculations) and **1Bb** (X-ray analysis data).

between the atomic orbitals of N_1 and N_3 and the π-system of the substituent.

The spatial structure of **1Bb** and **1Ab** according to X-ray analysis data and ab initio calculations is shown in Fig. 2. The hydroxyl oxygen atom in tautomer **1Bb** and the hydrogen atom of the N–H bond in **1Ab** are out of the plane of π-conjugation (N_1–C_2–N_3), which hinders effective involvement of the lone electron pairs of nitrogen and oxygen in conjugation (Table 5). The N_1–C_2 bond in form **B** is long, the bond order being thus lower than that of C_2–N_3 in form **A** (Table 4). For N_1–O, the bond order is slightly higher than single (Table 4), indicating that the π-overlap is insignificant and the transmission of the mesomeric effect from substituent to this center is inefficient. Hence, the mesomeric effect of substituent does not change electron density on oxygen as greatly as it does on N-3. This is confirmed by the calculated Mulliken charges on N-3 and O (Table 6). According to calculations, charge variation is 0.017 $\bar{e}$ on oxygen and 0.048 $\bar{e}$ on N-3. Hence, when we introduce a substituent with a positive (+M) mesomeric effect, greater stabilization is achieved for the nitrone form. Introduction of phenyl or substituted phenyl groups into

Table 4
N_1–C_2, C_2–N_3, and N_1–O bond lengths (Å) in **1A(a–k)** and **1B(a–k)** according to X-ray data and HF/6-31G (d,p) ab initio quantum-mechanical calculations

R	A		B			
	Ab initio	X-ray	Ab initio		X-ray	
	C_2–N_3	C_2–N_3	N_1–C_2	N_1–O	N_1–C_2	N_1–O
a	1.384		1.395	1.383		
b	1.383		1.394	1.386	1.357	1.407
c	1.385		1.403	1.386		
d	1.391		1.408	1.386	1.394	1.415
e	1.392		1.405	1.386		
f	1.391		1.408	1.386		
g	1.388		1.410	1.386		
h	1.388		1.407	1.385		
I	1.377[a]	1.357	1.402[a]	1.383[a]		
j	1.367	1.346	1.391	1.387		
k	1.389		1.405	1.385		

[a] The bromine atom was exchanged for chlorine for simplification of calculations.

Table 5
$N_1C_2N_3H$ and $N_3C_2N_1O$ dihedral angles in **1A(a–k)** and **1B(a–k)** according to X-ray data and HF/6-31G (d,p) ab initio quantum-mechanical calculations

R	A		B	
	∠$N_1C_2N_3H$		∠$N_3C_2N_1O$	
	Ab initio	X-ray	Ab initio	X-ray
a	147.40		148.93	
b	146.37		148.98	153.26
c	147.33		149.88	
d	143.74		146.83	150.74
e	143.21		146.62	
f	143.49		147.22	
g	147.29		146.38	
h	146.61		147.93	
I	147.21[a]	155.94	147.53[a]	
j	152.85	164.02	145.97	
k	146.61		150.03	

[a] Bromine atom was exchanged for chlorine for the simplification of calculations.

Table 6
The values of Mulliken charges at N-3 and O for **A** and **B** in ē, calculated ab initio HF/6-31G(d,p)

R	A (N_3)	B (O)
a	−0.670	−0.490
b	−0.655	−0.497
c	−0.675	−0.496
d	−0.701	−0.488
e	−0.701	−0.488
f	−0.703	−0.488
g	−0.674	−0.489
h	−0.679	−0.491
i[a]	−0.701	−0.482
j	−0.685	−0.499
k	−0.691	−0.494

[a] Bromine atom was exchanged for chlorine for the simplification of calculations.

molecule **1** significantly increases the content of nitrone form **A** (Table 3). Introduction of a substituent with an appreciable −M (NO_2) or +M (OCH_3) effect into the *para*-position of the phenyl group markedly changes the π-donor properties of the substituent, incidentally changing its inductive effect. The *para*-nitrophenyl group decreases the content of the nitrone form because of its minor stabilization effect, whereas the *para*-methoxypnenyl group provides additional stabilization of this form compared to the unsubstituted phenyl group (Table 3).

The spatial structure of the molecule, namely, the planarity of the R substituent is another factor essential to the state of the tautomeric equilibrium. According to quantum-mechanical calculations, the phenyl group and the heteroatom fragment cannot be planar because of steric hindrance (Fig. 3). As the dihedral angle between the phenyl ring and the $N_1-C_2-N_3$ plane increases, the efficiency of conjugation decreases along with the degree of stabilization of the respective form. The distinctive peculiarity of

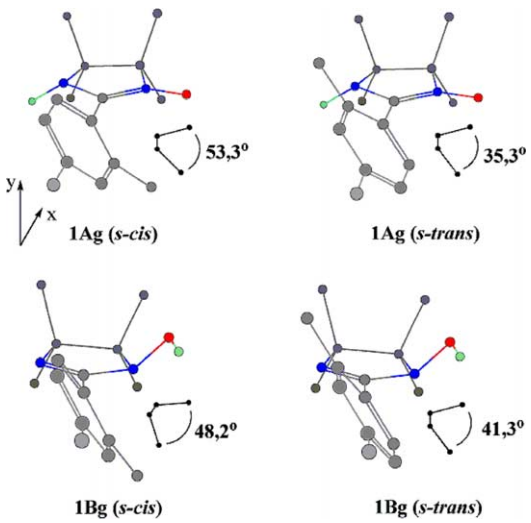


Fig. 3. The spatial structure of *s-cis* and *s-trans* conformers of **1Ag** and **1Bg** (ab initio calculations).

Table 7
Dihedral angles $N_1C_2C_{1'}C_{2'}$ in **1A(d–k)** and **1B(d–k)** according to X-ray analysis data and quantum-mechanical calculations ab initio HF/6-31G (d,p)

R	A		B	
	Ab initio	X-ray	Ab initio	X-ray
d	18.78		30.53	35.38
e	19.28		30.74	
f	17.80		27.37	
g	53.27		41.34	
h	63.03		83.98	
I	32.18[a]	33.82	14.95[a]	
j	27.83	27.24	7.71	
k	2.57		9.12	

[a] Bromine atom was exchanged for chlorine for the simplification of calculations.

a molecule **1** is the different spatial hindrance for coming into being planar for different tautomers **1Ad–k** and **1Bd–k**. Thus, according to quantum-mechanical calculations for tautomers **1Bd–h**, **k**, the bulky hydroxy group is a greater obstacle than the oxygen atom of the nitrone group in **1Ad–h**, **k** (Table 7). Hence, the smaller $N_1C_2C_{1'}C_{2'}$ dihedral angle, typically found in the nitrone form, provides more efficient stabilization of this form compared to the *N*-hydroxyaminoimino form.

Sequential introduction of methyl groups into the *ortho*-position of the phenyl ring results in increased $N_1C_2C_{1'}C_{2'}$ dihedral angle. Thus, the hypsochromic shift of the long-wave maximum in the UV spectra of the series of nitroxides **4d** (596 nm) > **4g** (556 nm) > **4h** (537 nm) is obviously caused by an increase in the $N_1C_2C_{1'}C_{2'}$ dihedral angle. Another evidence for this is an upfield shift of the proton signals of the acyl group in **2g** (1.70 ppm) relative to **2d** (1.95 ppm), of the methoxy group in **3Bg** (δ 3.43 ppm) relative to **3Bd** (3.68 ppm), and of the *N*-methyl group in **3Ag** (δ 2.45 ppm) relative to **3Ad** (δ 2.59 ppm), obviously resulting from the turning of the cone of magnetic anisotropy for the phenyl group.

As the $N_1C_2C_{1'}C_{2'}$ dihedral angle increases, the efficiency of conjugation in molecules **1g**, **h** decreases compared to **1d**; this results in less resonance stabilization of the nitrone form, whose content in these compounds is thus lower than that in **1d** (Table 3). In **1h**, however, the content of the nitrone form is higher than that in **1g**; the reason for this is the different symmetry of substituents. Molecule **1g** with a 2,4-dimethylphenyl group can exist as two different conformers, one of which, s-*trans* **1Bg**, is more stable (Fig. 3). In this conformer, the $N_1C_2C_{1'}C_{2'}$ dihedral angle is smaller than that in s-*cis*[1] **1Ag**; this results in less destabilization of **1Bg** compared to **1Ag**.

[1] *s-trans* and *s-cis* conformers are considered here regarding to the position relatively to the plane (*XY*) of methyl groups in phenyl ring and nitrone oxygen atom in tautomer **A** or hydroxyl group in tautomer **B**.

Table 8
Experimental and calculated (HF/6-31G(d,p)) $\Delta E_{comb.}$ for **B** and **A**

R	HF/6-31G (d,p)			Experimental, $\Delta E_{comb.}$ (kcal/mol)	
	$E_{comb.}$ (a.u.) **1**	$E_{comb.}$ (a.u.) **1′**	$\Delta E_{comb.}$ (kcal/mol)	C_2	$C_{1'}$
a	−792.554374	−792.527966	−16.572	−5.32	–
b	−456.939488	−456.916487	−14.434	−3.59	–
c	−495.988442	−495.968135	−12.743	−2.52	−2.98
d	−686.500728	686.485036	−9.848	4.13	3.70
e	−889.970252	−889.953368	−10.595	3.09	2.78
f	−800.385015	−800.369650	−9.642	5.32	3.93
g	−764.578012	−764.561751	−10.205	0.70	0.23
h	−803.615043	−803.597985	−10.704	2.26	1.21
i[a]	−1220.26753	−1220.26025	−4.568	–	–
j	−777.36469	−777.35756	−4.474	–	–
k	−763.392777	−763.375949	−10.560	3.20	2.39

[a] Bromine atom was exchanged for chlorine for the simplification of calculations.

The moving aside of the bulky phenyl group with preservation of the conjugate chain prevents rotation of the conjugation plane relative to the imidazoline ring in molecule **1k**. In this case, in both **A** and **B**, the $N_1C_2C_{1'}C_{2'}$ dihedral angles become smaller (Table 7), resulting in relatively more efficient stabilization of *N*-hydroxyaminoimino form **1Bk** compared to nitrone form **1Ak** (cf. **1Bk** : **1Ak** and **1Bd** : **1Ad**, Table 3).

The **B** : **A** ratio is determined from the difference between the formation heats of the forms ΔE_{comb} according to the equation $\mathbf{B} : \mathbf{A} = \exp[-\Delta E_{comb}/RT]$. The *N*-hydroxyaminoimino form is generally preferable according to calculations, so that in the crystalline state imidazolines **1b**, **d** exist in this form. Hence, substituents capable of stabilizing the nitrone form relative to the *N*-hydroxyaminoimino form lead to decreased values of ΔE_{comb} (Table 8). A comparison of the calculated and experimental values of ΔE_{comb} shows that they change symbatically, confirming that the state of equilibrium depends on the nature of the substituent and not only on solvation effects (Fig. 4).

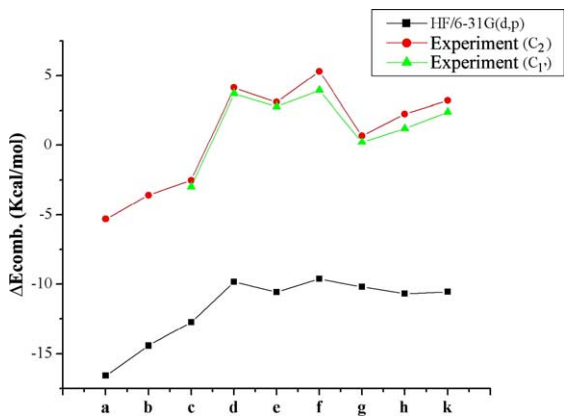


Fig. 4. The comparison of calculated and experimental $\Delta E_{comb.}$ (according to C-2 and C-1′).

3. Conclusions

Thus, the state of the aminonitrone-*N*-hydroxyaminoimino tautomeric equilibrium in the series of 1-hydroxy-2-imidazolines in solutions depends on various factors, including the nature of the solvent and the structure of the substituent in the 2-position of heterocycle. The increase of the inductivity of a solvent and its protic character leads to the increase of the content of nitrone form. On the contrary, aprotic solvents increase the content of *N*-hydroxyaminoimino form due to specific solvation. Electron-donating substituents (particularly those with the +M effect) stabilize the aminonitrone form, whereas the *N*-hydroxyaminoimino form is stabilized by electron-withdrawing substituents. The planarity of the whole π-system, including the aryl substituent, is also a very important factor affecting the state of the tautomeric equilibrium.

Therefore, it is believed that varying of a substituent at position 2 of the 2-imidazoline heterocycle and the nature of the solvent may change the path in reactions of these compounds with dipolarophiles. Further studies are under way to investigate these effects.

4. Experimental

IR spectra were recorded on a Bruker IFS 66 spectrometer for KBr pellets (concentration 0.25%, pellet thickness 1 mm). UV spectra were measured on a Specord M-40 spectrophotometer in EtOH. NMR spectra were recorded on Bruker WP 200 SY, Bruker AC-200, and Bruker AM-400 spectrometers for 5% solutions using the solvent as the internal standard. For ^{19}F NMR, C_6F_6 was used as internal standard. High-resolution mass spectra were recorded on a Finnigan MAT 8200 mass spectrometer with direct sample injection at a resolution of 10,000. The melting points were measured on a 'Boetius' plate and are uncorrected. Thin layer chromatography control was carried out with the use of Aluminum oxide TLC-cards (Fluka) with chloroform or chloroform–methanol (30:1 or 20:1) as eluent. The solutions were evaporated in vacuo in all cases. 2-Substituted 4,4,5,5-tetramethylimidazolidine-1,3-diols were synthesized according to Ref. [17]; imidazolines **1c**, **d**, according to Ref. [7]. Imidazolines **1i**, **j** were kindly granted by Dr E. V. Tretyakov [8].

For single crystals **1c**, **d**, data were collected on a Smart Apex Bruker AXS automatic diffractometer at room temperature using the standard procedure (Mo radiation, $2 < \theta < 25°$). The structures were solved by direct methods. Full-matrix least-squares refinement was performed anisotropically for nonhydrogen atoms and isotropically for hydrogens. H atoms were localized in difference electron density syntheses. All structure solution and refinement calculations were carried out with SHELXTL software.

Crystal data for **1c**: $C_7H_{14}N_2O$, $M = 142.20$, orthorhombic, space group $Pna2_1$, $a = 13.066(2)$, $b = 6.3291(8)$, $c = 10.372(1)$ Å, $V = 857.7(2)$ Å^3, $Z = 4$, $D_c = 1.101$ g cm^3, $\mu = 0.075$ mm^{-1}, 3390 reflections collected, 1061 unique ($R_{int} = 0.0456$), 148 parameters, Goof = 0.994, $R_1 = 0.0305$, $wR_2 = 0.0704(I > 2\sigma(I))$, $R_1 = 0.0329$, $wR_2 = 0.0719$ for all data (CCDC 215579).

Crystal data for **1d**: $C_{13}H_{18}N_2O$, $M = 218.29$, monoclinic, space group $C2/c$, $a = 17.435(3)$, $b = 13.748(2)$, $c = 11.014(2)$ Å, $\beta = 110.977(4)°$, $V = 2465.0(7)$ Å^3, $Z = 8$, $D_c = 1.176$ g cm^3, $\mu = 0.075$ mm^{-1}, 5223 reflections collected, 1783 unique ($R_{int} = 0.1101$), 218 parameters, Goof = 0.840, $R_1 = 0.0508$, $wR_2 = 0.0972(I > 2\sigma(I))$, $R_1 = 0.0931$, $wR_2 = 0.1148$ for all data (CCDC 215580).

All computations were carried out with the GAMESS program package [16]. Full geometry optimization was carried out at the Hartree–Fock (HF) level of theory. The standard 6-31G (d, p) basis set was employed, which is 6-31G quality plus six d-like polarization functions on heavy atoms and three p-like polarization functions on hydrogen atoms. The basis set used (HF/6-31G (d, p)) was chosen by comparing the experimental (X-ray) data with the geometrical characteristics and energies of compounds **1** (Tables 4, 5, 7 and 8). The harmonic vibration frequencies were determined by analytic second derivative methods at the 6-31G (d, p) level for equilibrium geometries **2(b,c,d,g)**.

*4.1. 4,4,5,5-tetramethyl-2-(trifluoromethyl)-4, 5-dihydro-1H-imidazol-1-ol **1a***

Trifluoroacetaldehyde hydrate (3.61 g, 31.1 mmol) emulsion in chloroform (10 ml) was slowly added dropwise with stirring to a boiling solution of 2,3-bis(hydroxyamino)-2,3-dimethylbutane (2.97 g, 20.05 mmol) in chloroform (15 ml). The reaction mixture was boiled for 5 h, then cooled to 20 °C, and washed with brine (2 × 15 ml). The chloroform solution was dried with $MgSO_4$, the solvent removed, and the residue chromatographed on alumina with a (1:20) methanol-chloroform mixture as eluent to give **4,4,5,5-tetramethyl-2-(trifluoromethyl)imidazolidine-1,3-diol**. Yield 1.9 g (65% after recrystallization from hexane). ^{1}H NMR ($CDCl_3$, 200.13 MHz, δ, ppm): 1.05 (s, 6H), 1.15 (s, 6H, 4,5-$(CH_3)_2$), 4.33 (q, 1H, $J_{H-C-C-F} = 5.9$ Hz, 4-H), 5.29 (s, 2H, NOH).

A solution of 4,4,5,5-tetramethyl-2-(trifluoromethyl)imidazolidine-1,3-diol (0.170 g, 0.75 mmol) in toluene (10 ml) with $MgSO_4$ (0.5 g) was boiled for 3 h with stirring and air bubbling. $MgSO_4$ was filtered off, and the solvent removed to give imidazoline **1a**, which was recrystallized from an ethyl acetate–hexane mixture; yield 0.10 g (60%).

^{1}H NMR ($CDCl_3$, 200.13 MHz, δ, ppm): 1.14 (s, 6H), 1.15 (s, 6H, 4,5-$(CH_3)_2$), 5.9 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 50.32 MHz, δ, ppm): 18.1, 22.8 (4,5-$(CH_3)_2$), 68.4 (C-4), 73.4 (C-5), 117.5 (q. J_{C-F} 275.8 Hz, CF_3), 155.6 (q. J_{C-C-F} 35.5 Hz, C-2). ^{19}F NMR ($CDCl_3$, 188.28 MHz, δ, ppm): 92.8 (s, CF_3). λ_{max}, (ethanol), nm (log ε) : 246 (4.21), ν, cm^{-1}: 3124 (OH), 1627 (C=N), 1187, 1163 (CF_3). m.p. 144–146 °C (from an ethyl acetate–hexane mixture). Found: C 45.7, H 6.2, F 27.1, N 13.3. Calculated for $C_8H_{13}F_3N_2O$: C 45.7, H 6.2, F 27.1, N 13.2.

*4.2. 4,4,5,5-Tetramethyl-4,5-dihydro-1H-imidazol-1-ol **1b***

Procedure A: A solution of 4,4,5,5-tetramethylimidazolidine-1,3-diol (2.69 g, 16.8 mmol) in toluene (30 ml) was boiled for 10 h while bubbling air through the solution. After solvent removal, the residue was recrystallized from an ethyl acetate–hexane mixture to give 1.2 g (41%) of **1b**.

Procedure B: A solution of $NaNO_2$ (1.62 g, 25.8 mmol) in water (20 ml) was added to a solution of **4b** (2.25 g, 14.34 mmol) in chloroform (50 ml). To the resulting mixture, hydrochloric acid (5% solution, 1 ml) was added dropwise while vigorously stirring the solution. The stirring was continued for 30 min, the organic layer was separated, and the aqueous solution extracted with chloroform (2 × 50 ml). The combined extracts were dried with $MgSO_4$, and the solvent was removed. The residue was dissolved in anhydrous tetrahydrofuran (15 ml), a catalyst (0.15 g, 5% Pd on charcoal) was added, and the mixture was hydrogenated with hydrogen while stirring for 4 h at 20 °C. The catalyst was filtered off and the solvent removed to give (96%) pure **1b** (2.0 g), which could be additionally purified by recrystallization from an ethyl acetate–hexane mixture. ^{1}H NMR ($CDCl_3$, 200.13 MHz, δ, ppm): 1.14 (s, 12H, 4,5-$(CH_3)_2$), 6.34.(s, 1H, OH), 7.19 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$, 50.32 MHz, δ, ppm): 18.5, 23.6 (4,5-$(CH_3)_2$), 67.7 (C-4), 71.0 (C-5), 153.3 (C-2). λ_{max}, (ethanol), nm (log ε) : 269 (4.71). ν, cm^{-1}: 3100 (OH), 1596 (C=N).

*4.3. 4,4,5,5-Tetramethyl-2-(4-nitrophenyl)-4, 5-dihydro-1H-imidazol-1-ol **1e***

A solution of 4,4,5,5-tetramethyl-2-(4-nitrophenyl)imidazolidine-1,3-diol (0.677 g, 2.41 mmol) (Ref. [18]) in chloroform (25 ml) was stirred with MnO_2 (3 g) for 1 h at 20–25 °C. Manganese oxides were filtered off and a water solution (10 ml) containing $NaNO_2$ (0.25 g, 3.62 mmol) was added to the filtrate; then 5% hydrochloric acid (0.4 ml) was added dropwise with vigorous stirring. The stirring was continued for 1 h at 20 °C, the organic solution was separated, and the water solution extracted with chloroform (3 × 20 ml). The combined extract was dried with $MgSO_4$ and the residue obtained after solvent removal was dissolved in a methanol solution (10 ml) containing hydroxylamine hydrochloride (0.83 g, 12.05 mmol) and sodium methoxide (0.39 g, 7.23 mmol). The resulting solution was kept for 24 h at 10 °C, the solvent was removed, and the residue dissolved in water (10 ml) and extracted with chloroform (3 × 20 ml). The combined extract was dried with $MgSO_4$, and the residue (after solvent removal) recrystallized from an ethyl acetate-hexane mixture to give 0.54 g (85%) of imidazoline **1e**.

^{1}H NMR ($CDCl_3$, 200.13 MHz, δ, ppm): 1.22 (s, 6H), 1.23 (s, 6H, 4,5-$(CH_3)_2$), 5.82 (s, 1H, OH), 8.07 (dd, 2H, J_3 9 Hz, J_4 2 Hz, 2′-H, Ph), 8.29 (dd, J_3 9 Hz, J_4 2 Hz, 3′-H, Ph). The spectrum also contains signals of the ethyl acetate crystalline solvate. ^{13}C NMR ($CDCl_3$, 50.32 MHz, δ, ppm): 19.2, 23.9 (4,5-$(CH_3)_2$), 62.7 (C-4), 74.3 (C-5), 123.1 (C3′), 128.2 (C2′), 132.7 (C1′), 148.0 (C-2), 148.1 (C4′). m.p. 115–116 °C. Found: C 59.00, H 6.65, N 14.52. Calculated for $C_{13}H_{17}N_3O_3 \times (1/4)C_4H_8O_2$: C 58.93, H 6.71, N 14.73.

4.4. 2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-ol **1f**

A solution of 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulphate (1.13 g, 4.28 mmol) and 4-methoxybenzaldehyde (0.47 ml, 3.9 mmol) in a (1:1) water–methanol mixture (20 ml) was boiled for 72 h. Sodium acetate (0.7 g, 8.54 mmol) was added after cooling and methanol was evaporated. The precipitate was filtered off and washed with water and hexane to give 0.76 g (75%) of crude 2-(4-methoxyphenyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (cf. Ref. [19]), which was used without further purification. ^{1}H NMR ($CDCl_3$, 200.13 MHz, δ, ppm): 1.26 (s, 6H), 1.28 (s, 6H, 4,5-$(CH_3)_2$), 3.93 (s, 3H, CH_3O), 4.75 (s, 1H, 2-H), 7.00 ppm (d, $J = 8.4$ Hz, 2′-H, Ph), 7.61.(d, $J = 8.4$ Hz, 3′-H, Ph), 7.78 (s, 1H, OH).

A mixture of 2-(4-methoxyphenyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (0.12 g, 0.45 mmol) and MnO_2 (3 g) in chloroform (10 ml) was stirred for 30 min at 20–25 °C. Manganese oxides were filtered off, and an aqueous solution (5 ml) containing $NaNO_2$ (0.1 g, 1.45 mmol)was added to the filtrate; then 5% hydrochloric acid (0.1 ml) was added with stirring to the resulting mixture. The stirring was continued for 30 min, the organic layer was separated, and the aqueous solution extracted with chloroform (3 × 10 ml). The combined organic extract was dried with $MgSO_4$, and the residue obtained after solvent evaporation, 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxyl, was purified by flash chromatography on alumina with chloroform as eluent. The eluate containing iminonitroxide was evaporated, and the residue was dissolved in anhydrous tetrahydrofuran (7 ml). A catalyst (5% Pd on charcoal, 0.1 g) was added, and the mixture was hydrogenated with hydrogen with stirring for 1 h at 20 °C. The catalyst was filtered off and the solvent removed to give crude **1f**, which was purified chromatographically on alumina with chloroform as eluent to remove traces of the starting iminonitroxide and then with a (10:1) chloroform-methanol mixture. The eluate containing **1f** was evaporated to give (after recrystallization from chloroform) 0.070 g (63%) of pure **1f**. ^{1}H NMR ($CDCl_3$, 200.13 MHz, δ, ppm): 1.18.(s, 6H), 1.23 (s, 6H, 4,5-$(CH_3)_2$), 3.73.(s, 3H, OCH_3), 4.77(s, OH), 6.77 (d, $J = 9$ Hz, 2′-H, Ph), 8.18 (d, $J = 9$ Hz, 3′-H, Ph). ^{13}C NMR ($CDCl_3$, 50.32 MHz, δ, ppm): 19.3, 24.2 (4,5-$(CH_3)_2$), 55.2 (OCH_3), 61.0 (C-4), 73.7 (C-5), 113.6 (C3′), 118.2 (C1′), 128.9 (C2′), 144.0 (C-2), 161.2 (C4′). m.p. 196–198 °C (in a sealed capillary). Found, *m/z*: 248.15320. Calculated for $C_{14}H_{20}N_2O_2$, *m/z*: 248.15247.

4.5. 2-(2,4-Dimethylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-ol **1g**

2,3-Bis(hydroxyamino)-2,3-dimethylbutane sulphate (2.45 g, 9.28 mmol), sodium acetate (1.4 g, 17.1 mmol), and 2,4-dimethylbenzaldehyde (1.13 g, 8.43 mmol) in a (1:1) water–methanol mixture (30 ml) was boiled for 48 h. Methanol was evaporated, and the 2-(2,4-dimethylphenyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol precipitate was filtered off and washed with water and hexane. Yield 1.18 g (53%). ^{1}H NMR (DMSO-d_6, 200.13 MHz, δ, ppm): 1.04 (s, 6H), 1.07 (s, 6H, 4,5-$(CH_3)_2$), 2.23 (s, 3H), 2.33 (s, 3H, 2,4-$(CH_3)_2$Ph), 4.84 (s, 1H, 2-H), 7.2 ppm (s, 1H, 3′-H, Ph), 6.96 (d, 1H, $J = 7.8$ Hz, 5′-H, Ph), 7.5 ppm (d, 1H, $J = 7.8$ Hz, 6′-H, Ph), 7.60 (s, 2H, OH).

A solution of 2-(2,4-dimethylphenyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (0.90 g, 3.41 mmol) in chloroform (40 ml) was stirred with MnO_2 (5 g) for 2 h at 20 °C. Manganese oxides were filtered off, and the filtrate was evaporated to dryness to give nitronylnitroxide **4g**, 20 mg of which was purified chromatographically on alumina with chloroform as eluent. λ_{max}, (ethanol), nm (log ε): 207 (4.23), 253 nm. (3.95), 327 (3.85), 556 (2.99). The remainder of **4g** was converted into imidazoline **1g** in the same manner as described for **1f**; yield 0.53 g (63%). ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.31 (s, 6H), 1.33 (s, 6H, 4,5-$(CH_3)_2$), 2.50 (s, 3H), 2.52 (s, 6H, 2,4-$(CH_3)_2$Ph), 5.71 (s, 1H, OH), 7.21 (d, 1H $J = 7.6$ Hz), 7.24 (s, 1H), 7.35 (d, 1H, $J = 7.6$ Hz, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 18.6, 23.5 (4,5-$(CH_3)_2$), 19.5, 20.9 (2,4-$(C H_3)_2$Ph), 63.4 (C-4), 71.8 (C-5), 125.1 (C1′), 125.5 128.4 130.5 (C3′, C5′, C6′), 137.1, 139.1 (C2′, C4′), 154.6 (C-2). m.p. 193–195 °C (from an ethyl acetate–hexane mixture). Found: C 73.00, H 9.41, N 11.37. Calculated for $C_{15}H_{22}N_2O$: C 73.13, H 9.00, N 11.37.

2-Mesityl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-ol **1h** and nitroxide **4h** were obtained as described for **1g** and **4g**, respectively. The yield of 2-mesityl-4,4,5,5-tetramethylimidazolidine-1,3-diol was 10%.

4h: λ_{max}, (ethanol), nm (log ε) : 240 (4.09), 319 (3.87), 537 (3.13).

1h: Yield 58%. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.28 (s, 6H), 1.32 (s, 6H, 4,5-$(CH_3)_2$), 2.26 (s, 6H), 2.95 (s, 3H) (2′, 4′, 6′-CH_3), 6.83 (s, 2H, 3,5-H, mesityl). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 19.4, 24.4 (4,5-$(CH_3)_2$), 21.2 (2,4,6-$(C H_3)_3$Ph), 63.3 (C-4), 72.4 (C-5), 123.9 (C1′), 128.3 (C3′), 137.4 (C2′), 139.5 (C4′), 152.0 (C-2). m.p. 215–217 °C (from an ethyl acetate–hexane mixture). Found: C 73.81, H 9.72, N 10.68. Calculated for $C_{16}H_{24}N_2O$: C 73.81, H 9.29, N 10.76.

4.6. 4,4,5,5-Tetramethyl-2-[(E)-2-phenylvinyl]-4,5-dihydro-1H-imidazol-1-ol **1k**

A solution of hydroxylamine obtained by alkalization of a solution of hydroxylamine hydrochloride (0.07 g, 1 mmol) in anhydrous methanol (5 ml) with sodium methoxide to pH 8–9 was added dropwise to a solution of 4,4,5,5-tetramethyl-2-[(*E*)-2-phenylvinyl]-4,5-dihydro-1H-imidazol-1-oxyl (0.090 g, 0.37 mmol) (for synthesis, see Ref. [17]) in anhydrous methanol (10 ml) at 5 °C with stirring until the color vanished. The solvent was removed and imidazoline **1k** was purified chromatographically on alumina with chloroform as eluent to remove traces of the starting iminonitroxide and then with a (10:1) chloroform-methanol mixture. The eluate containing **1k** was evaporated to give 0.080 g (89%) of pure **1k**. Oil ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.18.(s, 6H), 1.23 (s, 6H 4,5-$(CH_3)_2$), 5.10 (s, 1H, OH), 7.05 (d, $J = 16.8$ Hz), 7.32 (d, $J = 16.8$ Hz, HC=CH), 7.17–7.41 (m, Ph). NMR ^{13}C ($CDCl_3$, 50.3 MHz, δ, ppm): 19.1, 23.8 (4,5-$(CH_3)_2$), 61.2 (C-4), 72. ppm (C-5), 110.8 (C1′), 126.9, 128.3 (C4′, C5′), 128.8 (C6′), 135.2 (C3′), 136.4 (C2′), 145.9 (C-2). Found, *m/z* : 244.15700. Calculated for $C_{15}H_{20}N_2O$, *m/z* : 244.15756.

4.7. 1-Methoxy-4,4,5,5-tetramethyl-2-(trifluoromethyl)-4,5-dihydro-1H-imidazole **3Ba**

A solution of dimethyl sulphate (0.028 ml, 0.29 mmol) in anhydrous tetrahydrofuran (2 ml) was added to a solution of **1a** (0.056 g, 0.27 mmol) in anhydrous tetrahydrofuran (5 ml) with stirring, while the temperature was kept below 10 °C. The stirring was continued for 1 h at this temperature, and the solvent was carefully removed (imidazoline **3Ba** is volatile). The residue was flash-chromatographed on alumina with chloroform as eluent. Yield 40 mg (67%). Oil ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.14(s, 6H), 1.18 (s, 6H 4,5-$(CH_3)_2$), 3.70 (s, OCH_3). NMR ^{13}C ($CDCl_3$, 50.3 MHz, δ, ppm): 18.8, 22.4 (4,5-$(CH_3)_2$), 64.2 (OCH_3), 68.6 (C-4), 73.6 (C-5), 117.3 (q. $J_{C-F} = 275.6$ Hz, CF_3), 154.8 (q. J_{C-C-F} 35.6 Hz, C-2). ^{19}F NMR ($CDCl_3$, 188.2 MHz, δ, ppm): 92.9 (CF_3). Found, *m/z* : 224.11361. Calculated for $C_9H_{15}F_3N_2O$, *m/z* : 224.11365.

4.8. 1-Methoxy-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole **3Bb**

Sodium hydride (0.030 g, 1.25 mmol) was added to a solution of **1b** (0.166 g, 1.17 mmol) in anhydrous tetrahydrofuran (5 ml). The resulting mixture was stirred for 5 min, and a solution of dimethyl sulphate (0.12 ml, 1.27 mmol) in tetrahydrofuran (3 ml) was added dropwise with stirring at a temperature below 15 °C. The stirring was continued for 10 min, the solvent was carefully evaporated, and imidazoline **3Bb** was purified by flash chromatography on alumina with chloroform as eluent. Yield 0.090 g (50%). Oil ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 0.95 (s, 6H), 0.97 (s, 6H, 4,5-$(CH_3)_2$), 3.53 (s, OCH_3). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 18.8, 23.0 (4,5-$(CH_3)_2$), 64.0 (OCH_3), 69.6 (C-4), 70.8 (C-5), 156.32 (C-2). Found, *m/z* : 156.12671. Calculated for $C_8H_{16}N_2O$, *m/z* : 156.12626.

4.9. 1-Methoxy-2,4,4,5,5-pentamethyl-4,5-dihydro-1H-imidazole **3Bc**

A solution of **1c** (0.265 g, 1.70 mmol) and dimethyl sulphate (0.162 ml, 1.71 mmol) in anhydrous chloroform (4 ml) was kept for 30 min at 20 °C, then washed with a 5% water solution of $KHCO_3$, dried with $MgSO_4$ and evaporated. Imidazoline **3Bc** was isolated by flash chromatography on alumina with chloroform as eluent; yield 90 mg (31%). Oil. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 0.99 (s, 6H), 1.01 (s, 6H, 4,5-$(CH_3)_2$), 1.86 (s, 3H, 2-CH_3), 3.59 (s, OCH_3). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 13.1 (2-CH_3), 18.3, 23.4 (4,5-$(CH_3)_2$), 63.3 (OCH_3), 65.5 (C-4), 70.1 (C-5), 163.5 (C-2). Found, *m/z* : 170.14175. Calculated for $C_9H_{18}N_2O$, *m/z* : 170.14191.

4.10. 1-Methoxy-4,4,5,5-tetramethyl-2-phenyl-4,5-dihydro-1H-imidazole **3Bd**

1-Methoxy-4,4,5,5-tetramethyl-2-phenyl-4,5-dihydro-1H-imidazole **3Bd** was synthesized similarly to imidazoline **3b**. Reaction time was 24 h at 10 °C; yield 80%. Oil. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.16 (s, 6H), 1.20 (s, 6H, 4,5-$(CH_3)_2$), 3.68 (s, OCH_3), 7.33–7.36 (m, 3H), 7.64 (dd. 2H, $J = 7.9$ Hz, $J = 1.7$ Hz, *ortho*-H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 19.5, 23.2 (4,5-$(CH_3)_2$), 63.7 (OCH_3), 66.9 (C-4), 71.9 (C-5), 127.7, 127.8 (C2′, C3′), 129.6 (C4′), 131.3 (C1′), 164.9 (C-2). λ_{max}, (ethanol), nm (log ε) : 227 (3.76). ν, cm^{-1}: 2815 (OCH_3), 1629 (C=N), 1601, 1576.5 (C=C, Ph). Found, *m/z* : 232.15800. Calculated for $C_{14}H_{20}N_2O$, *m/z* : 232.15755.

4.11. 1-Methoxy-4,4,5,5-tetramethyl-2-(4-nitrophenyl)-4,5-dihydro-1H-imidazole **3Be**

1-Methoxy-4,4,5,5-tetramethyl-2-(4-nitrophenyl)-4,5-dihydro-1H-imidazole **3Be** was synthesized similarly to imidazoline **3Bb**. Reaction time was 1 h at 20 °C; yield 85%. Oil. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.19 (s, 6H), 1.23 (s, 6H, 4,5-$(CH_3)_2$), 3.70 (s, 3H, OCH_3), 7.83 (t, 2H, $J_3 = 9.0$ Hz, $J_4 = 2.1$ Hz, 2′-H, Ph), 8.22 (t, 2H, $J_3 = 9.0$ Hz, $J_4 = 2.1$ Hz, 3′-H, Ph). NMR ^{13}C ($CDCl_3$, 50.3 MHz, δ, ppm): 19.5, 23.1 (4,5-$(CH_3)_2$), 63.8 (OCH_3), 67.9 (C-4), 72.6 (C-5), 123.0 (C3′), 129.0 (C2′), 137.6 (C1′), 148.5 (C4′), 163.1 (C-2). Found, *m/z* : 277.14288. Calculated for $C_{14}H_{19}N_3O_3$, *m/z* : 277.14263.

*4.12. 2-(2,4-Dimethylphenyl)-1-methoxy-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole **3Bg***

2-(2,4-Dimethylphenyl)-1-methoxy-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole **3Bg** was synthesized similarly to imidazoline **3Bb**. Reaction time was 1 h at 100 °C (dioxane as solvent); yield 69%. Oil. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.19 (s, 6H), 1.22 (s, 6H, 4,5-$(CH_3)_2$), 2.30 (s, 3H), 2.34 (s, 3H, 2,4-$(CH_3)_2$-Ph), 3.43 (s, 3H, OCH_3), 6.97 (d, 1H, $J_3 = 7.6$ Hz, 5′-H, Ph) 6.99 (s, 1H, 3′-H, Ph), 7.13 (d, 1H, $J_3 = 7.6$ Hz, 6′-H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 19.3, 23.2 (4,5-$(CH_3)_2$), 19.1, 21.0 (2,4-$(CH_3)_2$-Ph), 63.5 (OCH_3), 67.4 (C-4), 71.0 ppm (C-5), 128.3 (C1′), 125.4, 128.0, 130.4 (C3′, C5′, C6′), 136.1, 138.2 (C2′, C3′), 165.4 (C-2). Found, *m/z*: 260.18885. Calculated for $C_{16}H_{24}N_2O$, *m/z*: 260.18886.

*4.13. 1-(Acetyloxy)-2,4,4,5,5-pentamethyl-4,5-dihydro-1H-imidazole **2c***

Acetic anhydride (0.47 ml, 4.99 mmol) was added dropwise with stirring to a solution of **1c** (0.26 g, 1.66 mmol) in anhydrous chloroform (5 ml). The stirring was continued for 30 min; the solution was washed with an aqueous solution of $KHCO_3$, water, and then dried with $MgSO_4$. After solvent removal, **2c** (0.311 g, 94%) was obtained. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.03 (s, 6H), 1.09 (s, 6H, 4,5-$(CH_3)_2$), 1.83 (s, 3H, 2-CH_3), 2.09 (s, 3H, C*H*$_3$–CO). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 13.6 (2-CH_3), 18.2 (*C*H$_3$–CO), 18.9, 23.1 (4,5-$(CH_3)_2$), 66.9 (C-4), 71.7 (C-5), 162.8 (C-2), 168.4 (C=O). ν, cm^{-1}: 1796 (C=O), 1652 (C=N).

*4.14. 2-R-1-(Acetyloxy)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazoles **2d,e,f,g,k***

2-*R*-1-(Acetyloxy)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazoles **2d,e,f,g,k** were obtained similarly.

2d. Yield 82%. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.16 (s, 6H), 1.25 (s, 6H, 4,5-$(CH_3)_2$), 1.95 (s, 3H, C*H*$_3$CO), 7.31–7.38 (m, 3H, Ph), 7.52 (dd, 2H, $J_3 = 7.9$ Hz, $J_5 = 1.7$ Hz, 2′-H, Ph. ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 18.6 (*C*H$_3$CO), 19.7, 23.9 (4,5-$(CH_3)_2$), 68.3 (C-4), 72.4 (C-5), 127.3, 128.1 (C2′,C3′), 130.1 (C4′), 130.5 (C1′), 164.0 (C-2), 168.9 (C=O). λ_{max}, (ethanol), nm (log ε): 229 nm (4.02). ν, cm^{-1}: 3064 (Ar–H), 1779 (C=O), 1630 (C=N), 1602, 1578 (C=C).

2e. Yield 95%. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.18 (s, 6H), 1.27 (s, 6H, 4,5-$(CH_3)_2$), 1.99 (s, 3H, C*H*$_3$CO), 7.71 (dd, 2H $J_3 = 9.0$ Hz, $J_4 = 2.1$ Hz, 2′-H, Ph), 8.20 (dd, 2H, $J_3 = 9.0$ Hz, $J_4 = 2.1$ Hz, 3′-H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 18.6 (*C*H$_3$CO), 19.7, 23.8 (4,5-$(CH_3)_2$), 69.4 (C-4), 73.0 (C-5), 123.4 (C3′), 128.5 (C2′), 136.7 (C1′), 148.9 (C4′), 162.5 (C-2), 168.8 (C=O);

2f. Yield 90%. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.14 (s, 6H), 1.22 (s, 6H, 4,5-$(CH_3)_2$), 1.97 (s, 3H, C*H*$_3$CO), 3.76 (s, 3H, OCH_3), 6.83 (dd, $J_3 = 8.9$ Hz, $J_4 = 2.5$ Hz, 2′-H, Ph), 7.46 (dd, $J_3 = 8.9$ Hz, $J_4 = 2.5$ Hz, 3′-H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 18.6 (*C*H$_3$CO), 19.7, 23.9 (4,5-$(CH_3)_2$), 55.0 (OCH_3), 68.0 (C-4), 72.2 (C-5), 113.5 (C3′), 122.7 (C1′), 128.9 (C2′), 161.1 (C4′), 163.5 (C-2), 169.1 (C=O).

2g. Yield 85%. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.08 (s, 6H), 1.16(s, 6H, 4,5-$(CH_3)_2$), 1.70 (C*H*$_3$CO), 2.15 (s, 3H, 4′-C*H*$_3$Ph), 2.23 (s, 3H, 2′-C*H*$_3$Ph), 6.81 (d, 1H, $J = 7.8$ Hz, 5′-H, Ph), 6.86 (s, 1H, 3′-H, Ph), 6.98 (d, 1H, $J_3 = 7.8$ Hz, 6′-H, Ph); ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 18.8 (*C*H$_3$CO), 19.2, 23.3 (4,5-$(CH_3)_2$), 20.7, 21.5 (4,5-(*C*H$_3$)Ph), 68.0 (C-4), 71.6 (C-5), 126.6 (C1′), 125.4, 127.6, 130.6 (C3′, C5′, C6′), 136.3, 138.6 (C2′, C4′), 163.9 (C-2), 168.1 (C=O).

2k. Yield 90%. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.12 (s, 6H), 1.21 (s, 6H, 4,5-$(CH_3)_2$), 2.16 (s, 3H, C*H*$_3$CO), 6.37 (d, 1H, $J_3 = 16.3$ Hz, *H*C=CH–Ph), 7.46 (d, 1H, $J_3 = 16.3$ Hz, HC=C*H*–Ph), 7.24–7.31 (m, 3H), 7.39–7.4 ppm (m, 2H, Ph). ^{13}C NMR ($CDCl_3$, 50.32 MHz, δ, ppm): 18.5 (*C*H$_3$CO), 19.1, 20.5 (4,5-$(CH_3)_2$), 67.5 (C-4), 72.1 (C-5), 114.8 (C1′), 127.0, 128.3 (C4′, C5′), 128.8 (C6′), 135.2 (C3′), 138.0 (C2′), 161.1 (C-2), 168.8 (C=O).

*4.15. 1-(Acetyloxy)-2-mesityl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole **2h***

A solution of acetic anhydride (0.075 ml, 0.74 mmol) and triethylamine (0.20 ml, 1.35 mmol) in anhydrous chloroform (2 ml) was added dropwise with stirring to a solution of **1h** (0.080 g, 0.31 mmol) in anhydrous chloroform (3 ml). The stirring was continued for 1 h at 20 °C, the solvent was removed, and the residue dissolved in anhydrous ether (10 ml). The triethylammonium acetate precipitate was filtered off and the filtrate evaporated. Imidazoline **2h** was purified by chromatography on alumina with chloroform as eluent. Yield 0.050 g (54%). ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.22 (s, 6H), 1.28 (s, 6H, 4,5-$(CH_3)_2$), 1.76 (s, 3H, C*H*$_3$CO), 2.21 (s, 3H, 4′-CH_3Ph, 2.24 (s, 6H, 2′,6′-$(CH_3)_2$Ph), 6.75 (s, 3H). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 18.2 (*C*H$_3$CO), 19.2, 23.8 (4,5-$(CH_3)_2$), 20.3, 20.9 (2′,4′,6′-$(CH_3)_3$Ph), 68.7 (C-4), 71.2 (C-5), 126.7 (C1′), 127.6 (C3′), 136.6 (C2′), 138.2 (C4′), 163.5 (C-2), 168.2 (C=O).

*4.16. 1,2,4,4,5,5-Hexamethyl-4,5-dihydro-1H-imidazole 3-oxide **3Ac***

A solution of **2c** (0.311 g, 1.57 mmol) and dimethyl sulphate (0.44 ml, 4.65 mmol) in anhydrous ether (9 ml) was kept for 48 h at 10 °C. The precipitate was filtered off and washed with anhydrous ether to give 0.411 g of 1-(acetyloxy)-2,3,4,4,5,5-hexamethyl-4,5-dihydro-1H-imidazol-3-ium methylsulphate. The latter was dissolved in 5% NaOH (5 ml) and the resulting solution was kept for 10 min at 20 °C. The solution was extracted with chloroform

(4 × 10 ml), and the combined extract was dried with $MgSO_4$. Subsequent solvent evaporation gave 0.214 g (80%) of nitrone **3Ac**. Oil. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.04 (s, 6H), 1.16 (s, 6H, 4,5-$(CH_3)_2$), 1.99 (s, 3H, 2-CH_3), 2.58.(s, 3H, N-CH_3). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 8.7 (2-CH_3), 18.5, 18.7 (4,5-$(CH_3)_2$), 27.1 (N–CH_3), 64.8 (C-4), 71.0 (C-5), 146.4 (C-2); Found, *m/z* : 170.14300. Calculated for $C_9H_{18}N_2O$, *m/z* : 170.14190.

*4.17. 2-R-1,4,4,5,5-Pentamethyl-4,5-dihydro-1H-imidazole 3-oxides **3A(d–k)***

2-*R*-1,4,4,5,5-pentamethyl-4,5-dihydro-1H-imidazole 3-oxides **3A(d–k)** were synthesized similarly.

3Ad. Yield 65%. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.20 (s, 6H), 1.32 (s, 6H, 4,5-$(CH_3)_2$), 2.59 (s, 3H, N-CH_3), 7.34–7.42 (m, 3H), 7.60–7.65 (m, Ph); ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 19.3, 19.5 (4,5-$(CH_3)_2$), 29.5 (N–CH_3), 64.9 (C-4), 72.8 ppm (C-5), 125.5 (C1′), 128.1, 129.0 (C2′, C3′), 129.8 (C4′), 145.8 (C-2). mp 90–92 °C; Found: C 72.2, H 8.7, N 11.9. Calculated for $C_{14}H_{20}N_2O$: C 72.4, H 8.7, N 12.1.

3Ae. Yield 72%. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.26 (s, 6H), 1.36.(s, 6H, 4,5-$(CH_3)_2$), 2.66 (s, 3H, NCH_3), 7.89 (dd, 2H, $J_3 = 9$ Hz, $J_4 = 2.1$ Hz, 2′-H, Ph, 8.30 (dd, 2H, $J_3 = 9$ Hz, $J_4 = 2.1$ Hz, 3′-H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 19.5, 19.7 (4,5-$(CH_3)_2$), 29.8 (N–CH_3), 65.5 (C-4), 73.7 (C-5), 123.5 (C3′), 130.2 (C2′), 131.3 (C1′), 145.1 (C-2), 148.2 (C4′). m.p. 165.5–166.5 °C; Found, *m/z* : 277.142631. Calculated for $C_{14}H_{19}N_3O_3$, *m/z* : 277.14264.

3Af. Yield 85%. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.20(s, 6H), 1.31 (s, 6H, 4,5-$(CH_3)_2$), 2.62 (s, 3H, N–CH_3), 3.79 (s, 3H, OCH_3), 6.92 (dd, 2H, $J_3 = 9.0$ Hz, $J_4 = 2.5$ Hz, 2′-H, Ph), 7.59 (dd, 2H, $J_3 = 9.0$ Hz, $J_4 = 2.5$ Hz, 3′-H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 19.3 19.5 (4,5-$(CH_3)_2$), 29.4 (N–CH_3), 55.2 (OCH_3), 65.0 (C-4), 72.4 (C-5), 113.6 (C3′), 117.2 (C1′), 130.7 (C2′), 147.1 (C-2), 160.8 (C4′). m.p. 142–143 °C; Found, *m/z* : 262.16956. Calculated for $C_{15}H_{22}N_2O_2$, *m/z* : 262.16812.

3Ag. Yield 80%. Oil. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.22 (s, 6H), 1.33 (s, 6H, 4,5-$(CH_3)_2$), 2.45 (s, 3H, N–CH_3), 2.28 (s, 6H, 2,4-$(CH_3)_2$Ph), 7.01–7.05 (m, 2H), 7.23 (s, 1H, 3′-H, Ph). ^{13}C ($CDCl_3$, 50.3 MHz, δ, ppm): 18.9, 19.1, 19.2, 19.3, 21.2 (4,5-$(CH_3)_2$, 2,4-$(CH_3)_2$Ph), 28.1 (N–CH_3), 65.3 (C-4), 72.5 (C-5), 122.3 (C1′), 126.4, 128.5, 131.0 (C3′, C5′, C6′), 137.9, 140.1 (C2′, C4′), 147.3 (C-2). Found, *m/z* : 260.18910. Calculated for $C_{16}H_{24}N_2O$, *m/z* : 260.18885.

3Ah. Yield 60%. Oil. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.25 (s, 6H), 1.3 ppm (s, 6H, 4,5-$(CH_3)_2$), 2.19 (s, 6H), 2.26 (s, 3H, 2,4,6-$(CH_3)_3$Ph), 2.44 (s, 3H, N-CH_3), 6.86 (s, 3H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 19.1, 19.2 (CH_3), 19.5, 21.0 (4,5-$(CH_3)_2$, 2,4,6-$(CH_3)_3$Ph), 27.1 (N–CH_3), 65.4 (C-4), 72.5 (C-5), 121.7 (C1′), 128.4 (C3′), 137.2 (C2′), 139.9 (C4′), 148.0 (C-2).

3Ak. Yield 60%. Oil. ^{1}H NMR ($CDCl_3$, 200.1 MHz, δ, ppm): 1.14 (s, 6H), 1.29 (s, 6H, 4,5-$(CH_3)_2$), 2.44 (s, 3H, N–CH_3), 6.45 (d, 1H, $J_3 = 16.0$ Hz, *H*C=CHPh), 7.27–7.36 (m, 3H), 7.48–7.53 (m, 2H, Ph), 9.06 (d, 1H, $J_3 = 16.0$ Hz, HC=C*H*Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz, δ, ppm): 19.1, 19.2 (4,5-$(CH_3)_2$), 28.3 (N–CH_3), 64.9 (C-4), 72.6 (C-5), 109.2 (C1′), 127.2, 128.6 (C4′, C5′), 128.9 (C6′), 136.7 (C3′), 139.7 (C2′), 142.8 (C-2); Found, *m/z* : 258.17320. Calculated for $C_{16}H_{22}N_2O$, *m/z* : 258.17321.

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