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Cascade Reactions of Me_3Si-Substituted Imidazolidine-1,3-Diols with PbO_2, Including Oxidation of the Corresponding Diol and Subsequent Elimination of the Trimethylsilyl Fragment

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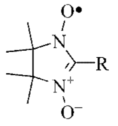
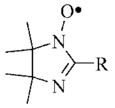
It was found that reactions of 2-Me_3Si-R-substituted (Si–C_{sp} or Si–C_{sp^2}) imidazolidine-1,3-diols with PbO_2 in MeOH are cascade reactions, which involve the oxidation of imidazolidine-1,3-diols into nitronyl nitroxide (NN–R–$SiMe_3$) and further elimination of the Me_3Si group to give NN–R–H. The efficiency of a one-pot approach in the synthesis of nitronyl nitroxides is demonstrated by reference to syntheses of 2-ethynyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (**2**), 2-(4-ethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (**8**), (*E*)-4,4,5,5-tetramethyl-2-[2-(pyrrolidin-1-yl)vinyl]-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (**3a**), (*E*)-2-[2-(diisopropylamino)vinyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (**3b**), and 4,4,5,5-tetramethyl-2-(1*H*-1,2,3-triazol-5-yl)-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (**H11**). Interaction of **2** with secondary amines formed only *trans* isomers **3a** and **3b**. X-ray investigation of **3a** and **3b** confirmed that the reaction is regiospecific. Static magnetochemical measurements detected weak exchange interactions between the odd electrons of the paramagnetic centers in the solid nitronyl nitroxide products, including **H11** whose crystals consist of helices formed by numerous intermolecular H bonds. The ESR spectra of **3a**, **3b**, and **H11** show substantial delocalization of spin density to the substituent. Modeling reproducibly gave equal hyperfine coupling constants (HFC) for the imidazoline nitrogen atoms of **3b** and different HFC for the nitrogen atoms of **3a** and **H11**, indicating that rotation of the two cyclic substituents is hindered.

Introduction

Nitronyl (NN–R) and imino nitroxides (IN–R) have attracted increased interest as paramagnetic organic components in the design of molecule-based magnets because of their potential for varying the spatial and electronic structure allows selective variation of the sign and magnitude of the exchange interaction energy inside heterospin exchange clusters.[1] This calls for the development of effective procedures for the synthesis of key nitroxides, leading to various polyfunctional spin-labeled derivatives.



NN–R



IN–R

An example of these nitroxides is NN–C≡C–H (**2**), which was recently synthesized by oxidation of 2-[2-(trimethylsilyl)ethynyl]-4,4,5,5-tetramethylimidazolidine-1,3-diol (**1**) with $NaIO_4$ in NN–C≡C–$SiMe_3$ with further removal of the Me_3Si group.[2]

Our efforts to improve the synthetic procedure of **2** revealed a nontrivial fact. If oxidation of **1** is carried out in a PbO_2/MeOH (or EtOH) system, it is accompanied by elimination of the Me_3Si group. In this process, which is actually a variation of the one-pot synthesis of **2**, this compound may be obtained in high yield (≈ 70%). The present investigation was stimulated by this result and showed that the suggested synthetic approach, namely, a cascade of two successive reactions is useful for syntheses of various NN–R, including unknown ones.

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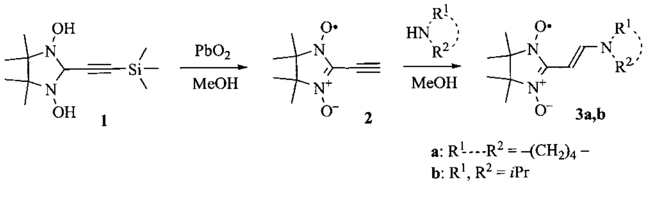
Results and Discussion

When PbO_2 was added to a MeOH or EtOH solution of **1**, the reaction mixture quickly became blue–violet, and compound **2** was the sole reaction product (Scheme 1). TLC monitoring of the oxidation of **1** in PbO_2/MeOH did not reveal the formation of nitroxide NN–C≡C–$SiMe_3$, which indicates that the C–Si bond is quickly split in intermediate NN–C≡C–$SiMe_3$. Elimination of the $SiMe_3$ group in the course of the oxidation of **1** in alcohols made it possible to avoid isolation of NN–C≡C–$SiMe_3$, which was previously mentioned[2] to be a rather labile compound, in pure form or in solution and significantly increased the yield of **2** (from 20 to 70%). The effective one-pot synthesis of polyfunctional nitronyl nitroxides naturally evolved as an elaboration of the given procedure for the transformation of **1** into **2**. Thus, the addition of pyrrolidine to the reaction mixture formed by the oxidation of **1** led to spin-labeled enamine **3a**, which formed within a few minutes as a sole product with ca. 90% yield based on **1** (Scheme 1). The reaction with $(i\text{Pr})_2NH$ proceeded in a similar way, but was a little more sluggish (≈3.5 h) and led to **3b** as a sole product with ≈75% yield based on **1**. The above examples demonstrate that the one-pot synthesis of **2** is possible and that this compound may be further subjected to one-pot functionalization by using reagents unreactive with PbO_2.



Scheme 1.

Nitronyl nitroxides were grown as X-ray quality single crystals by slowly evaporating the CH_2Cl_2/*n*-heptane solutions of **3a** and **3b**. Analysis of **3a** and **3b** indicated that the addition of secondary amines to the triple bond occurs regiospecifically and forms *trans* isomers. The structure of **3b** was described previously.[3] Crystals **3a** contain two crystallographically independent and structurally related nitronyl nitroxide molecules (Figure 1). In one of these molecules, the pyrrolidine cycle has a *gosh* conformation with C11A and C12A atoms deviating by –0.19 and 0.25 Å, respectively, from the plane; in the other molecule, the cycle has an envelope conformation, in which the C atom is similar to the one designated by C11A in Figure 1 departs from the plane by 0.24 Å. The angle between the planes through the CN_2 fragment of the imidazoline ring and the NC_2 fragment of the pyrrolidine ring is 12.8(3) and 16.6(3)°. In the imidazoline ring, the deviation of atoms from the plane is up to 0.02 Å. The N–O bond lengths are typical for nitroxides: 1.284(3)–1.295(3) Å. The intermolecular distances between the O atoms exceed 5.3 Å; that is, in the solid state, the paramagnetic centers are widely separated. For this reason, in the range 25–300 K the effective magnetic moment of **3a** and **3b** remains almost unchanged: 1.73 ± 0.01 B.M. (see Supporting Information). This indicates that in solids **3a** and **3b**, the intermolecular exchange interactions between the odd electrons of the paramagnetic centers are weak.

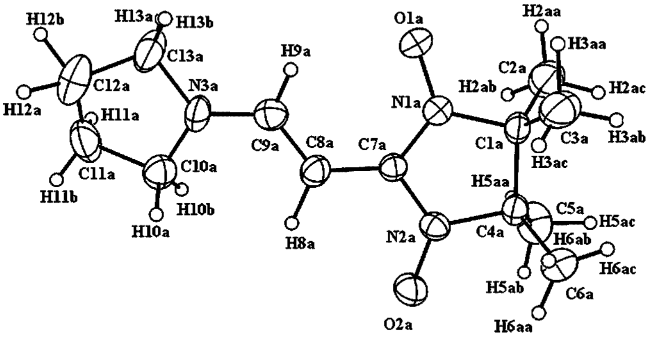
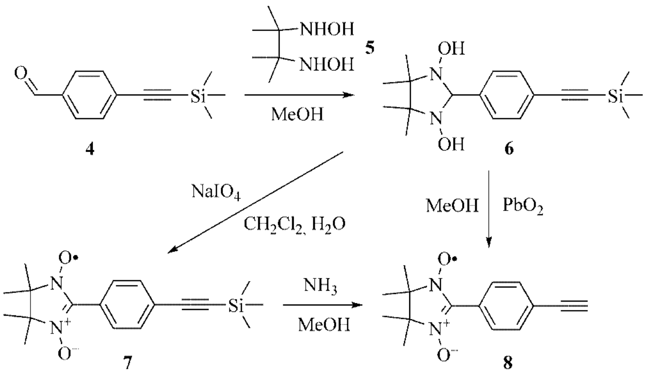


Figure 1. Molecular structure of **3a**.

Returning to the discussion of the transformation of **1** into **2** in PbO_2/MeOH, we note that Si–C_{sp} bond splitting requires the presence of a base in the reaction mixture.[4] Evidently, PbO_2 in itself cannot perform this function. Nevertheless, we carried out a special experiment to prove this. For this, authentic nitroxide, NN–C≡C–$SiMe_3$, was added to the PbO_2/MeOH system and remained unchanged in it. In contrast, the addition of $Pb(OH)_2$ suspended in tiny amount of water to a NN–C≡C–$SiMe_3$ solution in methanol followed with agitation for 5 h resulted in full transformation of NN–C≡C–$SiMe_3$ into **2**. This gave us grounds to assume that in the course of the transformation of **1** into **2**, Si–C_{sp} bond splitting had a provoking effect on $Pb(OH)_2$ that was formed in the reaction. Thus, in the PbO_2/MeOH system, compound **1** actually enters a cascade of transformations with NN–C≡C–$SiMe_3$ and $Pb(OH)_2$ formed at the first stage and with Me_3Si further removed from NN–C≡C–$SiMe_3$ under the action of $Pb(OH)_2$ that accumulates in the system.

To prove the efficiency of this approach we synthesized nitroxide NN–C_6H_4–C≡C–H (**8**). Previously, **8** was prepared by a reaction of OHC–C_6H_4–C≡C–H with bis(hydroxylamine) **5** with further oxidation of the imidazolidine-1,3-diol.[5] For the synthesis of OHC–C_6H_4–C≡C–H, the starting compound was OHC–C_6H_4–C≡C–$SiMe_3$ (**4**), and the sequence of stages was altered. At first, a reaction was performed between **4** and **5** to synthesize **6**, and then **6** was oxidized in the PbO_2/MeOH system. As a result, target compound **8** was isolated in 90–95% yield (Scheme 2). Note that specially synthesized nitroxide **7**, as well as NN–C≡C–$SiMe_3$, remained unchanged in the PbO_2/MeOH system, but transformed into **8** after the addition of a MeOH solution of NH_3. As in case of **1**, TLC monitoring of the oxidation of **6** in PbO_2/MeOH did not reveal the formation of nitroxide **7**, which indicates that the C–Si bond is quickly split in intermediate **7**. Thus **6**, as well as **1**, undergoes a cascade transformation (oxidation–desilylation) in the PbO_2/MeOH system, forming nitroxide **8**.



Scheme 2.

The oxidation–desilylation method proved to be highly effective for the synthesis of 1,2,3-triazolyl-substituted nitronyl nitroxide **H11**. To demonstrate the advantages of this method, let us first describe the products formed during classical synthesis of **H11**.

The reaction of aldehyde **9**[6] with bis(hydroxylamine) **5** in MeOH (Scheme 3) did not lead to the formation of expected imidazolidine-1,3-diol **10**. This was attributed to the fact that under these conditions, **10** is spontaneously dehydrated into 4,4,5,5-tetramethyl-2-(1*H*-1,2,3-triazol-5-yl)-4,5-dihydro-1*H*-imidazol-1-ol (**12**) (Scheme 3). Structural analysis of the methanol solvate of this compound, **12·MeOH**, indicated that in the solid state the compound exists as zwitterions (Figure 2a) linked via numerous H bonds into layers (Figure 2b).[7] The MeOH solvate molecules lie between layers.

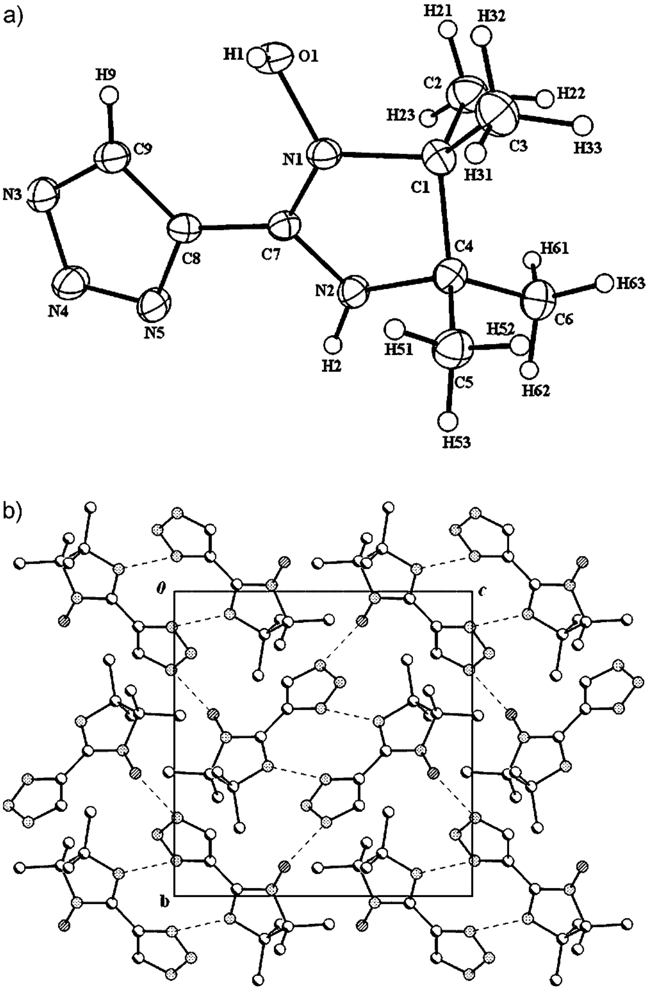
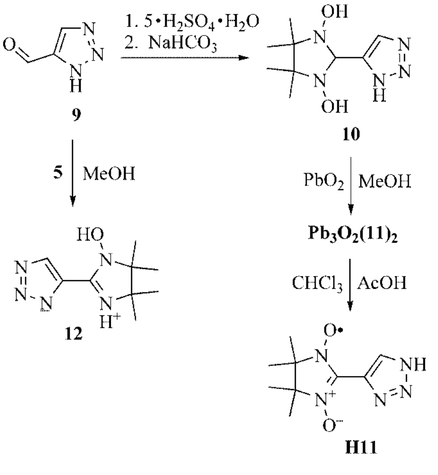


Figure 2. Structure of the zwitterion (a) and layer motif in the structure of **12·MeOH** (b).

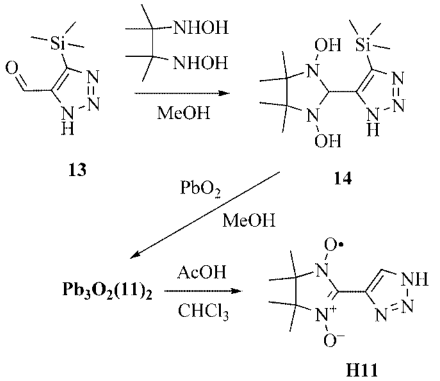


Scheme 3.

When condensation of **9** was carried out with sulfate **$5·H_2SO_4·H_2O$**, but not with compound **5** itself, and the reaction was conducted in water, but not in MeOH, a crude product was isolated, which contained imidazolidine-1,3-diol **10**. The product, however, could not be purified by recrystallization because the dehydrated derivative of **10** – compound **12** – was the only solid isolated from the mother solution. Oxidation of a suspension of the crude product with $NaIO_4$ in a mixture of $CHCl_3$ and H_2O did not form **H11** either. We could only observe red coloring of the reaction mixture; isolation of any individual compound from this mixture again led to crystallization of zwitterion **12**. However, oxidation of the crude product with PbO_2 in MeOH led to the isolation of a dark blue amorphous product, which corresponded to the molecular formula **$Pb_3O_2(11)_2$**, where **11** is deprotonated nitroxide **H11** (element analysis and LC–MSD data). Previously, we described the formation of lead complexes of this kind when we investigated the products of oxidation of pyrazolyl-substituted imidazolidine-1,3-diols with lead dioxide.[8] When a solution of **$Pb_3O_2(11)_2$** was kept for a few days in a MeOH/H_2O mixture in an open flask, we observed the formation of a gray finely divided precipitate and a solution of **H11**. To achieve faster decomposition of **$Pb_3O_2(11)_2$** to isolate **H11**, we added an excess amount of AcOH to its solution in $CHCl_3$.

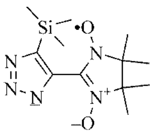
The above-described difficulties may be avoided if **H11** is synthesized from trimethylsilyl derivative **13**, but not from **9** itself, and if an oxidation–desilylation cascade process is employed (Scheme 4). Interaction of **13** and **5** in MeOH led to a voluminous precipitate of colorless thin needles of imidazolidine-1,3-diol **14** isolated from the solution. Unlike

10, compound **14** is not liable to dehydration on heating or prolonged storage in solution. Due to this property, it may be recrystallized and used in further transformations.



Scheme 4.

When **14** was oxidized in PbO_2/MeOH, we isolated a navy blue powder that contained $\mathbf{Pb_3O_2(11)_2}$ as the major product (LC–MSD data). The intense signal (m/z = 223.1) of ion **11** corresponded to the fundamental chromatographic peak in the LC–MSD. Signals with m/z = 295 and m/z = 207.1 from chromatographic peaks with small areas were also recorded and corresponded to insignificant amounts of ions **15** and **16** (see Supporting Information).



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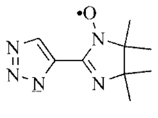

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Our numerous attempts to crystallize the dark blue finely disperse powder failed to give a crystal suitable for X-ray study. However, element analysis of the product of recrystallization indicated that the compound had a molecular formula $\mathbf{Pb_3O_2(11)_2}$. Dissolution of this complex in $CHCl_3$ containing AcOH led to gradual decomposition of the complex and to isolation of free nitroxide **H11** as a solution, which may be further isolated with ca. 45% yield.

Although **H11** crystallized as a conglomerate of crystals, single crystal fragments could be separated, which allowed us to determine the structure of nitronyl nitroxide. In molecule **H11**, (Figure 3a) the angle between the planes of the triazole ring and the CN_2 fragment of the imidazoline ring is 12.6(4)°. The N–O distances are 1.263(5) and 1.273(5) Å. In the solid state, the molecules that are arranged around the 4_1 axis are H-bonded into helices (Figure 3b).[9] However, although solid **H11** contains H-bonds that involve N–O groups, exchange interactions between the odd electrons of the paramagnetic centers of the individual molecules are weak. This is indicated by the effective magnetic moment of the compound (1.73 ± 0.01 B.M.), which remains almost invariable within a wide range of temperatures, 25–300 K (see Supporting Information).

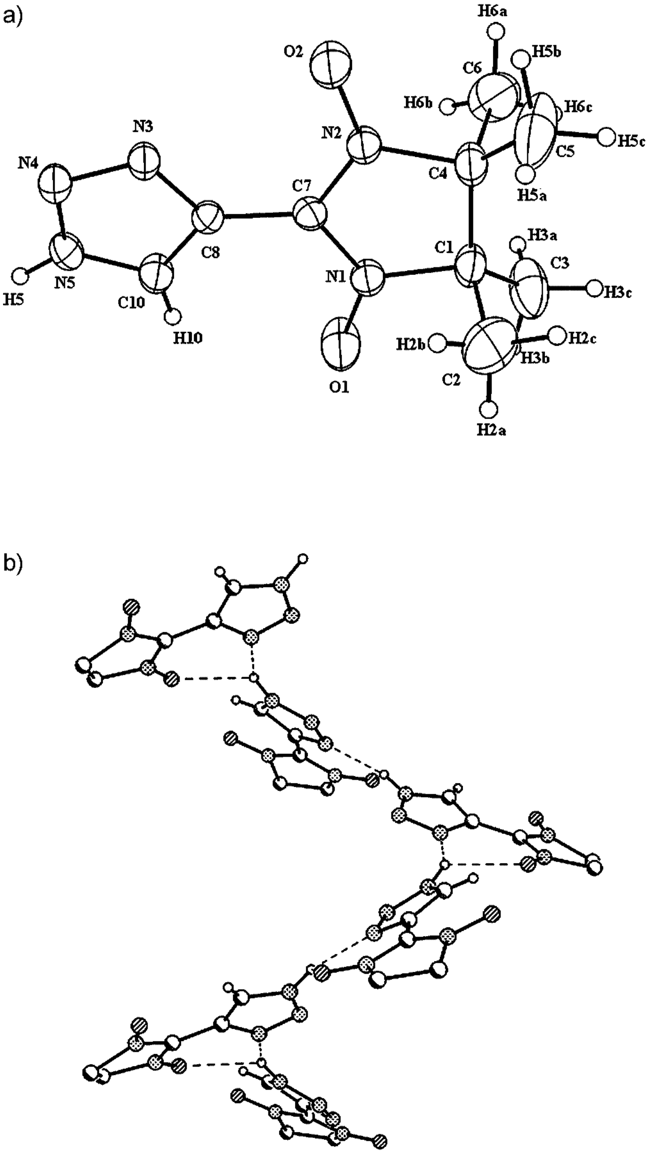

Figure 3. Molecular structure (a) and helix formation in **H11** (b).

Figure 4 shows the experimental and simulated ESR spectra of **3a**, **3b**, and **H11** in toluene. The overall spectra are very similar and rather typical for 2-imidazoline radicals, showing the dominant quintet from two nitrogen atoms of the imidazoline cycle.

All spectra show substantial delocalization of spin density into the substituent, as is evident from the better of less-resolved substructures of the lines. The latter conclusion is in good agreement with the spin density distribution from DFT calculations. The spin delocalization pattern could be clearly seen on the spin density plots from PBE0/EPR-II calculations shown in Figure 5.

The DFT estimations of hyperfine coupling constants were made to provide a clear correlation between the various structural elements and the electronic structure. In the present case, the DFT calculations are essential for the as-

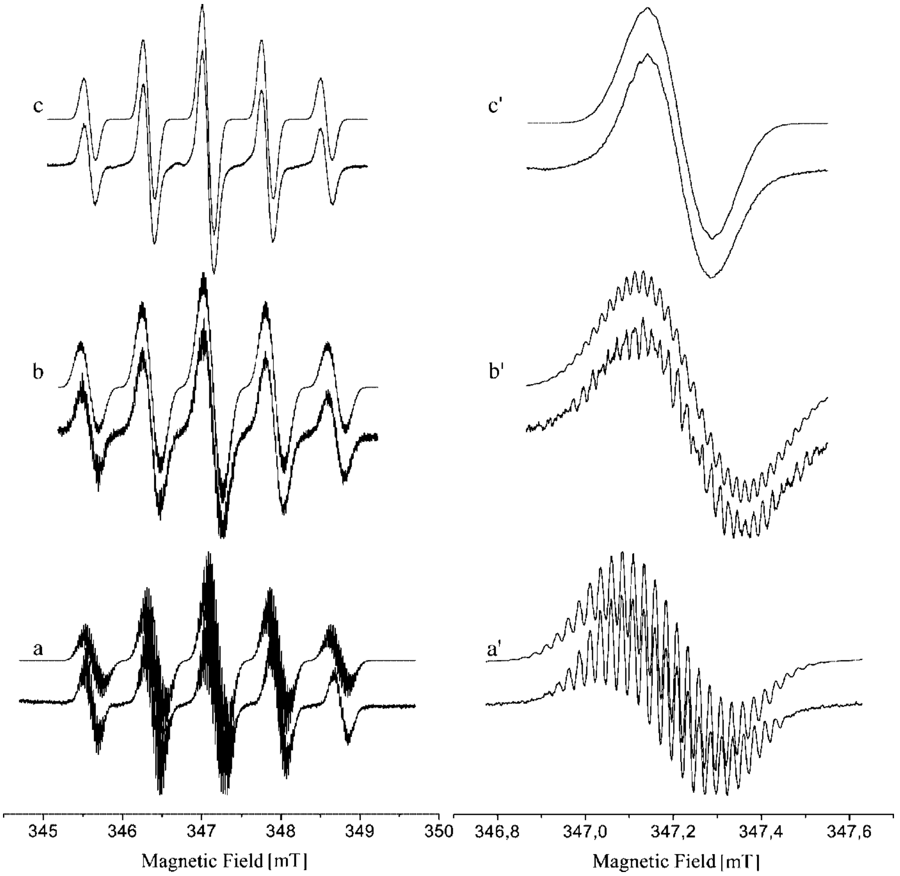

Figure 4. ESR spectra of **3b** (a, a′), **3a** (b, b′), and **H11** (c, c′) in toluene. Left column gives full spectra, and blowups of the corresponding central line are shown in the right column. The bottom trace of each pair gives the experimental spectrum, and the top trace shows the results of its simulation.

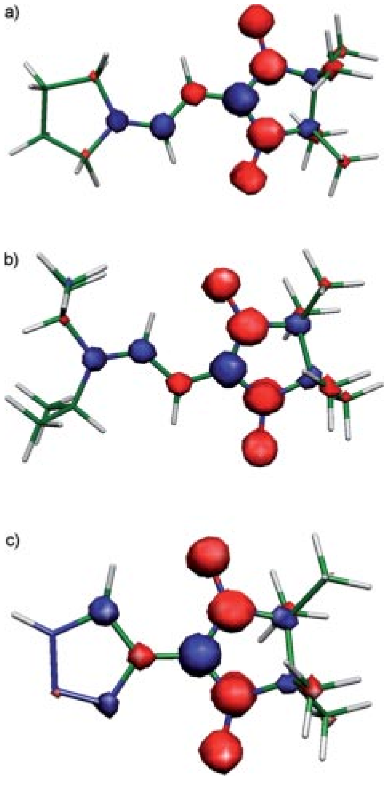

Figure 5. Spin density plots for **3a** (a), **3b** (b), and **H11** (c) from PBE0/EPR-II calculations.

signment of the signals providing important guidelines for spectral simulations of the EPR spectra. In general, a reasonably good agreement was obtained between the experimental and calculated ^{14}N hyperfine interactions of the imidazoline nitrogen atoms (Table 1). The slight underestimation of the N_{im} HFC by DFT calculations is in agreement with previous studies[10] and does not have any significant effect on the spin density distribution and other HFCs. For the nitrogen atoms in substituents and for the protons the DFT calculations give good predictions for the hyperfine couplings. These, in turn, were rather useful for EPR signal assignments and served as constraints on the simulation parameters.

Modeling of experimental spectra reproducibly gave equal hyperfine coupling constants (HFC) for the imidazoline nitrogen atoms of **3b** and different HFC for the nitrogen atoms of **3a** and **H11**, indicating that rotation of the two cyclic substituents is hindered (Table 1). This is also a possible reason for poorer resolution of the spectral substructure of these two radicals. Only N_{im} HFC could be determined for **H11** because of the unresolved structure. However, the lines of the nitrogen quintet are inhomogeneously broadened; to reproduce the broadening, according to the DFT calculations it is necessary to introduce not only HFC of 0.02 mT with 12 protons of the methyl groups typical for these radicals, but also additional couplings with the nuclei of the triazole substituent. The estimated accu-

Table 1. Experimental[a] and calculated[b] values of isotropic HFC (*a* in mT) of **3a**, **3b**, and **H11**.

	3a		**3b**		**H11**	
	PBE0	Exp	PBE0	Exp	PBE0	Exp
N_{1im}	0.677	0.801	0.686	0.775	0.677	0.751
N_{2im}	0.653	0.742	0.675	0.775	0.557	0.728
H_{im}	–0.026	0.02	–0.027	0.028	–0.023	
H_{8a}[c]	–0.156	0.056	–0.136	0.074		
H_{9a}	0.243	0.096	0.226	0.122		
N_{3a}	–0.076	0.067	–0.084	0.051		
H_{10a}, H_{10b}, H_{13a}, H_{13b}	–0.162	0.040				
N_3					–0.038	
N_4					0.007	
N_5					0.009	
H_{10}					0.180	
H_5					0.019	

[a] EPR experiment does not provide information on signs of HFCs and gives the absolute values only. Analysis of experimental spectra gave g_{iso} = 2.0067 for **3a**, g_{iso} = 2.0065 for **3b**, g_{iso} = 2.0065 for **H11**. [b] Average *a* values which are greater than 0.005 mT. [c] Numbering of atoms corresponds to the numbering scheme in Figures 1 and 3a.

racy in determining the HFC constants and the *g* values is 0.005 mT and 0.0001, respectively.

The final comment on modeling of the given spectra is that although reproduction of the finer substructure of well-resolved lines is consistent and reliable with the given sets of parameters, their uniqueness cannot be guaranteed because the spectra are overcrowded and the couplings are too small and close-lying. The dominant nitrogen HFC values, as well as the *g* values and the conclusion about spin density delocalization to the substituent, are quite reliable, but the actual values of HFC for the nuclei of substituents should probably be adopted with certain caution.

Conclusions

Thus, our study established that the interaction between $Me_3Si\text{-}C_{sp}$ and $Me_3Si\text{-}C_{sp^2}$ bearing imidazolidine-1,3-diols with PbO_2 in MeOH occurs as a cascade of reactions, involving oxidation of imidazolidine-1,3-diol into nitronyl nitroxide and further removal of the Me_3Si group under the action of $Pb(OH)_2$ formed in the course of the reaction. This approach permitted us to accomplish effective syntheses of NN–C≡C–H and $NN–C_6H_4–C≡C–H$, avoiding the stage of formation of the corresponding Me_3Si-substituted spin-labeled acetylenes. The resulting monosubstituted spin-labeled acetylene NN–C≡C–H may be introduced in further transformations without isolating it from the reaction mixture, which was demonstrated by the one-pot synthesis of enamine-substituted nitronyl nitroxides. We also succeeded in developing a synthetic procedure for 1,2,3-triazolyl-substituted nitronyl nitroxide; in the course of synthesis, a Me_3Si group was deliberately introduced at an early stage to ensure stability of the imidazolidine-1,3-diol intermediate against dehydration. The Me_3Si group was then eliminated in the course of the cascade reaction; this reaction involved the oxidation of imidazolidine-1,3-diol, C–Si bond cleavage, and the formation of a lead complex, from which the target nitroxide was isolated at the last stage. Thus, one can state that the suggested cascade reaction can serve as a convenient synthetic approach for the syntheses of other nitroxides.

Experimental Section

General Methods: 4,4,5,5-Tetramethyl-2-[2-(trimethylsilyl)ethynyl]-imidazolidine-1,3-diol[2] (**1**), 4-[(trimethylsilyl)ethynyl]benzaldehyde[4] (**4**), 1*H*-1,2,3-triazole-5-carbaldehyde[6] (**9**), *N*,*N*′-(2,3-dimethylbutane-2,3-diyl)bis(hydroxylamine)[11,12] (**7**), and 4-(trimethylsilyl)-1*H*-1,2,3-triazole-5-carbaldehyde[6] (**13**) were prepared according to the published procedures. All the solvents used were reagent quality. All of them were removed under reduced pressure, and all commercial reagents were used without additional purification. The reactions were monitored by TLC using silica gel 60 F_{254} aluminum sheets from Merck. The yields are given for pure substances obtained after recrystallization. IR spectra were obtained from KBr pellets with a Bruker VECTOR 22 infrared spectrometer. Melting points were obtained with a Boetius melting point apparatus. Microanalyses were performed with a Carlo Erba 1106 analyzer. Mass spectra were recorded with a Finnigan MAT-8200 instrument using the electron impact ionization technique (70 eV). X-band CW ESR spectra were recorded with a Bruker EMX spectrometer for dilute degassed toluene solutions at room temperature and modeled with the Winsim v.0.96 free package as described earlier.[13] LC–MSD analysis was performed with an Agilent 1100 Series LC–MSD instrument. The system included a binary pump, vacuum degasser, autosampler, thermostatted column compartment, diode array detector, and mass-selective detector in electrospray ionization (ESI) mode. Flow injection analysis was done for optimization of MS parameters. MS conditions: ionization mode – negative scan in the range *m*/*z* = 200–1300; Vcap 4000 V; nebulizer 50 psig; drying gas flow 10 L/min; drying gas temperature 340 °C; fragmentor 40 V. Chromatographic conditions: Zorbax Rx-C18 column (4.6 × 150 mm, 5 µm particles, 30 °C); water/MeOH mobile phase; gradient 50 to 90 % MeOH from 5th to 10th min; flow rate 0.5 mL/min; injection volume 5 µL; diode-array detector: signal 254/16 nm, 600/80 nm, reference 850/50 nm. The magnetochemical experiment was followed with an MPMS-5S ("Quantum Design") SQUID magnetometer at temperatures from 2 to 300 K in a homogeneous external magnetic field of up to 49.5 kOe. The molar magnetic susceptibility χ was calculated using Pascal's additive scheme including diamagnetic corrections.

2-Ethynyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (2): PbO_2 (500 mg, 2.1 mmol) was added at room temperature to a stirred solution of 4,4,5,5-tetramethyl-2-[2-(trimethylsilyl)ethynyl]imidazolidine-1,3-diol (**1**) (100 mg, 0.39 mmol) in MeOH (4 mL). The reaction mixture was stirred for 30 min and filtered. The solution was concentrated to a volume of ca. 2 mL. Then it was diluted with benzene (10 mL) and placed onto a column [silica gel Merck (0.063–0.100 mm for column chromatography), 15 × 1.5 cm, wetted with benzene]. The column was eluted with ethyl acetate, and a bluish violet fraction was collected; the fraction was evaporated. The solvent was distilled off, the residue ground with hexane, and the solvent decanted. Yield 50 mg (70 %). Spectral data for nitroxide **2** are identical to those obtained earlier.[2]

(*E*)-4,4,5,5-Tetramethyl-2-[2-(pyrrolidin-1-yl)vinyl]-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (3a): PbO_2 (500 mg, 2.1 mmol) was added at room temperature to a stirred solution of **1** (100 mg, 0.39 mmol) in MeOH (5 mL). After 30 min, pyrrolidine (50 µL) was added. The reaction mixture was stirred for 30 min and filtered. The mother solution was concentrated to a volume of ca. 2 mL. Then it was diluted with benzene (10 mL) and placed onto a column [silica gel Merck (0.063–0.100 mm for column chromatography), 5 × 1.5 cm, wetted with benzene]. The column was eluted with ethyl acetate, and a bluish violet fraction was collected; the fraction was evaporated. The solvent was distilled off, the residue ground with hexane, and the solvent decanted. Yield 90 mg (90%). M.p. 149–151 °C. IR: $\tilde{\nu}$ = 542, 617, 642, 772, 867, 881, 947, 966, 1131, 1192, 1206, 1266, 1298, 1323, 1357, 1428, 1453, 1484, 1615, 2853, 2964, 3044, 3076 cm^{-1}. $C_{13}H_{22}N_3O_2$ (252.33): calcd. C 61.9, H 8.8, N 16.7; found C 62.4, H 8.8, N 16.7. Perfect crystals were grown by slowly evaporating a CH_2Cl_2/*n*-heptane solution of nitroxide **3a** at ca. 5 °C.

(*E*)-2-[2-(Diisopropylamino)vinyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (3b): The compound was synthesized from **1** similarly to **3a** with 75% yield. Spectral data of nitroxide **3b** are identical to the data obtained earlier.[3]

4,4,5,5-Tetramethyl-2-{4-[(trimethylsilyl)ethynyl]phenyl}imidazolidine-1,3-diol (6): 4-[(Trimethylsilyl)ethynyl]benzaldehyde (**4**) (200 mg, 1 mmol) and *N*,*N′*-(2,3-dimethylbutane-2,3-diyl)bis(hydroxylamine) **5** (150 mg, 1 mmol) were dissolved in MeOH (10 mL). The solution was maintained at room temperature for 2 h, and then at ca. 5 °C for 48 h. Yield 80 mg (60%). M.p. 186–195 °C (dec.). IR: $\tilde{\nu}$ = 547, 650, 702, 760, 803, 825, 841, 873, 914, 994, 1018, 1086, 1144, 1218, 1250, 1301, 1379, 1464, 1508, 2161, 2921, 2958, 2993, 3283 (very broad band) cm^{-1}. $C_{18}H_{28}N_2O_2Si$ (332.51): calcd. C 65.0, H 8.5, N 8.4; found C 64.8, H 8.4, N 8.1.

2-{4-[(Trimethylsilyl)ethynyl]phenyl}-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (7): $NaIO_4$ (250 mg, 1.17 mmol) was added for 30 min in portions to a mixture of imidazolidine-1,3-diol **6** (260 mg, 0.78 mmol), CH_2Cl_2 (12 mL), and H_2O (6 mL), which was stirred at 10 °C. Then the reaction mixture was stirred for 3 h and filtered. The organic layer was separated, and the aqueous layer extracted with CH_2Cl_2 (2 × 10 mL). The consolidated organic extracts were dried with Na_2SO_4, and then filtered and the solvents evaporated. The residue was dissolved in a minimal amount of ethyl acetate, and the resulting solution was placed into a SiO_2 (2 × 5 cm) column. Ethyl acetate was used as an eluent. The dark blue fraction was diluted with heptane (30 mL) and concentrated at a pressure of 100 Torr until the volume reached ca. 10 mL. Nitroxide **7**, which precipitated as thin needles, was filtered off. Yield: 183 mg (70%). M.p. 174–175 °C. IR: $\tilde{\nu}$ = 547, 616, 653, 757, 836, 867, 1018, 1102, 1132, 1166, 1220, 1251, 1300, 1363, 1388, 1423, 1452, 2159, 2954 cm^{-1}. $C_{18}H_{25}N_2O_2Si$ (329.49): calcd. C 65.6, H 7.7, N 8.5; found C 65.9, H 7.7, N 8.7.

2-(4-Ethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (8): The compound was synthesized from 4,4,5,5-tetramethyl-2-{4-[(trimethylsilyl)ethynyl]phenyl}imidazolidine-1,3-diol (**6**) similarly to **2** with 94% yield. Spectral data and the m.p. of nitroxide **8** are identical to those obtained earlier.[5]

4,4,5,5-Tetramethyl-2-(1*H*-1,2,3-triazol-5-yl)imidazolidine-1,3-diol (10): Sulfate hydrate *N*,*N′*-(2,3-dimethylbutane-2,3-diyl)bis(hydroxylamine) (**7·H_2SO_4·H_2O**) (350 mg, 1.33 mmol) was added at room temperature to a stirred solution of 1*H*-1,2,3-triazole-5-carbaldehyde (**9**) (130 mg, 1.34 mmol) in H_2O (5 mL). The reaction mixture was stirred for 24 h at room temperature until yellow suspension formed. The mixture was neutralized with $NaHCO_3$ (300 mg); the organic layer was filtered off, washed with cold H_2O (5 mL), and dried in air. The resulting product was suspended in MeOH (15 mL); the mixture was kept in an ultrasound bath for a few minutes and then filtered. The filtrate was evaporated, and the yellowish brown crystalline residue was ground with ethyl acetate and filtered off. The yield of crude product **10** was from 25 to 50%. The product was used without additional purification. Storage of a solution of imidazolidine-1,3-diol **10** in MeOH for a few days led to the formation of 4,5-dihydro-1*H*-imidazol-1-ol **12**.

4,4,5,5-Tetramethyl-2-(1*H*-1,2,3-triazol-5-yl)-4,5-dihydro-1*H*-imidazol-1-ol (12): *N*,*N′*-(2,3-dimethylbutane-2,3-diyl)bis(hydroxylamine) **5** (270 mg, 1.82 mmol) was added at room temperature to a stirred solution of 1*H*-1,2,3-triazole-5-carbaldehyde (**9**) (175 mg, 1.80 mmol) in MeOH (5 mL). The reaction mixture was stirred for 2 h at room temperature until a yellow solution formed. Then the solution was kept at ca. 5 °C for 100 h. The solvent was evaporated. The viscous yellowish brown residue was ground with ethyl acetate, which caused fast crystallization of the residue. The resulting pale yellow powder was filtered off, washed with cool ethyl acetate on the filter, and dried in vacuo. Yield: 300 mg (80%). M.p. >300 °C. Compound **12·MeOH** solvate crystals suitable for an X-ray analysis were grown by slowly evaporating the solution of the product in MeOH/ethyl acetate (1:1) at room temperature. IR: $\tilde{\nu}$ = 444, 462, 522, 592, 641, 705, 729, 772, 855, 885, 962, 1062, 1125, 1148, 1184, 1210, 1247, 1326, 1377, 1450, 1617, 2399 (very broad band), 2937, 2982, 3123 cm^{-1}. $C_9H_{15}N_5O$·MeOH (241.29): calcd. C 49.8, H 7.9, N 29.0; found C 50.0, H 7.6, N 29.3.

4,4,5,5-Tetramethyl-2-[4-(trimethylsilyl)-1*H*-1,2,3-triazol-5-yl]imidazolidine-1,3-diol (14): *N*,*N′*-(2,3-dimethylbutane-2,3-diyl)bis(hydroxylamine) **5** (236 mg, 1.59 mmol) was added at room temperature to a stirred solution of 4-(trimethylsilyl)-1*H*-1,2,3-triazole-5-carbaldehyde (**13**) (270 mg, 1.60 mmol) in MeOH (10 mL). The reaction mixture was stirred for 10 h, within which bulk precipitate of colorless thin needles gradually formed. The precipitate was filtered off and washed with ethyl acetate on a filter. Yield: 340 mg (70%). For element analysis, a small amount of **14** was recrystallized from MeOH. M.p. 233–235 °C. IR: $\tilde{\nu}$ = 700, 765, 845, 870, 916, 996, 1019, 1159, 1189, 1256, 1321, 1377, 1456, 2954, 3239 cm^{-1}. $C_{12}H_{25}N_5O_2Si$ (299.45): calcd. C 48.1, H 8.4, N 23.4; found C 47.6, H 8.4, N 23.3.

4,4,5,5-Tetramethyl-2-(1*H*-1,2,3-triazol-5-yl)-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (H11): Procedure A: PbO_2 (500 mg, 2.1 mmol) was added at room temperature to a stirred solution of imidazolidine-1,3-diol **14** (150 mg, 0.50 mmol) in MeOH (5 mL). The reaction mixture was stirred for 24 h and filtered. The filtrate was evaporated; the navy blue residue was ground with a mixture of hexane with ethyl acetate, which led to crystallization of the residue. The precipitate was filtered off, washed with hexane, dried in air, and analyzed by HPLC–MSD (see Supporting Information). After recrystallization of the reaction product from DMF/Et_2O or $CHCl_3$/toluene, **$Pb_3O_2(11)_2$** (**11** is deprotonated **H11**) precipitated as amorphous dark blue powder. Yield: 290 mg (55%). The product is slowly hydrolyzed by water; it is sparingly soluble in toluene and Et_2O, but well-soluble in DMF, CH_2Cl_2, acetone, MeOH, and EtOH. IR: $\tilde{\nu}$ = 470, 542, 635, 691, 755, 845, 868, 975, 1043, 1088, 1137, 1169, 1215, 1244, 1334, 1372, 1412, 1453, 1577, 2984, 3418 (very broad band) cm^{-1}. LC–MS: *m*/*z* (%) = 223 [**11**]$^-$. $C_{18}H_{26}N_{10}O_6Pb_3$ (1100.06): calcd. C 19.7, H 2.4, N 12.7; found C 18.2, H 2.4, N 10.2.

$Pb_3O_2(11)_2$ (190 mg) was dissolved in $CHCl_3$ (15 mL), which contained AcOH (0.5 mL). The resulting solution was stirred for 24 h at room temperature, and then filtered. The filtrate was evaporated, and the viscous navy blue residue was dissolved in $CHCl_3$. The resulting solution was placed onto a column [silica gel Merck (0.063–0.100 mm for column chromatography), 10 × 1.5 cm, wetted with ethyl acetate]. The column was eluted with ethyl acetate/MeOH (5:1), which allowed the separation of the byproducts. After the eluate became colorless, MeOH/AcOH (10:1) was passed through the column. The blue fraction was collected and the solvents evaporated. The resulting navy blue oily residue was ground with ethyl acetate, which caused crystallization of the residue. The precipitate was filtered off and recrystallized from a mixture of MeOH with toluene using hot filtration. The filtrate was concentrated until a precipitate started to form, whereupon it was stored at ca. 5 °C for 10 h. The single crystal residue was filtered off, washed with hexane, and dried in vacuo. Yields were about 30 mg (80%). **H11** is well-soluble in MeOH and EtOH, not readily soluble in CH_2Cl_2, and insoluble in ethyl acetate and benzene. Heating of crystals **H11** to 180–190 °C formed a green liquid, which became orange after heating to 200 °C. IR: $\tilde{\nu}$ = 541, 602, 665, 822, 867, 965, 1057, 1136, 1171, 1214, 1234, 1315, 1374, 1410, 1451, 1508, 2868, 2982, 3052, 3177 cm^{-1}. $C_9H_{14}N_5O_2$ (224.24): calcd. C 48.2, H 6.3, N 31.2; found C 48.7, H 6.3, N 31.5. Crystals **H11** were grown by slowly evaporating a MeOH/toluene (3:1) solution of this compound at ca. 5 °C. Single crystal fragments suitable for an X-ray analysis were separated from the resulting navy blue crystals.

Procedure B: PbO_2 (350 mg, 1.46 mmol) was added at room temperature to a stirred solution of crude imidazolidine-1,3-diol **10** (70 mg, 0.31 mmol) in MeOH (5 mL). The reaction mixture was stirred for 14 h and filtered. The product (290 mg, dark blue amorphous powder) was separated from the filtrate as per Procedure A. IR: $\tilde{\nu}$ = 468, 542, 611, 691, 753, 818, 868, 976, 1038, 1083, 1137, 1171, 1216, 1334, 1372, 1414, 1453, 1580, 2987, 3441 (very broad band) cm^{-1} [the IR spectrum of the product is identical to the spectrum of **$Pb_3O_2(11)_2$**]. $C_9H_{14}N_5O_2$ (224.24): calcd. C 48.2, H 6.3, N 31.2; found C 18.0, H 2.0, N 8.7. **$Pb_3O_2(11)_2$** was transformed into **H11** by Procedure A with 45 mg (65%) yield.

X-ray Crystal Structure Determination of 3a, 12, and H11: Data for crystals of compounds were collected at room temperature with a Smart APEX CCD diffractometer using graphite-monochromated Mo-K_α (λ = 0.71073 Å), operating at 50 kV and 40 mA. In all cases, data were collected in a hemisphere of reciprocal space using a combination of five exposure sets. The cell parameters were determined and refined by least-squares fits of all reflections. The first 50 frames were recollected 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. All hydrogen atoms were included in their calculated positions and refined as riding on the respective carbon-bonded atoms. All structure solution and refinement calculations were performed with Bruker SHELXTL version 6.12.

Compound 3a: $C_{13}H_{22}N_3O_2$; *FW* = 252.34; orthorhombic, $P2_12_12_1$; a = 10.903(2), b = 14.211(3), c = 17.769(3) Å, V = 2753.3(8) Å^3; Z = 8, $D_{\text{calcd.}}$ = 1.217 g/cm^3; μ = 0.083 mm^{-1}; $2.19<\theta<23.31°$; 19145 collected, 3958 unique, R_{int} = 0.0901; 502 parameters; *Goof* = 0.927; R indices for $I>2\sigma$ R_1 = 0.0504, wR_2 = 0.1068; R indices (all data) R_1 = 0.0676, wR_2 = 0.1148.

Compound 12: $C_{10}H_{19}N_5O_2$; *FW* = 241.30; monoclinic, $P2_1/c$; a = 10.460(4), b = 10.994(4), c = 11.056(4) Å; β = 102.988(8)°; V = 1238.9(9) Å^3; Z = 4; $D_{\text{calcd.}}$ = 1.294 g/cm^3; μ = 0.094 mm^{-1}; $2.65<\theta<23.22°$; 6634 collected, 1773 unique, R_{int} = 0.0598; 231 parameters; *Goof* = 1.106; R indices for $I>2\sigma$ R_1 = 0.0683, wR_2 = 0.1799; R indices (all data) R_1 = 0.0910, wR_2 = 0.1929.

Compound H11: $C_9H_{14}N_5O_2$; *FW* = 224.25; tetragonal, $I4_1/a$; a = 20.743(3), c = 10.880(2) Å; V = 4681.3(12) Å^3; Z = 16; D_C = 1.273 g/cm^3; μ = 0.094 mm^{-1}; $1.96<\theta<23.29°$; 17693 collected, 1688 unique, R_{int} = 0.1248; 166 parameters; *Goof* = 1.047; R indices for $I>2\sigma$ R_1 = 0.0894, wR_2 = 0.2389; R indices (all data) R_1 = 0.1137, wR_2 = 0.2571.

CCDC-627770 (for **H11**), -627771 (for **3a**), and -628480 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: All calculations were done with the ORCA electronic structure package version 2.5.20.[14] Geometry optimizations were performed at the UPBE/6-31G(d) level, and the isotropic hyperfine coupling constants were obtained for the optimized structures at UPBE0/EPR-II level.[15] The calculated HFC values were then averaged over the fast internal molecular motions. The spin density plots were made by the Molekel program.[16]

Supporting Information (see footnote on the first page of this article): Temperature dependencies of the effective magnetic moments for nitroxides, LC–MSD analysis of the reaction product prepared by the oxidation of 4,4,5,5-tetramethyl-2-[4-(trimethylsilyl)-1*H*-1,2,3-triazol-5-yl]imidazolidine-1,3-diol (**14**) with PbO_2 in MeOH, and cartesian coordinates of optimized structures **3a**, **3b** and **H11**.

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