A New Class of Enehydroxylamino Ketones − (*R*)-2-(1-Hydroxy-4,4,5,5-tetraalkylimidazolidin-2-ylidene)ethanones: Synthesis and Reactions

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Three approaches to the synthesis of (*R*)-2-(1-hydroxy-4,4,5,5-tetraalkylimidazolidin-2-ylidene)ethanones **1** are described: (a) condensation of 1,2-bishydroxylamines with β-ketoaldehyde synthons, (b) treatment of metallated 1-hydroxy-2-methyl-4,5-dihydroimidazoles with esters, and (c) 1,3-dipolar cycloaddition between 1-hydroxy-4,5-dihydroimidazole-3-oxide and DMAD. The reactivity of **1** with electrophiles has been studied. The exocyclic methylene (enamine) carbon atom is shown to be the major site of electrophilic attack. Synthesized chloro-substituted 1-hydroxy-2-acetylideneimidazolidines react with sodium cyanide to form the corresponding nitriles. Oxidation of these nitriles occurs with formation of persistent vinyl nitroxides, which are of interest as potential paramagnetic ligands.

Introduction

This paper presents a study of methods for the synthesis of cyclic ketene *N*-hydroxyaminals [derivatives of (*R*)-2-(1-hydroxy-4,4,5,5-tetraalkylimidazolidin-2-ylidene)ethanones, **1**] and their properties. The distinctive feature of the structure of compound **1** is the presence of reactive enaminone and enehydroxylamino ketone groups in one molecule. While the reactivity of enaminones is well known,[1,2] data on the reactivity of enehydroxylamino ketones with heterolytic reagents − electrophiles and nucleophiles − are relatively scarce and mainly limited to our previous works.[3−14] More is known about the oxidative transformations of enehydroxylamino ketones, with intermediate formation of extremely unstable vinyl nitroxides capable of further transformations. In particular, recombination of type **A** vinyl-nitroxides, generated by oxidation of enehydroxylamino ketones **B**, results in C−C- (**C**) or C−O-type (**D**) dimer formation. The reason for this regiochemistry of nitroxides **A** is highly efficient spin delocalization in the conjugate π-system (Scheme 1).[4,15] At the same time, we have previously shown that oxidation of similar structures with endocyclic localization of the enehydroxylamino ketone group and with a cyano group as a strong electron acceptor at the enamine carbon atom produces persistent vinyl nitroxides, stable enough to be isolated as individual compounds.[7,12]

It is noteworthy that ketene aminals, including cyclic imidazolidines, which are analogues of **1**, are known to be highly reactive compounds, attracting the attention of investigators as convenient precursors for syntheses of fused heterocyclic systems. Syntheses and reactions of these compounds are discussed in detail in reviews,[16,17] and in more recent works by Huang's group. In contrast, no data on the reactivity of *N*-hydroxyketene aminals are available in the literature.

On the other hand, the synthesis of transition metal complexes with paramagnetic ligands, mainly complexes with stable nitroxides bearing functional groups suitable for coordination with the metal ion, is one of the more challenging fields in coordination chemistry.[18,19] Compounds with structure **1** seem to be promising precursors for syntheses of new magnetoactive heterospin complexes (cf. ref.[20]).

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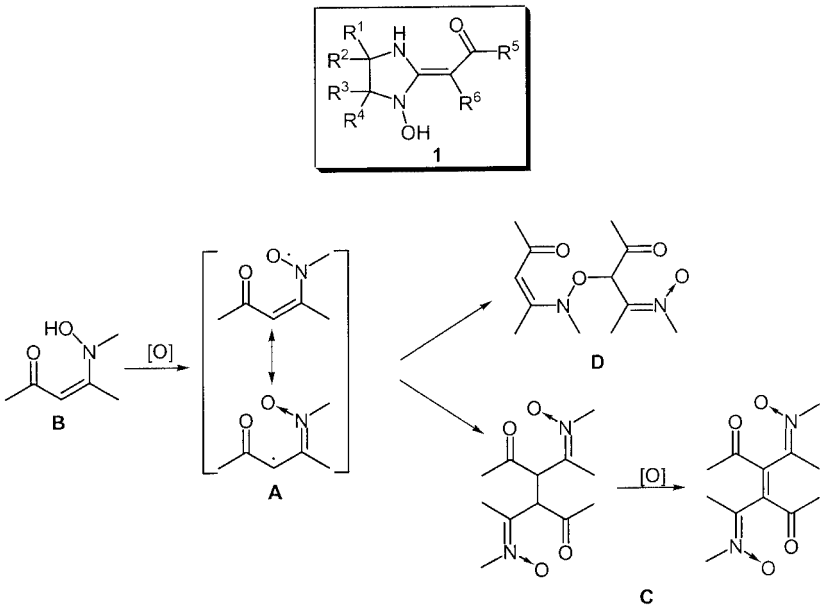


Scheme 1

Results and Discussion

Synthesis of (*R*)-2-(1-Hydroxy-4,4,5,5-tetraalkylimidazolidin-2-ylidene)ethanones

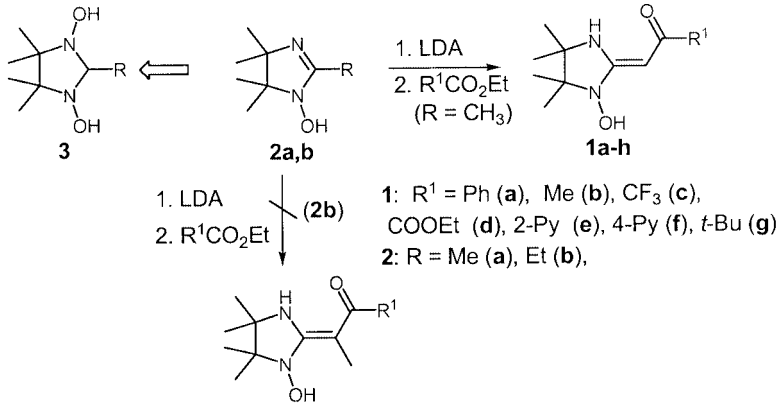
a. Treatment of Metallated 2,4,4,5,5-Pentamethyl-4,5-dihydro-1H-imidazol-1-ol with Esters

The first example of a synthesis of a type **1** compound was the reaction between a 2-imidazoline of type **2** and ethyl benzoate in the presence of LDA.[21] Recently, we have found that imidazoline **2a** can also be involved in this reaction, and a convenient method for the synthesis of **2a** based on thermal oxidative dehydration of dihydroxyimidazolidines **3** has been worked out (preliminary communication: ref.[21]). This method for the synthesis of **1** is shown here to be sufficiently general, and affording a series of enaminones **1** (Scheme 2). It is only viable, though, for compounds with a substituent the size of a methyl group at the 2-position of heterocycle **2**. Metallation of compound **2b** with R = Et and subsequent Claisen reaction with esters failed because of unfavorable steric and electronic effects (cf. ref.[23]).

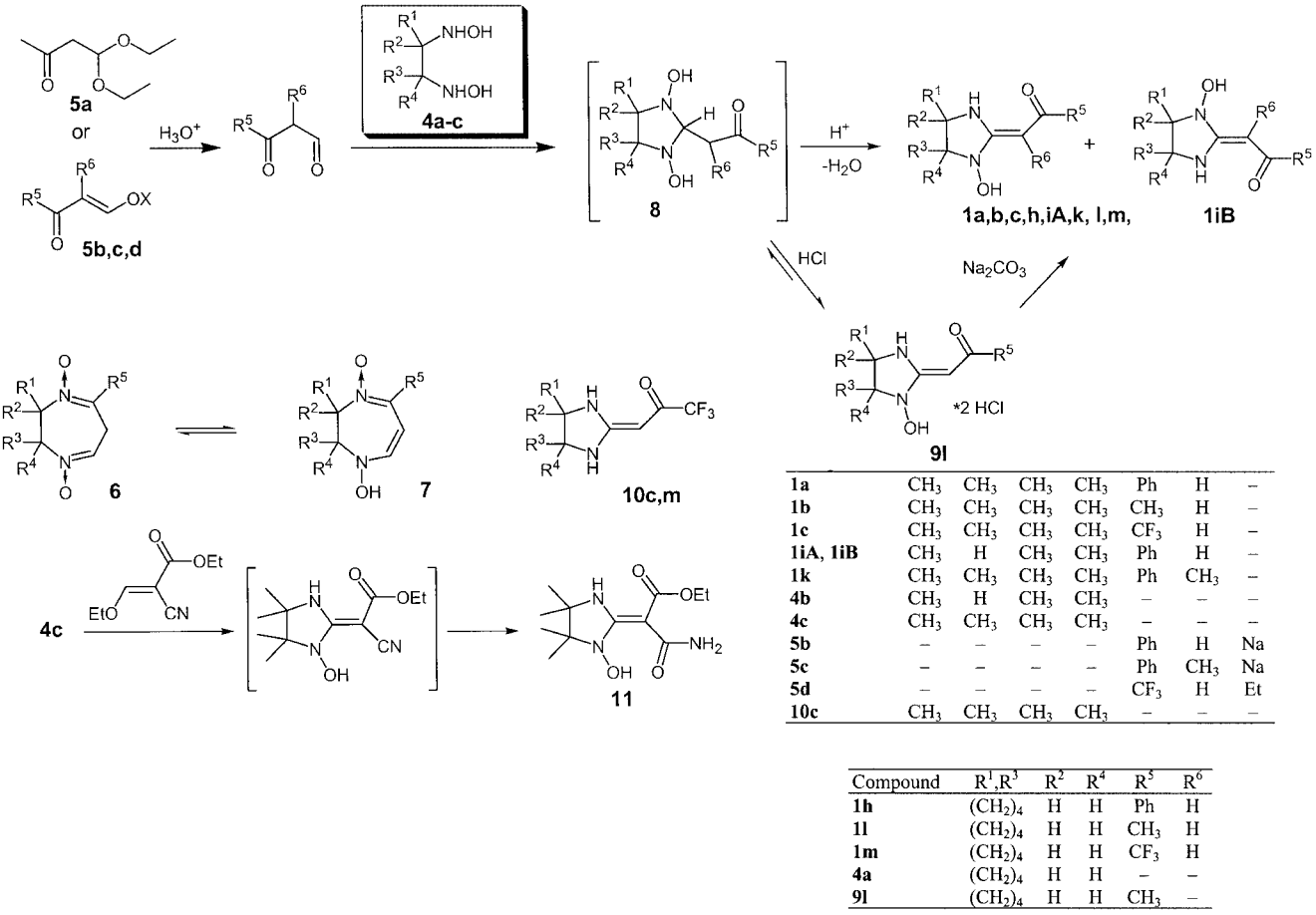
b. Condensation of 1,2-Bishydroxyamines with Synthetic Equivalents of 1,3-Keto Aldehydes

Aliphatic 1,2-diamines (1,2-DAs) are known to react with 1,3-dicarbonyl compounds (1,3-DCCs) in acidic media to form 2,3-dihydro-1,4-diazepinium salts.[24] The reactions of another type of *N*-binucleophile, aliphatic 1,2-bishydroxylamines (1,2-BHAs),[25,26] had not been studied previously, and it was considered that reactions between 1,3-ketoaldehydes (1,3-KAs) and 1,2-BHA **4** should result in the formation of *N*-oxide or *N*-hydroxy derivatives of 1,4-diazepine (preliminary communication: ref.[26]).

Since 1,3-KAs are unstable in the free state, protected forms of 1,3-KAs − namely, 1,3-keto acetal **5a**, salts **5b** and **5c**, and enol ether **5d** − were used in reactions with 1,2-BHAs **4a**−**c** (Scheme 3). The free form of the 1,3-KA was generated in situ by acid-catalyzed hydrolysis in acidic me-



Scheme 2



1a	CH_3	CH_3	CH_3	CH_3	Ph	H	–
1b	CH_3	CH_3	CH_3	CH_3	CH_3	H	–
1c	CH_3	CH_3	CH_3	CH_3	CF_3	H	–
1iA, 1iB	CH_3	H	CH_3	CH_3	Ph	H	–
1k	CH_3	CH_3	CH_3	CH_3	Ph	CH_3	–
4b	CH_3	H	CH_3	CH_3	–	–	–
4c	CH_3	CH_3	CH_3	CH_3	–	–	–
5b	–	–	–	–	Ph	H	Na
5c	–	–	–	–	Ph	CH_3	Na
5d	–	–	–	–	CF_3	H	Et
10c	CH_3	CH_3	CH_3	CH_3	–	–	–

Compound	R^1,R^3	R^2	R^4	R^5	R^6
1h	$(CH_2)_4$	H	H	Ph	H
1l	$(CH_2)_4$	H	H	CH_3	H
1m	$(CH_2)_4$	H	H	CF_3	H
4a	$(CH_2)_4$	H	H	–	–
9l	$(CH_2)_4$	H	H	CH_3	–

Scheme 3

dia at pH ≈ 2−5. The reaction between 1,2-BHA **4a** and sodium 3-oxo-3-phenylpropenoxide (**5b**) proceeds in glacial acetic acid at 20 °C in 30 h, giving, according to element analysis data, a product of addition of the 1,2-BHA at two carbonyl groups of the 1,3-KA with elimination of two water molecules. The compound obtained was neither 1,4-diazepine-1,4-dioxide **6** nor **7**; according to its spectroscopic data it has the structure of the cyclic *N*-hydroxyketene aminal 2-(1-hydroxyimidazolidin-2-ylidene)-1-phenylethanone **1h** (see Exp. Sect. for spectroscopic data).

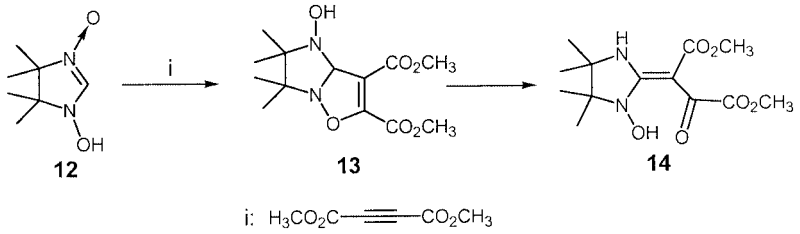
A similar reaction between the sterically hindered 1,2-BHA **4c** and the 1,3-KA **5b** gives the corresponding 1-hydroxy-2-phenacetylideneimidazolidine (**1a**). In the reaction between the asymmetric 1,2-BHA **4b** and **5b**, two isomers were obtained: **1iA** and **1iB**. Enaminones **1** are obviously formed by dehydration of the intermediate imidazolidines **8** (cf. ref.[28]) to enaminones **1A** and **1B**. Introduction of a methyl group at the C-2 atom of the 1,3-KA molecule does not influence the reaction pathway; condensation of the 1,2-BHA **4c** with the sodium salt of 3-hydroxy-2-methyl-1-phenylprop-2-en-1-one (**5c**) occurs similarly and yields the corresponding imidazolidine **1k**. Treatment of the 1,2-BHA **4a** with acetoacetaldehyde diethyl acetal **5a** in methanol saturated with HCl gives the dihydrochloride **9l** in a good yield; subsequent neutralization of the solution results in the isolation of enaminone **1l** (Scheme 3).

Treatment of the 1,2-BHAs **4a** or **4c** with *trans*-β-ethoxyvinyl trifluoromethyl ketone **5c**[29] in a water/methanol solution of HCl also gave the enaminones **1m** and **1c**, respectively. In the case of **4c**, an approximately equal amount of enaminone **10c** was formed together with **1c**. Moreover, according to the NMR spectroscopic data, a crude sample of **1m** contains enaminone **10m** as an impurity. This result cannot be attributed to insufficient purity of starting **4c**; most probably it is the result of some redox processes of unknown nature.

Treatment of **4c** with ethyl 2-cyano-3-ethoxyacrylate proceeds in a similar way, but is accompanied by hydrolysis of the nitrile group, giving rise to amide **11**, the crystal structure of which is shown in Figure 4.

c. Cycloaddition Reaction

Finally, the third approach to the synthesis of structures of type **1** is the 1,3-dipolar cycloaddition reactions between 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-ol 3-oxide (**12**) and activated alkynes (Scheme 4, cf. ref.[31]). While cycloadditions between 2,5-dihydroimidazole nitrones and different dipolarophiles, including activated alkynes, are well known (for recent papers, see ref.[32−35]), there is only one example of 1,3-dipolar cycloadditions of 4,5-dihydroimidazole nitrones as dipoles described in the literature.[35]



Scheme 4

Strictly speaking, compound **12** is an *N*-hydroxyamidoxime rather than a nitrone, and one cannot exclude the possibility of a nucleophilic addition of the hydroxy group to the activated CC multiple bond of the addend along with, or instead of, cycloaddition.

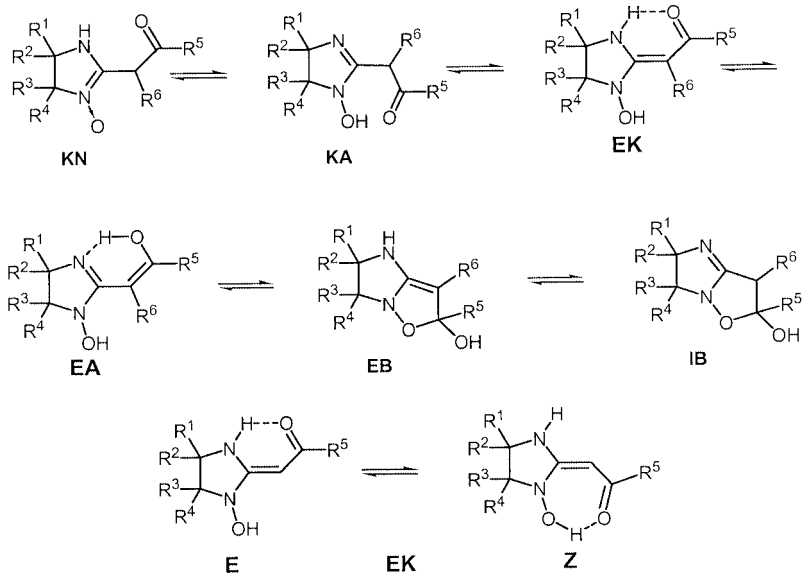
Nevertheless, treatment of **12** with dimethyl acetylenedicarboxylate (DMAD) gives the corresponding cycloadduct **13** as the sole product, and this is spontaneously transformed into the imidazolidine **14**, differing from the previously synthesized **1** in the presence of a methoxycarbonyl group at the enamine carbon atom. This reaction is characterized by the relatively high stability of cycloadduct **13**, which can readily be isolated; according to ^{1}H NMR spectroscopic data, its subsequent transformation into the imidazolidine **14** is much slower than its formation (cf. refs.[36–39]).

Structures of the (*R*)-2-(1-Hydroxyimidazolidin-2-ylidene)-ethanones 1

^{13}C NMR spectroscopic data have demonstrated that the (*R*)-2-(1-hydroxyimidazolidin-2-ylidene)ethanones **1**, **11**, and **14** exist in the conjugated enaminone tautomeric form **EK**; no signals of the ketone-amidine form **KA** have been observed. The signals may be assigned both to the enaminone form **EK** and to the enol-amidine form **EA**, existing in a fast (NMR timescale) equilibrium **EK** ⇄ **EA** as a result of intramolecular proton transfer from N to O. It seems unlikely that compounds **1** should exist in bicyclic tautomeric forms **EB** or **IB** (Scheme 5).

In contrast to other imidazolidines **1**, existing in conjugated form both in the solid state and in DMSO and $CDCl_3$ solutions, compound **1k** is found to exist in chloroform solution in the non-conjugated tautomeric form. Thus, the ^{1}H NMR spectrum of **1k** contains a doublet for a methyl group at δ = 1.48 ppm and a quadruplet for the proton at the exocyclic carbon atom at δ = 4.81 ppm. The tautomeric form **KA** seems to be more probable than **KN** because the signal of the C-2 atom in the ^{13}C NMR spectrum lies at δ = 162.0 ppm.

Since rotation around the exocyclic carbon−carbon double bond is hindered, one can imagine that the conjugate tautomeric forms **EK** and (or) **EA** may exist as *E* and *Z* (cf. ref.[30]) isomers (or conformers) and that the geometry of the exocyclic double bond cannot easily be determined from NMR spectroscopic data. The equilibrium may be slow or fast on the NMR timescale, so determination of the true geometry of **1** or of the isomer ratio and quantity is not an easy task. For instance, the ^{1}H NMR spectrum of **1e** contains low-field signals at δ = 8.8 and 9.7 ppm (NH and OH protons), but nothing can be said about the geometry of the exocyclic double bond in **1e**. X-ray analysis data show that crystalline enaminone **1a** exists in the conju-



Scheme 5

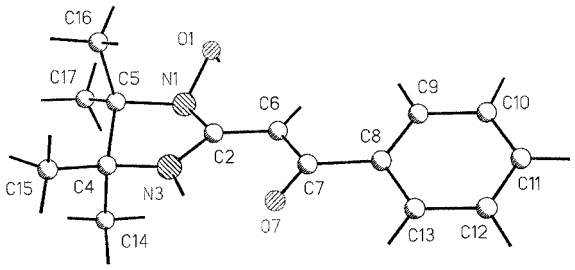


Figure 1. Atomic numbering scheme and structure of the (*R*)-2-(1-hydroxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)-1-phenylethanone molecule (**1a**); average bond lengths (in two crystallographically independent molecules, Å): N(1)−C(2) 1.362(4); C(2)−N(3) 1.337(4); N(3)−C(4) 1.376(4); C(4)−C(5) 1.554(4); C(5)−N(1) 1.488(4); N(1)−O(1) 1.405(3); C(2)−C(6) 1.388(4); C(6)−C(7) 1.381(4); C(7)−C(8) 1.505(4); C(7)−O(7) 1.270(4); the O(7)−C(7)−C(8)−C(13) torsion angles are 14.6 and −14.5°; hydrogen bond parameters (Å, deg, head-to-tail chains along the *a* axis): O(1)−H(1)···O(7)[1] 1.09(6), 1.53(6), 2.580(4), 158(5); O(1A)−H(1A)···O(7A)[1] 0.98(4), 1.67(4), 2.639(3), 174(5); symmetry operations: [1] $x-1, y, z$ (CCDC-214520)

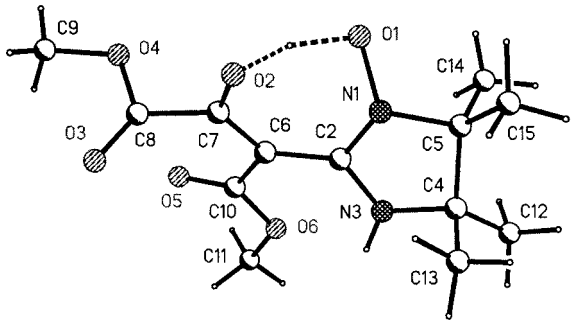


Figure 2. Atomic numbering scheme and molecular structure of dimethyl 2-(1-hydroxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)-3-oxosuccinate (**14**); selected bond lengths: $C-C_{Me}$ 1.504(4)−1.542(3), O(1)−N(1) 1.399(3), N(1)−C(2) 1.339(3), N(1)−C(5) 1.476(3), C(2)−N(3) 1.324(3), C(2)−C(6) 1.437(3), N(3)−C(4) 1.481(3), C(4)−C(5) 1.549(4), C(6)−C(10) 1.461(3), C(10)−O(5) 1.203(2), C(6)−C(7) 1.399(3), C(7)−O(2) 1.260(3), C(7)−C(8) 1.515(3), C(8)−O(3) 1.202(3); H-bond parameters: O(1)−H(1) 1.37(5), H(1)···O(2) 1.16(5), O(1)···O(2) 2.490(3) Å, O(1)−H(1)···O(2) 160(5)°, N(3)−H(3) 0.83(3), H(3)···O(3)[1] 2.21(3), N(3)···O(3)[1] 2.984(3) Å, N(3)−H(3)···O(3)[1] 155(2)°; symmetry operations: [1] $-x, -y+1, -z$ (CCDC-214521)

gated enaminone form **EK** as the *E* isomer (Figure 1). According to X-ray analysis data, diester **14** possesses the *E* configuration of the exocyclic carbon-carbon double bond in the crystalline state (Figure 2), with the carbonyl oxygen hydrogen-bonded to the endocyclic hydroxyamino group. As to the structure of compound **14** in solution, the problem is more complex − the spectra of different samples contain double sets of proton signals for NH, OH, and methoxy groups (see Exp. Sect.) and the comparative intensities of the signals in pairs differ from sample to sample. This obviously means that two forms (*E* and *Z*) are present in a solution of **14**, but we did not determine whether they equilibrate or not. The configuration of the exocyclic C=C bond in the crystalline state of amide **11** seems to be dictated not only by intramolecular hydrogen bonding involving the hydroxy group and the amide carbonyl atom, but also by intermolecular hydrogen bonding of the amide group (Figure 3).

It thus seems virtually impossible to predict the configuration of the exocyclic carbon−carbon double bond for solid (*R*)-2-(1-hydroxyimidazolidin-2-ylidene)ethanone (**1**) and to determine the geometry of **1** in solutions unambiguously because of possible *E*/*Z* isomerization.

This investigation coincided with the publication of another synthetic procedure for compounds of type **1**. The method is based on reactions between 1,2-BHA **4c** and another masked form of 1,3-ketoaldehydes − substituted phenylpropargyl aldehydes (Scheme 6).[43] Contrary to the

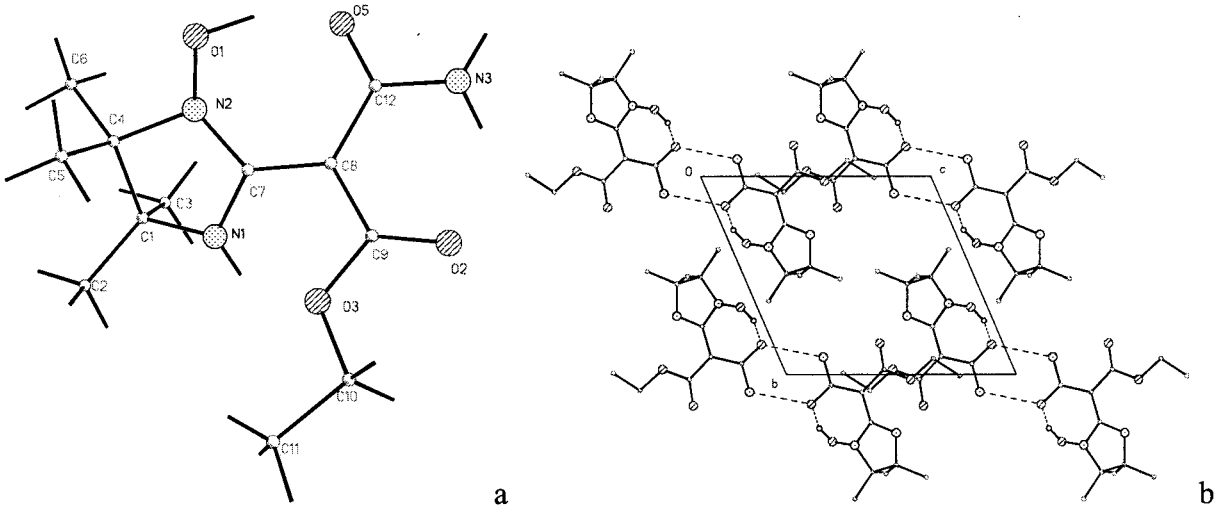
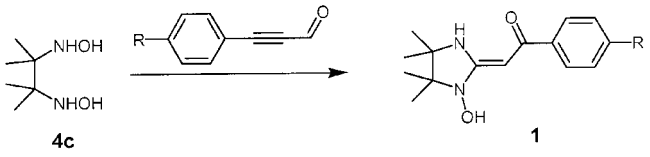


Figure 3. Molecular structure of **11** and atomic numbering scheme (a); projection of packing onto the (100) plane; (b) bond lengths (Å): N(1)−C(7) 1.343(4), N(1)−C(1) 1.471(4), C(1)−C(3) 1.517(5), C(1)−C(2) 1.518(4), C(1)−C(4) 1.563(4), C(4)−N(2) 1.484(4), C(4)−C(6) 1.510(4), C(4)−C(5) 1.529(5), N(2)−C(7) 1.341(4), N(2)−O(1) 1.396(3), C(7)−C(8) 1.431(4), C(8)−C(9) 1.440(4), C(8)−C(12) 1.453(4), C(9)−O(2) 1.226(4), C(9)−O(3) 1.345(4), O(3)−C(10) 1.441(4), C(10)−C(11) 1.486(6), C(12)−O(5) 1.257(4), C(12)−N(3) 1.343(4); hydrogen bond parameters (Å, deg): N(1)−H(1)···O(2)[1] 0.80(4), 2.28(4), 3.038(4), 157(3); O(1)−H(11)···O(5) 1.02(4), 1.52(4), 2.493(3), 158(4); N(3)−H(41)···O(2) 0.87(4), 1.94(4), 2.665(4), 140(4); N(3)−H(42)···O(5)[2] 0.92(5), 2.03(5), 2.950(4), 177(4); symmetry operations: [1] $-x, -y+2, -z+1$; [2] $-x, -y+2, -z+2$ (CCDC-215674)

statement of the authors, this seems to be a less general procedure than the first two methods described above, only suitable for syntheses of aryl-substituted derivatives.



Scheme 6

Reactions between (*R*)-2-(1-Hydroxyimidazolidin-2-ylidene)-ethanones and Some Electrophiles

Methods have thus been worked out for the synthesis of cyclic (*R*)-2-(1-hydroxy-4,4,5,5-tetraalkylimidazolidin-2-ylidene)ethanones **1**, thanks to which these compounds are available for further reactivity studies. There are five possible sites of electrophilic attack in molecule **1** (Scheme 7). Nitrosation of **1a** with amyl nitrite in the presence of sodium methoxide occurs at the enamine carbon atom and is accompanied by oxidation, giving an imino nitroxide − oxime **15**. In contrast, the reaction between **1a** and methyl nitrate under the same conditions results in the formation of *O*-methylation product **16a** together with the reduction product − enaminone **17**, the crystal structure of which is shown in Figure 4. The way in which **1a** undergoes reduction in the presence of methyl nitrate as an oxidant remains unknown.

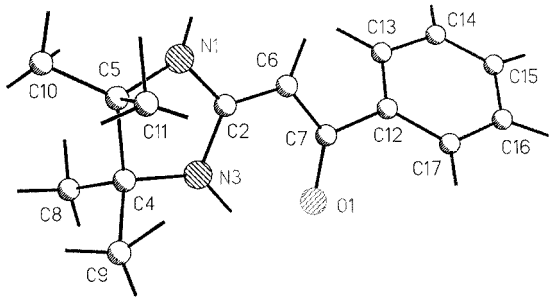
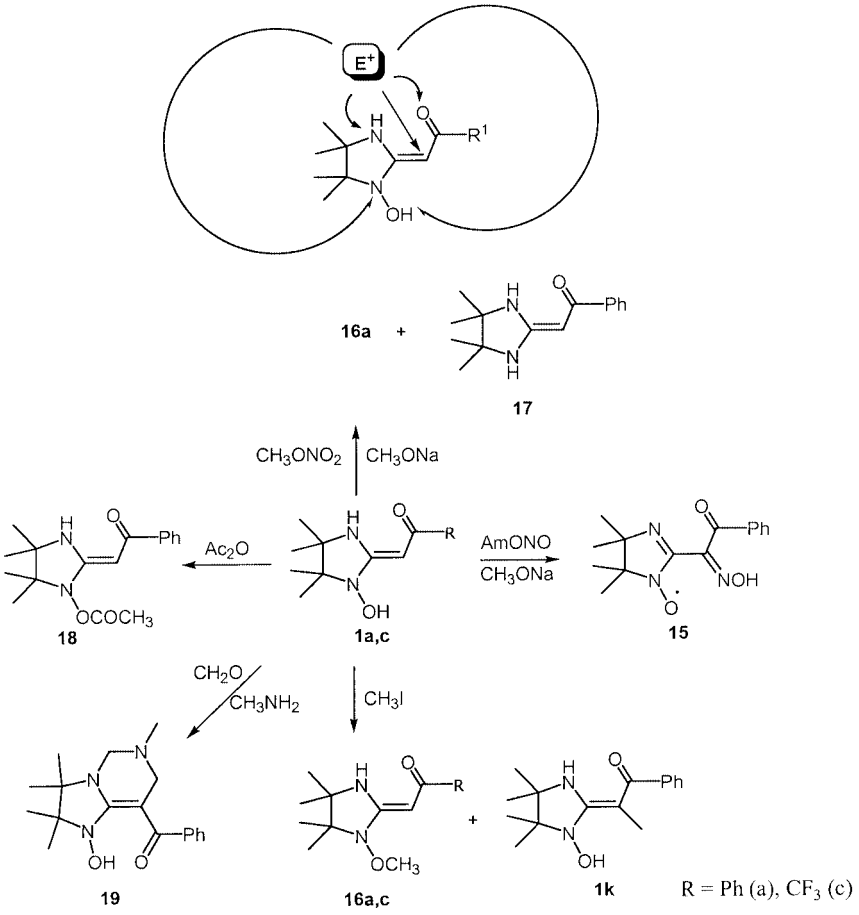


Figure 4. Atomic numbering scheme and molecular structure of **17**; bond lengths: N(1)−C(2) 1.332(5), C(2)−N(3) 1.332(5), N(3)−C(4) 1.454(6), C(4)−C(5) 1.565(7), C(5)−N(1) 1.458(7), C(2)−C(6) 1.393(6), C(6)−C(7) 1.376(6), C(7)−C(12) 1.510(6), C(7)−O(1) 1.272(5) Å; the O(1)−C(7)−C(12)−C(17) torsion angle is −45.6°; hydrogen bond parameters (Å, deg, head-to-tail chains along the *a* axis): N(1)−H(1)···O(1)[1] 0.76(5), 2.11(5), 2.865(5) Å, 169(6); symmetry operations: [1] $x - 1/2, 1/2 - y, 1 - z$ (CCDC-214521)

Alkylation of **1a** with methyl iodide occurs mainly at the oxygen atom of the hydroxyamino group, forming the methoxy derivative **16a**. *C*-Methylated product **1k** was also isolated from the reaction mixture, in a low yield, along with



Scheme 7

16a. Treatment of imidazolidine **1c** with CH_3I yields the methoxy derivative **16c** as the sole product. It is important to note that, according to literature data, an enehydroxylamino ketone with a similar structure reacts with CH_3I under similar conditions at the enamine carbon atom, forming a *C*-alkylated product.[8] Acylation of **1a** by acetic anhydride proceeds at the hydroxylamino oxygen atom and forms acetate **18**. The reaction of **1a** with methylamine and formaldehyde involves both the enamine carbon atom and the endocyclic nitrogen atom of the enamino ketone group and gives rise to 2,3,5,6,7-hexahydroimidazo[1,2-*c*]pyrimidine derivative **19** (cf. ref.[40], Scheme 7).

We had previously found that both enaminones and enehydroxylamino ketones react with *N*-chloro- and *N*-bromosuccinimides to form mono- or dihalo derivatives depending on the substrate/reagent ratio.[7,30,41] Treatment of **1** with an equimolar amount of *N*-chlorosuccinimide (NCS) gives moderate yields of monochloro derivatives **20**, of low stability and not isolable in pure form (cf. ref.[22]). The reaction is hindered by easy oxidation of the starting enehydroxylamino ketones (cf. Scheme 1) and by low selectivity. Thus, chlorination of **1a** gives a noticeable amount of dichloro derivative **21** along with monochloro derivative **20a**; the former is easily separated thanks to its low solubility in chloroform. In contrast, methoxy (**16a**) and acetoxy (**18**) derivatives give stable monochlorides **22a** and **22b** in high yields under the same conditions.

Synthesis of Persistent Vinyl Nitroxides – 2-(1-Oxyl-4,4,5,5-tetramethylimidazolidin-2-ylidene)-3-oxopropionitrile

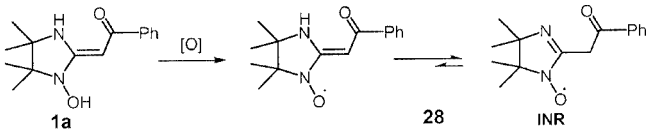
In view of the potential easy substitution of chlorine at the enamine carbon in the enaminone molecule (cf. refs.[22,30]) and also of the synthesis of persistent vinyl nitroxides of type **23**[7,12] through introduction of a cyano group at a similar position in the endocyclic β-oxonitrone molecule, we studied the reaction between **20** and sodium cyanide (Scheme 8).

The substitution reaction proceeds smoothly at room temperature in DMSO, forming nitriles **24** in moderate yields. Treatment of methoxy derivative **22a** and acetoxy derivative **22b** with cyanide gives nitriles **25** and **26**, respectively; the latter hydrolyzes during isolation, forming nitrile **24a** in a high yield, which seems to be a convenient alternative method for the synthesis of **24a**. We failed to obtain nitriles **24** by chlorination of enaminones **1d** or **1n** (amide **1n** was obtained by ammonolysis of ester **1d**) and subsequent treatment with NaCN, probably because of the hydrolysis of the ester or amide groups during the isolation of the desirable nitriles.

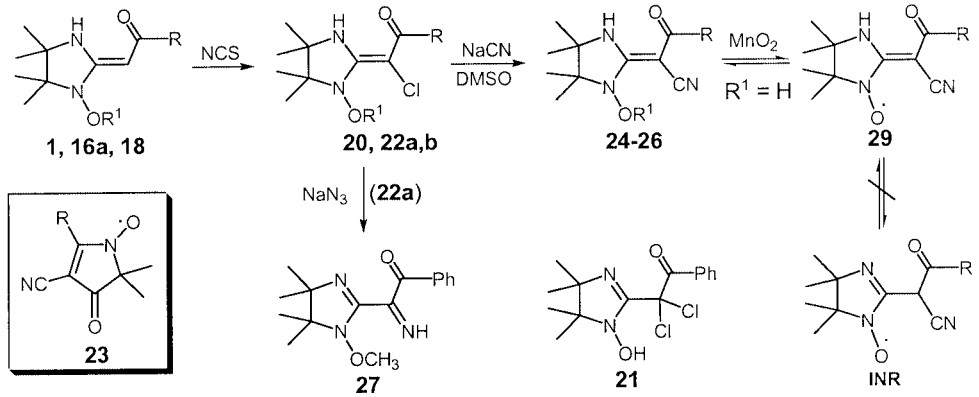
According to their NMR spectroscopic data, each of the nitriles **24**–**26** exists in the conjugated enehydroxylamino ketone form in solution. For example, the ^{13}C NMR spectrum of nitrile **24c** contain the signals for the nitrile carbon at δ = 115.8 ppm, the signals for the enamine carbon atoms at 63.6 [C(CN)=] and 162.8 ppm (C-2), and the signal for the carbonyl carbon at δ = 173.8 ppm (q, J = 32 Hz).

It is interesting to note that treatment of **22a** with NaN_3 occurs as observed earlier for chlorosubstituted enaminones (cf. ref.[42]), forming α-diketone monoimine **27**.

As mentioned above, sterically hindered 2-acylmethylene-1-hydroxyimidazolidines **1** (R^{1-4} = CH_3) are of interest as precursors of paramagnetic ligands for the synthesis of transition metal complexes with potentially unusual magnetic properties.[20] However, because of the strong tendency toward recombination of most radicals generated by oxidation of the corresponding enehydroxylamino ketones (Scheme 1), isolation of nitroxides **28** that could be generated by oxidation of **1** seems to be improbable (Scheme 9).



Scheme 9



1, **20**, **24**, **29**: R = Ph (a), Me (b), CF_3 (c), 2-Py (e), 4-Py (f), *tert*-Bu (g)
16a, **18**, **22a,b**, **25**, **26**: R = Ph
R^1 = H (**1**, **20**, **24**), CH_3 (**16a**, **22a**, **25**), CH_3CO (**18**, **22b**, **26**)

Scheme 8

Imidazolidine **1a** is oxidized by PbO_2 into the unstable radical **28**, the EPR spectrum of which demonstrates splitting on two nonequivalent nitrogen atoms. The values of the hfs constants (a_{N1} = 9.2 G, a_{N2} = 4.6 G) are similar to those of iminonitroxides. These data, along with the absence of splitting on hydrogen atoms, indicate that nitroxide **28** exists in the iminonitroxide tautomeric form (**INR**). Nitroxide **28** forms in very low concentrations not increasing with time; after a few minutes the solution becomes entirely diamagnetic and a complex mixture of compounds forms according to TLC. It might be thought that decomposition of this type of radical is the result of dimer-forming recombination (cf. Scheme 1). As a matter of fact, the reaction is a rather complex process producing a large variety of products depending strongly on the character of the oxidant and solvent. The only product isolated in the oxidation reaction of **1a** was enaminone **17**; formally, this is the product of the reduction of starting **1a,** which demonstrates that the oxidation is a complex process. At the same time, oxidation of Ni^{2+}, Co^{2+}, Cu^{2+}, and Pd^{2+} coordination compounds of **1c** by PbO_2 results in the formation of complexes containing the deprotonated nitroxide of type **28** as a ligand (cf. ref.[20]).

The introduction of the cyano group at the enamine carbon atom in molecule **24** obviously hinders recombination (cf. refs.[7,12,22]), and the oxidation of these compounds actually leads to the formation of persistent vinyl nitroxides **29**. These radicals could not be isolated in analytically pure form, but they exist in the crystalline state at about 0 °C for prolonged periods (months). The main decomposition route of these radicals is reduction to the corresponding hydroxylamines **24** on storage in ethanol solutions and even as crystals at room temperature. The EPR spectroscopic data (Figure 5) are summarized in Table 1. The distinguishing feature of these spectra is coupling on three nonequivalent nitrogen atoms, including the nitrogen atom of the cyano group, evidently the result of very efficient spin density delocalization over the conjugated π-system, and the high splitting constant on a hydrogen atom (≈ 2 G), apparently on the one lying at the N-3 atom. This could be explained by the existence of nitroxides **29** in imidazolidine rather than the **INR** tautomeric forms.

It is important to note that the magnetic susceptibility curve of nitroxide **29c** (Figure 6, d) shows the presence of a strong intermolecular exchange interaction in the solid sample, which hinders evaluation of the paramagnetic molecule content (cf. ref.[12]). Nevertheless, the structure of nitroxide **29c** was determined precisely, thanks to X-ray analysis data for its potassium salt, the structure of which is shown in Figure 7.

In an attempt to obtain nitroxide **28g** in crystalline form suitable for an X-ray analysis, we found that the sample contains an impurity of compound **30**, which was separated manually and its structure determined (Figures 8 and 9).

A possible scheme showing the formation of compound **30** in the course of the reaction between chloride **20g** and sodium cyanide and subsequent oxidation is given below (Scheme 10). It is believed that the reaction mechanism is quite similar to the mechanisms postulated earlier for the reactions of chlorosubstituted enaminones of imidazolidine nitroxide; the first stage is the nucleophilic attack of the cyanide anion at the carbonyl carbon, forming cyanohydrin anion **31**.

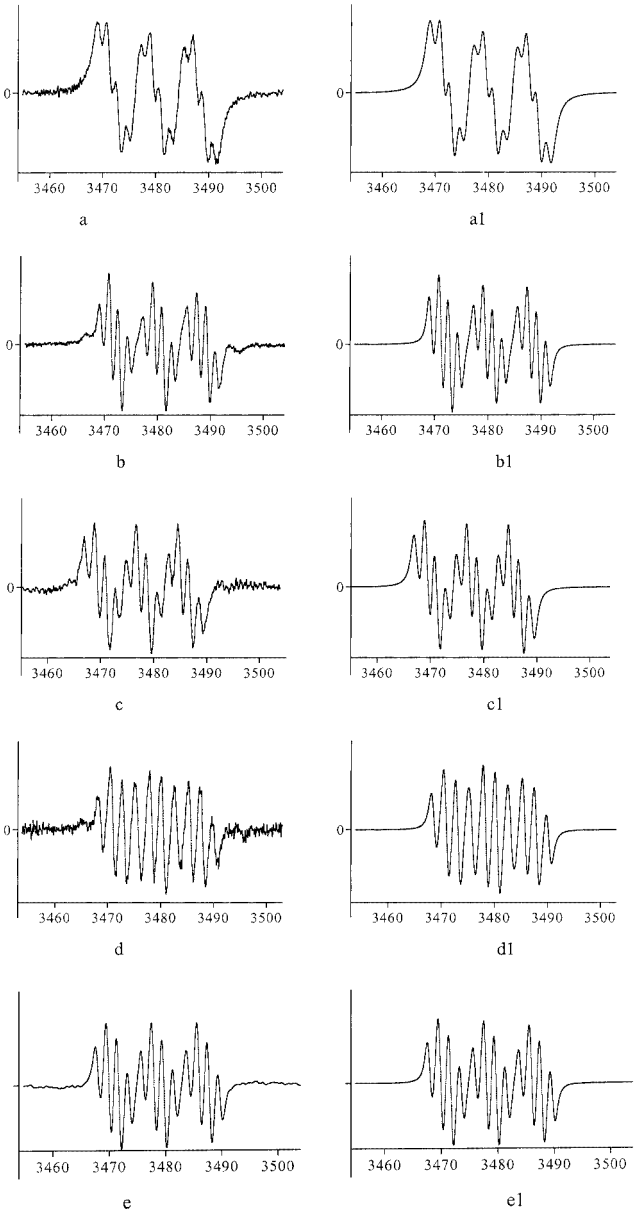


Figure 5. EPR spectra and simulations for nitroxides **29**: a: **29b**, b: **29g**, c: **29e**, d: **28c**, e: **29a**

Table 1. EPR spectral data for radicals **29**

	g factor	Hfs constants, *G*
28a	2.0044	8.03 ($^{14}N_1$), 1.80 ($^{14}N_3$), 0.27 ($^{14}N_{CN}$), 1.95 ($^{1}H_{NH}$)
29b	2.0040	8.13 ($^{14}N_1$), 1.72 ($^{14}N_3$), 0.41 ($^{14}N_{CN}$), 1.85 ($^{1}H_{NH}$)
28c	2.0043	7.37 ($^{14}N_1$), 2.19 ($^{14}N_3$), 0.30 ($^{14}N_{CN}$), 2.39 ($^{1}H_{NH}$)
28e	2.0051	7.86 ($^{14}N_1$), 1.82 ($^{14}N_3$), 0.40 ($^{14}N_{CN}$), 2.00 ($^{1}H_{NH}$)
28g	2.00451	8.29 ($^{14}N_1$), 1.67 ($^{14}N_3$), 0.30 ($^{14}N_{CN}$), 1.87 ($^{1}H_{NH}$)

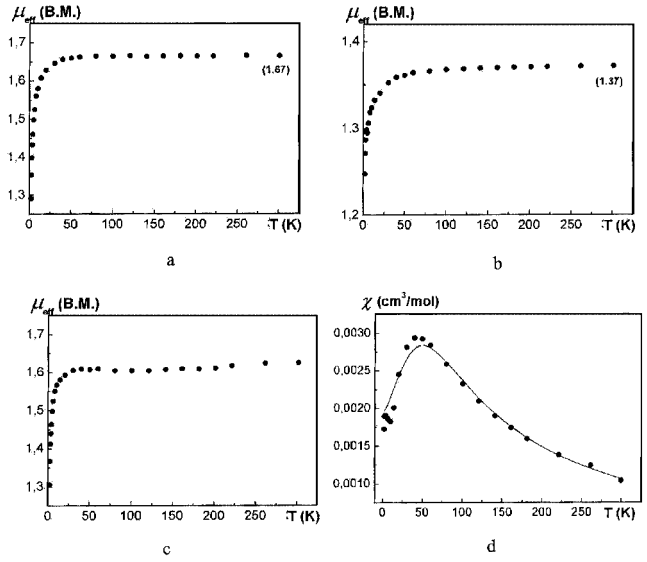


Figure 6. Effective magnetic moment curves (a−c) for nitroxides **29** (radical content, %): a: **29a** (93), b: **29e** (63), c: **29g** (85) and magnetic susceptibility for **29c** (d)

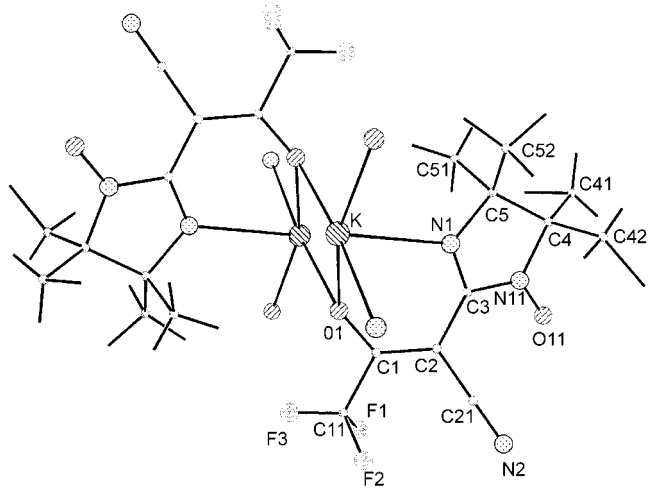


Figure 7. Crystal structure of the potassium salt of nitroxide **29c**[22]

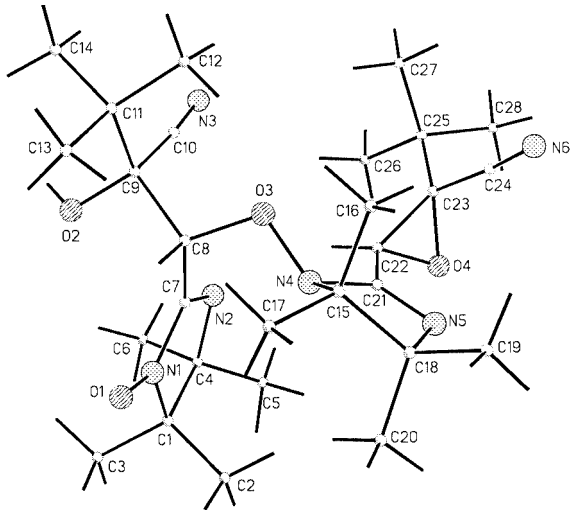


Figure 8. Atomic numbering scheme and structure of molecule **30**; average bond lengths (on two crystallographically independent molecules): C−C_{Me} 1.501(4)−1.541(3), O(1)−N(1) 1.260(3), N(1)−C(7) 1.383(3), N(1)−C(1) 1.485(3), C(1)−C(4) 1.555(4), C(4)−N(2) 1.493(3), N(2)−C(7) 1.267(3), C(7)−C(8) 1.498(3), C(8)−O(3) 1.437(2), C(8)−C(9) 1.547(3), C(9)−O(2) 1.403(3), C(9)−C(10) 1.473(4), C(9)−C(11) 1.568(4), C(10)−N(3) 1.140(4), O(3)−N(4) 1.433(2), N(4)−C(21) 1.396(3), N(4)−C(15) 1.495(3), C(15)−C(18) 1.564(4), C(18)−N(5) 1.500(3), N(5)−C(21) 1.273(3), C(21)−C(22) 1.475(3), C(22)−O(4) 1.427(3), C(22)−C(23) 1.477(3), O(4)−C(23) 1.429(3), C(23)−C(24) 1.462(4), C(23)−C(25) 1.515(3), C(24)−N(6) 1.135(3) Å

Subsequent migration of the multiple bond inside the heterocycle and intramolecular nucleophilic substitution give epoxide **32**. An epoxide with a similar structure has previously been isolated and characterized similar to the case of the reaction of enaminone of imidazolidin-4-ylidene with a *tert*-butyl group at the carbonyl function, which is one of the products of the reaction with sodium cyanide.[30] The relatively high kinetic stability of the epoxide with a *tert*-butyl group substituent in relation to the kinetic stability of other substituents, probably due to steric hindrance to subsequent nucleophilic cleavage of the epoxide heterocycle, permits an alternative to the normal route − epoxide cleavage in molecule **32** as a result of a nucleophilic attack

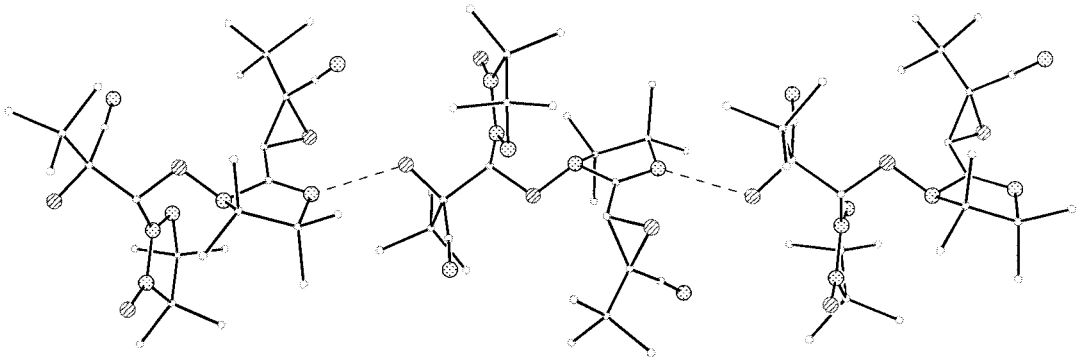
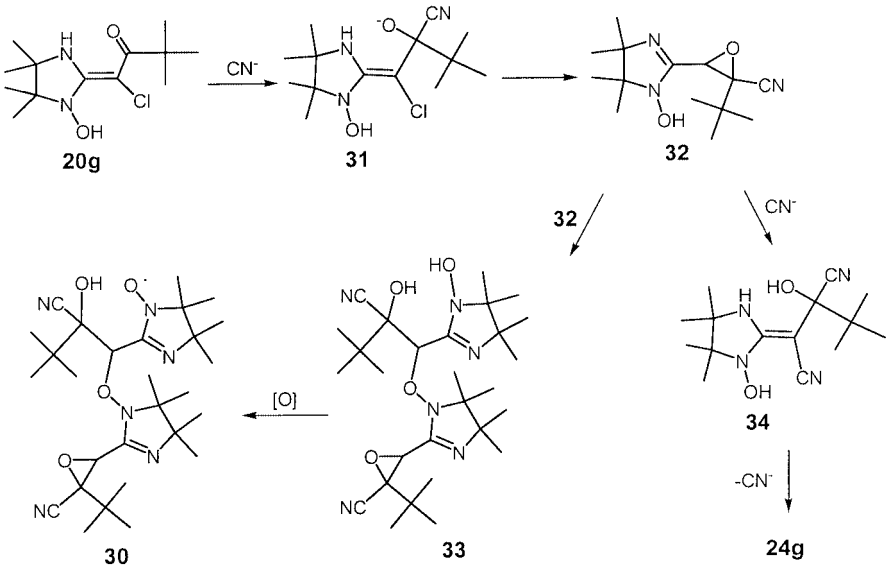


Figure 9. Chain in the structure of **30**; H-bond parameters: O(2)−H(2E) 0.82(3) Å, H(2E)···N(5)[1] 2.03(3) Å, O(2)···N(5)[1] 2.837(3) Å, O(2)−H(2E)−N(5)[1] 166(3)°, O(2A)−H(2AE)···N(5A)[2], 0.91(3) Å, H(2AE)···N(5A)[2] 1.93(3) Å, O(2A)···N(5A)[2] 2.828(3) Å, O(2A)H(2AE)N(5A)[2] 169(3)°; symmetry operations: [1] $-x$, $y + 1/2$, $-z + 1/2$; [2] $-x - 1$, $y + 1/2$, $-z + 1/2$ (CCDC-215673)



Scheme 10

of the hydroxy group of another molecule **32** instead of the cyanide anion. Subsequent oxidation of the resulting hydroxylamine **33** gives the nitroxide **30**. Compound **30** was formed as a minor by-product along with nitroxide **29g**, but its formation is good evidence in favor of the previously postulated mechanism for the reactions of halo-substituted enaminones and enehydroxylamino ketones with nucleophiles (cf. ref.[42])

Conclusions

Three approaches to the synthesis of a new class of compounds − (*R*)-2-(1-hydroxy-4,4,5,5-tetraalkylimidazolidin-2-ylidene)ethanones **1** − have been worked out:

(a) Claisen condensations between metallated 2,4,4,5,5-pentamethyl-4,5-dihydro-1*H*-imidazol-1-ol and esters,

(b) condensation of 1,2-bishydroxyamines with 1,3-keto aldehyde precursors, and

(c) cycloaddition between 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-ol 3-oxide and DMAD.

Route (a) permits variation of a substituent at carbonyl group and seems to be most versatile thanks to the availability of starting esters, but limited by the availability of the only known suitable precursor − imidazoline **2a**. The advantage of route (b) is its potential for the synthesis of a wide scope of starting 1,2-bishydroxyamines of type **4**. The third approach (c) is at the very beginning of its exploration, and further studies to investigate this reaction are underway.

The reactivity of (*R*)-2-(1-hydroxy-4,4,5,5-tetraalkylimidazolidin-2-ylidene)ethanones **1** with electrophiles mainly depends on the presence of an enaminone function in the molecule. The site of the electrophilic attack is the enamine carbon atom, but in some cases the reactions proceed at the oxygen atom of the endocyclic hydroxyamino group. The ease of substitution of chlorine at the enamine carbon atom by the cyano group and subsequent oxidation provide syntheses of a series of new persistent vinyl nitroxides, which are prospective paramagnetic ligands.

Experimental Section

IR spectra were recorded on a Bruker IFS 66 spectrometer as 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 and Bruker AC 200 spectrometers with 5−10% solutions in $CDCl_3$, or [D_6]DMSO and HMDS or solvent as the internal standard. High-resolution mass spectra were recorded on a Finnigan MAT 8200 mass spectrometer with direct sample injection at a resolution of 10000. X-ray data were measured on a Bruker P4 diffractometer with graphite monochromated Mo-K_α radiation. CCDC-214520, -214521, -215674, and -215673 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. ESR spectra were registered for $5\cdot10^{-4}$ M solutions of radicals **29** in chloroform on a Bruker ESP-300 spectrometer with a double resonator. The *g*-factors were calculated relative to the standard (MnO) positioned on the back shoulder of the resonator. ESR spectra were simulated by use of the WINSYM program with an LMB1 optimization algorithm. Melting points were measured on a "Boetius" plate and are uncorrected. Thin layer chromatography monitoring was carried out on Silufol UV-254 plates with chloroform and chloroform/MeOH (30:1 or 20:1) as eluents. Diethyl ether was dried with $CaCl_2$ and then over sodium wire; DMSO was dried with NaOH and distilled in vacuo over BaO. Alumina neutral (degree of activity II) and silica gel (Merck, 0.063−0.200 mm) were used for chromatographic purification of the synthesized compounds. The solutions were evaporated in vacuo in all cases.

Reactions between 2,4,4,5,5-Pentamethyl-4,5-dihydroimidazol-1-ol (2a) and Esters (General Procedure): The reaction was carried out under argon. Diisopropylamine (2.7 mL, 19.5 mmol) was added dropwise with stirring over 10 min to a solution of phenyllithium prepared from bromobenzene (3 g, 19.2 mmol) and lithium (0.27 g, 38.4 mmol) in anhydrous diethyl ether (30 mL). The stirring was continued for 30 min at room temperature, and finely powdered imidazoline **2a** (1 g, 6.4 mmol) was then added portionwise to the resulting solution of LDA. The stirring was continued for another 30 min at room temperature, and the reaction mixture was then cooled to 0 °C and an ester (ethyl benzoate, ethyl acetate, ethyl trifluoroacetate, ethyl pivalate, diethyl oxalate, or ethyl picolinate) solution (12 mmol) in diethyl ether was added rapidly. The reaction mixture was stirred for 2 h at 20 °C, cooled to 0 °C, and then quenched by slow addition of water (20 mL). The aqueous solution was separated, and the diethyl ether solution was extracted with water (5 mL) and discarded. The combined aqueous solution was washed with diethyl ether (2 × 20 mL) and neutralized with 5% HCl. After that, either the precipitate of enaminone **1** was filtered off, or the solution was extracted with $CHCl_3$ (5 × 30 mL). The combined extract was evaporated, and the residue was recrystallized.

Compound 1a: Yield 60%. ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.08 (s, 6 H), 1.19 [s, 6 H, 4,5-$(CH_3)_2$], 5.49 (s, 1 H, CH=), 7.33−7.44 (m, 3 H), 7.70−7.82 (m, 2 H, Ph), 8.80−9.20 (broad s, 1 H), 9.38 (s, 1 H, NH, OH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 18.0 [5,5-$(CH_3)_2$], 23.0, [4,4-$(CH_3)_2$], 60.2 (C-4), 68.2 (C-5), 74.2 (CH=), 126.4, 128.2, 130.0, 141.0 (Ph), 163.7 (C-2), 183.9 (C=O). IR (ṽ, cm^{-1}): 3300, 3110 (OH, NH), 1600, 1575, 1525, 1485 (HN−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 242 (4.13), 330 (4.41). m.p. 185−188 °C (from ethanol). $C_{15}H_{20}N_2O_2 \cdot H_2O$: calcd. C 66.9, H 7.9, N 10.4; found C 66.9, H 7.9, N 10.0.

$C_{15}H_{20}N_2O_2$, FW = 260.33, monoclinic, $P2_1/n$, a = 6.979(1), b = 13.429(2), c = 31.532(5) Å, β = 94.31(1)°, V = 2946.9(8) Å^3, Z = 8, D_C = 1.174 g/cm^3, μ(Mo-K_α) = 0.079 mm, 1.99 < θ < 22.50°, 4234 reflections collected, 3860 unique, R_{int} = 0.0290, data/parameters = 3860/504, $Goof$ = 1.006, R indices (2293, $I > 2\sigma_I$): R_1 = 0.0512, wR_2 = 0.1050; R indices (all data): R_1 = 0.1040, wR_2 = 0.1269. (For the crystal structure of ethyl acetate crystal solvate **1b**, see ref.[43]).

Compound 1b: Yield 40%. ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.02 (s, 6 H), 1.13 [s, 6 H, 4,5-$(CH_3)_2$], 1.82 (s, 3 H, CH_3CO), 4.75 (s, 1 H, CH=), 8.40−8.75 (broad s, 1 H), 9.00−9.35 (broad s, 1 H, NH, OH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 17.7 [4,4-$(CH_3)_2$], 22.9 [5,5-$(CH_3)_2$], 28.6 (CH_3), 59.7 (C-4), 67.6 (C-5), 77.2 (CH=), 162.2 (C-2), 190.1 (C=O). IR (ṽ, cm^{-1}): 3335, 3135 (OH, NH), 1610, 1545−1430 (HN−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 242 (3.40), 297 (4.48). m.p. 141−143 °C (from ether). $C_{10}H_{18}N_2O_2$: calcd. C 60.6, H 9.2, N 14.1; found C 60.5, H 9.3, N 13.9%.

Compound 1c: Yield 80%. ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.09 (s, 6 H), 1.20 [s, 6 H, 4,5-$(CH_3)_2$], 5.07 (s, 1 H, CH=), 8.68−8.86 (broad s, 1 H), 9.70 (broad s, 1 H, NH, OH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 17.8 [5,5-$(CH_3)_2$], 22.2 [4,4-$(CH_3)_2$], 61.2 (C-4), 68.7 (C-5), 71.5 (CH=), 118.2 (q, $J_{C,F}$ = 280, CF_3), 163.8 (C-2), 171.0 (q, $J_{C,F}$ = 30, C=O). IR (ṽ, cm^{-1}): 3325, 3150 (OH, NH), 1615, 1575, 1520 (HN−C=C−C=O), 1270, 1195, 1145 (CF_3). UV [λ_{max} (ethanol), nm (log ε)]: 302 (4.32). m.p. 208−211 °C (from an ethyl acetate/hexane mixture). $C_{10}H_{15}F_3N_2O_2$: calcd. C 47.6, H 6.0, F 22.6, N 11.1; found C 47.6, H 6.1, F 22.7, N 11.1%.

Compound 1d: Yield 40%, m.p. 153−156 °C (decomp., from ethanol). ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.06 (s, 6 H), 1.17 [s, 6 H, 4,5-$(CH_3)_2$], 1.21 (t, 3 H, CH_3, J = 7 Hz), 4.12 (q, J 0 7 Hz, 2 H, CH_2), 5.39 (s, 1 H, =CH-), 8.8 (s, 1 H, NH), 9.7 (s, 1 H, OH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 14.0 (OCH_2CH_3), 17.9, 22.5 [4,5-$(CH_3)_2$], 60.4 (OCH_2CH_3), 60.9 (C-4), 68.5 (C-5), 76.3 (=CH-), 163.7 (C-2), 164.9 (CO_2Et), 173.5 (C=O). IR (ṽ, cm^{-1}): 3320, 3140, 3000−2600 (NH, OH), 1730 (CO_2Et), 1600−1464 (N−C=CH−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 329 (4.29). $C_{12}H_{20}N_2O_4$: calcd. C 56.2, H 7.9, N 10.9; found C 56.5, H 8.3, N 11.0%.

Compound 1e: Yield 55%, m.p. 192−196 °C (decomp., from ethyl acetate/hexane mixture). ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.09 (s, 6 H), 1.21 [s, 6 H, 4,5-$(CH_3)_2$], 6.17 (s, 1 H, =CH-), 7.30 (m, 1 H), 7.86 (m, 1 H, 3,5-pyridyl), 7.94 (m, 1 H, 4-pyridyl), 8.55 (m, 1 H, 6-pyridyl), 9.0 (s, 1 H, NH), 9.35 (s, 1 H, OH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 17.7, 22.8 [4,5-$(CH_3)_2$], 60.1 (C-4), 68.0 (C-5), 74.0 (=CH-), 120.2, 124.6, 136.6, 148.1, 156.6 (pyridyl), 163.8 (C-2), 182.3 (C=O). IR (ṽ, cm^{-1}): 3285, 3121, 2976, 2873, 3200−2600 (NH, OH), 1600, 1570, 1532, 1504, 1463 (N−C=CH−C=O, C=C). UV [λ_{max} (ethanol), nm (log ε)]: 250 (3.91), 342 (4.22). $C_{14}H_{19}N_3O_2$: calcd. C 64.35, H 7.33, N 16.08; found C 64.09, H 7.46, N 15.87%.

Compound 1f: Yield 35%, m.p. 238−241 °C (from an ethyl acetate/hexane mixture). ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.08 (s, 6 H), 1.20 [s, 6 H, 4,5-$(CH_3)_2$], 5.49 (s, 1 H, CH=), 7.64 (d, J = 3 Hz, 2 H, β-pyridyl), 8.62 (d, J 3 Hz, 2 H, α-pyridyl), 9.08 (broad s, 1 H, NH), 9.53 (broad s, 1 H, OH). IR (ṽ, cm^{-1}): 3270, 2600−3000 (OH, NH), 1599, 1561, 1535 (N−C=C−C=O, C=C). UV [λ_{max} (ethanol), nm (log ε)]: 240 (3.96), 343 (4.23). $C_{14}H_{18}N_3O_2$: calcd. C 64.60, H 6.97, N 16.14; found C 64.36, H 7.18, N 15.96%.

Compound 1g: Yield 60%. m.p. 215−219 °C (from an ethyl acetate/hexane mixture in a sealed capillary). ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.02 [s, 6 H, 5-$(CH_3)_2$], 1.03 (s, 9 H, *tert*-Bu), 1.18 [s, 6 H, 5-$(CH_3)_2$], 4.91 (s, 1 H, CH=), 8.72 (broad s, 1 H, NH), 9.11 (broad s, 1 H, OH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 17.5, 22.7 [4,5-$(CH_3)_2$], 27.7 [C(CH_3)$_3$], 59.3 [C(CH_3)$_3$], 67.3 (C-4), 71.8 (=CH-), 78.8 (C-5), 163.0 (C-2), 198.8 (C=O). IR (ṽ, cm^{-1}): 3424, 3325, 3115, 3009, 2971, 2898, 2864, 3200−2600 (NH, OH), 1606, 1521, 1504, 1483, 1455, 1434 (N−C=CH−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 238 (3.42), 299 (4.35). $C_{13}H_{24}N_2O_2$: calcd. C 64.97, H 10.06, N 11.66; found C 64.96, H 10.24, N 11.61%.

2-(1-Hydroxyoctahydrobenzoimidazol-2-ylidene)-1-phenylethanone (1h): A solution of the sodium salt of benzoyl acetaldehyde **5b** (2.55 g, 15 mmol) in water (25 mL) was carefully acidified to pH 3 with 5% HCl and stirring. The resulting solution was extracted with diethyl ether (3 × 15 mL). The combined extract was washed with water (10 mL) and dried with $MgSO_4$, and the solution was evaporated to dryness. The residue was dissolved in ethanol (15 mL) and finely powdered 1,2-BHA **4a** (1.46 g, 10 mmol) was added to this solution portionwise over 20 min with stirring; the resulting mixture was stirred for 3 h at 20 °C and then kept for 30 h at that temperature. The light precipitate was filtered off, and the solution was evaporated. The residue was dissolved in diethyl ether (40 mL). The resulting solution was kept at −12 °C for 1 h, and the precipitated imidazolidine **1h** was filtered off; yield 1.13 g. Additional imidazolidine **1i** could be obtained after keeping the mother liquor at −12 °C for 3 days (0.50 g). The total yield was 63%. ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.15−1.98 [m, 8 H, $(CH_2)_4$],

3.71 (q, J = 6.5 Hz, 1 H, C-4), 3.35−3.50 (m, 1 H, C-5), 5.62 (s, 1 H, CH=), 7.35−7.45 (m, 3 H), 7.72−7.85 (m, 2 H, Ph), 9.05−9.40 (broad s, 1 H), 9.52 (s, 1 H, OH, NH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 20.2, 21.3, 23.5, 28.9 [$(CH_2)_4$], 51.6 (C-4) 61.7 (C-5), 75.4 (CH=), 126.4, 128.1, 129.9, 140.9 (Ph), 166.9 (C-2), 184.2 (C=O). IR (ν̃, cm^{-1}): 3315, 3100 (OH, NH), 1615, 1580, 1525 (HN−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 243 (4.13),333 (4.44). m.p. 196−201 °C (from ethanol). $C_{15}H_{18}N_2O_2$: calcd. C 69.8, H 7.0, N 10.9; found C 69.7, H 7.2, N 10.8%.

2-(1-Hydroxy-4,5,5-trimethylimidazolidin-2-ylidene)-1-phenylethanone (1iA) and 2-(1-Hydroxy-4,4,5-trimethylimidazolidin-2-ylidene)-1-phenylethanone (1iB): A solution of 1,2-BHA **4b** (1.34 g, 10 mmol) in glacial acetic acid (10 mL) was added dropwise with stirring over 15 min to a solution of the sodium salt of benzoyl acetaldehyde **5b** (2.55 g, 15 mmol) in glacial acetic acid (20 mL). The reaction mixture was kept for 48 h at 20 °C, and the solution was evaporated. The residue was diluted with water (40 mL) and $CHCl_3$ (50 mL), and sodium carbonate was added slowly with shaking until carbon dioxide ceased to evolve. The chloroform solution was separated, and the aqueous solution was extracted with chloroform (3 × 10 mL). The combined extract was kept for 1 h at 5 °C, and the resulting precipitate was filtered off and washed with cold chloroform (10 mL) to give imidazolidine **1kA** (0.40 g). The filtrate was evaporated, and the solid residue was dissolved in hot MeOH (10 mL) and mixed with silica gel to give a thick suspension. The resulting mixture was dried and placed on a chromatographic column; subsequent elution with an (1:1) ethyl acetate/hexane mixture gave two fractions with $R_f \approx 0.20$ and 0.15. Evaporation of eluates and treatment of the residues with hexane gave **1iB** (0.45 g) and isomer **1iA** (0.35 g), respectively.

Compound 1iA: Yield 30%. ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 0.98 (s, 3 H), 1.21 [s, 3 H, 5,5-$(CH_3)_2$], 1.17 (d, J = 6.5 Hz, 4-CH_3), 3.49 (q, J = 6.5 Hz, 1 H, 4-H), 5.50 (s, 1 H, CH=), 8.90−9.15 (broad s, 1 H), 9.36 (s, 1 H, OH, NH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 14.2 (4-CH_3), 15.1, 22.4 [5,5-$(CH_3)_2$], 57.4 (C-4), 66.4 (C-5), 74.0 (CH=), 126.2, 128.0, 129.8, 140.9 (Ph), 164.6 (C-2), 183.8 (C=O). IR (ν̃, cm^{-1}): 3360, 3130 (OH, NH), 1600, 1575, 1520, 1485 (HN−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 242 (4.13), 332 (4.40). m.p. 202−203 °C (from ethanol). $C_{14}H_{18}N_2O_2$: calcd. C 68.3, H 7.4, N 11.4; found C 67.8, H 7.3, N 11.0%.

Compound 1iB: Yield 19%. ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.11 (s, 3 H), 1.31 [s, 3 H, 4,4-$(CH_3)_2$], 1.15 (d, J = 6.5 Hz, 5-CH_3), 3.18 (q, J = 6.5 Hz, 1 H, 5-H), 5.56 (s, 1 H, CH=), 9.10−9.32 (broad s, 1 H), 9.59 (s, 1 H, OH, NH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 11.3 (5-CH_3), 21.6, 26.5 [4-$(CH_3)_2$], 58.1 (C-4), 67.5 (C-5), 74.3 (CH=), 126.3, 128.0, 129.9, 140.8 (Ph), 165.3 (C-2), 184.0 (C=O). IR (ν̃, cm^{-1}): 3310, 3100 (OH, NH), 1600, 1575, 1520, 1485 (HN−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 242 (4.12), 334 (4.40). m.p. 198−199 °C (from ethyl acetate). $C_{14}H_{18}N_2O_2$: calcd. C 68.3, H 7.4, N 11.4; found C 68.5, H 7.4, N 11.0%.

2-(1-Hydroxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)-1-phenylethanone (1a): A solution of 3-hydroxy-1-phenylprop-2-en-1-one sodium salt **5b** (18.35 g, 108 mmol) in MeOH (200 mL) was added dropwise over 35 min to a stirred solution of 1,2-BHA **4c** hydrochloride (16.56 g, 90 mmol) in MeOH (100 mL). The reaction mixture was kept for 48 h at 20 °C. The NaCl residue was filtered off, and concentrated HCl (5 mL) was added to the filtrate. The resulting solution was boiled for 7 h and then cooled. The inorganic salt precipitate was filtered off, and the filtrate was evaporated to dryness. The oily residue was mixed with water (150 mL), and the mixture was made basic (pH 8) by shaking with a saturated solution of sodium carbonate. The resulting mixture was extracted with chloroform (1 × 300 mL and 2 × 100 mL) and ethyl acetate (100 mL). The combined extract was dried with $MgSO_4$, the solution was evaporated, and the residue was chromatographed on a silica gel column (h = 35 cm, d = 7 cm) with chloroform as eluent. After elution of all benzoyl acetaldehyde ($R_f \approx 0.80$), the elution was continued with a chloroform/MeOH (40:1) mixture, and the fraction containing imidazolidine **1b** was collected ($R_f \approx 0.15$). The residue obtained after evaporation of the eluate was suspended with hexane (100 mL), and the precipitate was filtered off to give imidazolidine **1b** (15.81 g, 68%).

1-(1-Hydroxyoctahydrobenzoimidazol-2-ylidene)propan-2-one Dihydrochloride (9l) and the Free Base (1l): A solution of freshly distilled acetoacetaldehyde dimethyl acetal **5a** (0.76 g, 5.75 mmol) in MeOH (3 mL) was added dropwise over 15 min at 20 °C to a solution of 1,2-BHA **4a** (0.73 g, 5 mmol) in MeOH (15 mL) saturated with hydrogen chloride. The reaction mixture was kept for 1 h at 20 °C, and the residue was filtered off and washed with a saturated solution of hydrogen chloride in MeOH (2 × 6 mL). The yield of **9l** was 0.91 g. To prepare free base **1l**, compound **10m** (0.40 g) was dissolved in water (10 mL) and the resulting solution was neutralized with sodium carbonate and then extracted with $CHCl_3$ (5 × 10 mL). The combined extract was dried with $MgSO_4$, the solution was evaporated to dryness, the residue was suspended with anhydrous diethyl ether, and the precipitate was filtered off to give 0.12 g of imidazolidine **1l**.

Compound 9l: Yield 60%. IR (ν̃, cm^{-1}): 2800−2600, 1635, 1590. UV [λ_{max} (ethanol), nm (log ε)]: 296 (4.25). m.p. 156−159 °C (from an ethyl acetate/MeOH mixture). $C_{10}H_{16}N_2O_2 \cdot 2HCl \cdot CH_3OH$: calcd. C 43.9, H 7.4, Cl 23.5, N 9.3; found C 43.7, H 7.4, Cl 23.6, N 9.3%.

Compound 1l: Yield 46%. ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.06−2.04 [m, 8 H, $(CH_2)_4$], 1.84 (s, 3 H, CH_3CO), 3.59 (q, J = 6.5 Hz, 1 H, 4-H), 3.22−3.50 (m, 1 H, 5 H), 4.85 (s, 1 H, CH=), 8.64−8.88 (broad s, 1 H), 9.34 (s, 1 H, NH, OH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 20.2, 21.4, 23.5, 28.9 [$(CH_2)_4$], 28.8 (CH_3), 51.3 (C-4), 61.4 (C-5), 78.6 (CH=), 165.3 (C-2), 190.5 (C=O). IR (ν̃, cm^{-1}): 3335, 3160 (OH, NH), 1610, 1550−1490 (HN−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 238 (3.62), 298 (4.49). m.p. 182−185 °C (from an ethyl acetate/MeOH mixture). $C_{10}H_{16}N_2O_2$: calcd. C 61.2, H 8.2, N 14.3; found C 60.8, H 8.1, N 14.0%.

1-(1-Hydroxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)propan-2-one (1b): This compound was synthesized as described above for imidazolidine **1l** from 1,2-BHA **4c** (0.74 g, 5 mmol, synthesized according to ref.[44]) and 1,3-ketoaldehyde acetal **5a** (0.76 g, 5.75 mmol). The reaction mixture was kept for 15 h at 20 °C, and the solvent was evaporated. The residue was treated with diethyl ether, and the semisolid mass was separated from diethyl ether by decantation and dissolved in water (15 mL). The aqueous solution was neutralized with sodium carbonate and extracted with chloroform (4 × 15 mL). The combined extract was dried with $MgSO_4$, the solution was removed, and crude enaminone **1b** was purified by silica gel chromatography and sequentially eluted with chloroform and a chloroform/MeOH (20:1) mixture; a fraction with $R_f \approx 0.5$ was collected. The residue obtained after eluate evaporation was dissolved in anhydrous diethyl ether (10 mL). After the solution has been cooled to −12 °C and kept for 24 h, the imidazolidine **1b** precipitate was filtered off; the yield of **1b** was 0.22 g (22%).

1,1,1-Trifluoro-3-(1-hydroxyoctahydrobenzoimidazol-2-ylidene)-propan-2-one (1m): A suspension of 1,2-BHA **4a** (2.19 g, 15 mmol) in MeOH (20 mL) was acidified with a mixture of concentrated HCl and MeOH (1:1, 6 mL), and a solution of *trans*-4-ethoxy-1,1,1-trifluorobut-3-en-2-one (**5d**) (3.02 g, 8 mmol, synthesized according to ref.[29]) in MeOH (3 mL) was then added dropwise with stirring over 8 min. The reaction mixture was kept for 0.5 h at 20 °C and then boiled for 3 h. The solvent was removed, the residue was dissolved in water (20 mL), and the solution was alkalized to pH 8 with a saturated solution of sodium carbonate. The precipitate of imidazolidine **1m** was filtered off and washed with water (2 × 10 mL); yield 33%. ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.10−1.94 [m, 8 H, (CH$_2$)$_4$], 3.74 (q, J = 6.5 Hz, 1 H, 4-H), 3.55 (dq, 1 H, J_1 = 7.0, J_2 = 4.5 Hz, 5-H), 5.15 (s, 1 H, CH=), 8.99 (broad s, 1 H), (s, 1 H, NH, OH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 19.9, 20.9, 23.1, 28.1 [(CH$_2$)$_4$], 52.1 (C-4), 61.6 (C-5), 72.5 (CH=), 118.1 (q, $J_{C,F}$ = 290 Hz, CF$_3$), 167.3 (C-2), 171.2 (q, $J_{C,F}$ = 30 Hz, C=O). IR (ṽ, cm^{-1}): 3345, 3190 (OH, NH), 1610, 1570 (HN−C=C−C=O), 1255, 1190, 1135 (CF$_3$). UV [λ$_{max}$ (ethanol), nm (log ε)]: 253 (3.44), 300 (4.35). m.p. 195−199 °C (from CHCl$_3$). C$_{10}$H$_{13}$F$_3$N$_2$O$_2$: calcd. C 48.0, H 5.2, N 11.2, F 22.8; found C 47.8, H 5.2, N 10.9, F 22.8%.

1,1,1-Trifluoro-3-(1-hydroxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)propan-2-one (1c) and 1,1,1-Trifluoro-3-(4,4,5,5-tetramethylimidazolidin-2-ylidene)propan-2-one (10c): Enol ether **5d** (18.9 g, 112.5 mmol) was added dropwise with stirring to a solution of 1,2-BHA hydrochloride **4c** (13.8 g, 75 mmol) in MeOH (150 mL) over 15 min. The reaction mixture was kept for 5 days at 20 °C and was then boiled for 7 h; the light precipitate was filtered off, and the solution was evaporated to a volume of ca. 20 mL. The residue was dissolved in water (50 mL), and the resulting solution was carefully alkalized with shaking with a concentrated solution of sodium carbonate. The precipitate formed was triturated, and the suspension was cooled to 5 °C for 15 h. [If crystallization did not occur, the mixture was extracted with ethyl acetate (4 × 100 mL), the combined extract was dried with MgSO$_4$, the solution was evaporated, and the residue was dissolved in methanol and chromatographed as described in the given procedure.] After that, the precipitate, a mixture consisting mainly of **1c** and **10c**, was filtered off, washed three times with water (15 mL), and dried. The mixture of **1c** and **10c** was dissolved in MeOH (100 mL) with heating, the resulting solution was mixed with silica gel, and the solvent was removed. The obtained mixture was suspended with chloroform (200 mL) and placed on a chromatographic silica gel column (h = 50 cm, d = 7 cm). Elution with chloroform gave a fraction with $R_f \approx 0.1$ (Silufol TL plate, CHCl$_3$/MeOH mixture, 50:1). Elution was continued with a chloroform/MeOH mixture (30:1), and a fraction with $R_f \approx 0.07$ (Silufol TL plate, CHCl$_3$/MeOH mixture, 50:1) was collected. The residues obtained after eluate evaporation were treated with a pentane/CH$_2$Cl$_2$ mixture, and the precipitates of imidazolidines **10c** (5.94 g) and **1c** (5.20 g, 33%), respectively, were filtered off.

Compound 10c: Yield 34%. ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.15 [s, 12 H, 4,5-(CH$_3$)$_2$], 4.78 (s, 1 H, CH=), 8.25−8.43 (broad s, 2 H, NH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 22.4 [4,5-(CH$_3$)$_4$], 62.3 (C-4,5), 71.5 (CH=), 117.5 (q, $J_{C,F}$ = 280, CF$_3$), 161.9 (C-2), 169.4 (q, $J_{C,F}$ = 30). IR (ṽ, cm^{-1}): 3160 (NH), 1605, 1570, (HN−C=C−C=O), 1265, 1175, 1135 (CF$_3$). UV [λ$_{max}$ (ethanol), nm (log ε)]: 290 (4.39). m.p. 193−194 °C (from CHCl$_3$). C$_{10}$H$_{15}$F$_3$N$_2$O: calcd. C 50.8, H 6.4, F 24.1, N 11.9; found C 50.9, H 6.5, F 24.3, N 11.8%.

2-(1-Hydroxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)-1-phenylpropan-1-one (1k): A suspension of 1,2-BHA **4c** sulfate (5 g, 18.9 mmol) and the sodium salt of 2-methyl-1-phenylpropane-1,3-dione **5c** (3.5 g, 18.9 mmol) in a water/MeOH mixture (1:2, 75 mL) was stirred for 48 h at 50 °C. MeOH was removed, and the aqueous solution was washed with diethyl ether (30 mL) and extracted with chloroform (2 × 50 mL). The combined extract was dried with MgSO$_4$, and the solution was evaporated. Imidazolidine **1k** was purified chromatographically on silica gel with a (20:1) chloroform/MeOH mixture as eluent. Yield 2.1 g (40%), oil. ^{1}H NMR (CDCl$_3$, 200.13 MHz, δ, ppm): 0.98 (s, 3 H), 1.06 (s, 3 H), 1.15 [s, 6 H, 4,5-(CH$_3$)$_2$], 1.48 (d, J = 6.9 Hz, 3 H, -CH-CH_3), 4.81 (q, J = 6.9 Hz, 1 H, CH-CH$_3$), 7.84 (m), 7.35 (m, 5 H, Ph), 10.05 (broad s, 1 H, OH). ^{13}C NMR (CDCl$_3$, 50.32 MHz, δ, ppm): 13.5 (-CHCH$_3$), 18.3, 22.3 [4,5-(CH$_3$)$_2$], 39.4 (-CHCH$_3$), 64.1 (C-4), 71.9 (C-5), 128.5, 133.4, 134.9 (Ph), 162.0 (C-2), 194.6 (C=O). IR (ṽ, cm^{-1}): 1691 (C=O), 1596, 1579 (C=N). UV [λ$_{max}$ (ethanol), nm (log ε)]: 246 (4.09). Found, m/z: 274.16797; calculated for C$_{16}$H$_{22}$N$_2$O$_2$ m/z: 274.16812.

Ethyl 2-(1-Hydroxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)malonamic Acid Ester (11): A solution of 1,2-BHA **4c** (1.0 g, 6.75 mmol) and ethyl 2-cyano-3-ethoxyacrylic ester (1.14 g, 6.74 mmol) in MeOH (25 mL) was kept for 24 h at 20 °C, the solvent was removed, and the solid residue of imidazolidine **11** was recrystallized from diethyl ether. Yield 60%, m.p. 125−128 °C (from ether).

C$_{12}$H$_{21}$N$_3$O$_4$, FW 271.32, space group $P\bar{1}$, unit cell dimensions a = 7.633(2), b = 9.993(2), c = 10.691(2) Å, α = 65.52(3), β = 79.86(3), γ = 81.18(3)°, V = 727.6(2) Å^3, Z = 2, D_C = 1.238 g/cm^3, μ(Mo-K_α) = 0.093 mm, 2.11 < θ < 24.99°, 2675 reflections collected/2470 unique (R_{int} = 0.0339), data/parameters = 2470/257, Goof = 0.870, R indices ($I > 2\sigma_I$): R_1 = 0.0508, wR_2 = 0.1272, R indices (all data): R_1 = 0.1154, wR_2 = 0.1683.

^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.13 (s, 6 H), 1.18 [s, 6 H, 4,5-(CH$_3$)$_2$], 1.19 (t, J = 7.00 Hz, 3 H, CH$_3$), 4.03 (q, J = 7 Hz, 2 H, CH$_2$), 6.83 (s, 1 H), 7.72 (s, 1 H), 8.25 (s, 1 H), 13.02 (s, 1 H, OH, NH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 14.2 (-OCH$_2$CH$_3$), 18.4, 22.3 [4,5-(CH$_3$)$_2$], 58.6 (OCH$_2$CH$_3$), 60.8 (C-4), 68.5 (C-5), 72.1 (=C), 160.6 (C-2), 167.9, 171.5 (C=O). IR (ṽ, cm^{-1}): 3378, 3309, 2980, 2937, 2901, 3500−2800 (NH, OH), 1618, 1527, 1504, 1476, 1441 (N−C=CH−C=O). UV [λ$_{max}$ (ethanol), nm (log ε)]: 239 (4.21), 274 (4.17), 350 (2.03). C$_{12}$H$_{21}$N$_3$O$_4$: C 53.12, H 7.80, N 15.49; found C 53.22, H 7.89, N 15.42%.

Dimethyl 2-(1-Hydroxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)-3-oxosuccinate (14): Imidazoline **12** was synthesized by hydrogenation of 4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole 3-oxide 1-oxyl with Pd/C as a catalyst in tetrahydrofuran as a solvent. After the catalyst had been filtered off and the solvent had been evaporated, crude imidazoline **12** was obtained, and was used without further purification.

A solution of imidazoline **12** (0.135 g, 0.87 mmol) in CHCl$_3$ (3 mL) was cooled to freezing point, and a solution of DMAD (0.12 mL, 0.96 mmol) in CHCl$_3$ (1 mL) was added. The resulting mixture was heated to 20 °C. The solution was placed on a silica gel column cooled to about 10 °C. Flash chromatography with ethyl acetate gave an eluate containing a cycloadduct − **dimethyl 1-hydroxy-2,2,3,3-tetramethyl-1,2,3,7a-tetrahydroimidazo[1,2-*b*]isoxazole-6,7-dicarboxylate** (**13**) in a yield of 0.06 g. Cycloadduct **13** is stable as a solid at 0 °C for prolonged periods, but in solution at 20 °C it quantitatively transforms into imidazolidine **14**. Evaporation of a solution gave imidazolidine **14** as the sole product. After recrystalli-

zation, the yield of **14** was 0.05 g (85%), m.p. 125−126 °C (from an ethyl acetate/hexane mixture). ^{1}H NMR ($CDCl_3$, 200.13 MHz, δ, ppm): 1.14 (s, 6 H), 1.17 [s, 6 H, 4,5-$(CH_3)_2$], 3.57(s, 3 H), 3.58 (s, 3 H, -CO_2CH_3), 3.70 (s, 3 H), 3.71 (s, 3 H, -$COCO_2CH_3$), 7.73, 7.89 (broad s, NH), 9.07, 10.89 (broad s, OH), the ratio of forms was 1:2. IR (ν̃, cm^{-1}): 3500−2500 (OH, NH), 1737, 1666, 1596 (C=O), 1557 (C=C). UV [λ_{max} (ethanol), nm (log ε)]: 234 (4.18), 273 (4.16).

$C_{13}H_{20}N_2O_6$, *FW* = 300.31, orthorhombic, *Pbca*, *a* = 14.7171(12), *b* = 12.6034(5), *c* = 16.2410(7) Å, *V* = 3012.5(3) Å^3, *Z* = 8, D_C = 1.324 g/cm^3, μ (Mo-K_α) = 0.105 mm, 2.47 < θ < 25.01°, absorption correction by integration, max. and min. transmission 0.966 and 0.934, 2589 reflections collected, 2589 unique, data/parameters = 2589/271, *Goof* = 1.025, *R* indices 1962 ($I > 2\sigma_I$): R_1 = 0.0456, wR_2 = 0.1221; *R* indices (all data): R_1 = 0.0637, wR_2 = 0.1358.

1-(1-Oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-2-phenylethane-1,2-dione 1-Oxime (15): A solution of enaminone **1a** (1.04 g, 4 mmol), sodium methoxide (0.87 g, 16 mmol), and amyl nitrite (1.2 mL, 8 mmol) in MeOH (40 mL) was kept for 2 h at 20 °C and then evaporated. The residue was dissolved in water (30 mL), and the solution was washed with diethyl ether (2 × 20 mL), neutralized with 5% HCl, and extracted with chloroform (4 × 30 mL). The combined extract was dried with $MgSO_4$, and the solution was evaporated to give crude oxime **15**, which was purified chromatographically on alumina with a chloroform/MeOH (30:1) mixture as eluent. Yield 0.63 g (55%). IR (ν̃, cm^{-1}): 3500−2500 (OH), 1659 (C=O), 1600, 1580 (C=N). UV [λ_{max} (ethanol), nm (log ε)]: 265 (4.22). m.p. 142−143 °C (from an ethyl acetate/hexane mixture). $C_{15}H_{18}N_3O_3$: C 62.5, H 6.3, N 14.6; found C 63.1, H 6.6, N 14.6%.

Treatment of **1a** with methyl nitrate was carried out in the same manner. A mixture of unchanged **1a** (yield 40%), methoxy derivative **16a** (yield 10%), and enaminone **17** (yield 15%) was separated chromatographically on alumina by elution of (in sequence) **16a** (chloroform as eluent), **1a**, and **1-phenyl-2-(4,4,5,5-tetramethylimidazolidin-2-ylidene)ethanone** (**17**) (50:1 chloroform/MeOH mixture as eluent).

Compound 16a: ^{1}H NMR ($CDCl_3$, 200.13 MHz, δ, ppm): 1.17 (s, 6 H), 1.20 [s, 6 H, (4,5-$(CH_3)_2$], 3.80 (s, 3 H, -OCH_3), 5.54 (s, =CH-), 7.35 (m, 2 H), 7.85 (m, 3 H, Ph), 9.1 (broad s, NH). ^{13}C NMR ($CDCl_3$, 50.32 MHz, δ, ppm): 18.2, 23.2 (4,5-$(CH_3)_2$], 60.4 (C-4), 65.0 (-OCH_3), 69.5 (C-5), 74.5 (=CH-), 126.7, 127.8, 130.0, 140.6 (Ph), 163.3 (C-2), 186.8 (C=O). IR (ν̃, cm^{-1}): 3303, 3270 (NH), 2816 (OCH_3), 1614, 1579, 1540 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 241 (4.14), 328 (4.38). m.p. 128−129 °C (from an ethyl acetate/hexane mixture). $C_{16}H_{22}N_2O_2$: calcd. C 70.0, H 8.1, N 10.2; found C 70.4, H 8.4, N 10.3%.

Compound 17: $C_{15}H_{20}N_2O$, *FW* = 244.33, orthorhombic, $P2_12_12_1$, *a* = 10.850(2), *b* = 11.043(3), *c* = 11.797(2) Å, *V* = 1413.5(5) Å^3, *Z* = 4, D_C = 1.148 g/cm^3, μ (Mo-K_α) = 0.073 mm, 2.53 < θ < 24.99°, 1436 unique reflections collected, data/parameters = 1436/244, *Goof* = 1.048, *R* indices (965 $I > 2\sigma_I$): R_1 = 0.0607, wR_2 = 0.1421; *R* indices (all data): R_1 = 0.0997, wR_2 = 0.1669. ^{1}H NMR ($CDCl_3$, 200.13 MHz, δ, ppm): 1.20 (s, 12 H), 5.27 (s, 1 H, =CH-), 7.32, 7.78 (m, 5 H, Ph), 8.65 (broad s, 1 H, NH), 9.30 (broad s, 1 H, NH). IR (ν̃, cm^{-1}): 3430−3127 (NH), 1610, 1582, 1547 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 236 (4.03), 319 (4.11), m.p. 236−238 °C (from an ethyl acetate/hexane mixture). $C_{15}H_{20}N_2O$: C 73.74, H 8.25, N 11.47; found C 73.35, H 8.39, N 11.46%.

2-(1-Methoxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)-1-phenylethanone (16a): A solution of imidazolidine **1a** (0.26 g, 1 mmol), sodium methoxide (0.11 g, 2 mmol), and methyl iodide (0.21 g, 0.1 mL, 1.5 mmol) in MeOH (25 mL) was kept for 10 h at 20 °C. The solvent was removed, and the residue was chromatographed on silica gel. The first fraction, containing methoxy derivative **16a**, was eluted with a chloroform/MeOH (30:1) mixture; yield 0.15 g (55%). Subsequent elution with a chloroform/MeOH (10:1) mixture resulted in collection of the second fraction, containing imidazolidine **1k**; yield 0.04 g (15%).

Similarly, treatment of **1c** with CH_3I gave **1,1,1-trifluoro-3-(1-methoxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)propan-2-one** (**16c**) in a yield of 60%. ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.37 (s, 6 H), 1.20 [s, 6 H, 4,5-$(CH_3)_2$], 3.77 (s, 3 H, OCH_3), 5.03 (s, 1 H, =CH-), 9.04 (broad s, NH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 18.1, 21.9 [4,5-$(CH_3)_2$], 61.6 (C-4), 65.2 (OCH_3), 68.5 (C-5), 71.1 (=CH-), 117.9 (q, $J_{C,F}$ = 290 Hz, CF_3), 163.5 (C-2), 171.8 (q, $J_{C,F}$ = 31 Hz, C=O). IR (ν̃, cm^{-1})): 3305 (NH), 2813 (OCH_3), 1628, 1590 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 250 (3.60), 301 (4.43). m.p. 142−143 °C (from an ethyl acetate/hexane mixture). $C_{11}H_{17}F_3N_2O_2$: C 49.6, H 6.5, F 21.4, N 10.5; found C 50.8, H 7.2, N 10.7, F 21.2%.

2-[4,4,5,5-Tetramethyl-2-(2-oxo-2-phenylethylidene)imidazolidin-1-yl Acetate (18): A solution of imidazolidine **1a** (0.26 g, 1 mmol) and acetic anhydride (0.11 mL, 1.2 mmol) in chloroform (10 mL) was kept for 1 h at 20 °C, washed with aqueous sodium hydrogencarbonate, and dried with $MgSO_4$. The residue obtained after solvent removal crystallized after addition of hexane, and the precipitate of acetoxy derivative **18** was filtered off; yield 0.22 g (75%), m.p. 141−142 °C (from hexane). ^{1}H NMR (CCl_4, 200.13 MHz, δ, ppm): 1.16 (s, 6 H), 1.35 [s, 6 H, (4,5-$(CH_3)_2$], 2.21 (s, 3 H, CH_3CO), 5.14 (s, 1 H, =CH-), 7.30 (m, 3 H), 7.72 (m, 2 H, C_6H_5), 9.43 (broad s, 1 H, NH). IR (ν̃, cm^{-1}): 3428, 3301 (NH), 1800 (C=O), 1621, 1581, 1522 (N−C=C−C=O, C=C). UV [λ_{max} (ethanol), nm (log ε)]: 239 (4.10), 326 (4.37). $C_{17}H_{22}N_2O_2$: C 67.53, H 7.33, N 9.26; found C 67.42, H 7.33, N 9.26%.

(1-Hydroxy-2,2,3,3,6-pentamethyl-1,2,3,5,6,7-hexahydroimidazo-[1,2-*c*]pyrimidin-8-yl)phenylmethanone (19): A solution of imidazolidine **1a** (0.3 g, 1.1 mmol), a formaldehyde solution (30%, 0.5 mL), and aqueous ammonia (20%, 0.6 mL) in MeOH (5 mL) was kept for 15 min at 20 °C, and the MeOH was evaporated. The precipitate of **19** was filtered off and washed with water. Yield 0.2 g (55%). ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.17 (s, 6 H), 1.20 [s, 6 H, 4,5-$(CH_3)_2$], 2.14 (s, 3 H, N-CH_3), 3.31 (s, 2 H, 1-CH_2), 4.03 (s, 2 H, 3-CH_2), 7.3 (m, 5 H, Ph). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 18.6, 19.4 [4,5-$(CH_3)_2$], 39.1 (N-CH_3), 52.6 (C-3), 62.5 (C-1), 64.3 (C-7), 69.4 (C-6), 83.3 (C-4), 127.2, 127.9, 128.7, 141.0 (Ph), 156.9 (C-4a), 181.8 (C=O). IR (ν̃, cm^{-1}): 2787 (N−CH_3), 1525 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 235 (3.90), 334 (4.11). m.p. 153−154 °C (from a hexane/ethyl acetate mixture). $C_{18}H_{25}F_3N_3O_2$: C 68.5, H 8.0, N 13.3; found C 69.1, H 8.0, N 13.1%.

2-Chloro-2-(1-methoxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)-1-phenylethanone (22a): NCS (0.21 g, 1.54 mmol) was added to a solution of enaminone **16a** (0.4 g, 1.47 mmol) in CCl_4 (20 mL), and the resulting mixture was stirred for 40 min at 20 °C. The succinimide precipitate was filtered off, and the solution was evaporated to dryness. The residue was treated with hexane, and the precipitate of **22a** was filtered off and recrystallized from a hexane/ethyl acetate mixture to give 0.32 g (70%) of monochloro derivative **22a**. ^{1}H NMR ($CDCl_3$, 200.13 MHz, δ, ppm): 0.88 (s, 3 H), 1.27 [s, 9 H,

4,5-$(CH_3)_2$], 3.82 (s, 3 H, OCH_3), 7.29 (m, 3 H), 7.48 (m, 2 H, Ph), 10.11 (broad s, NH). IR ($\tilde{\nu}$, cm^{-1}): 3235 (NH), 1590, 1524 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 243 (3.99), 336 (3.86). m.p. 125−127 °C (from a hexane/ethyl acetate mixture). $C_{16}H_{21}ClN_2O_2$: calcd. C 62.23, H 6.85, N 9.07; found C 61.84, H 6.60, N 9.19%.

2-(1-Chloro-2-oxo-2-phenylethylidene)-4,4,5,5-tetramethylimidazolidin-1-yl Acetate (22b): NCS (0.29 g, 2.1 mmol) was added portionwise with stirring to a solution of enaminone **18** (0.62 g, 2 mmol) in chloroform over 10 min. The stirring was continued for 4 h at 20 °C, and the reaction mixture was evaporated to dryness. The residue was dissolved in a minimum amount of DMSO, and the solution was cooled to 0 °C and poured into ice-cold brine (15 mL). The precipitate of **22b** was filtered off and washed with brine and water. Yield 0.63 g (95%); m.p. 165−167 °C (from a hexane/ethyl acetate mixture). ^1H NMR ($CDCl_3$, 200.13 MHz, δ, ppm): 1.22 (s, 6 H), 1.34 [s, 6 H, 4,5-$(CH_3)_2$], 2.15 (s, 3 H, CH_3CO), 7.3 (m, 3 H), 7.5 (m, 2 H, C_6H_5), 10.1 (broad s, 1 H, NH). IR ($\tilde{\nu}$, cm^{-1}): 3245 (NH), 1803 (C=O), 1592, 1576, 1523 (N−C=C−C=O, C=C). UV [λ_{max} (ethanol), nm (log ε)]: 244 (3.98), 337 (3.98). $C_{17}H_{21}ClN_2O_2$: calcd. C 60.62, H 6.28, N 8.32; found C 60.80, H 6.46, N 8.41%.

2-(1-Hydroxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)-3-oxo-3-phenylpropionitrile (24a): NCS (0.56 g, 4.23 mmol) was added portionwise over 10 min to a stirred solution of imidazolidine **1a** (1 g, 3.85 mmol) in chloroform (10 mL) dried with $CaCl_2$. The stirring was continued for 10 min, and the residue of dichloride **21** was filtered off. The solvent was removed at a temperature below 30 °C. The residue was dissolved in a solution of NaCN (0.38 g, 0.77 mmol) in DMSO (5 mL) and the resulting mixture was stirred for 2 h at 20 °C. The mixture was then cooled to 0 °C and diluted with ice-cold brine (20 mL), and the precipitate of nitrile **24a** was filtered off, washed with water, and recrystallized from ethyl acetate. Yield 0.38 g (35%). ^1H NMR ([D_6]DMSO/[D_6]acetone, 200.13 MHz, δ, ppm): 1.18 (s, 6 H), 1.29 [s, 6 H, (4,5-$(CH_3)_2$], 7.5 (m, 5 H, Ph), 9.6 (broad s, 1 H, NH), 10.1 (s, 1 H, OH). ^{13}C NMR (CD_3OD, 50.32 MHz, δ, ppm): 18.5, 23.1 (4,5-$(CH_3)_2$], 62.6 (C-4), 71.6 (C-5), 72.4 (=*C*-CN), 121.7 (C≡N), 128.7, 128.9, 131.6, 141.5 (Ph), 166.3 (C-2), 194.0 (C=O). IR ($\tilde{\nu}$, cm^{-1}): 3200−2800 (NH, OH), 2209 (C≡N), 1600, 1577, 1534 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 235 (4.01), 304 (4.06). m.p. 213−214 °C (decomp. from ethyl acetate). $C_{16}H_{19}N_3O_2$: calcd. C 67.3, H 6.7, N 14.7; found C 65.9, H 6.6, N 14.6%.

The yield of **2,2-dichloro-2-(1-hydroxy-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-phenylethanone** (**21**) was 15%. ^1H NMR ([D_6]DMSO, 200.13 MHz, δ, ppm): 0.80 (s, 6 H), 1.09 [s, 6 H, (4,5-$(CH_3)_2$], 7.55 (m, 3 H), 7.96 (m, 2 H, Ph). IR ($\tilde{\nu}$, cm^{-1}): 1716 (C=O), 1608 (C=N). UV [λ_{max} (ethanol), nm (log ε)]: 229 (4.17). m.p. 134−136 °C (from chloroform). Found, *m*/*z*: 328.07529; calculated for $C_{15}H_{18}N_2O_2Cl_2$ *m*/*z*: 328.07452.

Enaminones **1b**, **1c**, **1e**, **1f**, and **1g** were converted into nitriles **24b**, **24c**, **24e**, **24f**, and **24g** in a similar manner.

Compound 24b: Yield 35%, m.p. 193−195 °C (from ethyl acetate). ^1H NMR ([D_6]DMSO, 200.13 MHz, δ, ppm): 1.06 (s, 6 H), 1.26 [s, 6 H, (4,5-$(CH_3)_2$], 2.13 (s, 3 H, CH_3), 9.31 (s, 1 H), 9.99 (s, 1 H, OH, NH). ^{13}C NMR ([D_6]DMSO, 50.32 MHz, δ, ppm): 22.9, 27.3 [4,5-$(CH_3)_2$], 32.4 (CH_3CO), 65.8 (C-4), 72.3 (=*C*-CN), 74.3 (C-5), 125.5 (C≡N), 168.0 (C-2), 197.2 (C=O). IR ($\tilde{\nu}$, cm^{-1}): 3424, 3252, 3119, 2985, 2871 (NH, OH), 2194 (C≡N), 1598, 1543 (N−C=CH−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 220 (3.99), 285 (4.12). $C_{11}H_{17}N_3O_2$: C 59.2, H 7.7, N 18.8; found C 59.1, H 7.6, N 18.8%. Found, *m*/*z*: 223.13261; calculated for $C_{11}H_{17}N_3O_2$ *m*/*z*: 223.13208.

Compound 24c was purified by reprecipitation by water from pyridine and subsequent recrystallization from ethyl acetate; yield 50%. ^1H NMR ([D_6]DMSO, 200.13 MHz, δ, ppm): 1.11 (s, 6 H), 1.21 [s, 6 H, 4,5-$(CH_3)_2$], 9.30 (s, NH), 10.4 (s, OH). ^{13}C NMR ([D_6]DMSO, δ, ppm): 18.3, 22.2 [4,5-$(CH_3)_2$], 61.9 (C-4), 63.6 (=*C*-CN), 70.3 (C-5), 115.8 (C≡N), 117.2 (q, $J_{C,F}$ = 291 Hz, CF_3), 162.8 (C-2), 173.8 (q, $J_{C,F}$ = 32 Hz, C=O). IR ($\tilde{\nu}$, cm^{-1}): 3400−3200 (NH, OH), 2218 (C≡N), 1620, 1547 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 241 (4.25), 294 (4.21). m.p. 189−191 °C (from ethanol). $C_{11}H_{14}F_3N_3O_2$: C 47.7, H 5.1, N 15.2; found C 47.6, H 4.8, N 14.4%.

Compound 24e: Yield 50%, m.p. 196−200 °C (decomp., from ethyl acetate/hexane). ^1H NMR ([D_6]DMSO, 200.13 MHz, δ, ppm): 1.13 (s, 6 H), 1.24 [s, 6 H, 4,5-$(CH_3)_2$], 7.45 (m, 1 H), 7.54 (m, 1 H, 3,5-H, pyridyl), 7.69 (m, 1 H, 4-H, pyridyl), 8.56 (m, 1 H, 6-H, pyridyl), 9.54 (s, 1 H, NH), 10.11 (s, 1 H, OH). ^{13}C NMR ([D_6]DMSO, 50.32 MHz, δ, ppm): 18.0, 22.3 [4,5-$(CH_3)_2$], 60.1 (C-4), 67.0 [C=*C*(CN)], 69.6 (C-5), 119.1 (C≡N), 121.6, 124.6, 136.6, 148.0, 157.4, (pyridyl), 163.8 (C-2), 188.6 (C=O). IR ($\tilde{\nu}$, cm^{-1}): 3259, 3145, 2981, 2882, 3200−2600 (NH, OH), 2111 (C≡N), 1602, 1566, 1537 (N−C=CH−C=O, C=C). UV [λ_{max} (ethanol), nm (log ε)]: 241 (3.90), 305 (4.09). $C_{15}H_{18}N_4O_2$: C 62.92, H 6.34, N 19.57; found C 62.69, H 6.39, N 19.31%.

Compound 24f: Yield 40%. ^1H NMR ([D_6]DMSO, 200.13 MHz, δ, ppm): 1.12 (s, 6 H), 1.18 (t, 3 H, OCH_2CH_3, ethyl acetate), 1.23 [s, 6 H, 4,5-$(CH_3)_2$], 1.98 (3 H, CH_3CO, ethyl acetate), 4.02 (q, 3 H, OCH_2CH_3, ethyl acetate), 7.49 (d, *J* = 6 Hz, 2 H, β-H, pyridyl), 8.65 (d, *J* = 6 Hz, 2 H, α-H, pyridyl), 9.57 (1 H, broad s, NH), 10.22 (1 H, broad s, NH). IR ($\tilde{\nu}$, cm^{-1}): 3275, 2600−3000 (NH, OH), 2201 (C≡N), 1600, 1554, 1532 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 247 (3.95), 307 (4.03). m.p. 231−235 °C (from an ethyl acetate/MeOH mixture). $C_{15}H_{18}N_4O_2 \cdot 1/2\ C_4H_8O_2$: C 61.80, H 6.71, N 16.96; found C 61.45, H 6.60, N 17.11%.

Compound 24g: Yield 30%. ^1H NMR ([D_6]DMSO, 200.13 MHz, δ, ppm): 1.07 (s, 6 H), 1.17 [s, 6 H, 4,5-$(CH_3)_2$], 1.25 [s, 9 H, $C(CH_3)_3$], 9.57 (broad s, 1 H), 9.81 (broad s, 1 H, NH, OH). ^{13}C NMR ([D_6]DMSO, 50.32 MHz, δ, ppm): 17.6, 22.1 [4,5-$(CH_3)_2$], 26.5 [$C(CH_3)_3$], 42.4 [$C(CH_3)_3$], 60.0 (C-4), 64.0 [C=*C*(CN)], 68.9 (C-5) 120.6 (C≡N), 164.7 (C-2), 200.0 (C=O). IR ($\tilde{\nu}$, cm^{-1}): 3362, 3247 (NH, OH), 2203 (C≡N), 1606, 1549, 1539 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 223 (4.02), 287 (4.18) m.p. 225−229 °C (from ethyl acetate). $C_{14}H_{23}N_3O_2$: C 63.37, H 8.74, N 15.84; found C 63.37, H 8.92, N 15.76%.

Treatment of **22a** and **22b** with NaCN was carried out in the same way. To isolate nitrile **24a**, the resulting solution was extracted with chloroform (4 × 20 mL) after pouring into brine. The combined extract was washed with brine (2 × 10 mL) and with water and dried with $MgSO_4$. The residue obtained after solvent removal was dissolved in MeOH (20 mL) and the solution was boiled for 1 h and then evaporated. The residue was treated with hexane, and the precipitate of nitrile **24a** was filtered off and washed with a small amount of ethyl acetate; yield 60%.

2-(1-Methoxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)-3-oxo-3-phenylpropanenitrile (25): Yield 60%, m.p. 180−183 °C (from a hexane/ethyl acetate mixture). ^1H NMR ($CDCl_3$, 200.13 MHz, δ, ppm): 1.29 [s, 12 H, 4,5-$(CH_3)_2$], 3.90 (s, 3 H, OCH_3), 7.38 (m, 3 H), 7.72 (m, 2 H, C_6H_5), 10.10 (broad s, 1 H, NH). IR ($\tilde{\nu}$, cm^{-1}): 3252 (NH), 2203 (C≡N), 1604, 1550 (N−C=C−C=O, C=C). UV

[λ_{max} (ethanol), nm (log ε)]: 234 (4.13), 305 (4.25). $C_{17}H_{21}N_3O_2$,%: calcd. C 68.20, H 7.07, N 14.04; found C 67.97, H 7.21, N 14.23%.

3-(1-Hydroxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)-2-oxopropionamide (1n): A solution of ester **1d** (0.5 g, 1.95 mmol) in a saturated MeOH solution of ammonia (10 mL) and aqueous ammonia (20%, 3 mL) was kept for 8 h at 20 °C. The MeOH was evaporated from the mixture, and the precipitate was filtered off and washed with water to give 0.39 g (90%) of amide **1n**. ^{1}H NMR ([D$_6$]DMSO, 200.13 MHz, δ, ppm): 1.06 (s, 6 H), 1.17 [s, 6 H, 4,5-$(CH_3)_2$], 1.18 (t, J = 7 Hz, 3 H, CH_3CH$_2$ ethyl acetate), 1.98 (s, 3 H, CH_3CO ethyl acetate), 4.02 (q, J = 7 Hz, 2 H, CH$_3$CH_2O ethyl acetate), 5.62 (s, 1 H, =CH-), 7.20 (broad s, 2 H, NH$_2$), 9.48 (s, 2 H, OH). ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, δ, ppm): 14.0 (-OCH$_2$*C*H$_3$ ethyl acetate), 20.7 (*C*H$_3$CO ethyl acetate), 17.8, 22.6 (4,5-$(CH_3)_2$], 59.7 (O*C*H$_2$CH$_3$ ethyl acetate), 60.6 (C-4), 68.3 (C-5), 73.4 (=CH-), 164.0 (C-2), 166.7 (*C*ONH$_2$), 177.7 (C=O). IR (ν̃, cm^{-1}): 3500−2500 (OH), 1690 (CONH$_2$), 1584, 1539 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 327 (4.31). m.p. 226−228 °C (from an ethyl acetate-ethanol mixture) $C_{10}H_{17}N_3O_3 \cdot 1/2C_4H_8O_2$: calcd. C 53.1, H 7.8, N 15.5; found C 52.5, H 7.7, N 15.3%.

2-Imino-2-(1-methoxy-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-phenylethanone (27): Crude monochloro derivative **20a** (0.16 g, 0.52 mmol) was added portionwise to a stirred solution of NaN_3 (0.07 g, 1 mmol) in DMSO (5 mL), and the resulting mixture was stirred for 2 h at 20 °C. The solution was cooled to 0 °C and diluted with cold brine (20 mL). The precipitate of imine **27** was filtered off and washed with water. Yield 0.10 g (65%), m.p. 88−91 °C (from hexane). ^{1}H NMR (CCl_4, 200.13 MHz, δ, ppm): 1.12 (s, 6 H), 1.14 [s, 6 H, 4,5-$(CH_3)_2$], 3.26 (s, 3 H, OCH_3), 7.41 (m, 3 H), 8.0 (m, 3 H, C_6H_5), 11.49 (s, 1 H, NH). IR (ν̃, cm^{-1}): 3216 (NH), 1666 (C=O), 1625, 1595, 1578 (C=N, C=C). $\tilde{\nu}_{max}$ (ethanol), nm (log ε): 255 (4.12). $C_{16}H_{21}N_3O_2$: calcd. C 66.88, H 7.20, N 14.62; found C 66.78, H 7.20, N 14.34%.

2-(1-Oxyl-4,4,5,5-tetramethylimidazolidin-2-ylidene)-3-oxo-3-phenylpropionitrile (29a): Lead dioxide (3 g, 12.5 mmol) was added to a solution of **24a** (1 g, 3.5 mmol) in chloroform (100 mL), and the resulting mixture was stirred for 20 min at 20 °C. The lead oxides were filtered off, and the filtrate was evaporated at a temperature below 20 °C to half the original amount. The residue was diluted with hexane (50 mL), and the precipitate was filtered off to give 0.68 g (70%) of nitroxide **29a**. IR (ν̃, cm^{-1}): 3300−3200 (NH), 2201 (C≡N), 1608, 1578, 1550 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 303 (4.09), 602 (2.60). m.p. ≥ 200 °C (decomp., from ethyl acetate/hexane). Found, *m*/*z*: 284.14052; calculated for $C_{16}H_{18}N_3O_2$ *m*/*z*: 284.13989.

Nitroxides **29b**, **29c**, **29e**, **29f**, and **29g** were synthesized similarly by oxidation of the corresponding hydroxylamines **24b**, **24c**, **24e**, **24f**, **24g**.

Compound 29b: Yield 40%, m.p. 130−133 °C, IR (ν̃, cm^{-1}): 3239 (NH), 2197 (C≡N), 1642, 1576 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 265 (3.60), 294 (3.51), 324 (3.35), 600 (2.88). $C_{11}H_{16}N_3O_2$: calcd. C 59.4, H 7.3, N 18.9; found C 59.0, H 7.1, N 18.6%. Found, *m*/*z* = 222.12434, calculated for $C_{11}H_{16}N_3O_2$, *m*/*z*: 222.12424.

Compound 29c: Yield 90%. IR (ν̃, cm^{-1}): 3260 (NH), 2216 (C≡N), 1650, 1576 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 280 (4.02), 355 (3.56), 573 (3.22). m.p. ≥ 150 °C. Found, *m*/*z*: 276.09553; calculated for $C_{11}H_{13}F_3N_3O_2$ *m*/*z*: 276.09598.

Compound 29e: Yield 40%, IR (ν̃, cm^{-1}): 3432, 3206, 2980, 3600−3000 (NH), 1629, 1585, 1543 (N−C=CH−C=O, C=C).

Compound 29f: Yield 30%, IR (ν̃, cm^{-1}): 3426, 3243 (NH), 2204 (C≡N), 1629, 1609, 1563 (N−C=C−C=O). λ_{max}, (chloroform), nm (log ε): 242 (3.47), 302 (3.61), 592 (2.70), m.p. 203−211 °C (decomp. from an ethyl acetate/hexane mixture).

Compound 29g: Yield 40%, m.p. 73 °C (decomp. from hexane), IR (ν̃, cm^{-1}): 3440−3241 (NH), 2198 (C≡N), 1631, 1562 (N−C=C−C=O). UV [λ_{max} (ethanol), nm (log ε)]: 270 (3.91), 322 (3.53), 593 (3.10). $C_{14}H_{22}N_3O_2$: calcd. C 63.61, H 8.39, N 15.90; found C 63.23, H 8.45, N 15.73%.

Oxidation of imidazolidine **1a** afforded a complex mixture of products. Enaminone **17** was isolated chromatographically on alumina with a chloroform/MeOH (50:1) mixture in a yield of about 10%.

Potassium Salt of Deprotonated 4,4,4-Trifluoro-2-(1-oxyl-4,4,5,5-tetramethyl-imidazolidin-2-ylidene)-3-oxobutyronitrile (29c): Lead dioxide (3 g, 12.5 mmol) was added to a solution of imidazolidine **24c** (1 g, 3.6 mmol) in ethyl acetate (100 mL), and the resulting mixture was stirred for 20 min at 20 °C. The lead oxides were filtered off, a solution of KOH (4.0 mmol) in MeOH (5 mL) was added to the filtrate, and the solution was stirred for 20 min. The precipitate of inorganic salts was filtered off, and the filtrate was evaporated at a temperature below 20 °C. The residue was diluted with toluene (50 mL), and the precipitate of the potassium salt of **29c** was filtered off and dried in vacuo. Yield 0.57 g (50%). Crystals of the potassium salt of **29c** suitable for an X-ray analysis were obtained by slow diffusion of benzene into an ethyl acetate solution of this salt. IR (ν̃, cm^{-1}): 2190 (C≡N), 1603, 1553 (N=C−C=C−O). UV [λ_{max} (ethanol), nm (log ε)]: 280 (4.22), 518 (2.65). m.p. 257−262 °C (from an ethyl acetate/benzene mixture). $C_{11}H_{12}F_3N_3O_2K$: C 42.0, H 3.9, F 18.1, N 13.3; found C 41.8, H 3.9, F 18.5, N 13.1%.

Crystals of **2-*tert*-butyl-3-{1-[2-cyano-2-hydroxy-1-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-3,3-dimethylbutoxy]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl}oxirane-2-carbonitrile (30)** suitable for an X-ray analysis were obtained in an attempt to grow crystals from crude radical **29g** from an ethyl acetate/heptane mixture. Two types of crystal formed: dark-blue crystals of nitroxide **29g**, unsuitable for an X-ray analysis, and dark-red crystals of nitroxide **30**, which were separated manually.

Compound 30: $C_{28}H_{45}N_6O_4$, *FW* = 529.70, monoclinic, $P2_1/c$, a = 19.549(1), b = 18.259(1), c = 20.335(1) Å, β = 117.655(1)°, V = 6428.9(6) Å^3, Z = 8, D_C = 1.095 g/cm^3, μ(Mo-K_α) = 0.074 mm, $1.18 < \theta < 23.31°$, 27676 reflections collected, 9255 unique, R_{int} = 0.0916, data/parameters = 9255/1046, *Goof* = 0.931, R indices ($I > 2\sigma_I$): R_1 = 0.0484, wR_2 = 0.1097; R indices (all data): R_1 = 0.0854, wR_2 = 0.1241.

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