A guanine-substituted nitronyl nitroxide radical forming a one-dimensional ferromagnetic chain

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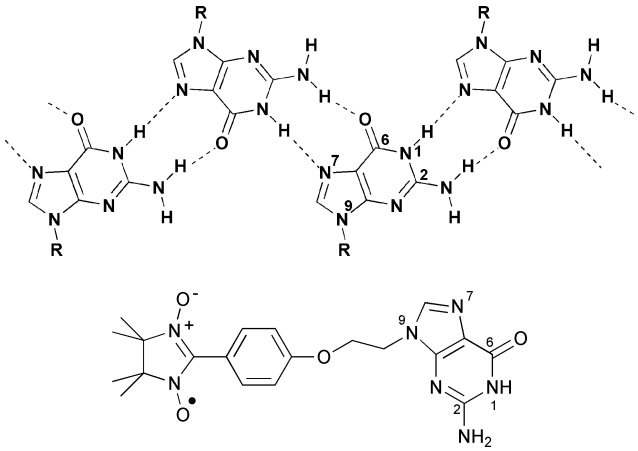
A stable guanine-substituted nitronyl nitroxide radical **1** has been synthesized and characterized. The single-crystal structure analyses and magnetic susceptibility measurements exhibit a one-dimensional architecture of guanine base resulting from carbonyl-amino hydrogen bonds in the solid state, giving a 1D ferromagnetic chain of the radical moieties.

Introduction

In molecule-based magnetism as an interdisciplinary field, molecular packing or arrangement of open-shell molecules in a crystalline solid state crucially links the magnetic properties of molecular assemblages such as ferromagnetism.[1] Hydrogen bonding is a promising noncovalent bonding for controlling molecular packing. Hydrogen-donating and accepting molecules such as phenol, carboxylic acid, and pyridine have been introduced to stable radical families of nitroxides and imino- or nitronyl nitroxides.[2] Biomolecule-based architecture such as a DNA duplex with nucleobase pairing is fascinating as well in controlling molecular packing. Whereas biologically important molecules with unpaired electrons have been exploited mainly in spin labeling chemistry and biochemistry,[3,4] solid-state chemistry has been reported for some nucleobases and nucleosides substituted with nitroxide or nitronyl nitroxide radicals.[5,6] There have been several examples of stable organic radicals with well-characterized crystal structures, to which naturally-found nucleobases such as cytosine and uracil have been introduced.[5] The magnetic properties of these compounds have been examined in view of the hydrogen-bonded assemblage of the open-shell building blocks. As for guanine-substituted radicals, however, little has been known about the X-ray crystal structures and magnetic properties, while the solution chemistry of spin-labeled guanines and guanosines has been explored.[3] Non-oligomeric N9-substituted guanines[7] and guanosine[8] have a marked tendency to form infinitely extended molecular assemblies in crystalline solid states, which results from intermolecular two-fold hydrogen bonding at N1H–N7 and N2H–O6. Such iteratively propagating hydrogen bonds[9] are attractive from the viewpoint of hydrogen bonding-based crystal engineering for open-shell molecular crystalline materials. In this paper, we report, for the first time, the synthesis, the crystal structure and the magnetic properties of a nitronyl nitroxide radical (**1**) substituted with a guanine base. The magneto-structural relationship of **1** is discussed.



Results and discussion

Synthesis of radical 1

The synthetic route is shown in Scheme 1. After the TBDMS-protected hydroxylamine **4** was introduced to the N9 position of 2-amino-6-chloropurine, the chloro group of **5** was replaced by the methoxy group using NaOMe, and subsequent treatment of **6** with TMSI afforded the guanine form **7**. Deprotection of **7** gave the nitronyl nitroxide radical **1**. Single crystals of **1** suitable for X-ray crystallography experiments were obtained by recrystallization from a mixed solution of chloroform and methanol.† The crystalline solid of **1** is stable under aerated conditions at ambient temperature.

Crystal structure of radical 1

An ORTEP drawing of the asymmetric unit of **1** is shown in Fig. 1. The asymmetric unit contains 1 mol of $CHCl_3$ as a crystal solvent. In Fig. 2 is depicted the molecular packing of **1**. The carbonyl-amino hydrogen bonds, N(7)H–O(4*) and N(5)H–N(4*), between

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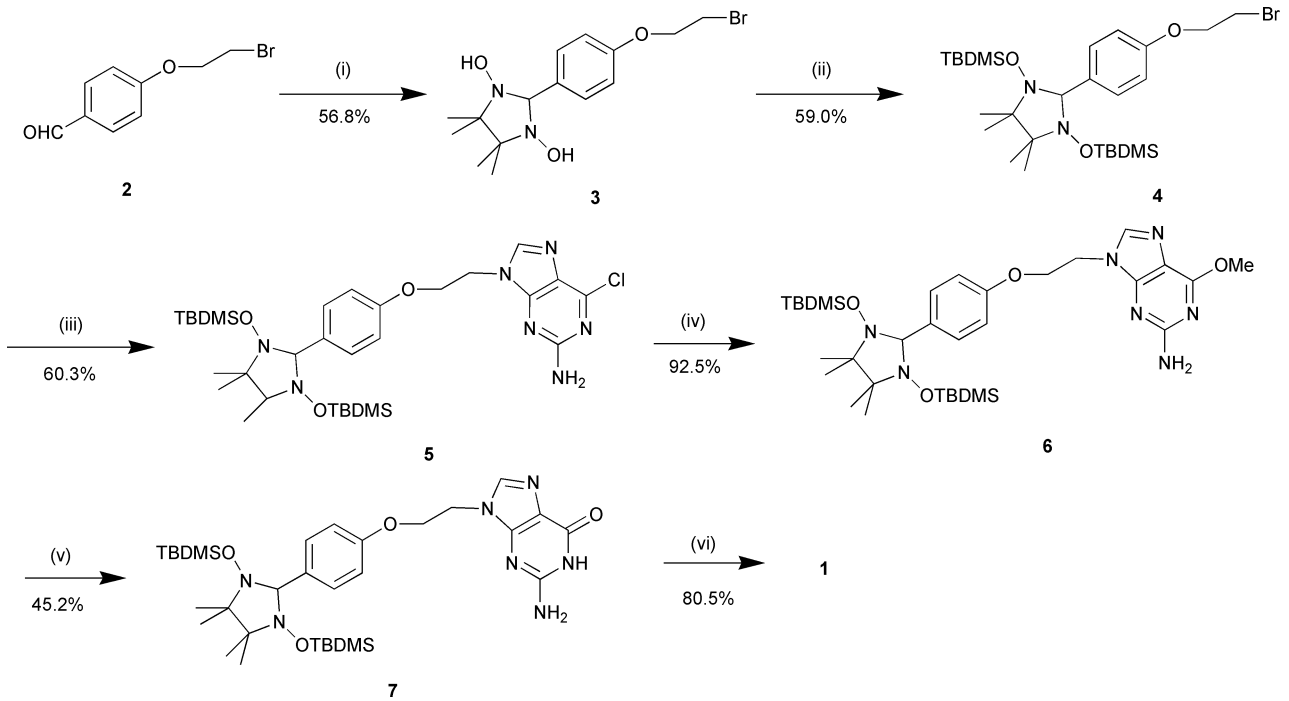
† Crystallographic data for $C_{21}H_{25}N_7O_4Cl_3$: $M = 545.83$, $0.20 \times 0.30 \times 0.50$ mm^3, Mo Kα, 183 K, monoclinic, $P2_1/n$, $a = 8.380(7)$ Å, $b = 10.583(8)$ Å, $c = 29.23(3)$ Å, $\beta = 99.424(10)°$, $V = 2558(4)$ Å^3, $Z = 4$, $D_{calc} = 1.417$, $R1 = 0.0819$, $R_w = 0.1968$ optimized on F^2 (GOF = 1.002) for 5494 reflections (all reflections) and 341 parameters. CCDC reference number 617741. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702606d



Scheme 1 The synthesis of the guanine-substituted radical. Conditions: (i) 2,3-dimethyl-2,3-dihydroxylaminobutane, benzene, 23 h; (ii) *tert*-butyldimethylchlorosilane, imidazole, DMF, 50 °C, 29 h; (iii) 2-amino-6-chloropurine, K_2CO_3, KI, DMF, 60 °C, 25 h; (iv) 28% NaOMe in methanol solution, CH_2Cl_2, MeOH, rt, 35 min; (v) TMSI, DMF, MeCN, rt, 23 h; (vi) 1.0 M TBAF in THF solution, THF, DMF, rt, 14 h.

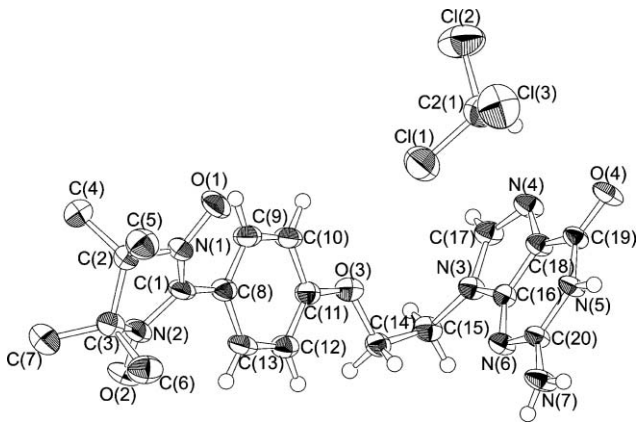


Fig. 1 An ORTEP drawing of **1** with the thermal ellipsoids of 50% probability. The hydrogen atoms of the methyl groups are omitted for clarity.

the guanine moieties lead to one-dimensional chains along the *b*-axis, as depicted in Fig. 2(a). The hydrogen bonding motif and its bond lengths (N(7)H–O(4*) = 2.781(3) Å and N(5)H–N(4*) = 2.825(3) Å) are close to those of non-oligomeric guanine and guanosine derivatives[7,8] as previously studied by X-ray single-crystal structure analyses. Little magnetic interactions are expected to propagate *via* the hydrogen bonds, since the hydrogen bonding sites of guanine have little spin density, as anticipated. The guanine moiety plays a primary role in governing the molecular packing, instead of propagating intermolecular exchange interactions.

Primitive *a*-axis translation of the two nearest-neighboring molecules connected by the carbonyl-amino hydrogen bonds gives a double chain of the radical moieties, as shown in Fig. 2(b). An intermolecular short contact close to the van der Waals contact[10] is found at O(1)–C(12#) = 3.439(3) Å between the phenyl nitronyl nitroxide radical moieties. A short contact between a nitroxide oxygen atom and a carbon atom of the *meta*-position such as O(1)–C(12#) of **1** is expected to give rise to an intermolecular ferromagnetic exchange interaction, as observed in many nitronyl nitroxide derivatives.[11] No short contacts around the nitroxide groups leading to exchange interactions were found between the chains.

Magnetic properties of radical 1

The temperature dependence of paramagnetic susceptibility χ_p for a randomly-oriented polycrystalline sample of **1** is shown in Fig. 3 in the χ_pT *vs.* T plots. The χ_pT value at room temperature is 0.37 emu K mol^{-1}, as expected for 1 mol of $S = 1/2$ spins. An upturn of χ_pT was found below 30 K, indicating the occurrence of intermolecular ferromagnetic exchange interactions. The temperature dependence of χ_p was analyzed using the Curie–Weiss law

$$\chi_p = \frac{C}{T - \theta} \quad (1)$$

where the fitting provides the Curie constant of $C = 0.37$ emu K mol^{-1} and the Weiss constant of $\theta = 0.16$ K.

As suggested from the crystal structure analyses, an $S = 1/2$ Heisenberg ferromagnetic chain model[12]

$$H = -2J \sum_i S_i \cdot S_{i+1} \quad (2)$$

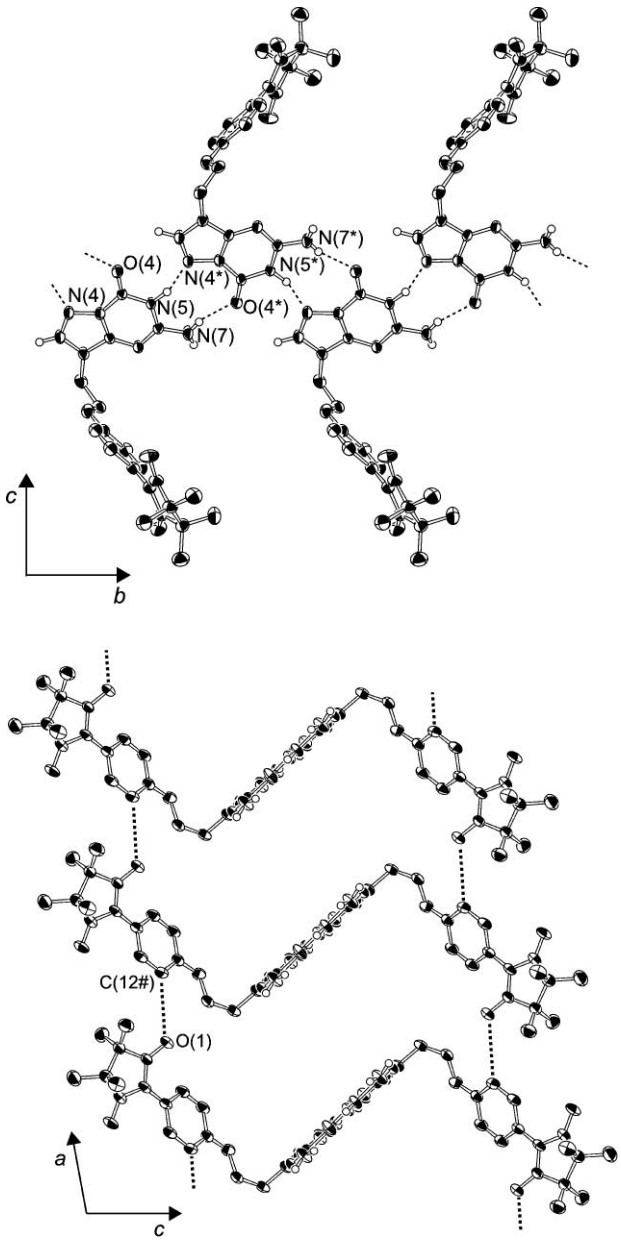


Fig. 2 (a) The chain of the guanine moieties running along the *b*-axis. The neighboring molecules related by the two-fold screw axis along the *b*-axis are connected by carbonyl-amino hydrogen bonds, as depicted by the dotted lines. (b) The double chain of the nitronyl nitroxide moieties along the *a*-axis. Intermolecular short contacts are depicted by the dotted lines. Symmetry transformations used to generate equivalent atoms: * $\{-x + 1/2, y + 1/2, -z + 1/2\}$; # $\{x - 1, y, z\}$.

should be more appropriate for describing the magnetic behavior of the molecular assemblage of **1**. The parameter J in eqn (2) denotes the intermolecular exchange coupling, which is primarily attributed to the O(1)–C(12#) contact. The calculation with the parameter of $2J/k_B = 0.09 \pm 0.01$ K is consistent with the observed temperature dependence of susceptibility.[13] The calculated curve of the Heisenberg chain model is identical to that of the Curie–Weiss law, as depicted in Fig. 3. When the magnitude of the exchange interaction is very small as compared with the thermal energy of the susceptibility measurement ($J \ll k_B T$ or $\theta \ll T$), we are not

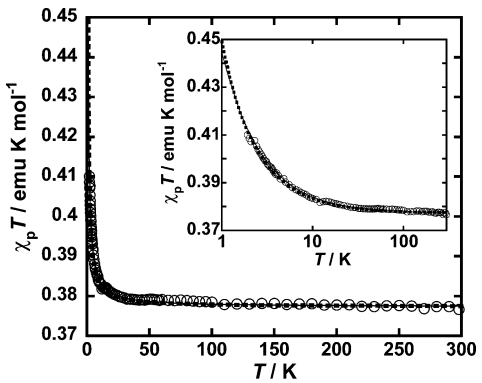


Fig. 3 The temperature dependence of magnetic susceptibility χ_p of **1** measured on a SQUID magnetometer with the static magnetic field of $B = 0.1$ T in the $\chi_p T$ *vs.* T plot. The solid and dotted lines represent theoretical calculations from eqn (1) and eqn (2), respectively.

allowed to distinguish the low-dimensional model, eqn (2), from the three-dimensional mean-field model, eqn (1). In view of the molecular packing, the exchange parameter of $2J/k_B = 0.09$ K is a good estimate for the intermolecular interaction of **1**.

Conclusions

The guanine-substituted nitronyl nitroxide radical **1** has been synthesized and isolated as a crystalline solid which is stable under ambient atmosphere. Introduction of the radical substituent into the nucleobase results in little disturbance to the intermolecular hydrogen bonding motifs as found in non-oligomeric guanines, demonstrating marked selectivity and directionality of the hydrogen bonding of guanine governing the molecular packing in a crystalline solid state: a bio-inspired approach to genuinely organic molecule-based magnetism described here has the potential to control the molecular packing of open-shell molecular assemblages.

Experimental

X-Ray crystallographic analysis

The X-ray diffraction measurements were made on a Rigaku Mercury CCD diffractometer at 183 K with graphite monochromated Mo Kα radiation up to $2\theta_{max} = 55°$. The crystal structure was solved by direct methods (SIR92)[14] and subsequent Fourier syntheses followed by a full-matrix least-squares refinement with the anisotropic approximation for non-hydrogen atoms. Positions of the hydrogen atoms were calculated and included in the final refinement. All the calculations were made using a program package *CrystalStructure* by the Rigaku/Molecular Structure Corporation.[15]

Magnetic susceptibility measurements

Magnetic susceptibility was measured on a Quantum Design SQUID magnetometer MPMS-XL in a temperature range of down to 1.9 K with a static magnetic field of 0.1 T.

Synthetic procedure

All commercially available materials for the synthesis shown in Scheme 1 were used without further purification. NMR spectra were recorded on an LA-400 spectrometer (JEOL). High-resolution mass spectra (HRMS) were recorded on a JMS-700T spectrometer.

2-[4-(2-Bromoethoxy)phenyl]-4,4,5,5-tetramethylimidazolidine-1,3-diol (3). Starting material, 4-(2-bromoethoxy)benzaldehyde **2**, was prepared according to a procedure previously reported.[16] A suspension of **2** (2.01 g, 8.77 mmol) and 2,3-dimethyl-2,3-dihydroxylaminobutane (1.30 g, 8.77 mmol) in dry benzene (120 ml) was refluxed under Ar atmosphere for 23 h to give a colorless powder of the adduct **3**. The precipitate was filtered and washed with benzene. Product **3** was used without further purification for the next reaction (1.79 g, 4.98 mmol, 56.8%).

2-[4-(2-Bromoethoxy)phenyl]-1,3-bis-(*tert*-butyldimethylsilanyloxy)-4,4,5,5-tetramethylimidazolidine (4). To a solution of **3** (1.77 g, 4.93 mmol) in dry DMF (15.6 ml) were added *tert*-butyldimethylchlorosilane (3.82 g, 25.3 mmol) and imidazole (3.35 g, 49.2 mmol). The mixture was stirred for 29 h at 50 °C. The resulting mixture was treated with water, and the solution was extracted with hexane, and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was purified on silica gel. Elution with hexane–CH_2Cl_2 (5 : 1) gave **4** as a colorless solid (1.71 g, 2.91 mmol, 59.0%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm): −0.854 (bs, 6H), −0.045 (s, 6H), 0.788 (s, 18H), 1.145 (s, 12H), 3.798 (t, 2H), 4.232 (t, 2H), 4.559 (bs, 1H), 6.837 (d, 2H), 7.281 (d, 2H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ(ppm): −5.051, −3.852, 17.943, 26.234, 41.776, 67.717, 68.152, 93.406, 113.956, 131.973, 134.629, 158.058.

9-(2-{4-[1-(*tert*-Butyldimethylsilanyloxy)-4,4,5,5-tetramethyl-3-(1-methyl-1-trimethylsilanylethoxy)-imidazolidin-2-yl]phenoxy}-ethyl)-6-chloro-9*H*-purin-2-ylamine (5). A mixture of **4** (2.37 g, 4.08 mmol), 2-amino-6-chloropurine (0.972 g, 5.73 mmol), K_2CO_3 (0.956 g, 6.92 mmol) and KI (0.700 g, 4.22 mmol) in dry DMF (25 ml) was stirred for 25 h at 60 °C. After the precipitate was filtered, to the filtrate were added CH_2Cl_2 and a small amount of hexane, and the solution was washed with brine. The solvent was evaporated under reduced pressure, and the residue was purified on silica gel. Elution with CH_2Cl_2–MeOH (54 : 1) gave **5** as a colorless solid (1.68 g, 2.46 mmol, 60.3%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm): −0.896 (bs, 6H), −0.061 (s, 6H), 0.772 (s, 18H), 1.134 (s, 12H), 4.291 (t, 2H), 4.466 (t, 2H), 4.542 (bs, 1H), 5.102 (s, 2H), 6.795 (d, 2H), 7.271 (d, 2H), 7.917 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ(ppm): −5.051, −3.906, 17.874, 26.157, 42.883, 65.534, 67.694, 93.352, 113.590, 125.110, 132.003, 134.988, 143.164, 151.249, 153.676, 157.486, 159.036. HRMS (FAB): *m*/*z* calcd for $C_{32}H_{55}ClN_7O_3Si_2$ ([M + H]$^+$) 676.35, found 676.35.

9-(2-{4-[1-(*tert*-Butyldimethylsilanyloxy)-4,4,5,5-tetramethyl-3-(1-methyl-1-trimethylsilanylethoxy)-imidazolidin-2-yl]-phenoxy}-ethyl)-6-methoxy-9*H*-purin-2-ylamine (6). To a solution of **5** (2.46 g, 3.62 mmol) dissolved in dry MeOH (30 ml) and dry CH_2Cl_2 (30 ml) was added dropwise a solution of 28% sodium methoxide in MeOH (7.59 ml, 37.3 mmol) at room temperature. The reaction mixture was stirred for 35 min at room temperature, and the solution was washed with brine, dried over $MgSO_4$ and concentrated. Product **6** was obtained as a colorless solid (2.25 g, 3.35 mmol, 92.5%) and used without further purification for the next reaction. ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm): −0.882 (bs, 6H), −0.051 (s, 6H), 0.782 (s, 18H), 1.143 (s, 12H), 4.083 (s, 3H), 4.287 (t, 2H), 4.446 (t, 2H), 4.548 (bs, 1H), 4.918 (s, 2H), 6.797 (d, 2H), 7.269 (d, 2H), 8.020 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ(ppm): −5.097, −3.951, 17.813, 26.119, 42.563, 53.762, 65.839, 67.610, 93.268, 113.590, 115.346, 131.912, 134.584, 140.057, 153.623, 157.661, 159.295, 161.532. HRMS (FAB): *m*/*z* calcd for $C_{33}H_{58}N_7O_4Si_2$ ([M + H]$^+$) 672.40, found 672.41.

2-Amino-9-(2-{4-[1-(*tert*-butyldimethylsilanyloxy)-4,4,5,5-tetramethyl-3-(1-methyl-1-trimethylsilanylethoxy)imidazolidin-2-yl]-phenoxy}ethyl)-1,9-dihydro-purin-6-one (7). To a solution of **6** (716.5 mg, 1.07 mmol) dissolved in dry DMF (17 ml) and dry MeCN (6 ml) was added dropwise Me_3SiI (0.75 ml, 5.55 mol). The reaction mixture was stirred at room temperature for 23 h, and then was treated with water, basified with 10% NaOH aq. The organic layer was extracted with a mixed solvent of CH_2Cl_2 and MeOH, washed with brine, and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was purified on silica gel. Elution with CH_2Cl_2–MeOH (12 : 1) gave **7** as a colorless solid (318.2 mg, 0.484 mmol, 45.2%). ^{1}H NMR (DMSO, 400 MHz): δ(ppm): −0.900 (bs, 6H), −0.066 (s, 6H), 0.755 (s, 18H), 1.111 (s, 12H), 4.243 (d, 2H), 4.309 (d, 2H), 4.477 (bs, 1H), 6.462 (s, 2H), 6.894 (d, 2H), 7.216 (d, 2H), 7.680 (s, 1H), 10.554 (s, 1H). ^{13}C NMR (DMSO, 300 MHz): δ(ppm): −5.083, −3.945, 17.575, 26.056, 42.088, 65.685, 67.273, 93.125, 113.672, 116.436, 131.452, 133.101, 137.697, 151.178, 153.606, 156.774, 157.942. HRMS (FAB): *m*/*z* calcd for $C_{32}H_{56}N_7O_4Si_2$ ([M + H]$^+$) 658.39, found 658.39.

2-Amino-9-{2-[4-(1-oxyl-3-oxido-4,4,5,5-tetramethyl-imidazolidin-2-yl)phenoxy]ethyl}-1,9-dihydropurin-6-one (1). To a solution of **7** (152.0 mg, 0.231 mmol) dissolved in DMF (2 ml) and THF (14 ml) was added dropwise a 1.0 M solution of tetrabutylammonium fluoride in THF (2.85 ml, 2.85 mol). The reaction mixture was stirred at room temperature for 14 h, and the solvent was evaporated, and the crude product was purified on silica gel. Elution with CH_2Cl_2–MeOH (15 : 1) and CH_2Cl_2–MeOH (5 : 1) gave **1** as a blue solid (79.3 mg, 0.186 mmol, 80.5%). HRMS (FAB): *m*/*z* calcd for $C_{20}H_{25}N_7O_4$ ([M + H]$^+$) 427.19, found 427.19.

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