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New Cascade Syntheses of Nitronyl Nitroxides and a New Synthetic Approach to Imino Nitroxides

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Suspensions of M_xO_y (MnO_2, Co_2O_3, Ni_2O_3) in protic solvents (MeOH, EtOH) have been found to be suitable systems for use in a cascade transformation of 4,4,5,5-tetramethyl-2-[2-(trimethylsilyl)ethynyl]imidazolidine-1,3-diol (**1a**) into 2-ethynyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (**3**). In MnO_2/MeOH, the products of further transformation of **3**, (*Z*)- and (*E*)-2-(2-methoxyvinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxides, were obtained by the regiospecific addition of MeOH to the triple bond of **3**. In the reaction in MnO_2/MeOH+H_2O (1:1), the *Z* isomer was the sole product. A multistep one-pot transformation of **1** into 4,4,5,5-tetramethyl-2-[2-oxo-1-(4,4,5,5-tetramethylimidazolidin-2-ylidene)ethyl]-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide occurred in MnO_2/EtOH. For (*E*)-2-[2-(diethylamino)vinyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide, it was shown that use of the MnO_2/secondary amine system provided a one-pot transformation of **1a** and gave (*E*)-aminovinyl-substituted nitronyl nitroxide as the sole product. In combined MnO_2/ROH/K_2CO_3 systems (R = Me, Et), the imidazolidine-1,3-diol **1a** was transformed into (*E*)-2-(2-ethoxyvinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide and the acetals 2-(2,2-dimethoxyethyl)- and 2-(2,2-diethoxyethyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide. In MnO_2/$MeNO_2$ we obtained the products of the transformations of different 2-substituted 4,4,5,5-tetramethylimidazolidine-1,3-diols (R = C≡C–$SiMe_3$, aryl, hetaryl, alkyl) or nitronyl nitroxides into the corresponding imino nitroxides (13 products); this reaction is a new method for the preparation of imino nitroxides and allowed us to synthesize the first α-acetylenyl-substituted imino nitroxides. The majority of paramagnetic compounds, including the derivatives of **1a**, were obtained as perfect crystals, and their structures were determined by X-ray structure analysis (14 solved structures).

Introduction

Nitronyl nitroxides (NNs) and imino nitroxides (INs)[1] are member compounds of the unique class of persistent organic paramagnets, widely used in the design of molecular magnets,[2] paramagnetic materials with giant thermostriction,[3] and contrastive substances for magnetic resonance tomography.[4] Interest in specially designed nitronyl and imino nitroxides has dramatically increased, which has stimulated the development of procedures for the synthesis of the key derivatives of nitronyl and imino nitroxides (e.g., α-ethynyl derivatives), leading to wide series of desired polyfunctional derivatives. Until recently, the α-acetylene derivatives of nitronyl and imino nitroxides were inaccessible compounds; their precursors each contained a combination of an N–OH group and a triple bond, rearrangement of which led to the aminoenone fragment,[5] also formed in reactions between 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxides and activated alkynes.[6,7] Thanks to the discovery of the cascade reaction between **1a** and PbO_2 in MeOH, leading to 2-ethynyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (**3**), however, compound **3** became accessible and could be used in various transformations.[8] To study the synthetic potential of the cascade reaction here, we concentrated on how the heterophase oxidation of **1a** could be changed by varying the oxidant, reaction time, and protic and aprotic polar and low-polar solvents. Here we wish to report the results of these studies, extending the available preparative scope of nitronyl and imino nitroxide chemistry.

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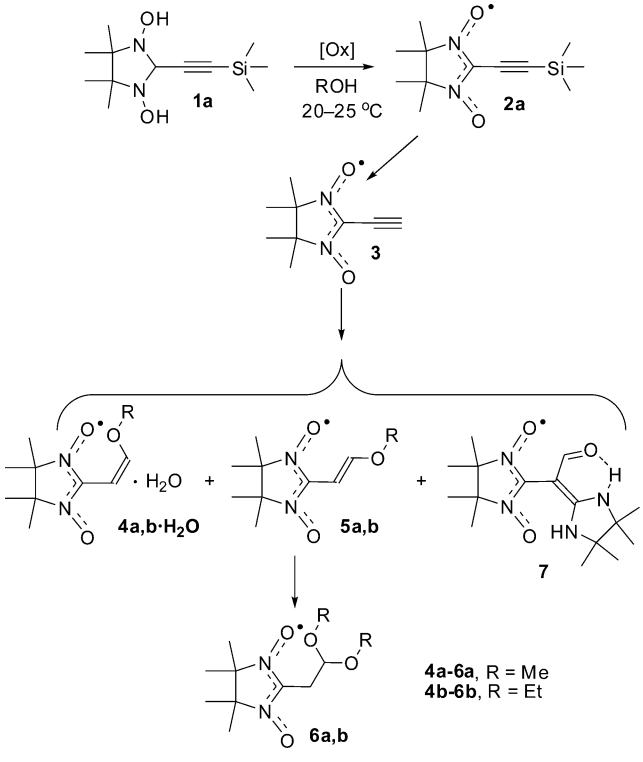
Results and Discussion

M_xO_y (MnO_2, Co_2O_3, Ni_2O_3)/Protic Solvent System

Experiments performed under normal conditions showed that after the addition of excess MnO_2, Co_2O_3, or Ni_2O_3 to

a solution of **1a** in MeOH or EtOH, the reaction mixtures became deep dark violet *after a minute*, as was also the case in the previously described reaction of **1a** in MeOH in the presence of PbO_2. Spin-labeled acetylene **3** was then quickly[8] isolated from the reaction mixture (Scheme 1). According to TLC data, other products formed in relatively small amounts over this time (Entries 1–3, Table 1), and **3** was obtained in a high yield (ca. 60–85%). Compound **3** also formed quickly under special conditions: namely, in absolute EtOH and under a dry atmosphere. At the same time, an authentic sample of **2a**[9] did not change in the presence of MnO_2, Co_2O_3, or Ni_2O_3 over the first 20 min. Consequently, the fast formation of **3** after treatment of **1a** with M_xO_y indicated that the basic reagent, responsible for splitting the Si–C bond, appeared during the course of the reaction. It can be assumed that the reduction of MnO_2, Co_2O_3, or Ni_2O_3 gives the corresponding hydroxides, and that these cause ionization of solvent molecules into RO^- ions, the concentrations of which are high enough for fast solvolysis of the Si–C bond. If so, larger radicals R should impede this reaction because the approach of RO^- to the sterically crowded Si–C bond should be hindered. Indeed, the reaction between MnO_2 and **1a** in *t*BuOH mainly gave **2a** in a 76% yield (Entry 4, Table 1). The interaction of the imidazolidine-1,3-diol **1a** with MnO_2, Co_2O_3, or Ni_2O_3 (as well as with PbO_2) in MeOH or EtOH was therefore a cascade reaction. Its first stage was the oxidation of **1a**, accompanied by the simultaneous generation of a base, and because of this the second stage was the removal of the Me_3Si group, finally forming compound **3**.



Scheme 1. Reactions between **1a** and M_xO_y in ROH (for details, see Table 1).

The maximum yield of **3** was isolated when excess M_xO_y was used; in this case, **1a** was completely converted in 30 min. Use of stoichiometric ratios of $\nu(M_xO_y)/\nu(\mathbf{1a})$ was less effective for the synthesis of **3**. At $\nu(MnO_2)/\nu(\mathbf{1a})$ = 3:1,[10] for example, complete oxidation of **1a** required longer times, and product **3** was obtained in much lower yields because of its further transformation into **4a**·H_2O, **5a**, and **6a** (Scheme 1, Entries 5 and 6, Table 1). We examined these transformations and found that higher reaction times decreased the yield of **3**, generally increased the contents of **4a**·H_2O and **5a** in the reaction mixture, and led to other products, with the product ratios depending on the $\nu(M_xO_y)/\nu(\mathbf{1a})$ ratio and the solvent used. Thus, at $\nu(MnO_2)/\nu(\mathbf{1a}) \approx 15:1$, the reaction between **1a** and MnO_2 in MeOH over 24 h mainly led to the *cis* isomer **4a**·H_2O, the *trans* isomer **5a**, and compounds **6a** and **7** in low yields (Entry 9, Table 1). If the reaction was performed in a mixture of equal volumes of MeOH and H_2O at the same $\nu(MnO_2)/\nu(\mathbf{1a})$ ratio, the major product was **4a**·H_2O, whereas the content of **5a** was low and that compound was not isolated (Entry 8, Table 1). The yields of **4a**·H_2O and **5a** obtained in the above experiments proved to be maxima and decreased when the stoichiometric $\nu(MnO_2)/\nu(\mathbf{1a})$ ratio was used or when other oxidants were used at different $\nu(M_xO_y)/\nu(\mathbf{1a})$ ratios (Entries 7, 12, 14, 16; Table 1), or when the reaction time was varied.

The reaction between **1a** and MnO_2 in EtOH gave a mixture of **3**, **4b**–**6b**, and **7**. The product ratio changed as the reaction time increased. After 60 h, the reaction mixture mainly contained **7**, which was formed in a 34% yield when the initial reagent ratio was $\nu(MnO_2)/\nu(\mathbf{1a})$ = 3:1 (Entries 10, and 11 in Table 1).

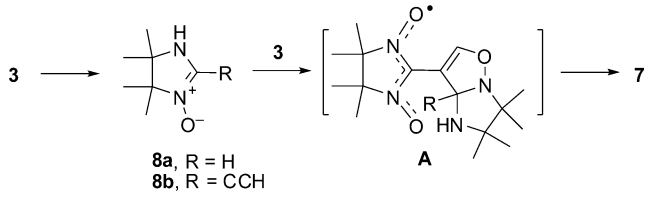
The distinctive feature of the cascade reaction between **1a** and M_xO_y in MeOH was thus the regiospecific addition of MeOH molecules to the triple bond in **3**, which occurred after the splitting of the C–Si bond (i.e., the cascade reaction involved one more stage). Products **4a**·H_2O and **5a**, which formed under one-pot synthesis conditions, proved to be kinetically stable in MnO_2/MeOH and were obtained in satisfactory yields. When the cascade reaction was performed in EtOH, the rate of the transformation of **3** into **4b** and **5b** was lower than that of the similar transformation in MeOH. The composition of the reaction mixture therefore depended strongly on decomposition, indicated by the formation of 4,4,5,5-tetramethyl-2-[2-oxo-1-(4,4,5,5-tetramethylimidazolidin-2-ylidene)ethyl]-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (**7**). Previously, aminoenal **7** had been prepared by treatment of **3** with 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-oxide (**8a**).[11] On this basis, it is reasonable to assume that under the reaction conditions, **3** was gradually reduced to 2-ethynyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-oxide (**8b**); by analogy with **8a**, this was then involved in 1,3-dipolar cycloaddition at the triple bond of **3** to form intermediate **A**, which rearranged into **7** (Scheme 2).

Compounds **6a**, **5b**, and **6b**, formed in small amounts in the oxidation of **1a** with M_xO_y, were identified by comparison of their IR spectra, R_f values, and spot colors (TLC)

Table 1. Identified products of the reactions between **1a** and M_xO_y in ROH.

Entry	[Ox]	ROH	$\nu(M_xO_y)/\nu(\mathbf{1a})$	Time [h]	Identified products (% isolated yield)[a]		
1	MnO_2	MeOH or EtOH	≈15:1	0.2–0.5	**3** (80–85)	**4a**·H_2O (+)	**5a** (+)
2	Co_2O_3	MeOH	≈8:1	0.2–0.4	**3** (60–75)	**4a**·H_2O (+)	**5a** (+)
3	Ni_2O_3	MeOH	≈8:1	0.2–0.4	**3** (60–80)	**4a**·H_2O (+)	**5a** (+)
4	MnO_2	*t*BuOH	≈15:1	0.2 or 6	**2a** (76)	**3** (+)	
5	MnO_2	MeOH	3:1[b]	0.4	**3** (46)	**1a** (+)	
6	MnO_2	MeOH	3:1[b]	6[c]	**3** (32)	4a·H_2O, 5a, 6a (+)	
7	MnO_2	MeOH	3:1[b]	26[d]	**4a**·H_2O (18)	**5a** (6)	**6a** (+)
8	MnO_2	MeOH/H_2O 1:1, v/v	≈15:1	18[d]	**4a**·H_2O (67)	**5a** (+)	
9	MnO_2	MeOH	≈15:1	20[d]	**4a**·H_2O (46)	**5a** (22)	**6a** (4), **7** (+)
10	MnO_2	EtOH	≈15:1	50[d]	**4b**–**6b**, **7** (+)[e]		
11	MnO_2	EtOH	3:1[b]	60[d]	**7** (34)	4b–6b (+)	
12	PbO_2	MeOH	5:1	24[d]	**4a**·H_2O (11)	**5a** (14)	
13	PbO_2	MeOH	3:2[b]	28[d]	**4a**·H_2O (12)	**5a** (18)	**6a** (+)
14	Ni_2O_3	MeOH	≈8:1	70[d]	**4a**·H_2O, 5a (+)		
15	Ni_2O_3	MeOH	3:2[b]	20	[f]		
16	Co_2O_3	MeOH	≈8:1	50[d]	**4a**–**6a** (+)[e]		

[a] The "+" symbol denotes that, according to TLC data, the product was present in the reaction mixture in relatively small amounts and was not isolated. [b] The stoichiometric ratio $\nu(M_xO_y)/\nu(\mathbf{1a})$. [c] The total consumption time of **1a**. [d] The total consumption time of **3**. [e] Unidentified products formed in addition to **4**–**7**. [f] Products **2**–**7** were not detected.



Scheme 2. Possible mechanism for the formation of **7**.

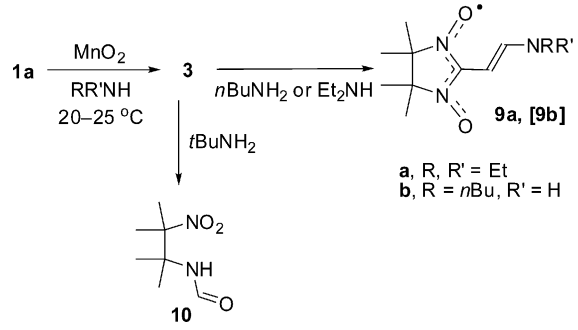
with those of authentic samples. For their preparation we used a MnO_2/ROH/K_2CO_3 combination, which involved the cascade reaction for the synthesis of **3**. Thus, in MeOH in the presence of K_2CO_3, nitroxide **3** was completely transformed into **4a**·H_2O and **5a** after 1 h and into **4a**·H_2O and **6a** after 24 h. In the course of these experiments, we came to believe that the acetal **6a** was formed exclusively from *trans* isomer **5a**, and this prompted a series of additional experiments. At room temperature, unaccompanied **4a**·H_2O in MeOH in the presence of K_2CO_3 did not change for at least 4 h, whereas the *trans* isomer **5a** was quantitatively transformed into **6a** under the same conditions.

Remarkably, solid **4a**·H_2O held its water molecule so tightly that did not lose it after recrystallization, SiO_2 chromatography (**4a**·H_2O has a much lower R_f than **5a**), or drying in vacuo. Attempts to perform dehydration of **4a**·H_2O under more rigid conditions, however, led to the formation of **5a** (along with the decomposition products). All this indicated that **4a**·H_2O existed as a stable hydrate, **4a**·H_2O_{Solv}, both in the solid state and in solution. The inertness of **4a**·H_2O_{Solv} relative to **5a** in MeOH/K_2CO_3 as described above could then be explained by the water molecule held by the *cis* isomer blocking the attack on the double bond by the MeO^- anion.

In EtOH/K_2CO_3, the time needed for the consumption of **3** increased to 50 h, and a mixture mainly containing **4b**·H_2O, as well as **5b**, **6b**, and **7**, formed. At 50–60 °C, the reaction gave a slightly increased yield of **6b**, whereas the content of **7** in the reaction product was comparable to that of **4b**·H_2O. The hydrate **4b**·H_2O was obtained several times as a solution by preparative chromatography, but evaporation of the solution and all attempts to crystallize the residue from hexane led to the formation of a mixture of **4b**·H_2O and *trans* isomer **5b**. This indicated that **4b**·H_2O was more readily dehydrated than **4a**·H_2O because of the increased size of the alkyl substituent; the product, *cis* isomer **4b**, was also unstable and isomerized into **5b** even under mild conditions (this actually gave satisfactory yields of **5b**.) Heating of **5b** by itself at 50–60 °C in EtOH in the presence of K_2CO_3 (7 h) gave acetal **6b** with a 52% yield. In view of the behavior of **3** in EtOH/K_2CO_3 at 50–60 °C described above, this is indirect evidence that neither **4b**·H_2O nor **4a**·H_2O added an EtOH molecule in the presence of K_2CO_3. Therefore, if **6b** is the target product, it is much more convenient to stir a ready-made ethanol solution of **3** at 20–25 °C in the presence of KOH (10 h). As in the case of K_2CO_3, a mixture of **5b** and **4b**·H_2O, with the latter dominant, initially formed under these conditions (TLC data); in the presence of a stronger base, however, not only **5b**, but also **4b**·H_2O, transformed into acetal **6b** (*cis* isomer **4b**·H_2O reacted much more slowly than **5b**). This ensured that the four stages of the transformation of **1a** into **6b** could be performed without isolation of intermediate nitroxides (the yield of **6b** reached 33%).

It was appealing to expand the potential of this one-pot synthesis of nitronyl nitroxides from **1a** by performing it in amines, which were chosen from a range of radically different representatives of this class of compounds. Dihydroxyimidazolidine **1a** was thus treated with 15-fold excesses of MnO_2 in different amines (Et_2NH, nBuNH$_2$, or tBuNH$_2$) at 20 °C (Scheme 3). Under these conditions, **1a** was completely transformed into **3** in 5–10 min. Further transformations of **3** depended on the amine solvent. In Et_2NH or nBuNH$_2$ a greenish blue product had formed after 1.5–2 h

(major product, TLC data). The diethylaminovinyl-substituted nitroxide **9a** was isolated in ca. 90% yield. An attempt to isolate **9b** showed that this nitroxide was unstable and quickly decomposed during concentration of its solution. In *t*BuNH$_2$, **3** was transformed into a crimson-colored product, which gave colorless **10** during its isolation. The oxidation of **1a** with MnO_2 in sterically uncrowded RR′NH or RNH$_2$ thus makes it possible to perform three stages in a one-pot synthesis to prepare diethylaminovinyl-substituted nitronyl nitroxides.



Scheme 3. Reactions between **1a** and MnO_2 in amines.

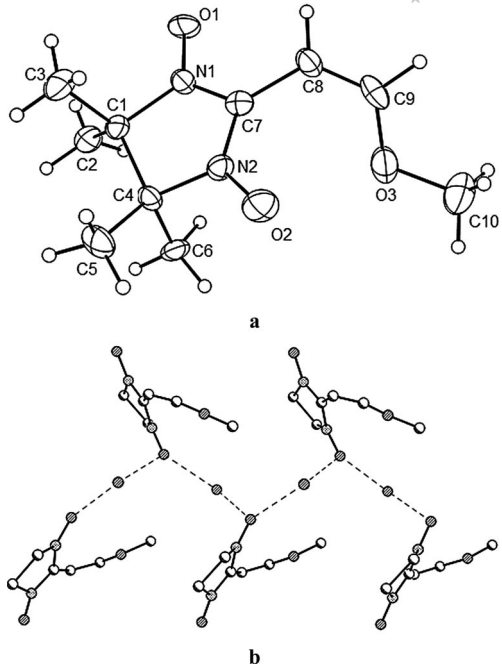


Figure 1. a) Molecule and b) crystal packing in **4a**·H$_2$O.

The structures of the products were supported by X-ray structure analyses (see Supporting Information), by satisfactory C, H, and N microanalyses, and by high-resolution mass spectroscopy. The compounds were also characterized by IR and ESR spectroscopy and magnetochemical measurements.

Discussion of the X-ray data can start with the group consisting of **4a**·H$_2$O, **5a**, and **5b**, which are the first alkoxyvinyl-substituted nitronyl nitroxides. For **4a**·H$_2$O (Figure 1), the X-ray study revealed short C(9)–O(3) [1.339(6) Å] and C(7)–C(8) [1.446(6) Å] bond lengths, which are indicative of substantial conjugation in the side fragment.[12] In the nitronyl nitroxide fragment, the N(1)–O(1) bond length [1.290(4)] is slightly larger than N(2)–O(2) [1.280(4) Å] because of O(1) being involved in H-bonding with water molecules [the O···O distances are 2.870(7) and 2.872(7) Å] (Figure 1, b).

After recrystallization, nitronyl nitroxide **5a** was always isolated from mother solutions in the form of an oil, which gradually solidified into an amorphous phase. It crystallized only as a trinuclear complex with copper(II) hexafluoroacetylacetonate [Cu(hfac)$_2$]$_3$(**5a**)$_2$, isolated as green plate-like crystals by slow evaporation of a mixture of hexane with CH_2Cl_2 containing equivalent amounts of Cu(hfac)$_2$ and **5a**. An X-ray study of [Cu(hfac)$_2$]$_3$(**5a**)$_2$ showed that **5a** performed the function of an O,O′ bridge in the trinuclear molecule (Figure 2, a). The Cu(1) atom has centrosymmetric surroundings in the form of an elongated octahedron, in which the O(1s) atom lies in the axial position [Cu(1)–O(1s) 2.379(4) Å]. The equatorial positions are occupied by the O_{hfac} atoms, lying 1.929(4) and 1.937(5) Å away from the Cu(1) atom. The Cu(2) atom is surrounded by a square pyramid with one of the O_{hfac} atoms at the apex [Cu(2)–O_{hfac} 2.219(4) Å] and the O(2s) atom of the second N–O group of the bridging nitroxyl and three O_{hfac} atoms [Cu(2)–O_{hfac} 1.925(4)–1.960(4) Å and Cu(2)–O(2s) 2.003(3) Å] at the base. The pyramid is completed to an elongated octahedron by the O(2s′) atom, lying at a distance of 2.538(4) Å; this leads to the formation of chains in the structure of the complex (Figure 2, b). The N–O distances in coordinated **5a** differ significantly – N(1s)–O(1s) 1.277(5) Å and N(2s)–O(2s) 1.310(5) Å – because of the different modes of their coordination to Cu^{II} ions. In molecules of **5a**, the angle between the planes of the C(8s)C(9s)-O(3s) and N(1s)C(7s)N(2s) fragments is 11(1)°, which leads to more effective π conjugation than in **4a**·H$_2$O, in which this angle is 44(1)°. As a consequence, the C(9s)–O(3s) and O(7s)–C(8s) bond lengths are smaller [1.326(6) Å and 1.404(7) Å, respectively] than the similar bonds in **4a**·H$_2$O.

The replacement of MeO by EtO led to crystallization of **5b** in the form of perfect needles from hexane. An X-ray study of a selected single crystal showed that **5b**, like coordinated **5a**, had effective conjugation between the side and nitronyl nitroxide fragments. This is confirmed by the relatively short[12] C(7)–C(8), C(8)–C(9), and C(9)–O(3) bond lengths [1.421(2), 1.324(3), and 1.335(2) Å, respectively], and by the arrangement of the C(8)C(9)O(3) and N(1)C(7)-N(2) fragments in almost the same plane (Figure 3). The latter factor favors the formation of an intramolecular H-bond, O(2)···H(9) [C–H 0.98(2), H···O 2.24(2), C···O 2.915(3) Å, angle C–H–O 124.5(13)°]; because of this the N(2)–O(2) bond length [1.287(2) Å] is slightly greater than N(1)–O(1) [1.272(2) Å]. With regard to the crystal structure of **5b**, the paramagnetic molecules form centrosymmetric pairs with O(1)···O(1′) distances of 3.514 Å.

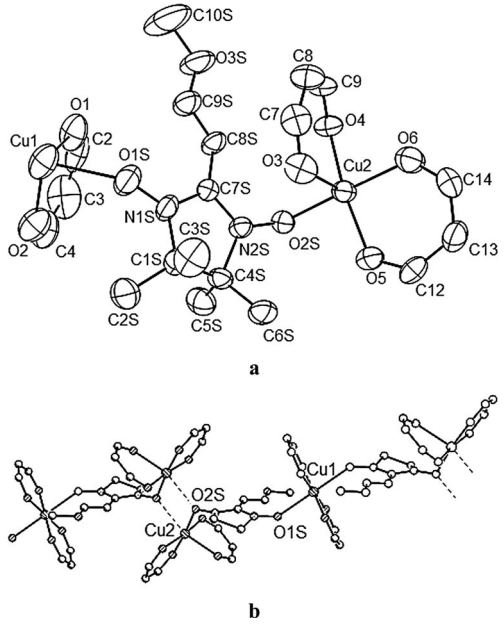


Figure 2. a) Independent part of $[Cu(hfac)_2]_3$(**5a**)$_2$ and b) polymer chain in the crystal structure of $[Cu(hfac)_2]_3$(**5a**)$_2$. CF_3 groups and H atoms are omitted for clarity.

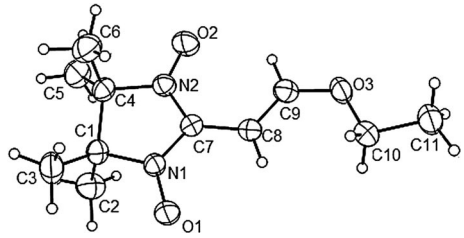


Figure 3. Molecule **5b**.

The effects of conjugation between the nitronyl nitroxide fragment and the substituents, mentioned in the discussion of the molecular structures of the alkoxyvinyl-substituted nitronyl nitroxides **5a** and **5b**, were also revealed in the ESR spectra of these compounds (see Figure 4 and Supporting Information). The overall spectra are very similar and rather typical of 2-imidazoline radicals in that they each contain the dominant quintet from the two nitrogen atoms of the imidazoline ring. All spectra show substantial delocalization of spin density to the substituent, which is evident from the resolved substructures from the two protons of the ethenyl bridge.

The experimentally measured ESR spectra were recorded in degassed toluene solutions at concentrations of 10^{-5} M at room temperature and modeled with Winsim v.0.96.[13] The isotropic g factors were determined by use of solid DPPH as a standard. Spectrum modeling yielded A_{N1} = 0.771 mT, A_{N2} = 0.747 mT, A_{H1} = 0.094 mT, A_{H2} = 0.113 mT, and g_{iso} = 2.0064 for **5a** and A_{N1} = 0.775 mT, A_{N2} = 0.753 mT, A_{H1} = 0.089 mT, A_{H2} = 0.117 mT, and g_{iso} = 2.0065 for **5b**. Further substructure from 12 protons of the four methyl groups of the imidazoline ring with A_{12H} = 0.02 mT was resolved for **5b**, but not for **5a**. The accuracy of hyperfine coupling constants and g factors is 0.005 mT and 0.0001, respectively.

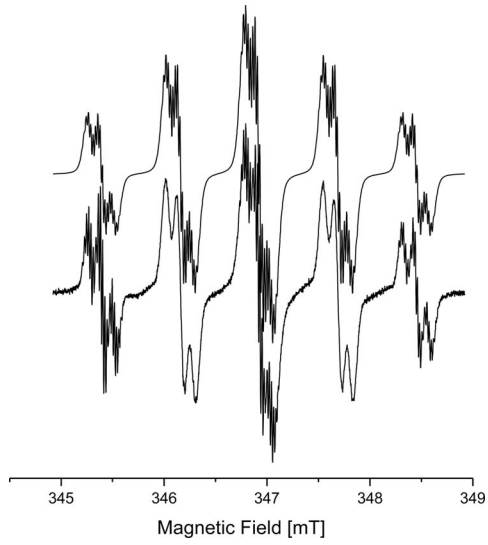


Figure 4. ESR spectrum of **5b** (bottom trace) and the result of its modeling (top trace).

In general, the two radicals have similar hyperfine parameters. Their nitrogen hyperfine couplings show that the two nuclei are not completely equivalent in solution. This can be explained by the relatively rigid extended π system, which includes the imidazoline moiety, the ethenyl bridge, and possibly methoxy/ethoxy oxygen, with the imidazoline ring having two distinguishable positions relative to the bridge. Furthermore, the ESR spectra, with a partially resolved finer substructure, show clear signs of the alternating linewidth effect due to the modulation of nitrogen couplings,[14] most probably because of the bending of the substituent with respect to the imidazoline ring. A typical spectrum of this type is shown in Figure 4. It can be seen that every other line of the dominant quintet (1, 3, 5) has a finer substructure, which is lacking in lines 2 and 4.

Figure 5 shows the experimentally measured and simulated ESR spectra for **4a**·H_2O. The modeling yielded A_{N1} = 0.746 mT, A_{N2} = 0.738 mT, A_{H1} = 0.089 mT, A_{H2} = 0.228 mT, and g_{iso} = 2.0066. The fine structure of the lines was not observed, and the spectrum was modeled as a conventional set of 12 protons from the four methyl groups of the imidazoline ring with A_{12H} = 0.02 mT. The spectra of **4a**·H_2O show closer hyperfine couplings (than those of **5a**) for the two nitrogen atoms, which became nearly equivalent, except that the coupling with one of the bridge protons was increased twofold. Because these spectra lack fine resolution, no dynamic effects could be observed.

In acetal **6a**, the oxygen atoms of the paramagnetic fragment are not involved in any specific interactions; according to XRD data, the N–O bond lengths are almost equal: 1.282(2) and 1.288(2) Å (Figure 6).

Radicals **6a** and **6b** have identical ESR spectra, in which each line of the dominant quintet is split into a 1–2–1 triplet from two apparently equivalent methene protons of the

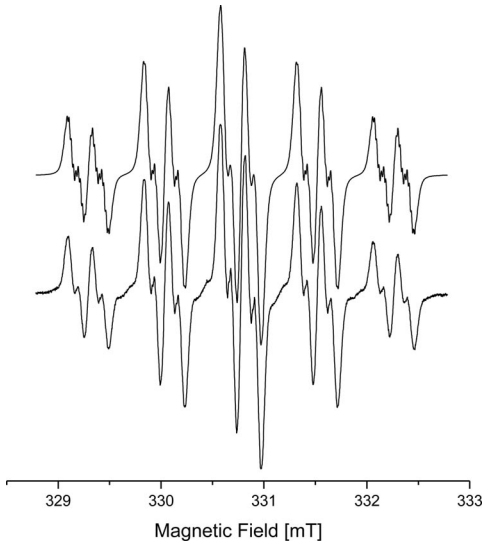


Figure 5. ESR spectrum of **4a**·H_2O (bottom trace) and the result of its modelling (top trace).

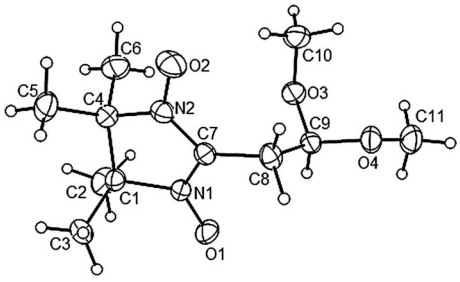


Figure 6. Molecule **6a**.

bridge, rotating relatively freely with respect to the imidazoline moiety (Figure 7 and the Supporting Information). The two side lines of the triplet, which do not exchange as the bridge rotates, have a resolved structure and are due to the imidazoline methyl groups, whereas the central line corresponding to the exchange averaging is not resolved. These spectra were modeled with use of two nearly equivalent protons of the methylene group. Modeling of the spectra of both **6a** and **6b** gave $A_{N1} = A_{N2} = 0.742$ mT, $A_{H1} = 0.219$ mT, $A_{H2} = 0.189$ mT, and $g_{iso} = 2.0066$. In both cases, 12 equiv. protons with $A_{12H} = 0.02$ mT were added to account for the four methyl groups of the imidazoline ring.

The data for **9a** are given in the Supporting Information section because the analogues of these compounds – pyrrolidin-1-ylvinyl- and diisopropylaminovinyl-substituted nitronyl nitroxides – have been studied previously.[8] The structure of diamagnetic **10** is not discussed here either.

For **4a**·H_2O, **5a**, **5b**, **6a**, and **9a** at 40–300 K, the effective magnetic moments (μ_{eff}) are 1.72–1.74 β, in agreement with the theoretical value of 1.73 β for noninteracting particles with spin $S = 1/2$ and $g = 2$ (see the Supporting Information). The weak temperature dependence of μ_{eff} indicates that the paramagnetic centers are well isolated from one another. This is confirmed by X-ray analysis data, namely

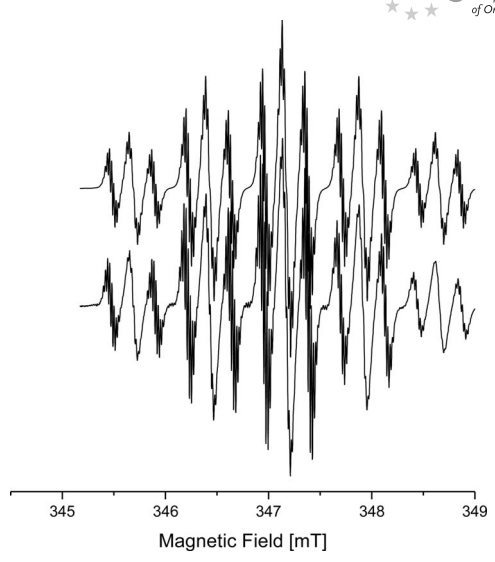


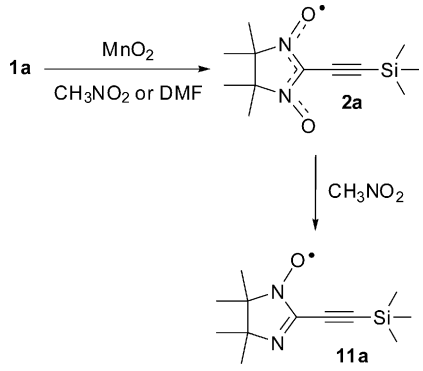
Figure 7. ESR spectrum of **6b** (bottom trace) and the result of its modelling (top trace).

by the fact that the intermolecular distances between the O atoms of N–O groups are large, the minimum distance (for solid **5b**) being 3.514 Å.

MnO_2/Aprotic Solvent (Benzene, DMF, Nitromethane) Systems

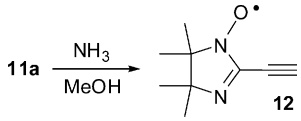
It was interesting to compare the products of the oxidation of **1a** in M_xO_y/protic solvent systems with the products of its oxidation in *aprotic* solvents, for which we chose benzene, nitromethane, and DMF, with very different polarities. Our experiments showed that the oxidation of **1a** with MnO_2, Ni_2O_3, and Co_2O_3 (and also PbO_2) in the weakly polar C_6H_6 was hindered. After the reaction mixture had been stirred for 1 day, it had merely become pale yellow. The same result was observed for the oxidation of **1a** with Ni_2O_3 and Co_2O_3 (and also PbO_2) in the polar solvents $MeNO_2$ and DMF. When the oxidation of **1a** with MnO_2 was carried out in $MeNO_2$ or DMF, however, the reaction mixture had become blue after 10–15 min because of the formation of **2a** in 90% yield (Scheme 4). With regard to the nature of the solvent here, it is important to emphasize that the oxidation of **1a** with MnO_2 in polar aprotic solvents was not accompanied by C–Si bond cleavage. Consequently, neither M_xO_y nor the reduction products can have been the bases that induced the splitting of this bond in the oxidations described in the previous section. For C–Si bond cleavage in **2a**, we need a protic solvent. We did not study the mechanism of bond splitting in this case, but it obviously did not occur in aprotic solvents. This is very important in that it forms a basis for the novel method of transformation of nitronyl nitroxides into imino nitroxides, which we found by studying the products of the reaction of **1a** with MnO_2 in $MeNO_2$.

After the reaction mixture had been stirred in DMF for 1 day, the nitronyl nitroxide **2a**, formed by the oxidation of **1a** with MnO_2, had been slowly deoxygenated, which led to



Scheme 4. Reactions of **1a** with MnO_2 in DMF or $MeNO_2$.

a decrease in its yield to 73%. If, however, the reaction of **1a** was performed with MnO_2 in $MeNO_2$, deoxygenation was much faster. Compound **2a** had been completely transformed into **11a** (ca. 80% yield) after 4 h; the TLC plate did not show any spots for other products. This unexpected result actually opened up an opportunity for the synthesis of the previously inaccessible α-ethynyl-substituted imino nitroxide **12**, because methods for splitting the Si–C bonds in Me_3Si-substituted acetylenes are well developed.[15] Indeed, treatment of **11a** with a methanol solution of NH_3 caused the transformation of this substrate into the ethynyl-substituted imino nitroxide **12**, isolated in ca. 85% yield (Scheme 5).



Scheme 5. Synthesis of the ethynyl-substituted imino nitroxide **12**.

Apart from being characterized by C, H, and N microanalyses and by high-resolution mass spectroscopy, which gave satisfactory results, **11a** and **12** were also studied by IR and ESR spectroscopic and magnetochemical measurements, whereas compound **12** was also characterized by X-ray diffraction. The presence of the terminal acetylene group in **12** can be inferred from the IR spectrum, which displays a low-intensity band due to the ν(C≡C) stretching vibrations at 2120 cm^{-1} and a strong band due to the ν(≡C–H) stretching vibrations at 3192 cm^{-1}. The free radical characters of **11a** and **12** are shown by the effective magnetic moments (μ_{eff}), which are almost constant at 40–300 K (1.78 and 1.73 β, respectively) for these compounds (see the Supporting Information).

The spectra show a triplet of triplets from two nitrogens of the imidazoline cycle and are very similar and typical for small 2-imidazoline-type iminonitroxyl radicals (Figure 8 and the Supporting Information). An additional splitting from the terminal proton can also be seen as a slight inflection in the spectra of **12**. Modeling of spectra yielded A_{N1} = 0.855 mT, A_{N2} = 0.426 mT, A_{12} = 0.02 mT, and g_{iso} = 2.0060 for **11a** and A_{N1} = 0.867 mT, A_{N2} = 0.432 mT, A_{Ht} = 0.071 mT, A_{12H} = 0.02 mT, and g_{iso} = 2.0060 for **12**. As would be expected, the only significant difference between the two radicals is additional proton splitting for **12**, whereas all other parameters of the spectra are very close.

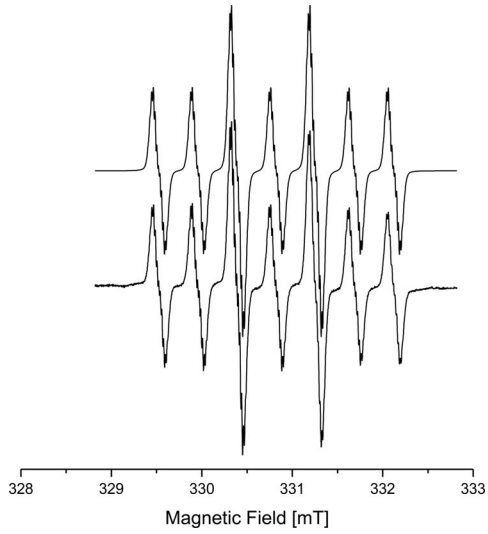


Figure 8. ESR spectrum of **12** (bottom trace) and the result of its modeling (top trace).

A comparison of the molecular structure of **12** with the structure of the related **3** shows that the lengths of the triple C(8)–C(9) [1.182(3) Å] and single C(7)–C(8) [1.433(3) Å] bonds in **12** are greater (Figure 9, a) than those in **3** [1.106(3) and 1.420(3) Å, respectively].[9] The motif of the crystal structure of **12** is similar to that of **3**. The structure of the solid is composed of zigzag chains with weak ≡C–H···N hydrogen bonds with the parameters C(9)···N(2′) 3.364(3), H(9)···N(2′) 2.45(3) Å, and angle C(9)H(9)N(2′) 168(2)° (Figure 9, b). Although these H-bonds involve the nitrogen atom of the N=C–N–O· fragment, the exchange

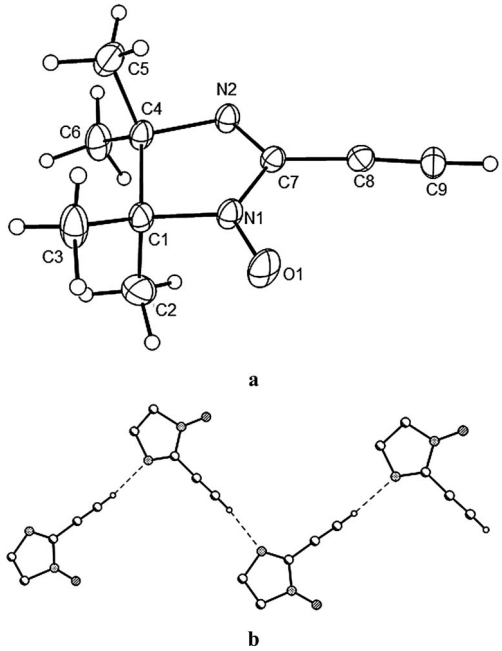
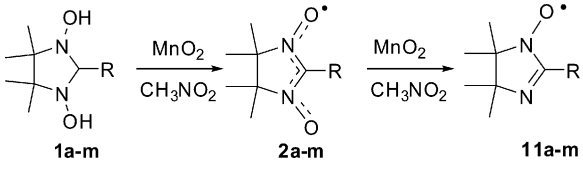


Figure 9. a) Molecule and b) crystal packing in **12**.

interactions between the odd electrons of the paramagnetic centers of the individual molecules are weak. This is indicated by the fact that μ_{eff} of **12** starts to decrease only at approximately liquid helium temperature (see the Supporting Information).

New Method for the Synthesis of Imino Nitroxides in MnO_2/$MeNO_2$

The transformation of **1a** into **11a** in MnO_2/$MeNO_2$ stimulated an attempt to extend this method to other nitronyl nitroxides to verify its generality. Indeed, in MnO_2/$MeNO_2$, different 1,3-dihydroxyimidazolidines **1** with alkyl, aryl, or hetaryl groups in their 2-positions gave the corresponding nitronyl nitroxides **2** after 10–20 min, and these were transformed into imino nitroxides **11** in high yields (Scheme 6). These results are summarized in Table 2. The structures of the new nitroxides **11** were supported by satisfactory C, H, and N microanalyses, by high-resolution mass spectroscopy, by magnetochemical measurements, and for well-crystallizable compounds **11** also by X-ray structure analysis.

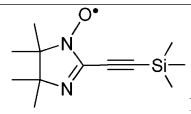
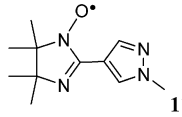
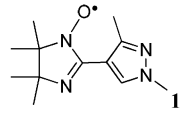
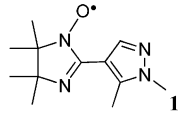
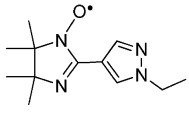
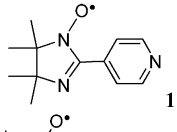
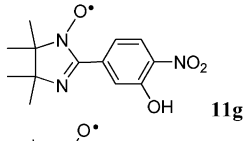
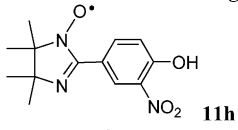
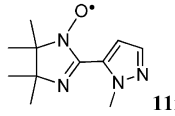
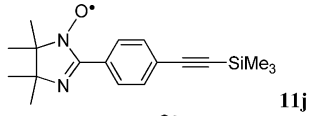
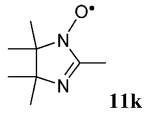
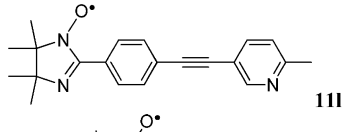
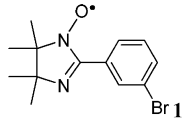


Scheme 6.

Two methods for the preparation of imino nitroxides **11** are currently available. The first is the oxidation of a dihydroxy derivative **1** into a nitronyl nitroxide **2**, which is then reduced with an appropriate reagent such as $NaNO_2$, PPh_3,[1c] or thiourea.[16] The second is the oxidation of a 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-oxide **13**, obtained by thermal[17] or SeO_2-catalyzed[18] dehydration of **1**. In both procedures, the reactions are performed in sequence. A distinction of our method for transforming **1** into **11** in MnO_2/$MeNO_2$ is a transition to a one-pot synthesis and the use of one reagent: MnO_2. The imino nitroxides **11** obtained in MnO_2/$MeNO_2$ were not contaminated with diamagnetic nitrones **13**, which are always present when compounds **11** are synthesized by the reduction of **2**.

Note that all transformations of **1** into **11** described in the Experimental Section were carried out at a MnO_2/**1** ratio of ca. 15:1 (i.e., with an excess of oxidant). At the minimum required ratio, MnO_2/**1m**[19] = 3:1, the oxidant was completely converted into brownish black MnO(OH), as it had been in MeOH, but **11m** did not form in this case. Thus, the one-pot synthesis of imino nitroxides **11** required that the reaction mixture contained MnO_2. This was also indicated by the fact that in $MeNO_2$ the addition of a tenfold excess of MnO_2 to a solution of **2m** (or **3**) caused its transformation into **11m** (or **12**) within 30 min. When the amount of MnO_2 was decreased to MnO_2/**2m** = 1:10 in $MeNO_2$, the time required for complete deoxygenation of **2m** increased to 60 h; in C_6H_6, DMF, MeOH, and EtOH, ca. 40% of the **2m** reacted over the same time. In the absence of MnO_2 (with stirring of a solution of **2m** in $MeNO_2$), no **11m** had formed after one day, but TLC

Table 2. Preparation of imino nitroxides **11a**–**m** from the corresponding imidazolidine-1,3-diols **1a**–**m** in MnO_2/$MeNO_2$.

Entry	Product **11**	Time [h]	Yield [%][a]
1	 **11a**	4	81
2	 **11b**	3	89
3	 **11c**	8	90
4	 **11d**	2.5	94
5	 **11e**	4.5	84
6	 **11f**	4.5	65
7	 **11g**	2	75
8	 **11h**	2.5	66
9	 **11i**	3	85
10	 **11j**	3	88
11	 **11k**	4	40
12	 **11l**	5	93
13	 **11m**	3	87

[a] Yield of the pure isolated product.

showed the presence of **11m** after 60 h. Consequently, deoxygenation of nitroxides **2** in solution was considerably accelerated in the presence of MnO_2. Active deoxygenation in $MeNO_2$, in which MnO_2 also easily oxidized compound **1**, made it possible to perform one-pot conversion of **1** into **11** in $MnO_2/MeNO_2$.

Conclusions

In this study, cascade reactions have been used for the synthesis of nitronyl nitroxides. As reaction systems, we used MnO_2/protic solvent (+ K_2CO_3), in which we performed one-pot transformations of 4,4,5,5-tetramethyl-2-[2-(trimethylsilyl)ethynyl]imidazolidine-1,3-diol (**1a**) into the nitronyl nitroxides (*Z*)- and (*E*)-2-(2-methoxyvinyl)-, (*E*)-2-[2-(diethylamino)vinyl]-, (*E*)-2-(2-ethoxyvinyl)-, 2-(2,2-dimethoxyethyl)- and 2-(2,2-diethoxyethyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide and 4,4,5,5-tetramethyl-2-[2-oxo-1-(4,4,5,5-tetramethylimidazolidin-2-ylidene)ethyl]-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide. We have found a new method for the transformation of nitronyl nitroxides and their precursor 2-substituted 4,4,5,5-tetramethylimidazolidine-1,3-diols (R = C≡C–$SiMe_3$, aryl, hetaryl, alkyl) into the corresponding imino nitroxides. The high efficiency of this method with $MeNO_2$ and MnO_2 was confirmed by the syntheses of a representative series of imino nitroxides (**11a**–**m**). Our data thus suggest that the interactions of M_xO_y (PbO_2, MnO_2, Co_2O_3, Ni_2O_3) with imidazolidine-1,3-diols in different solvents can be effectively used for the synthesis of new polyfunctional nitronyl and imino nitroxides.

Experimental Section

General: Compounds **1a**,[9] **1b** and **1e**,[20] **1c** and **1d**,[21] **1i**,[22] **1j**,[8] and **1l**,[23] were synthesized by the method reported by Ullman et al.[1] $Cu(hfac)_2$ was prepared by the known procedure and purified by sublimation.[24] Nickel(III) oxide and cobalt(III) oxide were synthesized as described in the literature.[25] Manganese(IV) oxide (activated, 5 micron, ca. 85%) was purchased from Sigma–Aldrich, and lead(IV) oxide (97%, A.C.S. reagent) was purchased from Aldrich. Other reagents and solvents from commercial sources were of the highest purity available and were used as received. The reactions were monitored by TLC with "Silica gel 60 F_{254} aluminium sheets, Merck". Chromatography was carried out with the use of "Merck" silica gel (0.063–0.100 mm for column chromatography) for column chromatography. C, H, and N elemental analyses were carried out by the Chemical Analytical Center of the Novosibirsk Institute of Organic Chemistry. The melting points were determined on a Boethius apparatus and not corrected. Infrared spectra (4000–400 cm^{-1}) were recorded with a Bruker VECTOR 22 instrument in KBr pellets. ^1H and ^{13}C NMR spectra were recorded at 25 °C with a Bruker Avance 400 spectrometer locked to the deuterium resonance of the solvent; chemical shifts are reported in parts per million (ppm) with the solvent as internal standard. HRMS were recorded on a DFS instrument by the Electron Impact Ionization technique (70 eV). X-Band CW ESR spectra were recorded in dilute degassed toluene solutions at room temperature on a Bruker EMX spectrometer at MW power 2 mW, modulation amplitude 0.01 mT at 100 kHz, single scan of 4096 points at 1310 ms per point, time constant 1310 ms, and modeled in free package Winsim v.0.96 as described earlier.[13] The magnetochemical experiment was run on an MPMS-5S ("Quantum Design") SQUID magnetometer at temperatures from 2 K to 300 K in a homogeneous external magnetic field up to 5 kOe. The molar magnetic susceptibility χ was calculated by Pascal's additive Scheme including diamagnetic corrections.

4,4,5,5-Tetramethyl-2-(pyridin-4-yl)imidazolidine-1,3-diol (1f): Pyridine-4-carboxaldehyde (1.07 g, 10 mmol) was added at room temperature to a stirred suspension of 2,3-bis(hydroxyamino)-2,3-dimethylbutane (BHA, 1.48 g, 10 mmol) in MeOH (15 mL).[1] The reaction mixture was stirred for 3 h and kept at 5 °C for 1 day. The precipitate was filtered off, washed on the filter with ethyl acetate and recrystallized from a mixture of MeOH and ethyl acetate. Yield 1.68 g (71%); decomposition temperature 170–175 °C. ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 1.00 (s, 6 H, Me), 1.06 (s, 6 H, Me), 4.49 (s, 1 H, 2-H), 7.44 (d, $J \approx 6$ Hz, 2 H, 3′-H, 5′-H), 7.92 (s, 2 H, N–OH), 8.49 (d, $J \approx 6$ Hz 2 H, 2′-H, 6′-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 150.6 (C), 149.1 (CH), 123.4 (CH), 89.1 (CH), 66.5 (C), 24.2 (CH_3), 17.2 (CH_3) ppm. IR: $\tilde{\nu}$ = 2886 (w), 2978 (m, CH_3), 3019 (w, C–H_{Py}), 3186 (br., OH) cm^{-1}. MS: *m/z* (%): 237 $[M]^+$ (1.0), 202 (7), 148 (10), 147 (100), 123 (17), 105 (11), 98 (10), 84 (12), 69 (11). HRMS calcd. for $C_{12}H_{19}N_3O_2$ $[M]^+$ 237.1472; found 237.1482. $C_{12}H_{19}N_3O_2$ (237.30): calcd. C 60.7, H 8.1, N 17.7; found C 60.8, H 8.2, N 17.8.

2-(3-Hydroxy-4-nitrophenyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (1g): Compound **1g** was synthesized from 3-hydroxy-4-nitrobenzaldehyde (3.34 g, 0.02 mol) and BHA (2.96 g, 0.02 mol) by the general procedure for the synthesis of **1f**. The product was obtained as a yellow solid (5.40 g, 91%); decomposition temperature 180–190 °C. ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 1.01 (s, 6 H, Me), 1.04 (s, 6 H, Me), 4.45 (s, 1 H, 2-H), 7.05 (dd, $^3J_{5',6'}$ = 8.4, $^4J_{2',6'}$ = 1.5 Hz, 1 H, 6′-H), 7.24 (d, $^4J_{2',6'}$ = 1.5 Hz, 1 H, 2′-H), 7.83 (d, $^3J_{5',6'}$ = 8.4 Hz, 1 H, 5′-H), 7.88 (s, 2 H, N–OH), 10.8 (s, 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 152.3 (C), 150.5 (C), 136.0 (C), 124.9 (CH), 119.8 (CH), 119.0 (CH), 89.8 (CH), 66.7 (C), 24.6 (CH_3), 17.5 (CH_3) ppm. IR: $\tilde{\nu}$ = 2915 (w), 2990 (m, CH_3), 3238 (br., OH) cm^{-1}. HRMS calcd. for $C_{13}H_{19}N_3O_5$ 297.1319 $[M]^+$; found 297.1318. MS: *m/z* (%): 297 $[M]^+$ (0.7), 262 (8), 208 (10), 207 (100), 206 (17), 183 (5), 165 (12), 161 (7), 98 (11), 84 (12), 69 (10). $C_{13}H_{19}N_3O_5$ (297.31): calcd. C 52.5, H 6.4, N 14.1; found C 52.8, H 6.4, N 14.3.

2-(4-Hydroxy-3-nitrophenyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (1h): Compound **1h** was synthesized from 4-hydroxy-3-nitrobenzaldehyde (3.34 g, 0.02 mol) and BHA (2.96 g, 0.02 mol) by the general procedure for the synthesis of **1f**. The product was obtained as a yellow solid (5.80 g, 98%); decomposition temperature 160–165 °C. ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 1.01 (s, 6 H, Me), 1.04 (s, 6 H, Me), 4.46 (s, 1 H, 2-H), 7.07 (d, $^3J_{5',6'}$ = 8.7 Hz, 1 H, 5′-H), 7.57 (dd, $^3J_{5',6'}$ = 8.7, $^4J_{2',6'}$ = 2.2 Hz, 1 H, 6′-H), 7.81 (s, 2 H, N–OH), 7.93 (d, $^4J_{2',6'}$ = 2.2 Hz, 1 H, 2′-H), 10.8 (s, 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 151.9 (C), 136.4 (C), 135.9 (CH), 133.7 (C), 124.7 (CH), 118.7 (CH), 89.1 (CH), 66.5 (C), 24.6 (CH_3), 17.6 (CH_3) ppm. IR: $\tilde{\nu}$ = 2916 (w), 2991 (m, CH_3), 3060 (w, C–H_{Ar}), 3229 (br., OH) cm^{-1}. MS: *m/z* (%): 297 $[M]^+$ (0.4), 208 (11), 207 (100), 206 (10), 182 (5), 165 (7), 161 (8), 98 (8), 84 (11), 69 (11). HRMS calcd. for $C_{13}H_{19}N_3O_5$ $[M]^+$ 297.1319; found 297.1322. $C_{13}H_{19}N_3O_5$ (297.31): calcd. C 52.5, H 6.4, N 14.1; found C 52.4, H 6.6, N 14.1.

2,4,4,5,5-Pentamethylimidazolidine-1,3-diol (1k): CH_3CHO (6 mL) was added to a suspension of BHA·H_2SO_4·H_2O (20.0 g, 0.076 mol)

in water (30 mL), and the reaction mixture was stirred for 2 h. A solution of NaOH (5.4 g, 0.135 mol) in water (10 mL) was added dropwise to the solution; then Na_2CO_3 (2.0 g, 0.019 mol) was added in portions (because of strong foaming). The resulting product **1k** was filtered off, dried in vacuo, and recrystallized from MeOH. Yield 7.2 g (71%); m.p. 149–150 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 0.96 (s, 12 H, Me), 1.13 (d, $^3J_2$ = 5.9 Hz, 3 H, Me), 3.70 (q, $^3J_{Me}$ = 5.9 Hz, 1 H, 2-H), 7.58 (s, 2 H, N–OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 82.7, 65.5, 22.9, 18.8, 18.0 ppm. IR: $\tilde{\nu}$ = 2915 (w), 2977 (m, CH_3), 3252 (br., OH) cm^{-1}. MS: *m*/*z* (%): 174 [M]$^+$ (1.8), 101 (14), 100 (11), 98 (18), 84 (100), 69 (8). HRMS calcd. for $C_8H_{18}N_2O_2$ [M]$^+$ 174.1363; found 174.1364. $C_8H_{18}N_2O_2$ (174.24): calcd. C 55.2, H 10.4, N 16.1; found C 54.9, H 10.4, N 16.0.

2-(3-Bromophenyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (1m): Compound **1m** was synthesized from 3-bromobenzaldehyde (1.85 g, 10 mmol) and BHA (1.48 g, 10 mmol) by the general procedure for the synthesis of **1f**; the product was obtained as a pale yellow solid (1.90 g, 71%); m.p. 194–196 °C (from ethyl acetate). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.00 (s, 6 H, Me), 1.04 (s, 6 H, Me), 4.47 (s, 1 H, 2-H), 7.26 (distorted t, $^3J_{4',6'} \approx 8$ Hz, 1 H), 7.45 (m, 2 H), 7.66 (distorted t, $^4J_{4',6'} \approx 2$ Hz, 1 H, 2′-H), 7.84 (s, 2 H, N–OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 144.9 (C), 130.8 (CH), 130.1 (CH), 129.8 (CH), 127.6 (CH), 121.2 (C), 89.5 (CH), 66.3 (C), 24.4 (CH_3), 17.2 (CH_3) ppm. IR: $\tilde{\nu}$ = 2914 (w), 2992 (m, CH_3), 3224 (br., OH) cm^{-1}. MS: *m*/*z* (%): 316 [M + 2]$^+$ (0.9), 314 [M]$^+$ (0.9), 227 (13), 226 (99), 225 (14), 224 (100), 202 (7), 200 (7), 100 (8), 98 (15), 89 (6), 84 (10), 69 (9). HRMS calcd. for $C_{13}H_{19}BrN_2O_2$ [M]$^+$ 314.0624; found 314.0621. $C_{13}H_{19}BrN_2O_2$ (315.21): calcd. C 49.5, H 6.1, Br 25.4, N 8.9; found C 49.3, H 5.9, Br 25.1, N 8.9.

General Procedure for the Oxidation of 1a in M_xO_y/ROH Systems {with MnO_2/MeOH as an example (Entry 9, Table 1)}

Characterization of (*Z*)-2-(2-Methoxyvinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-Oxide Hydrate (4a·H$_2$O) and (*E*)-2-(2-Methoxyvinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-Oxyl 3-Oxide (5a): MnO_2 (2.5 g, 28.8 mmol) was added to a solution of **1a** (500 mg, 1.95 mmol) in MeOH (25 mL). The resulting reaction mixture was stirred at room temperature for 20 h and then filtered, and the solvents were evaporated. The residue was chromatographed on a column (25 × 1.5 cm, ethyl acetate as an eluent). A blue [compound **5a** with R_f = 0.52 (AcOEt)] and a crimson [compound **6a**, R_f = 0.40 (AcOEt)] fraction were collected. The column was then eluted with a mixture of ethyl acetate and MeOH (5:1, *v*/*v*), and a blue-violet fraction was collected [compound **4a**·H$_2$O with R_f = 0.14 (AcOEt)]. The fractions were concentrated and again chromatographed. The products **4a**·H$_2$O, **5a**, and **6a** were dissolved in hexane at 40–50 °C, and the solutions were filtered and cooled. The crystalline precipitate **4a**·H$_2$O was filtered off and washed on a filter with cold hexane. Nitroxide **5a** was initially isolated as a dense oil, which crystallized on grinding with cold hexane. The first portions of **6a** were isolated as a dense oil; the mother solution was then decanted and stored at –15 °C for 24 h, which gave **6a** in the form of intergrown crystals.

Product 4a·H$_2$O: Yield 210 mg (46%); blue-violet needle crystals; m.p. 48–50 °C. The mass of **4a**·H$_2$O had not changed after the product had been kept in vacuo (< 1 Torr) at room temperature for 24 h. According to TLC data, on boiling in C_6H_6, **4a**·H$_2$O gave a number of products, including **5a**. IR: $\tilde{\nu}$ = 2939 (w), 2991 (m, CH_3), 3455 (br), 3511 (br., OH) cm^{-1}. μ_{eff} = 1.74 B.M. (5–300 K). MS: *m*/*z* (%): 214 [M + 1]$^+$ (4.8), 213 [M]$^+$ (38.8), 151 (4), 114 (7), 85 (12), 84 (100), 83 (9), 70 (4), 69 (92), 56 (18). (Under the mass spectrum recording conditions, **4a**·H$_2$O was dehydrated, and product **4a** isomerized into **5a**.) HRMS calcd. for $C_{10}H_{17}N_2O_3$ [M]$^+$ 213.1239; found 213.1231. $C_{10}H_{19}N_2O_4$ (231.27): calcd. C 51.9, H 8.3, N 12.1; found C 52.0, H 8.0, N 12.3.

Product 5a: Yield 90 mg (22%); blue finely crystalline powder; m.p. 84–86 °C; at room temperature, **5a** in MeOH in the presence of K_2CO_3 quantitatively transformed into **6a**. μ_{eff} = 1.73 B.M. (5–300 K). MS: *m*/*z* (%): 214 [M + 1]$^+$ (9.5), 213 (100) [M]$^+$, 151 (5), 114 (8), 85 (18), 84 (95), 69 (71), 56 (18). HRMS calcd. for $C_{10}H_{17}N_2O_3$ [M]$^+$ 213.1239; found 213.1225. $C_{10}H_{17}N_2O_3$ (213.26): calcd. C 56.3, H 8.0, N 13.1; found C 56.3, H 8.1, N 13.1.

Product 6a: Yield 20 mg (4%).

Other experiments on the oxidation of **1a** with M_xO_y in ROH (Table 1) were carried out by similar procedures; compounds **2a**,[9] **5b**, **6a**, **6b**, and **7**[11] were identified by comparing their IR spectra, R_f values, and spot colors (TLC) with those of authentic samples.

2-(2,2-Dimethoxyethyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-Oxide (6a): MnO_2 (1.02 g, 11.7 mmol) was added at room temperature to a solution of **1a** (200 mg, 0.78 mmol) in MeOH (10 mL). The reaction mixture was stirred for 20 min and filtered. K_2CO_3 (100 mg) was added to the filtrate containing **3**. The mixture was stirred for 24 h (until **5a** had vanished) and was then filtered, and the solvents were evaporated. The residue was chromatographed on a silica gel column to give **6a**. Yield 105 mg (55%); claret red crystals; m.p. 69–70 °C. UV/Vis (EtOH): λ_{max} (ε, M^{-1}cm^{-1}) = 216 (10000), 263 (8800), 339 sh. (6200), 353 (11000), 607 (380), 655 (290) nm. μ_{eff} = 1.74 B.M. (75–300 K). MS: *m*/*z* (%):245 [M]$^+$ (6.8), 214 (6), 84 (25), 75 (100), 69 (14). HRMS calcd. for $C_{11}H_{21}N_2O_4$ [M]$^+$ 245.1496; found 245.1496. $C_{11}H_{21}N_2O_4$ (245.30): calcd. C 53.9, H 8.6, N 11.4; found C 53.7, H 8.9, N 11.4.

(*E*)-2-(2-Ethoxyvinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-Oxide (5b): MnO_2 (1.02 g, 11.7 mmol) was added to a solution of **1a** (200 mg, 0.78 mmol) in EtOH (10 mL). The mixture was stirred at room temperature for 20 min and filtered. K_2CO_3 (100 mg) was then added to the solution of **3**. The mixture was stirred for 50 h (until compound **3** had vanished) and filtered, and the solvents were evaporated. The residue was kept in vacuo for 24 h and then dissolved in hexane. The resulting solution was heated with boiling for 3 h and concentrated {according to TLC data, in the course of this procedure, the blue-violet compound with R_f = 0.19 (AcOEt), presumably (*Z*)-2-(2-ethoxyvinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide hydrate (**4b**·H$_2$O), mostly transformed into **5b** (R_f = 0.60, AcOEt)}. The resulting mixture was separated on a column {35 × 1.5 cm; eluents EtOAc for **5b** and a mixture of EtOAc and MeOH (5:1, *v*/*v*) for **4b**·H$_2$O}; product **5b** was isolated. Yield 75 mg (42%); blue crystals; m.p. 66–68 °C. IR: $\tilde{\nu}$ = 2936 (w), 2978 (m, CH), 3056 (w, =C–H) cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε, M^{-1}cm^{-1}) = 272 (11891), 266 (9572), 626 (1216), 630 sh. (1206), 683 sh. (1172) nm. μ_{eff} = 1.73 B.M. (75–300 K). MS: *m*/*z* (%): 228 [M + 1]$^+$ (11.7), 227 [M]$^+$ (79), 114 (13), 99 (9), 98 (8), 84 (100), 83 (18), 71 (12). HRMS calcd. for $C_{11}H_{19}N_2O_3$ [M]$^+$ 227.1390; found 227.1392. $C_{11}H_{19}N_2O_3$ (227.28): calcd. C 58.1, H 8.4, N 12.3; found C 58.3, H 8.5, N 12.3.

2-(2,2-Diethoxyethyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-Oxide (6b)

Procedure 1: K_2CO_3 (40 mg) was added to a solution of **5b** (40 mg, 0.18 mmol) in EtOH (10 mL). The mixture was stirred while boiling for 7 h (until **5b** had vanished) and was then filtered, and the solvents were evaporated. The residue was purified by column chromatography (30 × 1.5 cm, EtOAc as eluent). A claret red frac-

tion with R_f = 0.40 AcOEt was collected and evaporated to give **6b**. Yield 25 mg (52%); claret red oil. UV/Vis (EtOH): λ_{max} (ε, $M^{-1}cm^{-1}$) = 215 (10000), 260 (8800), 340 sh. (6100), 350 (11000), 610 (370), 650 (300) nm. MS: *m/z* (%): 273 $[M]^+$ (7.30), 228 (18), 195 (6), 156 (10), 114 (6), 103 (100), 98 (7), 84 (53). HRMS calcd. for $C_{13}H_{25}N_2O_4$ $[M]^+$ 273.1809; found 273.1821. $C_{13}H_{25}N_2O_4$ (273.35): calcd. C 57.1, H 9.2, N 10.3; found C 57.5, H 9.3, N 10.7.

Procedure 2: A mixture prepared by the addition of MnO_2 (1.02 g, 11.7 mmol) to a solution of **1a** (200 mg, 0.78 mmol) in EtOH (10 mL) was stirred at room temperature for 20 min and filtered. KOH (100 mg) was added to the resulting solution of **3**. The mixture was stirred at room temperature for 10 h (until **3** had vanished) and was then filtered, and the solvents were evaporated. The residue was ground with ethyl acetate (ca. 10 mL) and the solution was decanted; the process was repeated until the next portion of ethyl acetate ceased to be colored. The consolidated solutions were evaporated, and the residue was chromatographed to give **6b** with a yield of 70 mg (33%).

$[Cu(hfac)_2]_3(5a)_2$ Complex: $Cu(hfac)_2$ (11 mg, 0.023 mmol) was added to a solution of **5a** (5.1 mg, 0.024 mmol) in a mixture of CH_2Cl_2 (1 mL) and *n*-heptane (3 mL). The resulting solution was kept in an open flask at 5 °C. After the mother solution was almost completely decolorized, the crystals were filtered off and dissolved in *n*-heptane (5 mL) at 50–55 °C. The solution was filtered, and the filtrate was kept at –15 °C for 1 d. The resulting greenish-brown dichroic crystals were filtered off, washed with cold hexane on a filter (1 mL), and dried in air. Yield 8.4 mg (38% based on **5a**). IR: $\tilde{\nu}$ = 545, 596, 617, 680, 746, 801, 846, 864, 962, 989, 1150, 1207, 1262, 1337, 1400, 1482, 1531, 1558, 1644 cm^{-1} (the other absorption bands have an intensity of less than 5% of the intensity of the 1150 cm^{-1} band). $\mu_{eff} \approx 2.00$ B.M. (10–200 K). $C_{50}H_{40}Cu_3F_{36}N_4O_{18}$ (1859.45): calcd. C 32.3, H 2.2, N 3.0; found C 32.4, H 2.3, N 3.3.

4,4,5,5-Tetramethyl-2-[2-oxo-1-(4,4,5,5-tetramethylimidazolidin-2-ylidine)ethyl]-4,5-dihydro-1*H*-imidazole-1-oxyl 3-Oxide (7): MnO_2 (204 mg, 2.35 mmol) was added at room temperature to a solution of **1a** (200 mg, 0.78 mmol) in EtOH (5 mL). The reaction mixture was stirred for 60 h and filtered. Toluene (5 mL) was added to the filtrate, and the solution was concentrated in vacuo to a volume of ca. 2 mL and placed on a silica gel column (1.5 × 20 cm). The column was eluted with ethyl acetate, and a blue fraction of nitroxide **7** with R_f = 0.31 AcOEt was collected. The fraction was concentrated, the residue was dissolved in ether, and the resulting solution was filtered. The filtrate was diluted with *n*-heptane (a volume one third of the volume of the filtrate) and evaporated to give **7** (43 mg, 34%). The spectroscopic data and melting point of nitroxide **7** are identical to those obtained earlier.[11]

(*E*)-2-[2-(Diethylamino)vinyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-Oxide (9a): MnO_2 (260 mg, 3.0 mmol) was added at room temperature to a solution of **1a** (50 mg, 0.20 mmol) in Et_2NH (5 mL). The reaction mixture was stirred for 40 min and filtered, and the solvents were evaporated. The residue was chromatographed on a silica gel column (1.5 × 20 cm); the side products were eluted with ethyl acetate. The column was then eluted with a mixture of ethyl acetate with MeOH (5:1, *v*/*v*), and a turquoise-colored fraction with R_f = 0.44 AcOEt was collected. The solution was concentrated, and the residue was recrystallized from hexane to give **9a**. Yield 15 mg (30%); dark green needles; m.p. 105–106 °C. UV/Vis ($CHCl_3$): λ_{max} (ε, $M^{-1}cm^{-1}$) = 313 (31043), 389 sh. (3840), 748 (2617) nm. μ_{eff} = 1.73 B.M. (75–300 K). ESR: g_{iso} = 2.0064; $A_{N1}(1N)$ = 0.822 mT, $A_{N2}(1N)$ = 0.750 mT $A_{(CH3)}(12H)$ = 0.025 mT, $A_{Hsub}(1H)$ = 0.095 mT, $A_{Hsub}(1H)$ = 0.033 mT, $A_{Nsub}(1N)$ = 0.036 mT, $A_{(CH2)}(4H)$ = 0.044 mT, $A_{(CH_2CH_3)}(6H)$ = 0.027 mT (for details see the Supporting Information). MS: *m/z* (%): 255 $[M + 1]^+$ (16.9), 254 (100) $[M]^+$, 237 (15), 222 (10), 220 (12), 178 (12), 126 (73), 125 (35), 124 (67), 123 (23), 109 (32), 84 (34). HRMS calcd. for $C_{13}H_{24}N_3O_2$ $[M]^+$ 254.1863; found 254.1861. $C_{13}H_{24}N_3O_2$ (254.35): calcd. C 61.4, H 9.5, N 16.5; found C 61.1, H 9.8, N 16.4.

***N*-(2,3-Dimethyl-3-nitrobutan-2-yl)formamide (10):** MnO_2 (260 mg, 3.0 mmol) was added at room temperature to a solution of **1a** (50 mg, 0.20 mmol) in Bu^tNH_2 (3 mL). The reaction mixture was stirred for 24 h and then filtered, and the solvents were evaporated. The residue was filtered through a silica gel layer (1.5 × 15 cm, AcOEt), the solution was concentrated, and the residue was recrystallized from hexane to give **10**. Yield 26 mg (74%); colorless crystals; m.p. 189–190 °C. ^1H NMR (400 MHz, $CDCl_3$) (1:1.3 mixture of formamide rotamers, signals from major rotamer marked with an asterisk *): δ = 1.38* (s, 12 H, Me), 1.48 (s, 12 H, Me), 1.60* (s, 12 H, Me), 1.64 (s, 12 H, Me), 6.1 (br s, 1 H, NH), 7.0* (br d, *J* ≈ 11 Hz, 1 H, NH), 8.11 (d, *J* = 2.0 Hz, 1 H, CHO), 8.11* (d, *J* = 11.4 Hz, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $[D_6]DMSO$) (1:1.3 mixture of formamide rotamers): δ = 164.7, 162.6, 96.6, 95.9, 60.6, 59.0, 26.1, 24.8, 24.3, 24.2 ppm. IR: $\tilde{\nu}$ = 1308 (s), 1530 (s, NO_2), 1695 (s, C=O), 2932 (m), 2998 (m, CH_3), 3105 (s), 3211 (s, NH) cm^{-1}. MS: *m/z* (%): 128 $[M - NO_2]^+$ (2.5), 113 (7), 86 (100), 85 (5), 84 (7), 83 (39), 58 (61). HRMS calcd. for $C_7H_{14}NO$ $[M - NO_2]^+$ fragment ion 128.1070; found 128.1068. $C_7H_{14}N_2O_3$ (174.20): calcd. C 48.3, H 8.1, N 16.1; found C 48.2, H 8.4, N 16.3.

General Procedure for the Preparation of Imino Nitroxides 11. Example: 4,4,5,5-Tetramethyl-2-[2-(trimethylsilyl)ethynyl]-4,5-dihydro-1*H*-imidazole-1-oxyl (11a): MnO_2 (1.0 g, 11.5 mmol) was added at room temperature to a stirred solution of **1** (200 mg, 0.78 mmol) in $MeNO_2$ (12 mL). The reaction mixture was stirred for 4 h and filtered. The solution was diluted with *n*-heptane (12 mL) and concentrated to a volume of ca. 2 mL on a rotary evaporator with bath temperature 30–35 °C. The solution was placed on a column (10 × 1.5 cm, wetted with $CHCl_3$). The column was eluted with $CHCl_3$, and an orange fraction was collected and then evaporated. The residue was dissolved in a minimum amount of hexane (ca. 5 mL) at room temperature, and the solution was filtered and kept at –10 °C for 10 h. The deposited orange-colored flakes were rapidly filtered out and washed with cold hexane. The yield of the crystalline **11a** was 80 mg (43%). The mother solution was further evaporated, which produced an additional 70 mg of **11a** (total yield 81%) in the form of an amorphous powder with spectral and analytical data identical to those of the crystalline sample; m.p. 73–75 °C (hexane); R_f = 0.63 (CH_2Cl_2). μ_{eff} = 1.73 B.M. (50–300 K). MS: *m/z* (%): 237 $[M]^+$ (1.0), 165 (6), 114 (8), 97 (6), 85 (6), 84 (100), 69 (28). HRMS calcd. for $C_{12}H_{21}N_2OSi$ $[M]^+$ 237.1418; found 237.1417. $C_{12}H_{21}N_2OSi$ (237.40): calcd. C 60.7, H 8.9, N 11.8; found C 60.8, H 8.8, N 11.8.

4,4,5,5-Tetramethyl-2-(1-methyl-1*H*-pyrazole-4-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl (11b): Compound **11b** was obtained as red-orange crystals (90 mg, 89%) from **1b** (110 mg, 0.46 mmol) by the general procedure; R_f = 0.33 (EtOAc). MS: *m/z* (%): 221 $[M]^+$ (2.5), 149 (7), 114 (18), 108 (18), 85 (6), 84 (100), 69 (43). HRMS calcd. for $C_{11}H_{17}N_4O$ $[M]^+$ 221.1397; found 221.1399. The melting point and spectroscopic data were identical with those reported in the literature.[22]

4,4,5,5-Tetramethyl-2-(1,3-dimethyl-1*H*-pyrazole-4-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl (11c):[22] Compound **11c** was obtained as red-orange crystals (50 mg, 90%) from **1c** (60 mg, 0.24 mmol) by the general procedure; R_f = 0.58 (EtOAc). MS: *m/z* (%): 235 $[M]^+$ (2.6),

122 (17), 114 (17), 85 (5), 84 (100), 69 (42). HRMS calcd. for $C_{12}H_{19}N_4O$ $[M]^+$ 235.1553; found 235.1559.

4,4,5,5-Tetramethyl-2-(1,5-dimethyl-1*H*-pyrazole-4-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl (11d):[22] Compound **11d** was obtained as red-orange crystals (26 mg, 94%) from **1d** (30 mg, 0.12 mmol) by the general procedure. MS: *m*/*z* (%): 235 $[M]^+$ (1.4), 122 (16), 121 (100), 120 (86), 114 (10), 93 (8), 84 (53), 69 (21). HRMS calcd. for $C_{12}H_{19}N_4O$ $[M]^+$ 235.1553; found 235.1560.

2-(1-Ethyl-1*H*-pyrazole-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl (11e):[22] Compound **11e** was obtained as red-orange crystals (31 mg, 84%) from **1e** (40 mg, 0.16 mmol) by the general procedure; R_f = 0.48 (EtOAc). MS: *m*/*z* (%): 235 $[M]^+$ (1.1), 163 (6), 122 (15), 114 (15), 85 (6), 84 (100), 69 (44). HRMS calcd. for $C_{12}H_{19}N_4O$ $[M]^+$ 235.1553; found 235.1556.

4,4,5,5-Tetramethyl-2-(pyridin-4-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl (11f): Compound **11f** was obtained as red-orange crystals (180 mg, 65%) from **1f** (300 mg, 1.26 mmol) by the general procedure; m.p. 72–73 °C (hexane); R_f = 0.46 (EtOAc). μ_{eff} = 1.73 B.M. (75–300 K). MS: *m*/*z* (%): 218 $[M]^+$ (2.4), 146 (11), 114 (14), 105 (18), 84 (100), 69 (53). HRMS calcd. for $C_{12}H_{16}N_3O$ $[M]^+$ 218.1293; found 218.1293. $C_{12}H_{16}N_3O$ (218.28): calcd. C 66.0, H 7.4, N 19.3; found C 65.6, H 7.3, N 19.3.

2-(3-Hydroxy-4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl (11g): Compound **11g** was obtained as orange crystals (105 mg, 75%) from **1g** (150 mg, 0.50 mmol) by the general procedure; m.p. 111.5–112.5 °C (hexane); R_f = 0.89 (EtOAc). IR: $\tilde{\nu}$ = 2982 (m, CH_3), 3243 (br), 3454 (br., OH) cm^{-1}. μ_{eff} = 1.73 B.M. (40–300 K). MS: *m*/*z* (%): 278 $[M]^+$ (0.8), 206 (16), 165 (13), 114 (14), 84 (100), 69 (47). HRMS calcd. for $C_{13}H_{16}N_3O_4$ $[M]^+$ 278.1135; found 278.1134. $C_{13}H_{16}N_3O_4 \cdot 0.5\,H_2O$ (287.30): calcd. C 54.4, H 6.0, N 14.7; found C 54.6, H 6.1, N 15.0.

2-(4-Hydroxy-3-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl (11h): Compound **11h** was obtained as orange crystals (75 mg, 66%) from **1h** (120 mg, 0.40 mmol) by the general procedure; m.p. 121–123 °C (hexane); R_f = 0.87 (EtOAc). IR: $\tilde{\nu}$ = 2930 (w), 2979 (m, CH_3), 3103 (w, C–H_{Ar}), 3247 (br., OH) cm^{-1}. μ_{eff} = 1.73 B.M. (50–300 K). MS: *m*/*z* (%): 278 $[M]^+$ (0.74), 206 (23), 165 (16), 114 (14), 85 (7), 84 (100), 69 (45). HRMS calcd. for $C_{13}H_{16}N_3O_4$ $[M]^+$ 278.1135; found 278.1134. $C_{13}H_{16}N_3O_4$ (278.29): calcd. C 56.1, H 5.8, N 15.1; found C 56.3, H 5.7, N 14.9.

4,4,5,5-Tetramethyl-2-(1-methyl-1*H*-pyrazole-5-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl (11i):[22] Compound **11i** was obtained as red-orange crystals (43 mg, 85%) from **1i** (55 mg, 0.23 mmol) by the general procedure; R_f = 0.77 (EtOAc). MS: *m*/*z* (%): 221 $[M]^+$ (2), 205 (8), 149 (14), 148 (10), 114 (21), 108 (18), 84 (100), 69 (22). HRMS calcd. for $C_{11}H_{17}N_4O$ $[M]^+$ 221.1397; found 221.1399.

4,4,5,5-Tetramethyl-2-{4-[(trimethylsilyl)ethynyl]phenyl}-4,5-dihydro-1*H*-imidazole-1-oxyl (11j): Compound **11j** was obtained as red-orange crystals (66 mg, 88%) from **1j** (80 mg, 0.24 mmol) by the general procedure; m.p. 170–171.5 °C (hexane); R_f = 0.91 (EtOAc). IR: $\tilde{\nu}$ = 2158 (w, C≡C), 2971 (m, CH_3) cm^{-1}. μ_{eff} = 1.73 B.M. (30–300 K). MS: *m*/*z* (%): 313 $[M]^+$ (0.6), 241 (11), 200 (8), 184 (17), 114 (14), 85 (5), 84 (100), 69 (22). HRMS calcd. for $C_{18}H_{25}N_2OSi$ $[M]^+$ 313.1731; found 313.1740. $C_{18}H_{25}N_2OSi$ (313.49): calcd. C 69.0, H 8.0, N 9.0; found C 69.2, H 8.1, N 9.0.

2,4,4,5,5-Pentamethyl-4,5-dihydro-1*H*-imidazole-1-oxyl (11k):[1c] Compound **11k** was obtained as a peach-colored oil (main component in LC-MSD, 180 mg, 40%) from **1k** (0.5 g, 2.9 mmol) by the general procedure; R_f = 0.49 (EtOAc). ESR: g_{iso} = 2.0059; A_{N1}(1N) = 0.917 mT, A_{N2}(1N) = 0.404 mT, A_{Me}(3H) = 0.182 mT, A_{Me}(12H) = 0.018 mT. HRMS calcd. for $C_8H_{15}N_2O$ $[M]^+$ 155.1179; found 155.1182.

4,4,5,5-Tetramethyl-2-[4-(6-methylpyridin-3-ylethynyl)phenyl]-4,5-dihydro-1*H*-imidazole-1-oxyl (11l):[23] Compound **11l** was obtained as red-orange crystals (210 mg, 93%) from **1l** (240 mg, 0.68 mmol) by the general procedure; R_f = 0.68 (EtOAc). MS: *m*/*z* (%): 332 $[M]^+$ (1.4), 316 (8), 260 (23), 248 (20), 219 (54), 218 (63), 191 (6), 190 (25), 151 (8), 114 (23), 85 (7), 84 (100), 69 (41). HRMS calcd. for $C_{21}H_{22}N_3O$ $[M]^+$ 332.1757; found 332.1755.

2-(3-Bromophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl (11m): Compound **11m** was obtained as red crystals (257 mg, 87%) from **1m** (315 mg, 1 mmol) by the general procedure; m.p. 58–59 °C (hexane); R_f = 0.88 (EtOAc). μ_{eff} = 1.73 B.M. (30–300 K). MS: *m*/*z* (%): 297 $[M + 2]^+$ (0.56), 295 $[M]^+$ (0.51), 225 (6), 223 (6), 184 (8), 183 (8), 114 (16), 85 (6), 84 (100), 69 (41). HRMS calcd. for $C_{13}H_{16}BrN_2O$ $[M]^+$ 295.0441; found 295.0445. $C_{13}H_{16}BrN_2O$ (296.18): calcd. C 52.7, H 5.4, Br 27.0, N 9.5; found C 52.4, H 5.3, Br 27.4, N 9.7.

2-Ethynyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl (12): Nitroxide **11a** (50 mg, 0.21 mmol) was dissolved in a solution of NH_3 in MeOH (14%, 3 mL), and the resulting solution was stirred at room temperature. A TLC analysis of the reaction mixture indicated that after 60 min the orange spot with R_f = 0.63 (CH_2Cl_2) had vanished completely, while an orange spot with R_f = 0.26 (CH_2Cl_2) had formed. The solution was diluted with benzene (3 mL) and concentrated to a volume of about 1 mL on a rotary evaporator at 30–35 °C (bath temperature). The solution was placed on a column (8 × 1.5 cm, wetted with CH_2Cl_2). The column was eluted with CH_2Cl_2, and an orange fraction was collected and concentrated. The residue was dissolved in CH_2Cl_2 (3 mL), *n*-heptane (3 mL) was added to the solution, and the solution was kept in an open flask at ca. 5 °C to give orange needle-shaped crystals suitable for X-ray analysis. Yield 30 mg (86%); m.p. 58–60 °C, R_f = 0.26 (CH_2Cl_2). IR: $\tilde{\nu}$ = 2120 (s, C≡C), 2869 (w), 2977 (m, CH_3), 3192 (s, ≡C–H) cm^{-1}. μ_{eff} = 1.73 B.M. (30–300 K). MS: *m*/*z* (%): 165 $[M]^+$ (5), 149 (7), 114 (11), 93 (22), 92 (14), 84 (100), 69 (83). HRMS calcd. for $C_9H_{13}N_2O$ $[M]^+$ 165.1022; found 165.1023. $C_9H_{13}N_2O$ (165.22): calcd. C 65.4, H 7.9, N 17.0; found C 65.4, H 8.0, N 17.0.

X-ray Structure Determinations: Crystal data for compounds were collected on a Smart APEX CCD diffractometer with use of graphite-monochromated Mo-K_α (λ = 0.71073 Å). In all cases, data were collected in a hemisphere of reciprocal space with use of a combination of five exposure sets. The cell parameters were determined and refined by the least-squares method for all reflections. The first 50 frames were collected again in order to monitor crystal decay at the end of data collection, and no appreciable decay was observed. The structures were solved by direct methods and refined by least-squares procedures on F^2. All non-hydrogen atoms were refined anisotropically. Some of the hydrogen atoms were localized in Δρ syntheses and refined isotropically; the others were calculated geometrically and refined as riding on the corresponding carbon-bonded atoms. All structure solution and refinement calculations were performed with Bruker Shelxtl Version 6.12.

Compound 4a·H_2O: The crystals were grown from hexane at ca. 5 °C. Crystal data and details of experiment are T = 240 K, a = 8.217(9), b = 7.205(8), c = 10.667(11) Å, β = 101.82(2)°, V = 618.1(11) Å^3, $P2_1$, Z = 2, D_C = 1.243 g cm^{-3}, μ = 0.096 mm^{-1}, 1.95 < θ < 26.50°, I_{hkl} (coll/uniq) 6050/2513, R_{int} = 0.0665, Goof = 1.091, $R1$ = 0.0778, $wR2$ = 0.1657 ($I > 2\sigma_I$), $R1$ = 0.1070, $wR2$ = 0.1781 (all data).

Compound $[Cu(Hfac)_2]_3(5a)_2$: The crystals were grown by slow evaporation of a solution of the complex in a mixture of CH_2Cl_2 with *n*-heptane. Crystal data and details of experiment are T = 240 K, a = 10.738(3), b = 12.005(3), c = 15.630(4) Å, α = 71.096(4)°, β = 82.012(4)°, γ = 69.588(4)°, V = 1785.7(8) Å^3, $P\bar{1}$, Z = 2, D_C = 1.729 g cm^{-3}, μ = 1.045 mm^{-1}, 1.90 < θ < 26.46°, I_{hkl} (coll/uniq) 18063/7285, R_{int} = 0.0761, Goof = 0.884, $R1$ = 0.0495, $wR2$ = 0.0961 ($I > 2\sigma_I$), $R1$ = 0.0787, $wR2$ = 0.1058 (all data).

Compound 5b: The crystals were grown from hexane at –15 °C. Crystal data and details of experiment are T = 150 K, a = 6.2041(12), b = 12.195(2), c = 16.467(3) Å, β = 97.65(1)°, V = 1234.7(4) Å^3, $P2_1/n$, Z = 4, D_C = 1.223 g cm^{-3}, μ = 0.089 mm^{-1}, 2.08 < θ < 29.65°, I_{hkl} (coll/uniq) 14153/3248, R_{int} = 0.1312, Goof = 0.816, $R1$ = 0.0539, $wR2$ = 0.1186 ($I > 2\sigma_I$), $R1$ = 0.1200, $wR2$ = 0.1342 (all data).

Compound 6a: The crystals were grown from hexane at –15 °C. Crystal data and details of experiment are T = 240 K, a = 7.7576(16), b = 9.975(2), c = 17.270(4) Å, V = 1336.4(5) Å^3, $P2_12_12_1$, Z = 4, D_C = 1.219 g cm^{-3}, μ = 0.092 mm^{-1}, 2.36 < θ < 29.47°, I_{hkl} (coll/uniq) 14411/3364, R_{int} = 0.0589, Goof = 1.044, $R1$ = 0.0517, $wR2$ = 0.1256 ($I > 2\sigma_I$), $R1$ = 0.596, $wR2$ = 0.1304 (all data).

Compound 12: The crystals were grown from hexane. Crystal data and details of experiment are T = 200 K, a = 10.478(2), b = 11.330(3), c = 15.764(4) Å, V = 1871.6(7) Å^3, $Pbca$, Z = 7, D_C = 1.173 g cm^{-3}, μ = 0.078 mm^{-1}, 2.95 < θ < 26.42°, I_{hkl} (coll/uniq) 17410/1920, R_{int} = 0.0671, Goof = 1.166, $R1$ = 0.0651, $wR2$ = 0.1583 ($I > 2\sigma_I$), $R1$ = 0.0735, $wR2$ = 0.1628 (all data).

Nitronyl Nitroxide 9a, Formamide 10, Imino Nitroxides 11b–11e, 11g, 11i, and 11j: ORTEP diagrams and X-ray crystallographic data are provided in the Supporting Information.

CCDC-668098 (for **4a**·H_2O), -710697 {for $[Cu(hfac)_2]_3$(**5a**)$_2$}, -710698 (for **5b**), -710699 (for **6a**), -710700 (for **9a**), -710701 (for **10**), -683982 (for **11b**), -710702 (for **11c**), -710703 (for **11d**), -683983 (for **11e**), -718643 (for **11g**), -683985 (for **11i**), -683986 (for **11j**), and -668099 (for **12**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Temperature dependencies of the effective magnetic moments, ESR spectra, IR absorption bands, Crystal data and details of X-ray experiments.

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