

Supporting Information for:

**^2H , ^{15}N -Substituted Nitroxides as Sensitive Probes
for Electron Paramagnetic Resonance Imaging**

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SUPPLEMENTAL METHODS

EPR Spectroscopy. EPR spectra were recorded on an X-band spectrometer at the following settings: microwave power, 20 mW; microwave frequency, 9.55 GHz; field set, 3335 G for ^{14}N or 3324 G for ^{15}N ; modulation frequency, 1 kHz; modulation amplitude, 0.008 – 0.5 G; field sweep, 4 G at 13.3 G min^{-1} . These settings encompassed the central spectral peak of the ^{14}N spectrum, or the first spectral peak of the ^{15}N spectrum. EWWIN software was used to digitize spectral data.

EPR Spectral Linewidth Measurements. To assess the effect of O_2 on the EPR linewidths of the nitroxides, deionized H_2O ($18.3 \text{ M}\Omega\cdot\text{cm}$ resistivity) was sparged with N_2 , equilibrated with air, or sparged with O_2 at 24°C for 30 min, to yield samples containing O_2 at 0.003 mM, 0.25 mM and 1.25 mM (O_2 -saturated; 18), respectively. Stock solutions (10 mM) of the K^+ salt of nitroxide **2** or **7** were diluted 500-fold into the gas-equilibrated H_2O samples to a final nitroxide concentration of 20 μM . Each solution was transferred into a flat quartz EPR cell previously purged with the appropriate gas. The quartz cell was sealed, and immediately positioned in the EPR spectrometer. Duplicate spectroscopic measurements on the samples were performed in random order with a modulation amplitude of 0.5 G. Reported linewidths are the peak-to-peak width of the central spectral line of **2**, and the first spectral line of **7**.

SUPPLEMENTAL FIGURES

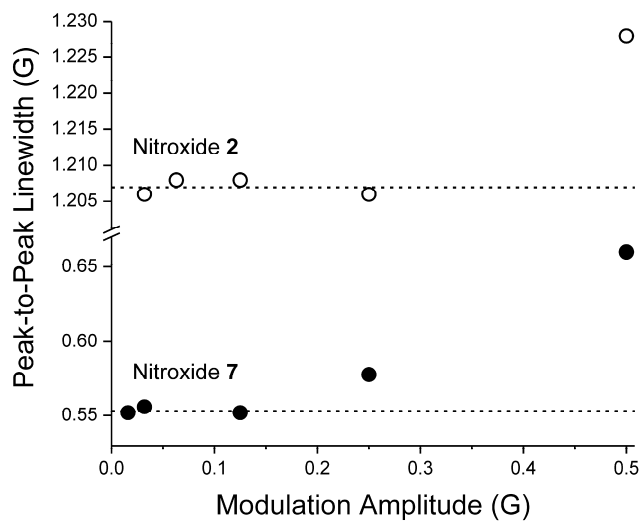


Figure S1. Effect of magnetic field modulation amplitude on EPR spectral linewidth of nitroxides **2** and **7**. Peak-to-peak linewidths were measured for nitroxides **2** and **7** at different values of the modulation amplitude in the range 0.008 – 0.5 G. Each point is the average of two measurements. Dashed lines indicate the limiting linewidths attained at low modulation amplitudes: 1.207 ± 0.001 G for **2** and 0.553 ± 0.002 G for **7**. The K^+ salt of each nitroxide was used at 20 μM in air-equilibrated H_2O .

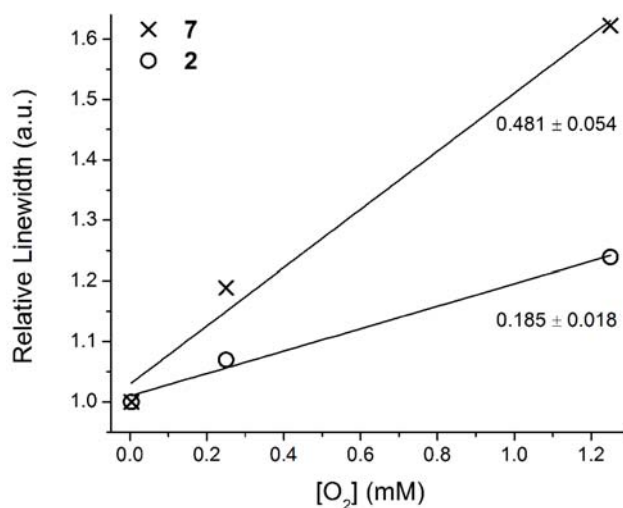


Figure S2. Relative linewidths of nitroxides **2** and **7** at different O_2 concentrations in water. For each nitroxide, the linewidths were normalized to the value measured at 0.003 mM O_2 (in N_2 -sparged water). The measurements were identical to those in Figure 2 of the main text, except that the modulation amplitude was increased to 0.5 G. Solid lines are least-squares fits of the data; the slope of each line is indicated on the graph.

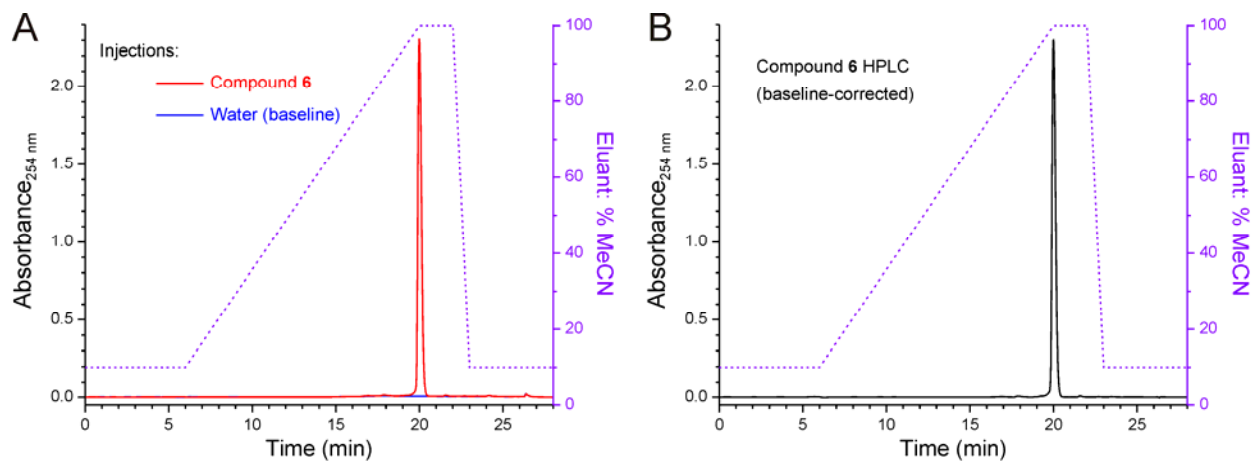


Figure S3. Reverse-phase HPLC analysis of compound **6**. A binary eluant system was used: water containing 0.1% v/v F_3CCO_2H , and acetonitrile. (A) HPLCs recorded after injection of water (blue) and after injection of compound **6** (red). Composition of the eluant (% MeCN) is indicated by the dashed line (violet). (B) Baseline-corrected HPLC of compound **6**, obtained by subtracting the baseline trace (blue) from the analytical trace (red) of panel (A). A C-18 column was used for the analysis.