Supporting Information

Synthesis and Electron Spin Relaxation of Tetra-Carboxylate Pyrroline Nitroxides

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1. Complete Reference 36.

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2. General Procedures and Materials.

Throughout the following paragraphs labels “JTP12-97f1C” and alike correspond to sample or experiment codes directly traceable to the laboratory notebooks or raw data.

3. X-ray Crystallography.

Data collection, structure solution, and refinement are briefly summarized below; more detailed descriptions may be found in the accompanying crystallographic information files (CIFs).

For nitroxides 1 and 2, the structures were determined using crystals obtained by slow evaporation of a DCM/heptane (1:1) solution (label: JTP12-97f1C) and vapor diffusion of pentane into a chloroform solution (label: HSD-1-1-26), respectively.

Nitroxide 1. A colorless crystal (approximate dimensions 0.25 × 0.18 × 0.10 mm³) was placed onto the tip of a 0.05 mm diameter glass capillary and mounted on a commercial diffractometer equipped with a detector at 150(2) K. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 30 seconds and a detector distance of 40 mm. The total exposure time was 18.12 hours. The frames were integrated with the SAINT software package using
a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 23212 reflections to a maximum θ angle of 26.45° (0.80 Å resolution), of which 2949 were independent (average redundancy 7.871, completeness = 99.6%, R_{int} = 3.33%, R_{sig} = 1.90%) and 2524 (85.59%) were greater than 2σ(F2). The final cell constants of a = 16.1787(15) Å, b = 7.8957(7) Å, c = 11.6365(10) Å, β = 105.489(5)°, volume = 1432.5(2) Å³, are based upon the refinement of the XYZ-centroids of 9945 reflections above 20 σ(I) with 5.225° < 2θ < 52.71°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.890. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9690 and 0.9870. Please refer to Table S1 for additional crystal and refinement information.

The space group P2₁/c was determined based on intensity statistics and systematic absences. The structure was solved and refined using the SHELX suite of programs. An intrinsic-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final anisotropic full-matrix least-squares refinement on F2 with 203 variables converged at R1 = 3.24%, for the observed data and wR2 = 8.65% for all data. The goodness-of-fit was 1.028. The largest peak in the final difference electron density synthesis was 0.326 e/Å³ and the largest hole was -0.204 e/Å³ with an RMS deviation of 0.040 e/Å³. On the basis of the final model, the calculated density was 1.466 g/cm³ and F(000), 660 e⁻. The remaining electron density is minuscule and located on bonds.

Nitrooxide 2 was studied with synchrotron radiation at the ChemMatCARS 15IDB beamline at the Advanced Photon Source at Argonne National Lab, Chicago, utilizing the SCrAPS program. A yellow crystal (approximate dimensions 0.115 × 0.061 × 0.055 mm³) was placed onto the tip of an ultra-thin glass rod and mounted on a D8 platform goniometer and measured at 100(2) K. The data collection was carried out using synchrotron radiation (λ=0.41328 Å, E =30 keV, silicon 111 and 113 monochromators, two mirrors to exclude higher harmonics) with a frame time 0.3 seconds and a detector distance of 60 mm. The total exposure time was 0.09 hours. The frames were integrated with
the SAINT software package\textsuperscript{S1} using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 13679 reflections to a maximum θ angle of 16.92° (0.71 Å resolution), of which 2333 were independent (average redundancy 5.863, completeness = 97.9%, R_{int} = 6.05%, R_{sig} = 4.49%) and 1988 (85.21%) were greater than 2σ(F2). The final cell constants of a = 16.3051(7) Å, b = 6.5192(3) Å, c = 15.4278(6) Å, β = 97.9090(10)°, volume = 1624.32(12) Å\textsuperscript{3}, are based upon the refinement of the XYZ-centroids of 5581 reflections above 20 σ(I) with 4.869° < 2θ < 33.70°. Data were corrected for absorption effects using the multi-scan method (SADABS).\textsuperscript{S2} The ratio of minimum to maximum apparent transmission was 0.841. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6260 and 0.7441. Please refer to Table S2 for additional crystal and refinement information.

The space group C2/c was determined based on intensity statistics and systematic absences. The structure was solved using and refined using the SHELX suite of programs.\textsuperscript{S3} An intrinsic methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final anisotropic full-matrix least-squares refinement on F2 with 113 variables converged at R1 = 4.94%, for the observed data and wR2 = 15.13% for all data. The goodness-of-fit was 1.230. The largest peak in the final difference electron density synthesis was 0.531 e/Å\textsuperscript{3} and the largest hole was -0.699 e/Å\textsuperscript{3} with an RMS deviation of 0.225 e/Å\textsuperscript{3}. On the basis of the final model, the calculated density was 1.408 g/cm\textsuperscript{3} and F(000), 724 e\textsuperscript{-}. Nonclassical hydrogen bonds were observed (Figure S3 and Table S3).
Table S1.  Crystal data and structure refinement for nitroxide 1 (X-ray label: 15131, sample label: JTP12-97f1C)

| Property                                      | Value                                           |
|----------------------------------------------|-------------------------------------------------|
| Empirical formula                            | C12 H14 N O9                                    |
| Formula weight                               | 316.24                                          |
| Crystal color, shape, size                   | colorless block, 0.25 × 0.18 × 0.10 mm³         |
| Temperature                                  | 150(2) K                                        |
| Wavelength                                   | 0.71073 Å                                       |
| Crystal system, space group                  | Monoclinic, P2₁/c                               |
| Unit cell dimensions                         | a = 16.1787(15) Å, α = 90°.  
|                                            | b = 7.8957(7) Å, β = 105.489(5)°.  
|                                            | c = 11.6365(10) Å, γ = 90°.                   |
| Volume                                       | 1432.5(2) Å³                                    |
| Z                                            | 4                                               |
| Density (calculated)                         | 1.466 Mg/m³                                     |
| Absorption coefficient                       | 0.128 mm⁻¹                                      |
| F(000)                                       | 660                                             |

**Data collection**

| Property                                      | Value                                           |
|----------------------------------------------|-------------------------------------------------|
| Diffractometer                               | APEX II Kappa Duo, Bruker                       |
| Theta range for data collection              | 1.306 to 26.451°                                |
| Index ranges                                 | -20 ≤ h ≤ 20, -8 ≤ k ≤ 9, -14 ≤ l ≤ 14         |
| Reflections collected                        | 23212                                           |
| Independent reflections                      | 2949 [R(int) = 0.0333]                          |
| Observed Reflections                         | 2524                                            |
| Completeness to theta = 25.242°              | 100.0 %                                         |

**Solution and Refinement**

| Property                                      | Value                                           |
|----------------------------------------------|-------------------------------------------------|
| Absorption correction                        | Semi-empirical from equivalents                 |
| Max. and min. transmission                   | 0.7454 and 0.6634                               |
| Solution                                      | Intrinsic methods                               |
| Refinement method                            | Full-matrix least-squares on F²                  |
| Weighting scheme                             | w = [σ²Fo² + AP² + BP]⁻¹, with                  |
|                                            | P = (Fo² + 2 Fc²)/3, A = 0.0412, B = 0.6339    |
| Data / restraints / parameters                | 2949 / 0 / 203                                  |
| Goodness-of-fit on F²                         | 1.028                                           |
| Final R indices [I>2sigma(I)]                | R1 = 0.0324, wR2 = 0.0819                       |
| R indices (all data)                          | R1 = 0.0395, wR2 = 0.0865                       |
| Largest diff. peak and hole                   | 0.326 and -0.204 e.Å⁻³                         |

Goodness-of-fit = [Σ[w(Fo² - Fc²)²]/Nobserved - Nparam]¹/², all data.
R1 = Σ[Fo - |Fc|] / Σ[Fo].  

wR2 = [Σ[w(Fo² - Fc²)²] / Σ [w(Fo²)]]¹/².
Table S2. Crystal data and structure refinement for nitroxide 2 (X-ray labels: S16003 and CMC1051, sample label: HSD-1-1-26).

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                             | C14 H18 N O9                               |
| Formula weight                                | 344.29                                     |
| Crystal color, shape, size                    | yellow block, 0.115 × 0.061 × 0.055 mm³   |
| Temperature                                   | 100(2) K                                   |
| Wavelength                                    | 0.41328 Å (30 keV)                         |
| Crystal system, space group                   | Monoclinic, C2/c                           |
| Unit cell dimensions                          | a = 16.3051(7) Å, α = 90°                 |
|                                              | b = 6.5192(3) Å, β = 97.909(1)°           |
|                                              | c = 15.4278(6) Å, γ = 90°                 |
| Volume                                        | 1624.32(12) Å³                             |
| Z                                            | 4                                          |
| Density (calculated)                          | 1.408 Mg/m³                                |
| Absorption coefficient                        | 0.072 mm⁻¹                                 |
| F(000)                                        | 724                                        |

Data collection

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Diffractometer                                | APS, ChemMatCARS, 15 IDB                   |
| Theta range for data collection               | 1.550 to 16.916°                         |
| Index ranges                                  | -20<=h<=22, -9<=k<=9, -18<=l<=21            |
| Reflections collected                         | 13679                                      |
| Independent reflections                       | 2333 [R(int) = 0.0605]                     |
| Observed Reflections                          | 1988                                       |
| Completeness to theta = 14.357°               | 97.8 %                                     |

Solution and Refinement

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Absorption correction                        | Semi-empirical from equivalents           |
| Max. and min. transmission                    | 0.7441 and 0.6260                          |
| Solution                                      | Intrinsic methods                         |
| Refinement method                             | Full-matrix least-squares on F²            |
| Weighting scheme                              | w = [σ²Fo² + AP² + BP] ¹, with             |
|                                              | P = (Fo² + 2 Fc²)/3, A = 0.0827, B = 0.2655 |
| Data / restraints / parameters                | 2333 / 0 / 113                            |
| Goodness-of-fit on F²                         | 1.230                                      |
| Final R indices [I>2sigma(I)]                 | R1 = 0.0494, wR2 = 0.1273                  |
| R indices (all data)                          | R1 = 0.0645, wR2 = 0.1513                  |
| Extinction coefficient                        | 0.35(3)                                   |
| Largest diff. peak and hole                   | 0.531 and -0.699 e.Å⁻³                    |

Goodness-of-fit = [Σ[w(Fo² - Fc²)²]/Nobs - Nparam)]¹/², all data.
R1 = Σ|Fo| - |Fc| / Σ |Fo|,         wR2 = [Σ[w(Fo² - Fc²)²] / Σ [w(Fo²)²]]¹/².
Figure S1. Nitroxide 1: formula unit obtained by Mo Kα radiation (X-ray label: 15131, sample label: JTP12-97f1C). Carbon, nitrogen, and oxygen atoms are depicted with thermal ellipsoids set at the 50% probability level.
Figure S2. Nitroxide 2: selected specimen and formula unit obtained by synchrotron radiation (X-ray labels: S16003 and CMC1051, sample label: HSD-1-1-26). Carbon, nitrogen, and oxygen atoms are depicted with thermal ellipsoids set at the 50% probability level.
Figure S3. Nitroxide 2: cell plots, views along $a$-axis (top plot) and $c$-axis (bottom plot), showing nonclassical H-bonding (Table S3).

Table S3. Hydrogen bonds for nitroxide 2 (X-ray labels: S16003 and CMC1051) [Å and $^\circ$].

| D-H...A               | d(D-H) | d(H...A) | d(D...A)     | <(DHA) |
|-----------------------|--------|----------|--------------|--------|
| C2-H2...O1#2          | 0.95   | 2.56     | 3.1251(16)   | 118.5  |
| C4-H4C...O3#3         | 0.98   | 2.53     | 3.4218(18)   | 151.8  |

* Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2  #2 x,y,-z  #3 -x+1/2,y-1/2,-z+1/2
4. **EPR spectroscopy at DU.**

X-band CW spectra were recorded on a commercial spectrometer with an SHQE resonator and 100 kHz modulation frequency. Variable temperature CW and pulse EPR experiments were obtained on a commercial spectrometer, which is equipped with an ER4118X-MS5 split ring resonator, a liquid helium cryostat, and a temperature controller for cryogenic temperatures. Q-band measurements were performed on a commercial instrument using an ER5107D2 resonator. Temperatures at the sample are accurate to within about 2 K. Spectra were simulated using the locally-written program Monmer, which is based on the equations in ref. S6. Parameters were adjusted to optimize agreement with spectra obtained at both X-band and Q-band. Relative g values were well defined in the Q-band spectra. The average g value was adjusted to agree with the values obtained for fluid solution spectra recorded with the dual mode resonator at the University of Nebraska (see below). $A_z$ is well defined at both X-band and Q-band, but $A_x$ and $A_y$ are not resolved, so values of $A_x$ and $A_y$ were adjusted to make the average value agree with $A_{iso}$ observed in fluid solution.
Figure S4. CW EPR (X-band, 9.862 GHz) spectra of tempol in trehalose at 20 °C.

A) magnetically dilute sample in well-formed glass obtained with 0.05 mT modulation amplitude at 100 kHz and 0.20 mW microwave power. B) Magnetically concentrated sample in a poorly-formed glass obtained with 0.1 mT modulation amplitude and 0.20 mW microwave power.

At room temperature the spectrum of tempol in a well-formed glassy matrix exhibits the anisotropic g and A-values that are characteristic of immobilized nitroxides (Figure S4A). However when there is not good glass formation and the solute is not magnetically dilute an exchange-narrowed spectrum is observed (Figure S4B). Samples may also be heterogenous resulting in spectra that are intermediate between those shown in Figure S4A and S4B. For small nitroxides such as tempol, it was difficult to reproducibly prepared well-formed glasses in trehalose. However, addition of 10% sucrose to the trehalose resulted in consistently well-formed glasses with magnetically dilute solute.
Figure S5. CW spectra of 1 in 9:1 trehalose:sucrose at 20°C (solid lines). A) X-band (9.857 GHz) spectrum obtained with 0.201 mW power and 0.1 mT modulation amplitude, and B) Q-band (33.84 GHz) spectrum obtained with 0.061 mW power and 0.1 mT modulation amplitude. The simulations (dashed red lines) were obtained with $g_x = 2.0099$, $g_y = 2.0060$, $g_z = 2.0025$, $A_x = 9.6$ MHz, $A_y = 9.8$ MHz, $A_z = 83.2$ MHz.
Figure S6. CW spectra of 2 in 9:1 trehalose:sucrose at 20 °C (solid lines). A) X-band (9.857 GHz) spectrum obtained with 0.201 mW power and 0.1 mT modulation amplitude, and B) Q-band (33.77 GHz) spectrum obtained with 0.061 mW power and 0.1 mT modulation amplitude. The simulations (dashed red lines) were obtained with $g_x = 2.0099$, $g_y = 2.0061$, $g_z = 2.0026$, $A_x = 12.0$ MHz, $A_y = 12.0$, MHz, $A_z = 89.0$ MHz

The broad underlying feature that is evident in the Q-band spectra of both 1 and 2, but not in the simulated spectra suggests the presence of a small amount of magnetically-concentrated radical. The relaxation times of the magnetically concentrated radicals are much shorter than for the magnetically dilute material, and do not contribute to the measured relaxation times reported in the main text.
5. **CW EPR spectroscopy at UNL.**

CW X-band EPR spectra for nitroxides in solution were acquired on a commercial EPR instrument, equipped with a frequency counter and nitrogen flow temperature control (130–300 K). The spectra were obtained using a dual mode cavity; all spectra were recorded using an oscillating magnetic field perpendicular (TE$_{102}$) to the swept magnetic field. DPPH powder ($g = 2.0037$) was used as a $g$-value reference. The spectra were simulated using Symphonia or EasySpin (Garlic).

![Figure S7. EPR ($v = 9.6505$ GHz) spectrum of nitroxide 1 (sample label: JTP13-21f1; 0.1 mM in CHCl$_3$; EPR label: HD174r1). Experimental spectrum: power, 20 dB, 2.046 mW; modulation amplitude 0.1 G; conversion time 40.96 ms; time constant 10.24 ms; resolution in X, 4k points. Simulation (EasySpin, Garlic): $g = 2.0061$, $A^{(14N)} = 34.223$ MHz ($n = 1$), $A^{(1H)} = 1.096$ MHz ($n = 2$), LW = 0.0105 mT (Gaussian) and 0.0132 mT (Lorenzian).](image-url)
Figure S8. EPR ($v = 9.6505$ GHz) spectrum of nitroxide 1 (sample label: JTP13-21f1; 0.1 mM in CHCl$_3$; EPR label: HD174r1).  Experimental spectrum: power, 20 dB, 2.046 mW; modulation amplitude 0.1 G; conversion time 40.96 ms; time constant 10.24 ms; resolution in X, 4k points. Simulation (Symphonia): $g = 2.0062$, $A(^{14}\text{N}) = 34.24$ MHz (n = 1), $A(^{1}\text{H}) = 1.096$ MHz (n = 2), $A(^{15}\text{N}) = 48.09$ MHz (n = 1), $A(^{13}\text{C}) = 25.30$ MHz (n = 4), $A(^{13}\text{C}) = 15.50$ MHz (n = 2), L/G = 0.4, LW = 0.020 mT. (All nuclei are at natural abundance.)
Figure S9. EPR ($\nu = 9.6499$ GHz) spectrum of nitrooxide 2 (sample label: HSD1-1-26; 0.1 mM in CHCl₃; EPR label: HD174r2). Experimental spectrum: power, 20 dB, 2.046 mW; modulation amplitude 0.1 G; conversion time 40.96 ms; time constant 10.24 ms; resolution in X, 4k points. Simulation (EasySpin, Garlic): $g = 2.0060$, $A(^{14}\text{N}) = 37.648$ MHz ($n = 1$), $A(^{1}\text{H}) = 1.864$ MHz ($n = 2$), $A(\text{H}) = 1.430$ MHz ($n = 2$), $A(\text{H}) = 1.087$ MHz ($n = 2$), LW (Lorentzian) = 0.0147 mT.
6. DFT Calculations.

Geometry optimizations and frequency calculations were performed using the Gaussian 09 program package\textsuperscript{S7} running on a workstation under Linux operating system.

Ground-state geometries of nitroxides were optimized at the UB3LYP/6-311G(d,p) level. Starting geometry for 2 was the $C_2$-symmetric conformation in the X-ray structure; this led to the lowest energy conformation for nitroxide 2. The geometry optimizations were followed by vibrational analyses to confirm that all reported structures are the minima on the potential energy surface (Tables S4 and S5). These geometries were used for single point calculations of EPR spectral parameters at the UB3LYP/EPR-III level of theory (Table S6).

Stick and space-filling plots for the lowest energy conformations of 1 and 2 the UB3LYP/6-311G(d,p)+ZPVE level are presented in Figure S10.

Table S4. The B3LYP/6-311G(d,p)+ZPVE calculations for tetraester nitroxide 1: energies ($E^\circ$, hartree), zero point vibrational energies (ZPVE, hartree),\textsuperscript{a} lowest vibrational frequencies (cm$^{-1}$), RMS gradient norms (a.u.),\textsuperscript{b} dipole moments ($\mu$, D), and relative energy (kcal mol$^{-1}$) of nitroxide.

| Point group | $<S^2>$ | $E^\circ$ | ZPVE | $E^\circ$ + ZPVE | Rel. energy | RMS gradient norm ($\times 10^4$) | Lowest vibrational frequencies (cm$^{-1}$) | $\mu$ (D) |
|-------------|---------|----------|------|----------------|-------------|-----------------------------------|------------------------------------------|---------|
| Con7/O1    | $C_2$   | 170.91, 99.65 99.65, 170.91 | 0.7537 | -1197.7046172 0.265110 | -1197.439572 0.00 | 0.28 | 21.3, 27.8 29.9, 49.1 | 2.10 |
| Of1        | $C_2$   | -8.78, 102.56 102.56, -8.78 | 0.7537 | -1197.70442342 0.264969 | -1197.439454 0.07 | 0.58 | 16.1, 35.1 44.1, 54.6 | 1.33 |
| Roe7/O1    | $C_2$   | 105.76, -4.23 -4.23, 105.76 | 0.7537 | -1197.7036057 0.268437 -1197.438224 0.85 | 1.19 | 18.9, 23.7 30.1, 55.0 | 6.28 |
| IRC of 1 and s3 | $C_1$ | 174.90, -96.06 96.31, -175.97 | 0.7538 | -1197.70293553 0.265031 -1197.437905 1.05 | 1.65 | 19.8, 22.5 25.8, 39.9 | 2.40 |
| Of2        | $C_1$   | -165.33, -107.96 -107.96, -165.33 | 0.7538 | -1197.70251344 0.264994 -1197.437519 1.28 | 1.71 | 20.6, 23.8 30.1, 44.3 | 4.25 |
| Of10       | $C_2$   | -160.99, -112.21 -112.21, -160.99 | 0.7538 | -1197.70173489 0.265169 -1197.436546 1.90 | 1.53 | 11.6, 22.7 30.2, 43.5 | 0.60 |
| Of12_Xray  | $C_2$   | -168.69, -104.62 -104.62, -168.69 | 0.7538 | -1197.70165525 0.265174 -1197.436482 1.94 | 1.11 | 20.0, 21.4, 26.3, 42.5 | 1.26 |
| Of3        | $C_2$   | -131.83, -131.83 -131.83, -131.83 | 0.7538 | -1197.69150284 0.264332 -1197.427171 7.78 | 0.05 | 159.6, 154.5 21.2, 24.5 | 4.64 |
| Of4        | $C_1$   | 111.94, -111.94 -111.94, 155.92 | 0.7538 | -1197.70184716 0.265008 -1197.436839 1.71 | 1.17 | 151.3, 25.0 35.6, 37.6 | 1.61 |
| Of5        | $C_1$   | 0.54, -0.54 0.54, -0.54 | 0.7538 | -1197.70147001 0.264694 -1197.436776 1.75 | 1.52 | 23.5, 24.5, 40.3, 47.4 | 2.06 |
| Of6        | $C_2$   | -19.20, -161.64 -161.64, -19.20 | 0.7535 | -1197.69274219 0.264729 -1197.428013 7.25 | 0.79 | 158.0, 159.1, 20.1, 36.6 | 6.45 |

\textsuperscript{a} 1 Hartree = 627.51 kcal mol$^{-1}$. \textsuperscript{b} In Cartesian coordinates.
Table S5. The UB3LYP/6-311G(d,p)+ZPVE calculations for nitroxide 2: energies (E°, hartree), zero point vibrational energies (ZPVE, hartree),<sup>a</sup> lowest vibrational frequencies (cm<sup>−1</sup>), RMS gradient norms (a.u.),<sup>b</sup> and dipole moments (D).

| Structure | Point group | O14-C11-C4-N7 | C36-C9-C1-N7 | O31-C30-C9-C1 | O13-C10-C1-N7 | C29-C12-C4-N7 | O32-C29-C12-C4 |
|-----------|-------------|---------------|---------------|----------------|----------------|---------------|---------------|
| Rot8/Xray | C2          | -118.39, -117.42, 23.74, -178.39, 23.74 | 0.7541 | 1276.37925199 | 0.322612 | -1276.056640 | 0.00 | 1.25 | 17.3, 25.0, 32.7, 38.6 | 1.35 |
| Rot9      | C2          | 69.01, -178.54, 10.73 | 0.7541 | 1276.37760243 | 0.322552 | -1276.050510 | 1.00 | 2.27 | 14.6, 25.1, 32.2, 32.6 | 0.90 |
| Rot11/12  | C2          | 122.65, 175.51, -155.06 | 0.7541 | 1276.37350109 | 0.322827 | -1276.05874 | 3.62 | 1.29 | 27.5, 28.2, 28.8, 41.3 | 5.90 |
| Rot10     | C2          | 73.90, 174.14, -162.51 | 0.7542 | 1276.37206363 | 0.322317 | 1276.049690 | 4.36 | 3.24 | 1276, 22.1, 26.7, 40.1 | 2.88 |
| Rot4/6/7  | C2          | -179.11, 66.48, 47.52, -179.11, 66.48, 47.52 | 0.7538 | 1276.37132281 | 0.322711 | 1276.048612 | 5.03 | 1.48 | 14.0, 23.8, 33.7, 36.6 | 0.12 |
| Rot2/5    | C2          | -172.13, 53.74, -127.64 | 0.7539 | 1276.37082435 | 0.322700 | 1276.048124 | 5.34 | 0.27 | 9.3, 29.8, 35.7, 42.1 | 1.07 |
| Rot1      | C2          | 8.03, -66.40, 57.51 | 0.7537 | 1276.37067335 | 0.322979 | 1276.047694 | 5.61 | 1.89 | 26.1, 32.7, 41.5, 53.8 | 1.50 |
| Start     | C2          | 155.07, -86.60, 46.43, 155.07, -86.60, 46.43 | 0.7538 | 1276.36990687 | 0.322673 | 1276.047234 | 5.90 | 2.93 | 20.6, 24.6, 38.2, 39.0 | 0.66 |
| Rot3      | C2          | 11.65, 61.85, -136.20, 11.65, 61.85, -136.20 | 0.7538 | 1276.36870924 | 0.322459 | 1276.046250 | 6.52 | 0.64 | 28.9, 39.6, 43.6, 52.1 | 4.57 |

1 Hartree = 627.51 kcal mol<sup>−1</sup>.  b In Cartesian coordinates.

Table S6. Single point energies and <sup>1</sup>H, <sup>13</sup>C hyperfine couplings (MHz) for the lowest energy conformations of 1 and 2 at the UB3LYP/EPR-III//UB3LYP/6-311G(d,p) level of theory vs. experimental values.<sup>a</sup>

|     | E° (UB3LYP/EPR-III) | <S°> | A(14N) (MHz) | A(1H) (MHz) |     |
|-----|------------------|-----|-------------|-------------|-----|
|     |                  |     | N-O | vinylic CH | OCH₃ | CH₂ |
|     |                  |     |     |            |      |     |
|     |                  |     | DFT | EPR<sup>a</sup> | DFT | EPR | NMR | DFT | NMR | DFT | EPR | NMR |
| 1   | -1197.91835553   | 0.7544 | 21.60       | 34.24         | -1.68 | 1.10 | -1.08 | x | +0.034 | x | x | x |
| 2   | -1276.60180954   | 0.7548 | 25.03       | 37.65         | -1.80 | 1.43 | -1.26 | x | +0.058 | +0.017 | -1.37 | 1.09 | 1.86 | -1.6<sup>a</sup> |

<sup>a</sup> Experimental values were obtained in chloroform or chloroform-d<sub>3</sub> at room temperature. For experimental and simulated EPR spectra of 1 and 2, see: Figures S7 – S9; for paramagnetic<sup>1</sup>H NMR spectra of 1 and 2 see: Figures S15, S16, S24 and S25. In DFT computations, no conformational analysis of the methyl groups was carried out, thus computed values of A(1H) for the methyl groups are not reported. For C₂-symmetric conformation of 1, computed A(13C) (in MHz) hyperfine coupling constants were as follows: −16.9 for C1 and C4 (quaternary carbons), +30.5 and +22.2 (avg. = +26.4) for C9-C13 (carbonyl carbons), 0.23 and −0.11 (avg. = +0.06) for C21, C25, C29 and C33 (methyl carbons), and −0.50 for C2 and C3 (vinyl carbons); for a simulation of EPR spectrum of 1, including <sup>15</sup>N and <sup>13</sup>C nuclei at natural abundance, see: Figures S7 and S8.

<sup>b</sup> In<sup>1</sup>H NMR spectrum of 2, a very broad peak at δ = − 40 ppm was tentatively assigned to diastereotropic CH₂ protons (Figures S24 and S25).
Figure S10. Stick and space-filling plots for the lowest energy conformations of nitroxides 1 (top) and 2 (bottom) computed at the UB3LYP/6-311G(d,p)+ZPVE level of theory.
7. Synthesis of Nitroxides.

Synthetic scheme for preparation of nitroxides 1 and 2 is summarized below.

HSD-1-56: Lithium (0.80 g, 0.113 mol, surface was refreshed with razor) was washed with heptane, dried under vacuum, charged with argon, and cut into small pieces immediately before using. Tetrahydrofuran (16 mL, freshly distilled from sodium and benzophenone) was added to lithium and cooled to 0 °C. A solution of 4,4′-di-tert-butylbiphenyl (0.94 g, 3.5 mmol) in tetrahydrofuran (40 mL) was added to lithium dropwise; a blue color appeared immediately. After stirring for 3 h, the mixture was cooled to −78 °C and a solution of SM 3 (2.0 g, 7.1 mmol) in tetrahydrofuran (40 mL) was added dropwise; the reaction mixture became red shortly after the
addition, and then slowly became dark brown, to produce dianion of 3.\textsuperscript{88} After 16 h, the liquid was cannulated to mostly frozen methyl chloroformate (1.36 mL, 17.6 mmol) and stirred for 1 day at –78 °C. The reaction was quenched with saturated aqueous ammonium chloride (100 mL) and allowed to warm to rt. The mixture was diluted with ethyl ether (100 mL\*3) and washed with brine (100 mL\*3), dried over sodium sulfate and concentrated in rotatory evaporator. The crude was purified by column chromatography (silica gel, pentane/ethyl acetate, 1:1, R\textsubscript{f} 0.32) to afford a light yellow solid (1.86 g, 66%).

JTP12-61: SM 4 (2.64 g, 6.57 mmol) and dichloromethane (350 mL) were charged to a round bottom flask and cooled in an ice water bath. Trifluoroacetic acid (145 mL, 1.95 mol) was added dropwise and stirred for five minutes before removing the ice water bath. The solution was stirred for one hour until starting material could not be observed by thin layer chromatography, then the dichloromethane and trifluoroacetic acid were evaporated in a rotary evaporator. The resulting brown oil was dissolved in methanol (50 mL) and evaporated three times to yield the crude as a brown solid. The crude was washed over silica (silica gel, hexanes/ethyl acetate, 3:2) then eluted (methanol/dichloromethane, 3:97, R\textsubscript{f} 0.48) to yield 5 as a sand colored solid (1.720 g, 87%).

| Product label | SM 4 \( (g/\text{mmol}) \) | DCM \( (\text{mL}) \) | Yield \( (g/\%) \) |
|---------------|-------------------------------|-----------------|-----------------|
| JTP10-92ppt1  | 0.157/0.391                  | 25              | 0.086/73        |
| JTP12-61I2    | 0.486/1.211                   | 78              | 0.420           |

JTP12-90: SM 5 \( (g/\text{mmol}) \) 0.017/0.057 0.8 0.027/0.156 0.005/27 JTP12-90f1 75
JTP12-91: SM 5 \( (g/\text{mmol}) \) 0.006/0.020 0.7, Et\textsubscript{2}O 0.008/0.046 Very low conversion
JTP12-92: SM 5 \( (g/\text{mmol}) \) 0.022/0.073 0.8, Et\textsubscript{2}O 0.031/0.180 Very low conversion
JTP12-93: SM 5 \( (g/\text{mmol}) \) 0.194/0.644 7.5 0.405/2.346 0.039/19 JTP12-97f1 85
JTP12-94: SM 5 \( (g/\text{mmol}) \) 0.038/0.126 3, benzene 0.086/0.498 Crude Broad amr, not isolated
JTP12-95: SM 5 \( (g/\text{mmol}) \) 0.849/2.817 33 1.826/10.58 0.145/16 JTP12-13f1 100
JTP12-96: SM 5 \( (g/\text{mmol}) \) 0.436/1.448 18 0.950/5.504 0.079/17 JTP12-21f1 99
JTP13-13: 5 (0.849 g, 2.82 mmol) was charged to a round bottom flask and evacuated for one hour then filled with nitrogen before being dissolved in dichloromethane (8.5 mL). The resulting solution was cooled in an ice water bath and purified m-CPBA\(^9\) (1.83 g, 10.6 mmol) in dichloromethane (24 mL) was added dropwise. The resulting solution was stirred for five minutes, then the ice bath was removed. After three hours the solution was evaporated and dissolved in ethyl ether (70 mL), washed with saturated aqueous sodium bicarbonate until the aqueous layer was no longer yellow, washed with brine (2 × 15 mL), dried over sodium sulfate, and evaporated to give white powdery crude. The crude was purified with column chromatography (silica gel, chloroform/ethyl acetate, 2:1, R\(_f\) 0.45) to afford nitroxide 1 contaminated with m-CPBA as a slightly orange powder. The m-CPBA was removed by washing with ethyl ether (~20 × 1 mL) to afford 1 as an orange powder (145 mg, 16%). LRMS (ESI, 0.1% formic acid in methanol, label: JTP13-21f1): m/z ion type (%RA = percent relative amplitude for m/z 150–1000) 339 [M+Na]\(^+\) (60%), 655 [2M+Na]\(^+\) (100%), 671 [2M+K]\(^+\) (5%). A crystal suitable for X-ray crystallography was obtained by slow evaporation from a 1:1 DCM:heptane solution (label: JTP12-97f1C).

**Reduction of nitroxide 1 to the corresponding hydroxylamine 1-H using ascorbate.**

Nitroxide 1 (5.1 mg) was dissolved in ascorbate solution (2 mL, 20 mM ascorbate, 125 mM phosphate, 20 mM glutathione, pH 7.4) and allowed to react for 15 minutes. The solution was then saturated with sodium chloride, extracted with ethyl acetate (3 × 1 mL), dried over sodium sulfate, and evaporated yielding 1-H. LRMS (ESI, 0.1% formic acid in methanol, label: JTP13-23-2): m/z ion type (%RA = percent relative amplitude for m/z 150–1000) 318 [M+H]\(^+\) (10%), 340 [M+Na]\(^+\) (30%), 657 [2M+Na]\(^+\) (100%).

![Chemical structure](image)

**Summary for preparation of compound 6**

| Label   | SM Label | SM (g/mmol) | THF (mL) | Li (g/mmol) | DBB (g/mmol) | BrCH\(_2\)CO\(_2\)Me (mL/mmol) | Yield (g/%) |
|---------|----------|-------------|----------|-------------|--------------|-------------------------------|-------------|
| HSD-1-1-10 | HSD-1-1-4 | 0.11/0.389 | 2.4 | 0.04/6.224 | 0.052/0.2 | 0.143/1.56 | 0.077/46 |
| HSD-1-1-12 | HSD-1-1-5 | 1.0/3.532 | 24 | 0.4/56.5 | 0.47/1.77 | 1.30/14.13 | 0.71/47 |
| HSD-1-1-24 | HSD-1-1-5 | 0.45/1.590 | 12 | 0.18/25.44 | 0.212/0.8 | 0.59/6.36 | 0.38/57 |
6 (label: HSD-1-1-12): Lithium (0.4g, 56.5 mmol, surface was refreshed with razor) was washed with heptane, dried under vacuum, charged with argon, and cut into small pieces immediately before using. Tetrahydrofuran (4 mL, distilled from sodium and benzophenone) was added to lithium and cooled to 0 °C. A solution of 4,4'-di-tert-butylbiphenyl (0.47 g, 1.77 mmol) in tetrahydrofuran (10 mL) was added to lithium dropwise, a blue color appeared immediately. After stirring for 3 h, the mixture was cooled to −78 °C and a solution of SM 3 (1.0 g, 3.532 mmol) in tetrahydrofuran (10 mL) was added dropwise. Following the addition, the reaction mixture became red, and then slowly turn to dark brown. After 16 h, the liquid was cannulated to mostly frozen methyl bromoacetate (1.30 mL, 14.13 mmol) and stirred for 1 day at −78 °C. The reaction was quenched with saturated aqueous ammonium chloride (30 mL) and allowed to warm to rt. The mixture was diluted with ethyl ether (30 mL*3) and washed with brine (30 mL*3), dried over sodium sulfate and concentrated in rotatory evaporator. The crude was purified by column chromatography (silica gel, pentane/ethyl acetate, 1:1, Rf 0.52) to afford a light yellow oil (710 mg, 47%). LRMS-ESI (0.1% HCOOH in MeOH, label: HSD-1-1-12), m/z (ion-type, % RA for m/z, 150-2000) at [M+Na]$^+$: 452.2.

### Summary for preparation of compound 7

| Label        | SM Label     | SM  (g/mmol) | TFA  (mL/mmol) | DCM  (mL) | Yield  (g/%) |
|--------------|--------------|--------------|----------------|----------|-------------|
| HSD-1-1-14   | HSD-1-1-12   | 0.4/0.932    | 2.4/31.7       | 12       | 0.127/42    |
| HSD-1-1-25   | HSD-1-1-12, 24 | 0.6/1.40     | 3.6/47.6       | 18       | 0.25/54     |

7 (label: HSD-1-1-14): SM 6 (400 mg, 0.932 mmol) and dichloromethane (12 mL) were charged to a round bottom flask and cooled in an ice water bath. Trifluoroacetic acid (2.4 mL, 31.7 mmol) was added dropwise and stirred for five minutes before removing the ice water bath. The solution was stirred for two hours until starting material could not be observed by thin layer chromatography, then the dichloromethane and trifluoroacetic acid were evaporated in a rotary evaporator. The resulting brown oil was dissolved in methanol (5 mL) and evaporated (the dissolution and evaporation repeated three times), to yield the crude as a brown solid. The crude was purified by column chromatography (silica gel, pentane/ethyl acetate, 3:1, Rf 0.15) to afford a brown solid (127 mg, 42%). LRMS-ESI
(0.1% HCOOH in MeOH, label: HSD-1-1-14), m/z (ion-type, % RA for m/z, 150-2000) at [M+Na]^+: 352.2.

Summary for preparation of compound 2

| Label       | SM Label        | SM (g/mmol) | DCM (mL) | mCPBA (g/mmol) | Yield (g/%) | Spin conc. |
|-------------|-----------------|-------------|----------|----------------|-------------|------------|
| HSD-1-1-15  | HSD-1-1-14      | 0.02/0.061 | 1.0      | 0.04/0.231     | 0.008/38    | --         |
| HSD-1-1-17  | HSD-1-1-14      | 0.098/0.3  | 4.9      | 0.196/1.135    | 0.0353/35   | ~100       |
| HSD-1-1-26  | HSD-1-1-25      | 0.25/0.76  | 12.5     | 0.498/2.89     | 0.19/73     | 91         |

2 (label: HSD-1-1-26): SM 7 (250 mg, 0.76 mmol) was charged to a round bottom flask and evacuated for one hour then filled with nitrogen before being dissolved in dichloromethane (5.0 mL). The resulting solution was cooled in an ice water bath and purified m-CPBA\(^{59}\) (498 mg, 2.89 mmol) in dichloromethane (7.5 mL) was added dropwise. The resulting solution was stirred for 5 min, then the ice bath was removed. After 2 h, the solvents were evaporated and the residue was dissolved in ethyl ether (15 mL), washed with saturated aqueous sodium bicarbonate until the aqueous layer was no longer yellow, washed with brine (3 \(\times\) 15 mL), dried over sodium sulfate, and evaporated to give pale yellow powdery crude. The crude was purified with column chromatography (silica gel, pentane/ethyl acetate, 3:1, R\(_f\) 0.31) to afford a light yellow solid (190 mg, 73%). LRMS-ESI (0.1% HCOOH in MeOH, label: HSD-1-1-26), m/z (ion-type, % RA for m/z, 150-2000) at [M+Na]^+: 367.6.

Single crystal growth for X-ray crystallography: 20 mg of nitroxide 2 was dissolved in 1 ml of chloroform, and then was filtered to a small vial. This small vial was placed into a big vial containing 2 ml of pentane, and then after sealing the big vial, the assembly was left at room temperature for overnight. The crystal formation was observed next day.

Summary for preparation of compound 2-H

2-H (label: HSD-1-1-36): Nitroxide 2 (label: HSD-1-1-26, 10.6 mg, 0.031 mmol, 1.0 equiv.) was dissolved into 2.5 ml of phosphate buffered saline (PBS; 12.4 mM) to give a homogenous solution. To this solution, L-ascorbic acid (ACS; 27.13 mg, 0.154 mmol, 5.0 equiv.) was added. The mixture
was stirred at ambient temperature with the protection from light for 3 hours. After 3 hours, the solutions was extracted with ethyl acetate (3 mL*3), and the organic layer was dried over Na₂SO₄ and concentrated under the reduced pressure, and then evacuated under high vacuum to afford the residue of the reaction of 7 mg (label: HSD-1-1-36). The residue was dissolved in CDCl₃ and characterized by NMR, IR and MS. LRMS-ESI (0.1% HCOOH in MeOH, HSD-1-1-36), m/z (ion-type, % RA for m/z, 150-2000) at [M+Na]^+: 368.1.
8. Spectra of Nitroxides (Paramagnetic $^1$H NMR and IR), and Spectra of Diamagnetic Synthetic Intermediates and Hydroxylamines.

Figure S11. $^1$H NMR spectrum (700 MHz, CDCl$_3$) of 4 (label: JTP10-63rc).

Figure S12. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4 (label: JTP10-63rc).
Figure S13. $^1$H NMR spectrum (600 MHz, CDCl$_3$) of 5 (label: JTP12-61f2).

Figure S14. $^{13}$C NMR spectrum (176 MHz, CDCl$_3$) of 5 (label: JTP12-61f2).
Figure S15. $^1$H NMR spectrum (400 MHz, 0.9 M in CDCl$_3$) of nitroxide 1 (label: JTP13-31f1).

Figure S16. $^1$H NMR spectrum (400 MHz, CDCl$_3$, ca. 0.9 M) of nitroxide 1 with one drop of CHCl$_3$ (label: JTP13-13f1).
Figure S17. $^1$H NMR spectrum (700 MHz, CDCl$_3$) of hydroxylamine 1-H (label: JTP13-23-2).

Figure S18. $^{13}$C NMR spectrum (176 MHz, CDCl$_3$) of hydroxylamine 1-H (label: JTP13-23-2).
Figure S19. $^1$H NMR spectrum (700 MHz, CDCl$_3$) of hydroxylamine 1-H after overnight in freezer (label: JTP13-23-2).

Figure S20. $^1$H-NMR spectrum (300 MHz, CDCl$_3$) of compound 6 (Label: HSD-1-1-12).
Figure S21. $^{13}$C-NMR spectrum (75 MHz, CDCl$_3$) of compound 6 (Label: HSD-1-1-12).

Figure S22. $^1$H-NMR spectrum (300 MHz, CDCl$_3$) of compound 7 (Label: HSD-1-1-14).
**Figure S23.** $^{13}$C-NMR spectrum (75 MHz, CDCl$_3$) of compound 7 (Label: HSD-1-1-14).

**Figure S24.** $^1$H NMR spectrum (400 MHz, CDCl$_3$, ca. 0.9 M) of nitroxide 2 (label: JTP13-13f1).
Figure S25. $^1$H NMR spectrum (400 MHz, CDCl$_3$, ca. 0.9 M) of nitroxide 2 with one drop of TMS (label: JTP13-13f1).

Figure S26. $^1$H-NMR spectrum (700 MHz, CDCl$_3$) of compound 2-H (Label: HSD-1-1-36).
Figure S27. $^{13}$C-NMR spectrum (176 MHz, CDCl$_3$) of compound 2-H (Label: HSD-1-1-36).

Figure S28. IR spectrum (ATR, diamond) of 4 (label: JTP10-53f3).
Figure S29. IR spectrum (ATR, diamond) of 5 (label: JTP12-61f2)

Figure S30. IR spectrum (ATR, diamond) of nitroxide 1 (label: JTP13-13f1)
Figure S31. IR spectrum (ATR, diamond) of hydroxylamine 1-H (label: JTP13-23-2).

Figure 32. IR spectrum (ATR, ZnSe) of compound 6 (label: HSD-1-1-12).
Figure S33. HRMS-ESI (1% CH₃COONa in 3:1 (v/v) MeOH/H₂O) of compound 6 (Label: HSD-1-1-12).

Figure S34. IR spectrum (ATR, ZnSe) of compound 7 (Label: HSD-1-1-14).
Figure S35. HRMS-EI (1% CH₃COONa in 3:1 (v/v) MeOH/H₂O) of compound 7 (Label: HSD-1-1-14).

Figure S36. IR spectrum (ATR, ZnSe) of nitroxide 2 (label: HSD-1-26).
Figure S37. HRMS-ESI (1% CH$_3$COONa in 3:1 (v/v) MeOH/H$_2$O) of nitroxide 2 (Label: HSD-1-1-15).

Figure S38. IR spectrum (ATR, ZnSe) of compound 2-H (label: HSD-1-1-36).
Figure S39. HRMS-EI (1% CH₃COONa in 3:1 (v/v) MeOH/H₂O) of compound 2-H (Label: HSD-1-1-36).
9. **Supporting References.**

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10. Cartesian Coordinates for UB3LYP/6-311G(d,p)+ZPVE Geometries of the Lowest Energy Conformations of Nitroxides 1 and 2.

Nitroxide 1, C2, Of11 (Table S4):

Stoichiometry  C12H14NO9(2)
Framework group  C2([C2(NO),X(C12H14O8)]
Deg. of freedom  51
Full point group  C2      NOp   2
Largest Abelian subgroup  C2      NOp   2
Largest concise Abelian subgroup  C2      NOp   2

Standard orientation:

| Number | Atomic Number | Atomic Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|--------|---------------|-------------|---------------|---------------|---------------|
| 1      | 6             | 0           | 0.030375      | 1.230842      | -0.508620     |
| 2      | 6             | 0           | 0.000000      | 0.663404      | -1.904304     |
| 3      | 6             | 0           | -0.000000     | -0.663404     | -1.904304     |
| 4      | 6             | 0           | -0.030375     | -1.230842     | -0.508620     |
| 5      | 1             | 0           | -0.001355     | 1.310298      | -2.769273     |
| 6      | 1             | 0           | 0.001355      | -1.310298     | -2.769273     |
| 7      | 7             | 0           | 0.000000      | 0.000000      | 0.315272      |
| 8      | 8             | 0           | 0.000000      | 0.000000      | -1.576706     |
| 9      | 6             | 0           | -1.218428     | 2.091651      | -0.206675     |
| 10     | 6             | 0           | 1.307612      | 2.077690      | -0.332340     |
| 11     | 6             | 0           | -1.307612     | -2.077690     | -0.332340     |
| 12     | 6             | 0           | 1.218428      | -2.091651     | -0.206675     |
| 13     | 8             | 0           | 1.405236      | 3.178877      | -0.809369     |
| 14     | 8             | 0           | -1.405236     | -3.178877     | -0.809369     |
| 15     | 8             | 0           | 2.268467      | 1.425864      | 0.317510      |
| 16     | 8             | 0           | -2.268467     | -1.425864     | 0.317510      |
| 17     | 8             | 0           | 1.064299      | 2.761591      | 0.935748      |
| 18     | 8             | 0           | -1.064299     | -2.761591     | 0.935748      |
| 19     | 8             | 0           | 3.519903      | 2.130805      | 0.454441      |
| 20     | 8             | 0           | -3.519903     | -2.130805     | 0.454441      |
| 21     | 6             | 0           | 3.063918      | 2.930520      | 1.504454      |
| 22     | 6             | 0           | -3.063918     | -2.930520     | 1.504454      |
| 23     | 6             | 0           | 3.933017      | 1.359197      | -0.528370     |
| 24     | 6             | 0           | -3.933017     | -1.359197     | -0.528370     |
| 25     | 1             | 0           | 3.063918      | 2.930520      | 1.504454      |
| 26     | 1             | 0           | -3.063918     | -2.930520     | 1.504454      |
| 27     | 1             | 0           | 4.171708      | 3.178877      | 1.004449      |
| 28     | 1             | 0           | -4.171708     | -3.178877     | 1.004449      |
| 29     | 1             | 0           | 4.71708       | 1.453864      | 1.004449      |
| 30     | 1             | 0           | -4.71708      | -1.453864     | 1.004449      |
| 31     | 1             | 0           | 2.410310      | 4.319182      | 0.600949      |
| 32     | 1             | 0           | -2.410310     | -4.319182     | 0.600949      |
| 33     | 1             | 0           | 1.880121      | 4.023952      | 2.280878      |
| 34     | 1             | 0           | -1.880121     | -4.023952     | 2.280878      |
| 35     | 1             | 0           | 3.369656      | 3.057295      | 1.009510      |
| 36     | 1             | 0           | -3.369656     | -3.057295     | 1.009510      |

Rotational constants (GHE): 0.378394 0.270209 0.194077
Standard basis: 6-311G(d,p) (5D, 7F)

SCF Done: E(UB3LYP) = -1197.7046172 A.U. after 4 cycles
Conv. = 0.0015000
V/T = 2.0032
<Sx> = 0.0000 <Sy> = 0.0000 <Sz> = 0.5000 <S**2> = 0.7537 S = 0.5019

Optimization completed.
-- Stationary point found.
Nitroxide 2 C2, Rot8 (Table S5): geometry optimization starting from X-ray structure geometry

| Center | Atomic Number | Atomic Number | X     | Y     | Z     |
|--------|---------------|---------------|-------|-------|-------|
| 1      | 6             | 0             | 0.000000 | 1.244858 | 0.019612 |
| 2      | 6             | 0             | 0.012295 | 0.664381 | -1.373934 |
| 3      | 6             | 0             | -0.012295 | -0.664381 | -1.373934 |
| 4      | 6             | 0             | 0.000000 | -1.244858 | 0.019612 |
| 5      | 1             | 0             | 0.017185 | 1.310765 | -2.238503 |
| 6      | 1             | 0             | -0.017185 | -1.310765 | -2.238503 |
| 7      | 0             | 0             | 0.000000 | 0.000000 | 0.832110 |
| 8      | 0             | 0             | -1.240824 | 2.081815 | 0.367091 |
| 9      | 1             | 0             | 1.240824 | -2.081815 | 0.367091 |
| 10     | 1             | 0             | 0.017185 | -1.310765 | 2.238503 |
| 11     | 1             | 0             | -0.017185 | 1.310765 | -2.238503 |
| 12     | 6             | 0             | 0.000000 | -1.240824 | 0.019612 |
| 13     | 6             | 0             | 1.273538 | 3.152807 | 0.842562 |
| 14     | 6             | 0             | -1.273538 | -3.152807 | 0.842562 |

Rotational constants (GHZ): 0.394073 0.151922 0.124088

```plaintext
S44
```