

Supporting Information

Diarylnitroxide Diradicals: Low-Temperature Oxidation of Diarylamines to Nitroxides

Andrzej Rajca, Matthew Vale, Suchada Rajca*

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588-0304

E-mail: arajca1@unl.edu

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1. Materials and general procedures.

Materials. Toluene was distilled from sodium in a nitrogen atmosphere. Chloroform-*d* (CDCl₃) for use in oxidation experiments and in NMR experiments was dried over 4-Å molecular sieves. Dichloromethane, GR grade, was used as purchased. Ammonium formate was recrystallized from ethanol and triphenylphosphine was recrystallized from acetone prior to use. *meta*-Chloroperbenzoic acid (*m*-CPBA) was recrystallized from dichloromethane and diethyl ether, and then stored at -20 °C. All major chemicals and perdeuterated solvents were obtained from commercial sources and used without further purification. Vacuum lines (10⁻³ Torr) were used for all air sensitive procedures. Standard techniques for synthesis under inert atmosphere, using Schlenk glassware, vacuum lines, and gloveboxes were employed.

Dimethyldioxirane (DMDO). Solution of DMDO in acetone (ca. 0.05–0.10 M) was prepared as reported previously.^{S1} Extraction and concentration into a solution in dichloromethane/acetone (~6:1, ca. 0.35–0.1 M) was carried out as reported in the literature.^{S2} Concentrations of DMDO were periodically determined by titrations carried out in duplicate with triphenylphosphine; molar ratio of unreacted phosphine to the corresponding oxide was determined by ¹H NMR spectroscopy.

Solutions of DMDO in acetone (ca. 0.05–0.10 M) were stored at -20 °C under a nitrogen atmosphere. Concentrated solutions of DMDO in dichloromethane/acetone (ca. 0.3 M) were either stored at -20 °C under a nitrogen atmosphere or were degassed three times using the pump and thaw method and stored frozen in liquid nitrogen under vacuum in a closed Schlenk vessel. The degassed DMDO solutions were carefully thawed and stored in an ice bath (0 °C) during all vacuum transfers. Concentrations of DMDO were periodically determined by titrations carried out in duplicate with triphenylphosphine. Two methods were used to determine concentration of DMDO in a degassed solution.

Titration of DMDO: method I. Chloroform-*d* (0.50 mL) was added to an NMR tube fitted with a Schlenk tap and degassed. A small portion of the DMDO solution was vacuum transferred, and then ¹H

NMR spectrum was recorded. The molar ratio of dichloromethane to acetone to DMDO ($\delta = 1.65$ ppm) was found to be 1 : 0.25 : 0.025. Triphenylphosphine (13.5 mg, 0.0515 mmol) was weighed into an oven dried and pre-weighed Schlenk vessel with a magnetic stirrer bar. After 5 min under vacuum, the weight of the vessel and contents were recorded. Dichloromethane (251.0 mg, 0.19 mL), and then DMDO in dichloromethane and acetone (30.0 mg) were vacuum transferred; after each transfer, the mass of the vessel and contents were recorded. The contents were stirred for 5 min at 0 °C, and then solvent was removed and ^1H NMR spectrum was recorded. The ratio of triphenylphosphine to the converted corresponding oxide was 6.14 : 1.00; using the estimate of density for the transferred DMDO solution ($d = 1.2$), a concentration of 0.29 M was determined. Another titration performed in the same manner gave a concentration of 0.31 M.

Titration of DMDO: method II. Dichloromethane (0.025 mL) was vacuum transferred into a home-made SQUID sample tube. The SQUID sample tube is described in the Experimental Section, main text. (The volume was determined using the calibration in which 1 mm in height corresponds to 0.0125 mL). DMDO in dichloromethane and acetone solution was then vacuum transferred (0.025 mL). Under a gentle stream of nitrogen triphenylphosphine in chloroform-*d* (0.094 M, 0.3 mL, 0.0282 mmol) was added by syringe, and then the walls of the vessel were washed with a further portion of chloroform-*d* (0.3 mL). The reaction mixture was mixed thoroughly at 0 °C for 5 min using a magnetic stirrer bar, and then ^1H NMR spectra recorded. The concentration of the DMDO solution was found to be 0.27 M.

NMR spectroscopy. Routine NMR spectra were obtained on commercial spectrometers (^1H , 500 MHz and 400 MHz) using chloroform-*d* (CDCl_3) as solvent. The chemical shift references were as follows: (^1H) CDCl_3 , 7.260 ppm (CHCl_3); (^{13}C) CDCl_3 , 77.0 ppm (CDCl_3). Typical 1D FID was subjected to exponential multiplication with an exponent of 0.3 Hz (for ^1H) and 1.0 Hz (for ^{13}C).

Other routine analyses. IR spectra were obtained using an FT-IR instrument, equipped with an ATR sampling accessory. A few drops of the compound in CH_2Cl_2 were applied to the surface of a ZnSe ATR plate horizontal parallelogram (45°). After the solvent evaporated, the spectrum was acquired.

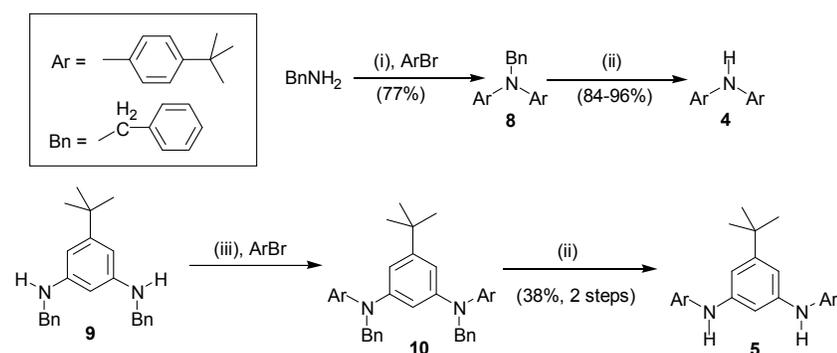
Routine MS analyses were carried out at the Nebraska Center for Mass Spectrometry. In FAB-MS data, 3-NBA is 3-nitrobenzyl alcohol and % RA is percent relative amplitude. ESI MS data were obtained on a time-of-flight mass spectrometer.

All melting points were obtained using a sealed tube under an atmosphere of argon.

Chromatographic separations. TLC grade silica gel was used for column chromatography. Preparative TLC plates (silica gel GF) were used. For selected separations, treated silica was prepared. Preparative TLC plates were treated 3–5% triethylamine in hexanes. After removal most of the solvents under a stream of nitrogen, the plates were heated at 100 °C for 30 min, and then evacuated in a vacuum dessicator over anhydrous calcium sulphate at 10 mmHg for 24 h. TLC grade silica (~50 g) for column chromatography was treated with 5% triethylamine in hexanes (500 mL). Solvents were removed under vacuo (10 mmHg) at 60 °C for 2 h, and then at 150–175 °C for 24 h. Treated silica was used when indicated below.

2. Preparation of amine **4** and diamine **5**, precursors to radical **1** and diradical **2** (Scheme S1).

Scheme S1.^a



^a Conditions: (i) Pd(OAc)₂ (5 mol %), DPPF (15 mol %), *t*-BuONa (3 equiv), ArBr (~10 equiv); (ii) ammonium formate (~15 equiv per monoamine), Pd/C (~0.2 equiv); (iii) Pd(OAc)₂ (4 mol %), (*t*-Bu)₃P (12 mol %), *t*-BuONa (3 equiv), ArBr (~20 equiv).

Bis(4-*tert*-butylphenyl)benzylamine 8. 4-*Tert*-butylbromobenzene (3.52 g, 16.5 mmol), benzylamine (161 mg, 1.50 mmol), *t*-BuONa (432 mg, 4.50 mmol), Pd(OAc)₂ (16.8 mg, 74.9 μmol), DPPF (125 mg, 0.225 mmol), and toluene (15 mL) were added in turn into an oven dried screw cap

Schlenk vessel (evacuated and back filled with dry nitrogen 2 times) in an atmosphere of nitrogen. After 18 h at 90–100 °C, the reaction mixture was allowed to attain room temperature. The usual aqueous workup with ammonium chloride (2 M) and extraction with ethyl acetate, gave a brown solid (3.67 g). Column chromatography (silica, 4% ethyl acetate in hexane), followed by recrystallization from chloroform and methanol, produced two crops of white crystals (430 mg, 77%) of the product. M.p. 132–134 °C; ¹H NMR (500 MHz, chloroform-*d*): δ = 7.361 (d, *J* = 7.6, 2 H), 7.299 (t, *J* = 7.5, 2 H), 7.210 (t, *J* = 7, 1 H), 7.238 (d, *J* = 9, 4 H), 6.985 (d, *J* = 9, 4 H), 4.958 (s, 2 H), 1.288 (s, 18 H); ¹³C NMR (125 MHz, chloroform-*d*): δ = 145.7, 143.8, 139.7, 128.5, 126.61, 126.46, 126.0, 120.0, 56.5, 34.1, 31.4; IR (ZnSe, cm⁻¹): 1604 (Ar); HR-FAB MS (3-NBA) cluster, *m/z* (ion type, % RA for *m/z* 200–650, deviation from the formula) at 372.2644 ([*M*+1]⁺, 40, 0.6 ppm for ¹³C₁¹²C₂₆¹H₃₃¹⁴N₁), 371.2602 ([*M*]⁺, 100, 2.9 ppm for ¹²C₂₇¹H₃₃¹⁴N₁).

Bis(4-*tert*-butylphenyl)amine 4. Using the general procedure for de-benzylation as described previously,^{S3} diarylamine **8** (72.7 mg, 0.196 mmol) was refluxed in ethanol for 2 h to give an off-white solid (65.0 mg). Recrystallization from hexane produced (54.0 mg, 96%) white crystals of secondary diarylamine **4**. From two other reactions, diarylamine **8** (501 mg), gave (316 mg, 84%) of secondary diarylamine **4**. M.p. 108–110 °C (lit.^{S4} m.p. 107–108 °C, under air); ¹H NMR (500 MHz, chloroform-*d*): δ = 7.295 (d, *J* = 8.6, 4 H), 7.019 (d, *J* = 8.6, 4 H), 5.571 (s (br), 1 H), 1.333 (s, 18 H).

5-*tert*-Butyl-N,N'-bis(4-*tert*-butyl-phenyl)benzene-1,3-diamine 5. Under an atmosphere of nitrogen, diamine **9** (379 mg, 1.10 mmol),^{S3} 4-*tert*-butylbromobenzene (4.26 g, 20.0 mmol), Pd(OAc)₂ (9.0 mg, 40.0 μmol), (*t*-Bu)₃P (24.3 mg, 0.120 mmol), and *t*-BuONa (96.1 mg, 1.00 mmol) were weighed in turn into an oven dried screw tap Schlenk vessel equipped with a magnetic stirrer bar. Toluene (10 mL) was syringed into the reaction vessel under a flow of nitrogen. After stirring at 100 °C for 24 h, the crude reaction mixture was allowed to cool, and then diluted with dichloromethane. The usual aqueous workup with ammonium chloride gave a yellow solid (4.20 g). Following the removal of the excess 4-*tert*-butylbromobenzene by vacuum distillation (100 mTorr/65–75 °C), diamine **10** was

obtained as an off-white solid (682 mg), which was used without further purification. ^1H NMR (500 MHz, chloroform-*d*): δ = 7.28–7.21 (m, 10 H), 7.178 (d, J = 9, 4 H), 6.915 (d, J = 9, 4 H), 6.680 (d, J = 2.0, 2 H), 4.875 (s, 4 H), 1.274 (s, 18 H), 1.141 (s, 9 H); ESI MS (0.3% CF_3COOH in dichloromethane), m/z (ion type (% RA for m/z 250–700)) at $[M+H]^+$ 609.5 (100), 610.4 (48), 611.4 (10); $[M+H]^+$, calcd. for $\text{C}_{44}\text{H}_{53}\text{N}_2$ at 609.4 (100), 610.4 (50), 611.4 (12).

Using the general procedure for de-benzylation, which was reported previously,^{S3} diamine **10** (34.7 mg, 57.0 μmol) was refluxed in ethanol for 4 h, to give a red/white solid (23.5 mg); the remaining diamine **10** (647 mg) from the previous step gave similar crude product (353 mg). Column chromatography (silica, toluene/hexanes, 40:60, v/v), followed by crystallization from ethanol, produced two crops of white crystals (170 mg, 38%) of secondary diamine **5**. M.p. 161–163 °C; ^1H NMR (400 MHz, chloroform-*d*): δ = 7.272 (d, J = 9, 4 H), 7.016 (d, J = 9, 4 H), 6.625 (d, J = 2, 2 H), 6.605 (t, J = 2, 1 H), 5.600 (br s, 2 H), 1.305 (s, 18 H), 1.273 (s, 9 H); ^{13}C NMR (100 MHz, chloroform-*d*): δ = 153.6, 144.2, 143.7, 140.6, 126.1, 117.9, 107.5, 103.0, 34.76, 34.12, 31.46, 31.28; IR (ZnSe, cm^{-1}): 3389 (NH), 1596 (Ar); LR-HR-FAB MS (3-NBA) cluster, m/z (ion type, % RA for m/z 200–1500, deviation from the formula) at 429.3252 ($[M+H]^+$, 57, 4.0 ppm for $^{12}\text{C}_{30}^{1}\text{H}_{41}^{14}\text{N}_2$), 428.3198 ($[M]^+$, 100, -1.4 ppm for $^{12}\text{C}_{30}^{1}\text{H}_{40}^{14}\text{N}_2$).

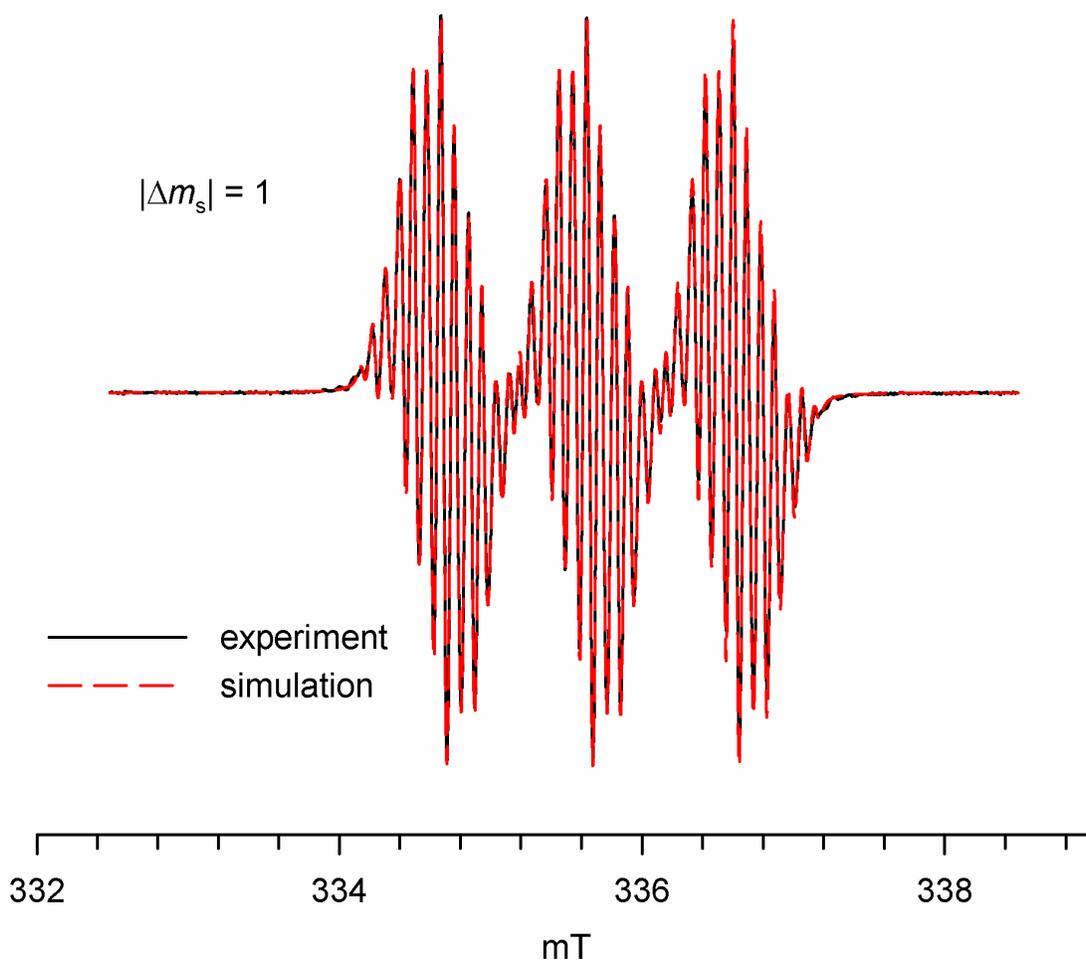


Figure S1A. EPR (X-band, 9.4229 GHz, diethyl ether) spectrum of 8×10^{-5} M nitroxide radical **1** (label: MV-686-38-1). Hyperfine splitting in mT (number of nuclei): $a_N = 0.965$ (1), $a_H = 0.185$ (4), $a_H = 0.080$ (4); 100% Lorentzian linewidth = 0.035 mT, $g \approx 2.005$, $R = 0.998$ (simulation label: simdata_mono5).

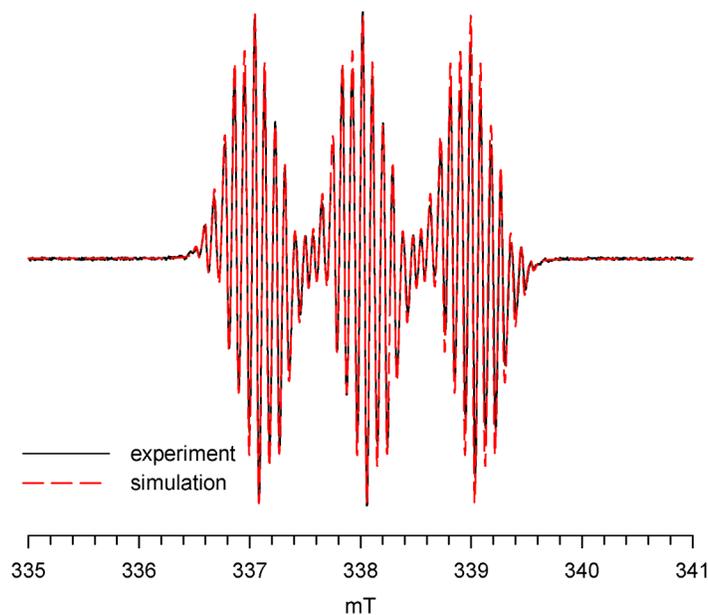


Figure S1B. EPR (X-band, 9.4900 GHz, toluene) spectrum of 7×10^{-5} M nitroxide radical **1** (label: MV-570-41-rest2-matt2). Hyperfine splitting in mT (number of nuclei): $a_N = 0.974$ (1), $a_H = 0.185$ (4), $a_H = 0.082$ (4); 100% Lorentzian linewidth = 0.036 mT, $g \approx 2.005$, $R = 0.989$.

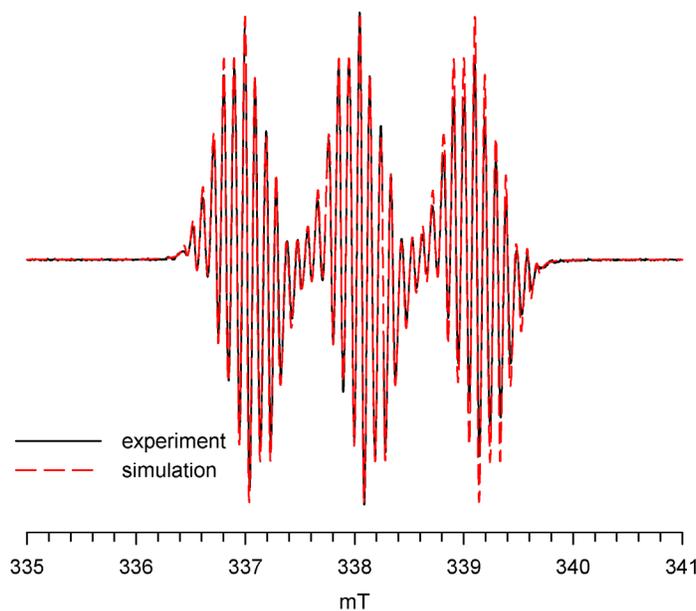


Figure S1C. EPR (X-band, 9.4891 GHz, ethanol) spectrum of 2×10^{-3} M nitroxide radical **1** (label: MV-570-41-rest2-Matt1). Hyperfine splitting in mT (number of nuclei): $a_N = 1.051$ (1), $a_H = 0.195$ (4), $a_H = 0.085$ (4); 100% Lorentzian linewidth = 0.033 mT, $g \approx 2.005$, $R = 0.989$.

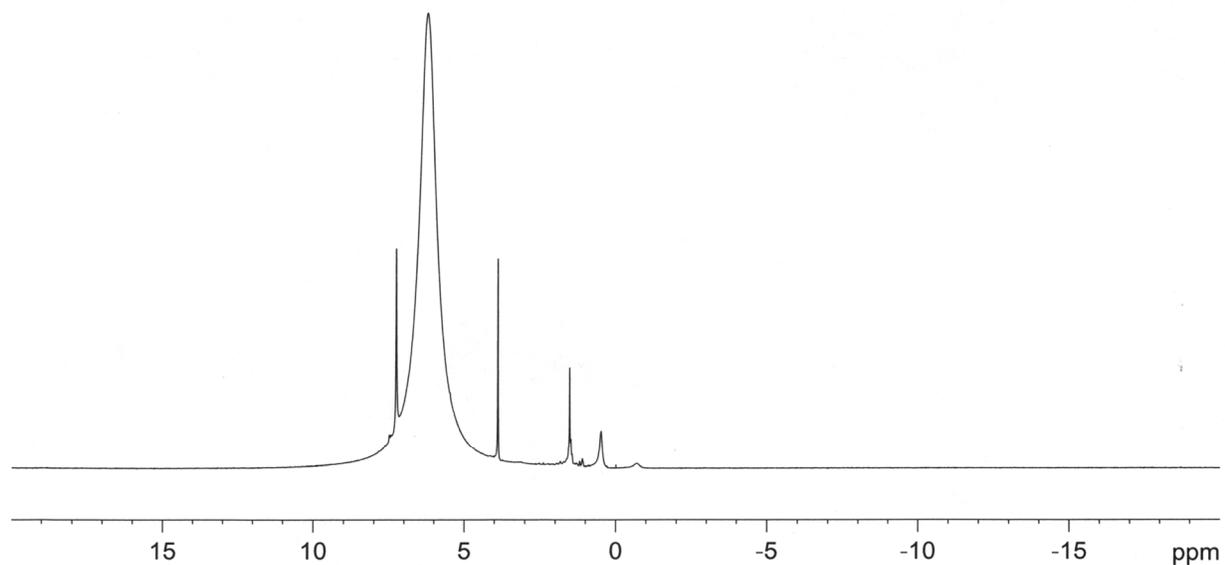


Figure S2. ¹H NMR (300 MHz, chloroform-*d*) spectrum of ~0.1 M nitroxide radical **1** (label: MV-266-27-1xst; NMR file: MV-5-monoradical). Chemical shifts are not corrected for bulk susceptibility. The singlet at 3.89 ppm corresponds to a residual solvent of crystallization (methanol); also, singlets corresponding to residual chloroform (7.27 ppm) and water (~1.5 ppm) are present.

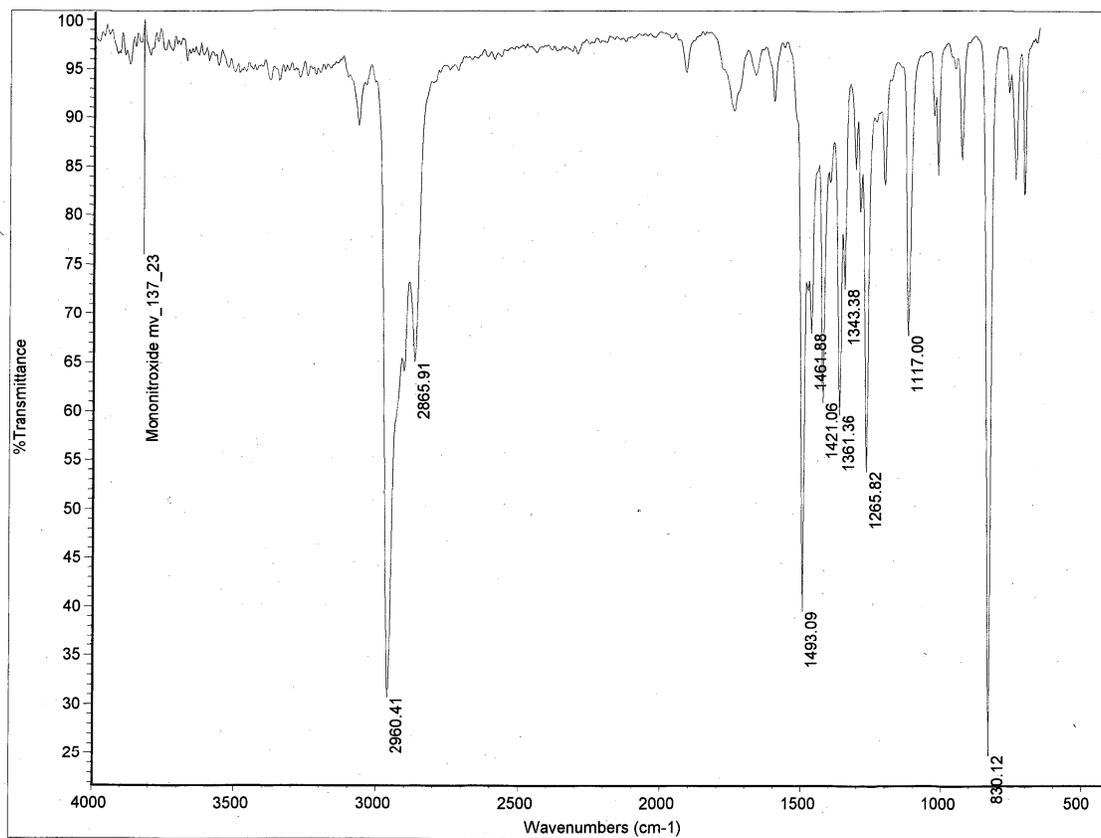


Figure S3. IR (ZnSe, cm⁻¹) spectrum for nitroxide radical **1** (label: Mononitroxide mv_137_23).

4. Detailed procedure for the EPR and EPR/SQUID/EPR monitoring of oxidation for amine 4, diamine 5, and aza[1₄]metacyclophane 6 (Figures S4A-C, 5A-C, and S6A-C).

Preparation of monoradical 1 (EPR monitoring). Dichloromethane (~0.1 mL) was added by vacuum transfer to amine 4 (2.5 mg, 1 equiv) in a 4-mm O.D. EPR quartz sample tube equipped with high-vacuum stopcock. Subsequently, DMDO (~0.25 M solution in dichloromethane, 0.04 – 0.05 mL, 2 – 2.5 equiv) was added. After stirring for 10 min at –95 °C, EPR spectrum for the faint orange reaction mixture was obtained at 140 K, as illustrated in Figure S4A (MV583-45-1). Subsequently, the reaction mixture was stirred –78 °C for several time consecutive intervals, and after each interval, EPR spectra were obtained, as selectively illustrated in Figures S4B and S4C (MV583-45-2 and MV583-45-8). Although the intense EPR spectra were obtained, the quantitative integration was not carried out because the reaction mixture was inhomogeneous with a precipitate above the orange solution. (The entire sample could not be contained in the EPR cavity.) After recording the EPR spectra, the sample tube was re-attached to vacuum line, and the reaction mixture was concentrated at –78 °C (~2 h). ¹H NMR (500 MHz, CDCl₃) spectrum (label: MV583-45-1) showed a broad peak for the *tert*-butyl group of the monoradical and sharp peaks 1.1 – 1.4 ppm region for the *t*-Bu groups of the diamagnetic byproducts, with relative integration of 3:1.

Preparation of diradical 2 (EPR/SQUID/EPR monitoring). Dichloromethane (~0.1 mL) was added by vacuum transfer to diamine 5 (2.5 mg, 1 equiv) in a SQUID sample tube. Subsequently, DMDO (~0.27 M solution in dichloromethane, ~0.1 mL, ~4.5 equiv) was added. After stirring for 2 h at –78 °C, EPR spectra for the red brown, homogeneous reaction mixture were obtained at 140 K, as illustrated in Figure S5A (MV559-32-3). After recording the EPR spectra, the SQUID sample tube was re-attached to vacuum line, and the reaction mixture was concentrated at –78 °C until the volume decreased to about 0.08 mL; subsequently, the sample tube was flame sealed. The sample tube, which was kept in liquid nitrogen, was transferred to a helium filled glove bag, and then rapidly inserted (<15 s) into the sample chamber of SQUID magnetometer at 10 K. The first set of magnetic data, obtained without melting the matrix in the 1.8–150 K range, is shown in Figure S5B (label: MV559r1G).

Following the magnetic measurements, the sample tube was rapidly withdrawn, and then EPR spectra were obtained as illustrated in Figure S5C (label: MV559-32-5).

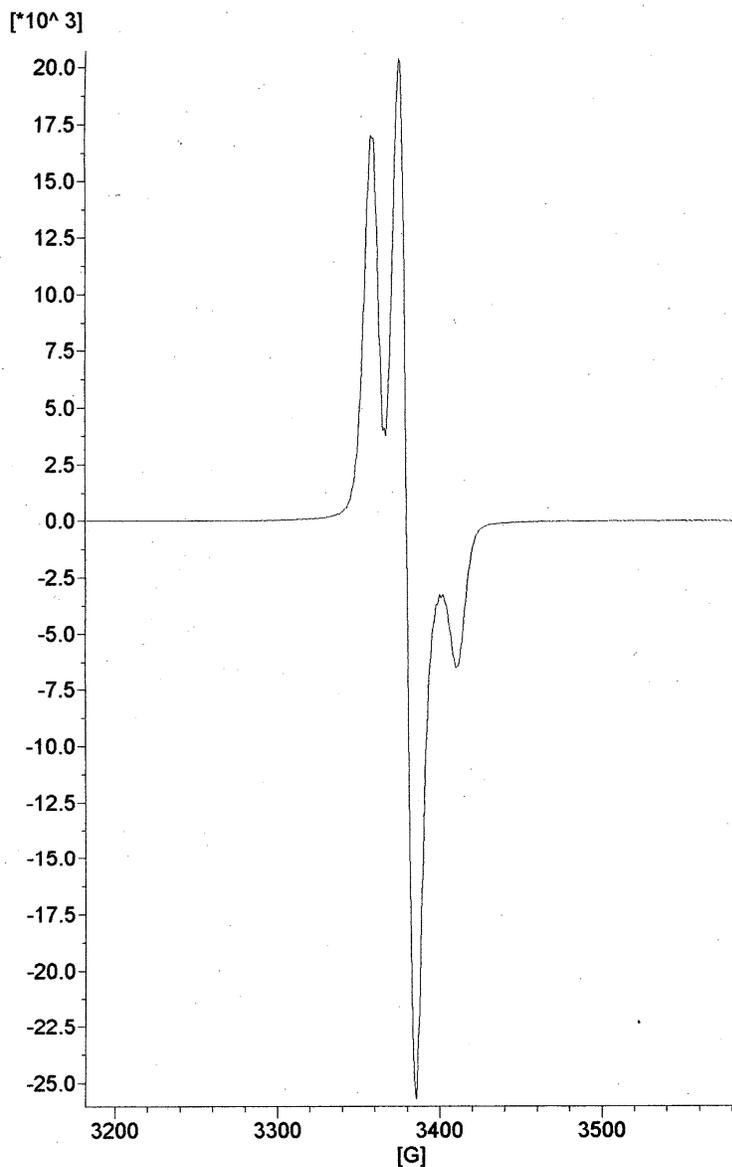
For another sample, which was prepared in an EPR tube and following similar procedure to that outlined for the EPR/SQUID/EPR sample above, except that the oxidation was carried out at $-90\text{ }^{\circ}\text{C}$, similar EPR spectra were obtained as illustrated in Figure 5, main text (label: MV562-33-6 and MV562-33-8). The initial concentration of the diamine was $\sim 30\text{ mM}$.

Attempted preparation of tetraradical 3 (EPR/SQUID/EPR monitoring). Dichloromethane ($\sim 0.05\text{ mL}$, $\sim 4\text{-mm}$ height) was added by vacuum transfer to aza[14]metacyclophane **6** (2.60 mg, 1 equiv) in a SQUID sample tube. The mixture was briefly stirred at $-95\text{ }^{\circ}\text{C}$, and then DMDO ($\sim 0.32\text{ M}$ solution in dichloromethane, $\sim 0.15\text{ mL}$, $\sim 16\text{-mm}$ height, ~ 10 equiv) was added by vacuum transfer. After mixing for 3 h at $(-90)\text{--}(-95)\text{ }^{\circ}\text{C}$, the first set of EPR spectra at 140 K for red brown reaction mixture were obtained. After additional 1.5 h at $-90\text{ }^{\circ}\text{C}$, the second set of EPR spectra was obtained as illustrated in Figure S6A (MV610/612-05-2). After recording the EPR spectra, the sample tube was re-attached to vacuum line, and the reaction mixture was concentrated at $-78\text{ }^{\circ}\text{C}$ until the volume decreased to about 0.08 mL; subsequently, the sample tube was flame sealed. The SQUID sample tube, which was kept in liquid nitrogen, was transferred to a helium filled glove bag, and then rapidly inserted ($<15\text{ s}$) into the sample chamber of SQUID magnetometer at 10 K. The first set of magnetic data, obtained without melting the matrix in the 1.8–150 K range, is shown in Figure S6B (label: MV612r1F). Following the magnetic measurements, the sample tube was rapidly withdrawn, and then EPR spectra were obtained as illustrated in Figure S6C (label: MV610/612-05-9).

For another sample, which was prepared in an EPR tube and following similar procedure to that outlined for the EPR/SQUID sample above, similar EPR spectra were obtained as illustrated in Figure S7 (label: MV608-03-7).



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Figure S4A. EPR (X-Band, $\nu = 9.485$ GHz, 140 K) spectra of the reaction mixture for generation of nitroxide radical **1** in CH_2Cl_2 ((label: MV583-45-1). Amine **4** was reacted with DMDO (2 – 2.5 equiv) for 10 min at 178 K.

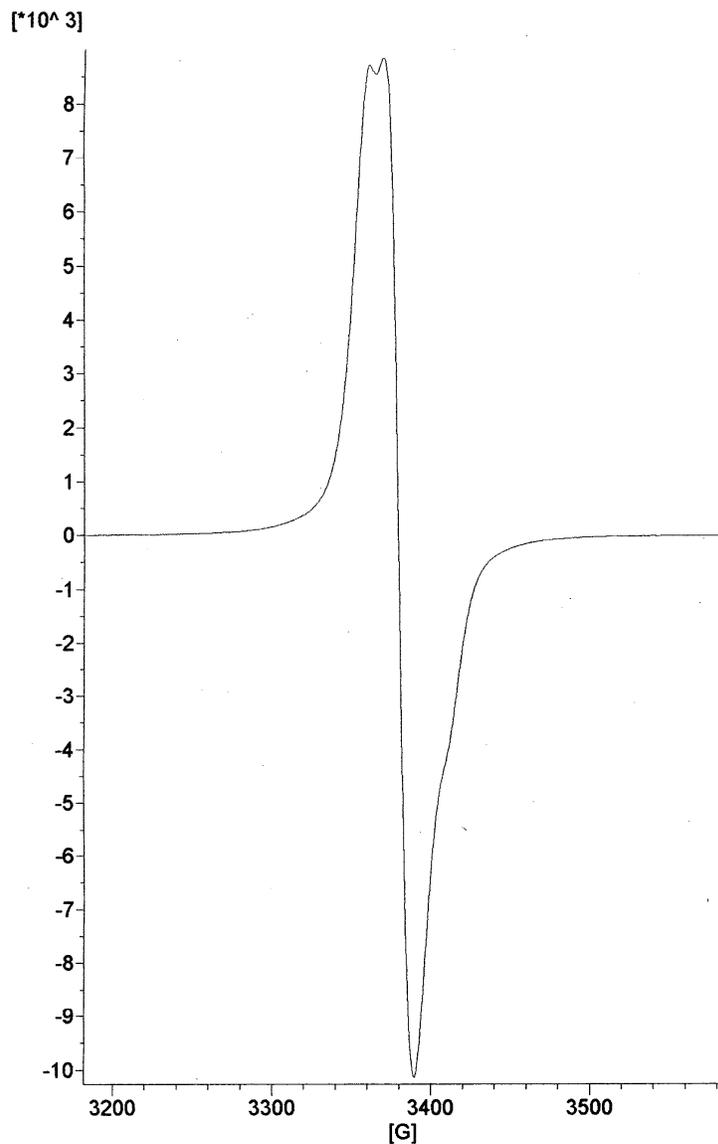
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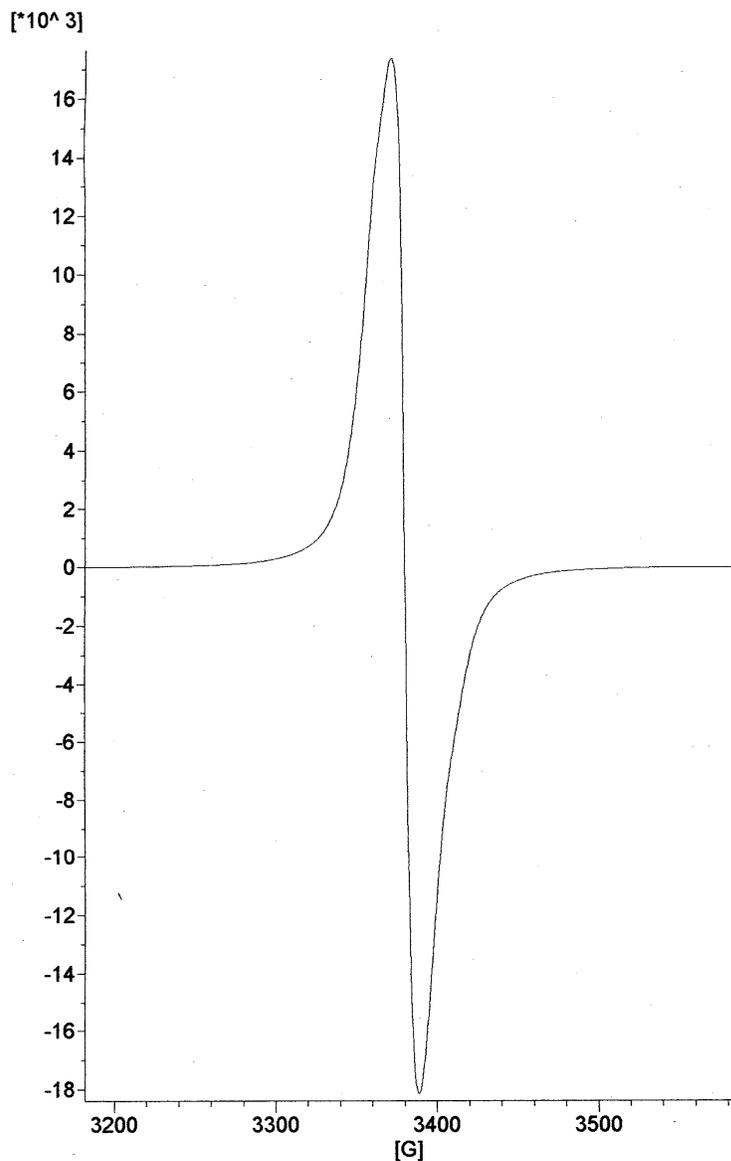


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Figure S4B. EPR (X-Band, $\nu = 9.487$ GHz, 140 K) spectrum of the reaction mixture for generation of nitroxide radical **1** in CH_2Cl_2 (label: MV583-45-2). Amine **4** was reacted with DMDO (2 – 2.5 equiv) for 10 min at 178 K, and then for 10 min at 195 K.



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Figure S4C. EPR (X-Band, $\nu = 9.488$ GHz, 140 K) spectrum of the reaction mixture for generation of nitroxide radical **1** in CH_2Cl_2 ((label: MV583-45-8). Amine **4** was reacted with DMDO (2 – 2.5 equiv) for 10 min at 178 K, and then for 110 min at 195 K. (Significant amount precipitate was observed.)

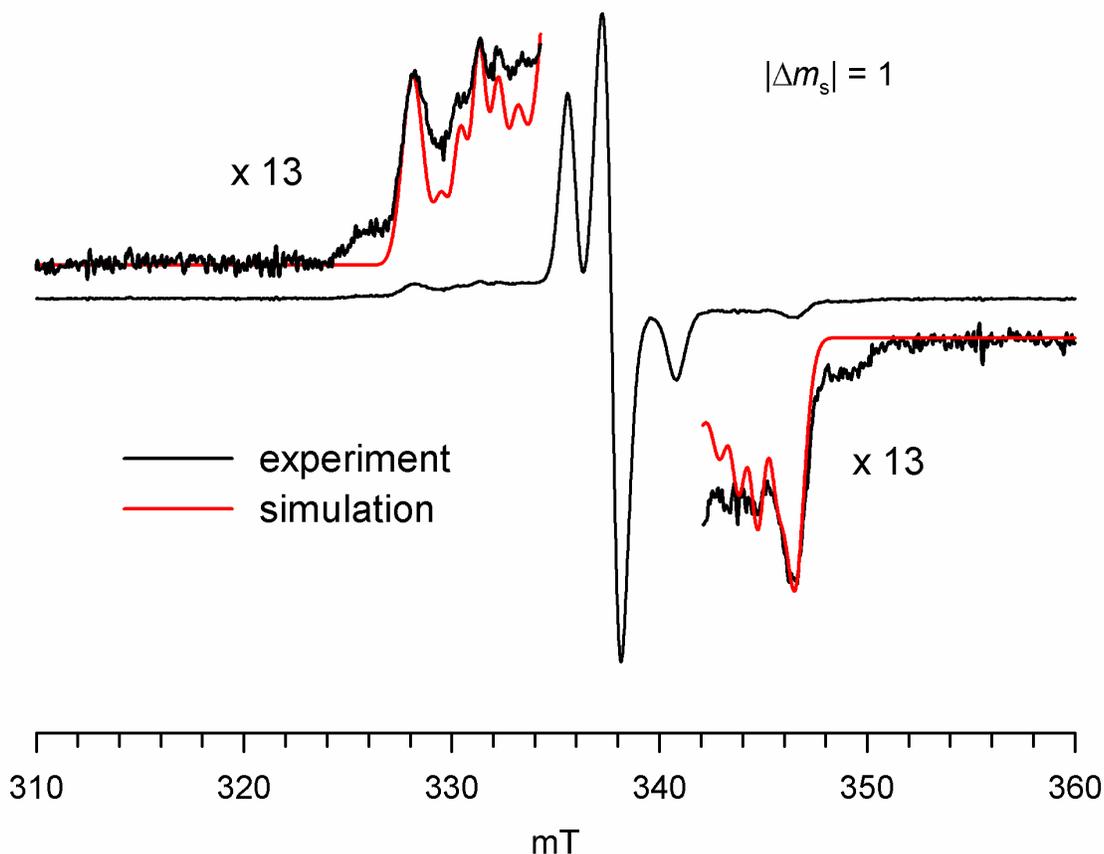


Figure S5A. EPR (X-Band, $\nu = 9.4763$ GHz, 140 K) spectra of the reaction mixture for generation of nitroxide diradical **2** in CH_2Cl_2 ((label: MV559-32-3). Diamine **5** was reacted with DMDO (4.5 equiv) for 2 h at 195 K. Based upon double integration of the spectrum, the side bands and the center peaks (334.3 – 341.8 mT) correspond have relative intensities of 0.3 and 0.7 respectively. The simulation parameters for the $S = 1$ state are: $|D/hc| = 8.6 \times 10^{-3} \text{ cm}^{-1}$, $|E/hc| = 1.3 \times 10^{-3} \text{ cm}^{-1}$, $|A_{yy}/2hc| = 8.5 \times 10^{-4} \text{ cm}^{-1}$, $g_x \approx 2.005$, $g_y = 2.0028$, $g_z = 2.0072$, Gaussian line ($L_x = 0.8$, $L_y = 0.65$, $L_z = 1.0$ mT). The most outer side bands correspond to the $S = 1$ state with the greater $|D/hc| = 1.10 \times 10^{-2} \text{ cm}^{-1}$ (simulation not shown). The center lines correspond to an $S = \frac{1}{2}$ product. Following these EPR spectra, the magnetic data (Figure S5B) were obtained.

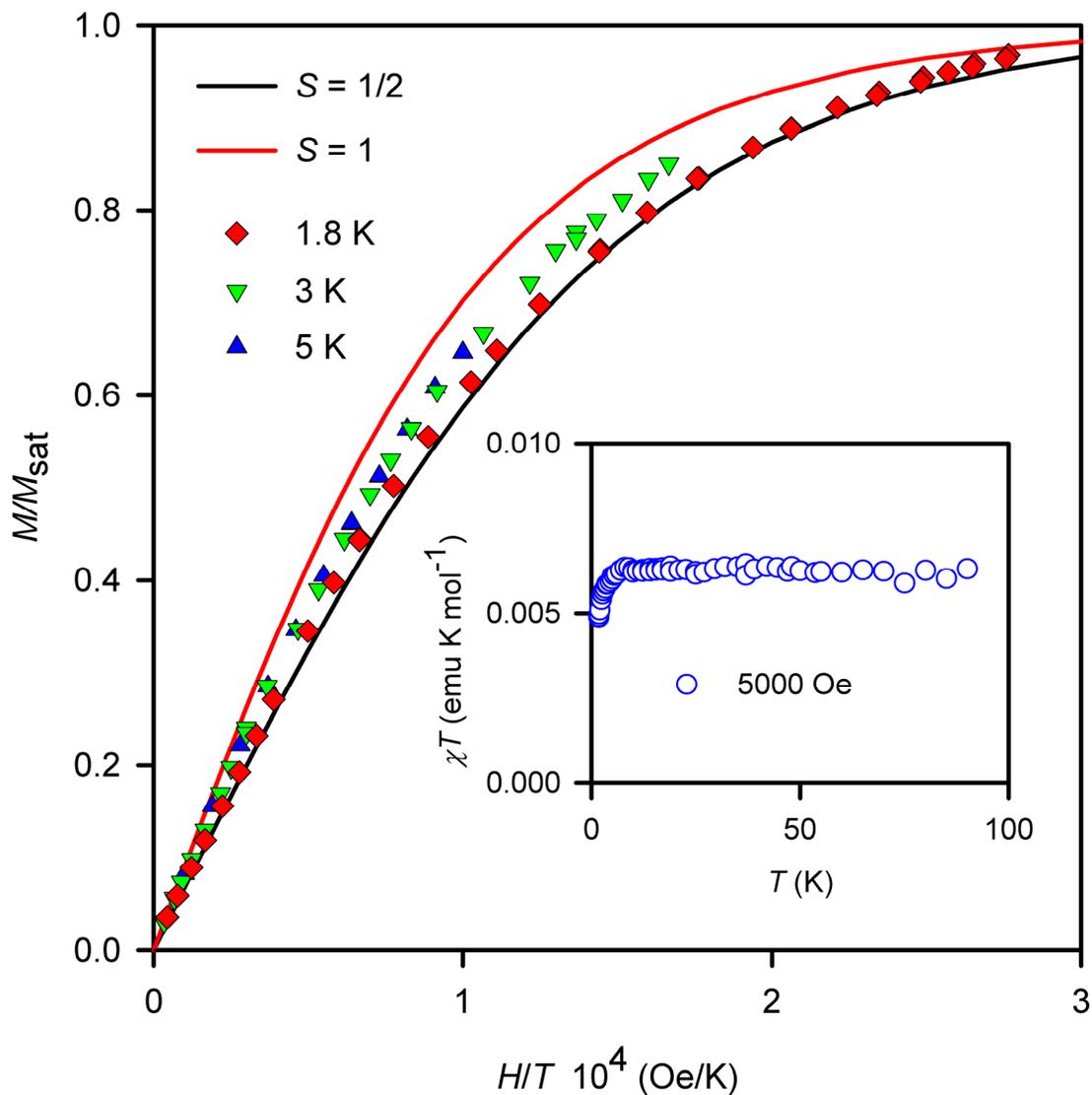


Figure S5B. SQUID magnetic data (label: MV559r1G) for the reaction mixture for generation of nitroxide diradical **2** in CH_2Cl_2 , following EPR spectra in Figure S5A. Main and inset plots: M/M_{sat} vs. H/T and χT vs. T , with $M_{\text{sat}} \approx 0.006 \mu_{\text{B}}$, $S \approx 0.5 - 0.8$, and $\chi T \approx 0.006 \text{ emu K mol}^{-1}$.

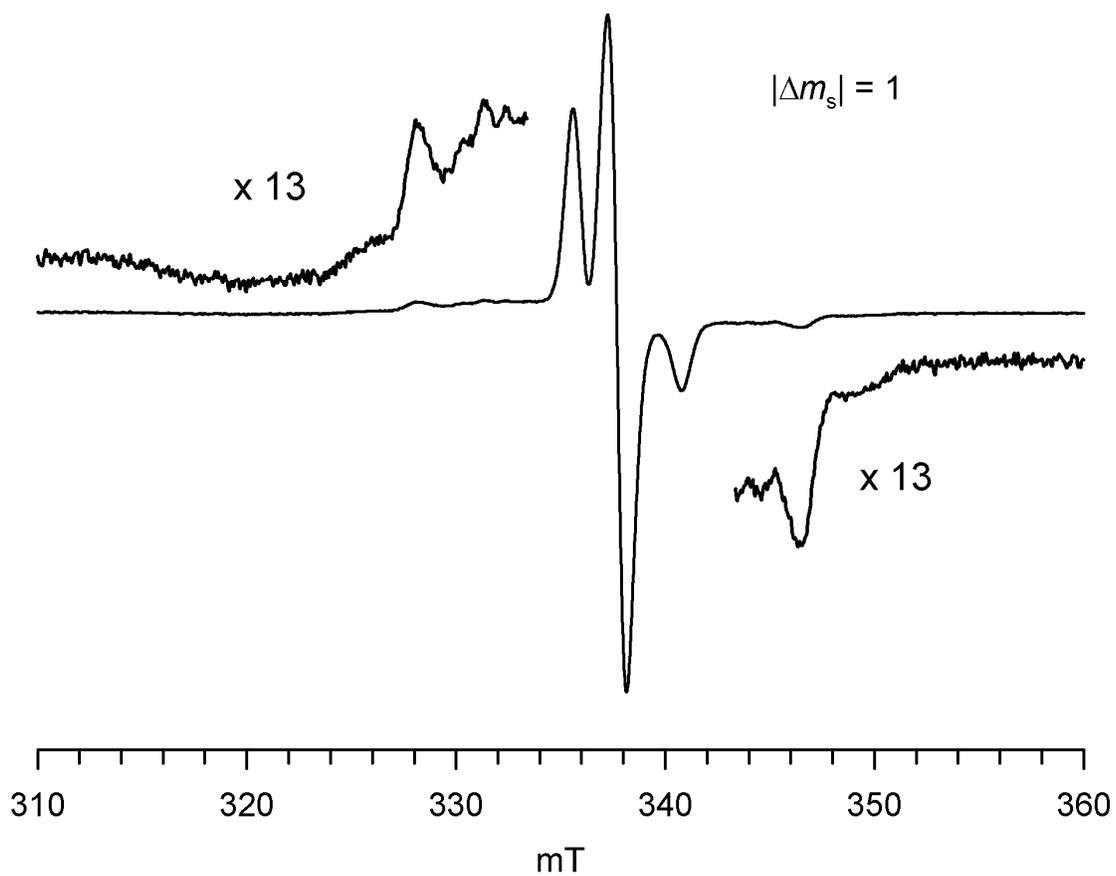


Figure S5C. EPR (X-Band, $\nu = 9.4764$ GHz, 140 K) spectra of the reaction mixture for generation of nitroxide diradical **2** in CH_2Cl_2 (label: MV559-32-5), following the magnetic data in Figure S5B. Based upon double integration of the spectrum, the side bands and the center peaks (334.3 – 341.8 mT) correspond have relative intensities of 0.3 and 0.7 respectively.

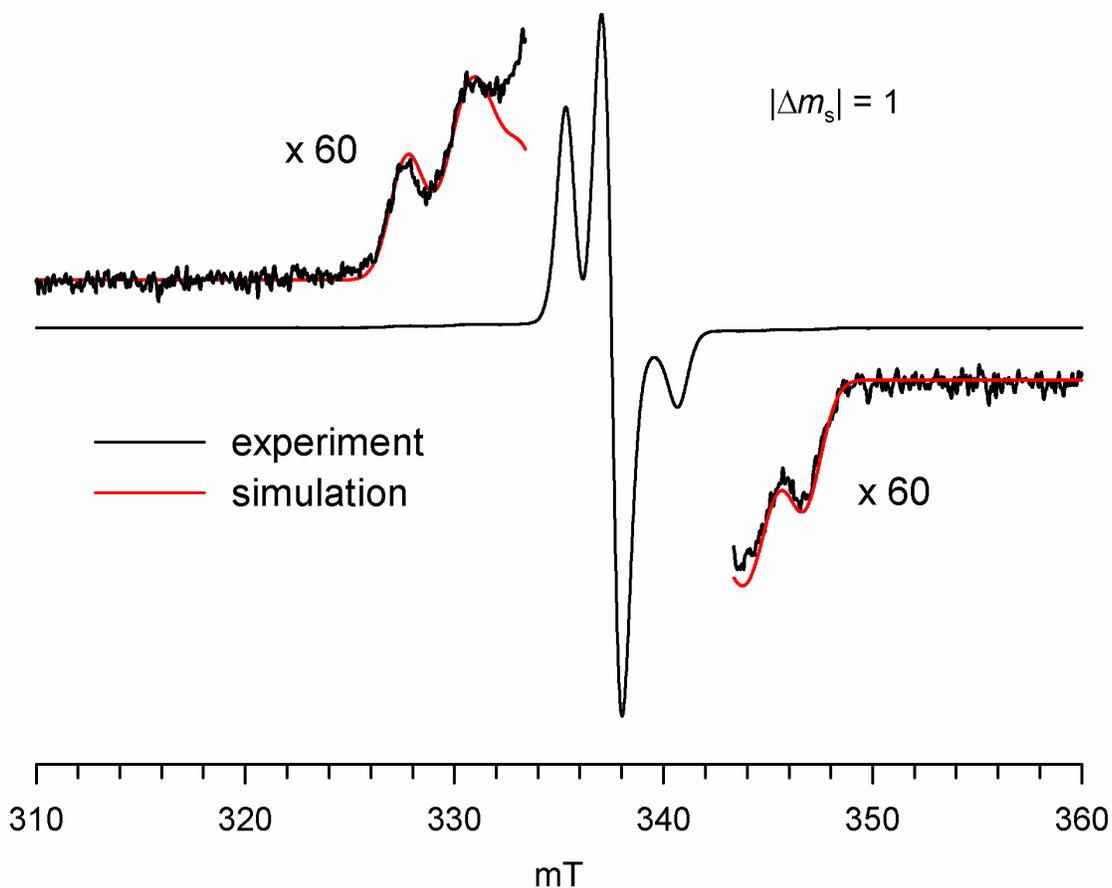


Figure S6A. EPR (X-Band, $\nu = 9.4710$ GHz, 140 K) spectra of the reaction mixture of attempted generation of nitroxide tetradical **3** in CH_2Cl_2 . Aza[1₄]metacyclophane **6** was reacted with DMDO (11 equiv) for 1.5 h at 183 K (label: MV610-05-2). The side bands were simulated with the following parameters for the $S = 1$ state: $|D/hc| = 8.9 \times 10^{-3} \text{ cm}^{-1}$, $|E/hc| = 1.15 \times 10^{-3} \text{ cm}^{-1}$, $|A_{yy}/2hc| = 0.0 \times 10^{-4} \text{ cm}^{-1}$, $g_x \approx 2.005$, $g_y = 2.0055$, $g_z = 2.0065$, Gaussian line ($L_x = 2.0$, $L_y = 2.2$, $L_z = 1.6$ mT) (label: SM610-2). The center lines correspond to an $S = \frac{1}{2}$ product. Following these EPR spectra, the magnetic data (Figure S6B) were obtained.

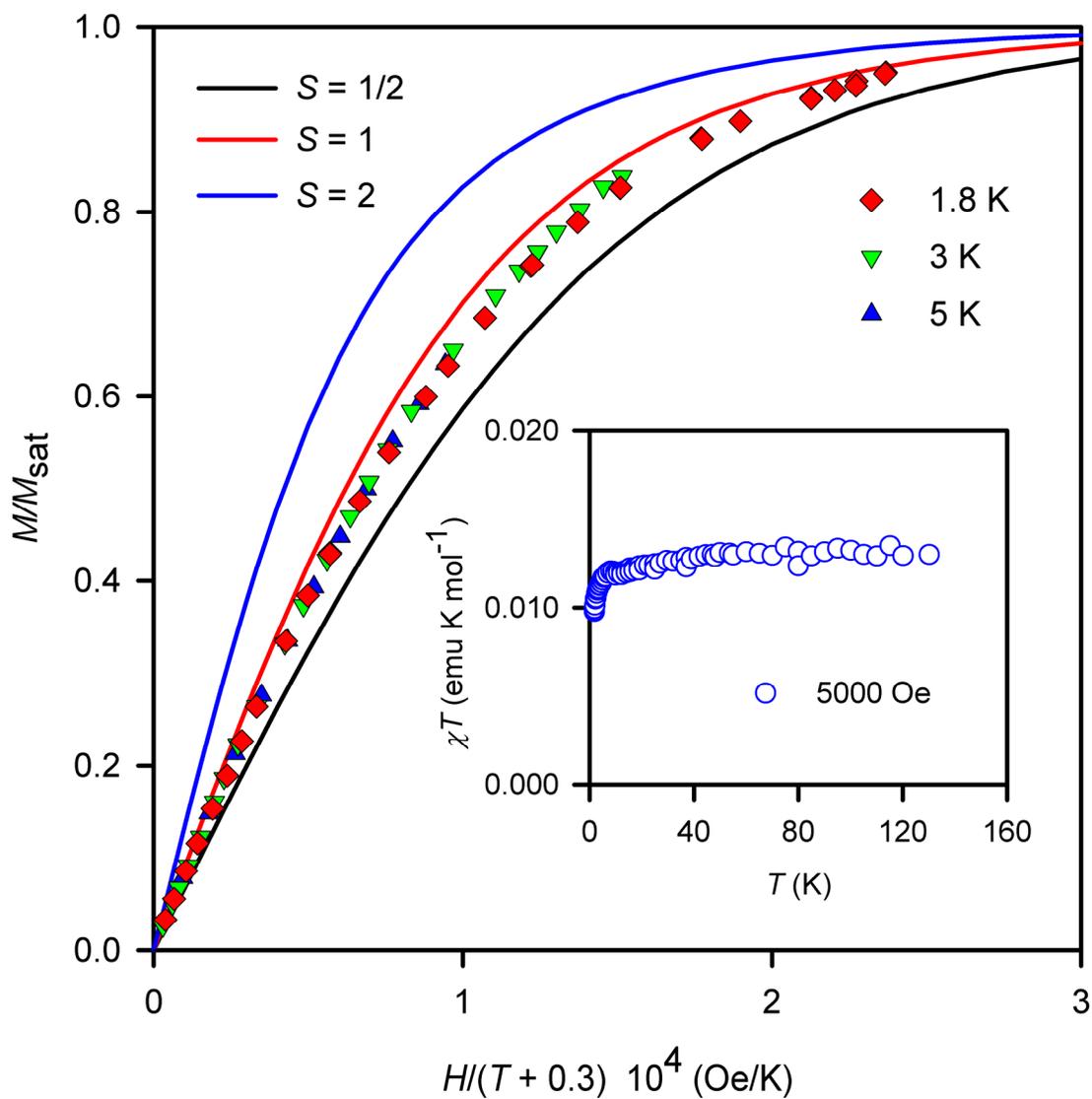


Figure S6B. SQUID magnetic data (label: MV612r1F) for the reaction mixture of attempted generation of nitroxide tetraradical **3** in CH_2Cl_2 , following EPR spectra in Figure S6A. Main and inset plots: M/M_{sat} vs. $H/(T - \theta)$ and χT vs. T , with $\theta \approx -0.3$ K, $M_{\text{sat}} \approx 0.006 \mu_{\text{B}}$, $S \approx 0.8$, and $\chi T \approx 0.013$ emu K mol $^{-1}$.

1.

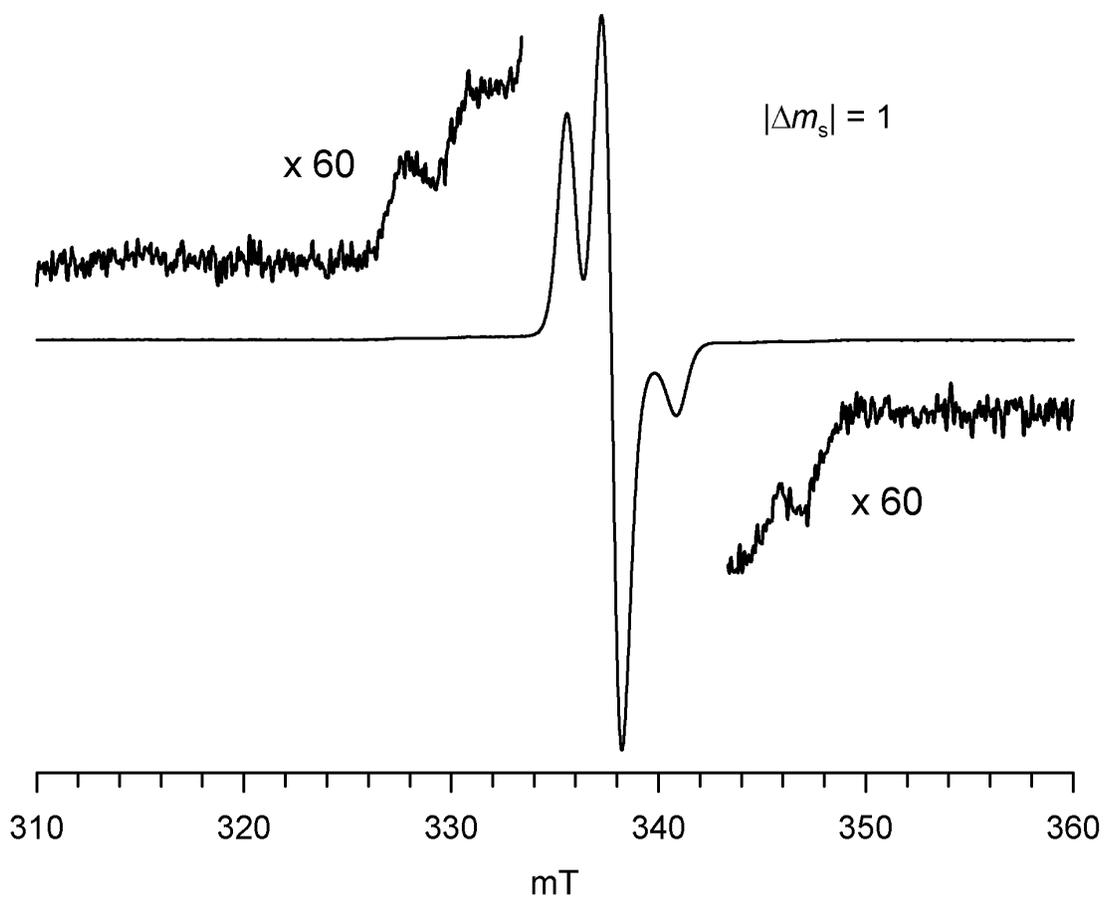


Figure S6C. EPR (X-Band, $\nu = 9.4771$ GHz, 140 K) spectra of the reaction mixture of attempted generation of nitroxide tetradical **3** in CH_2Cl_2 (label: MV610-05-9), following the magnetic data in Figure S6B.

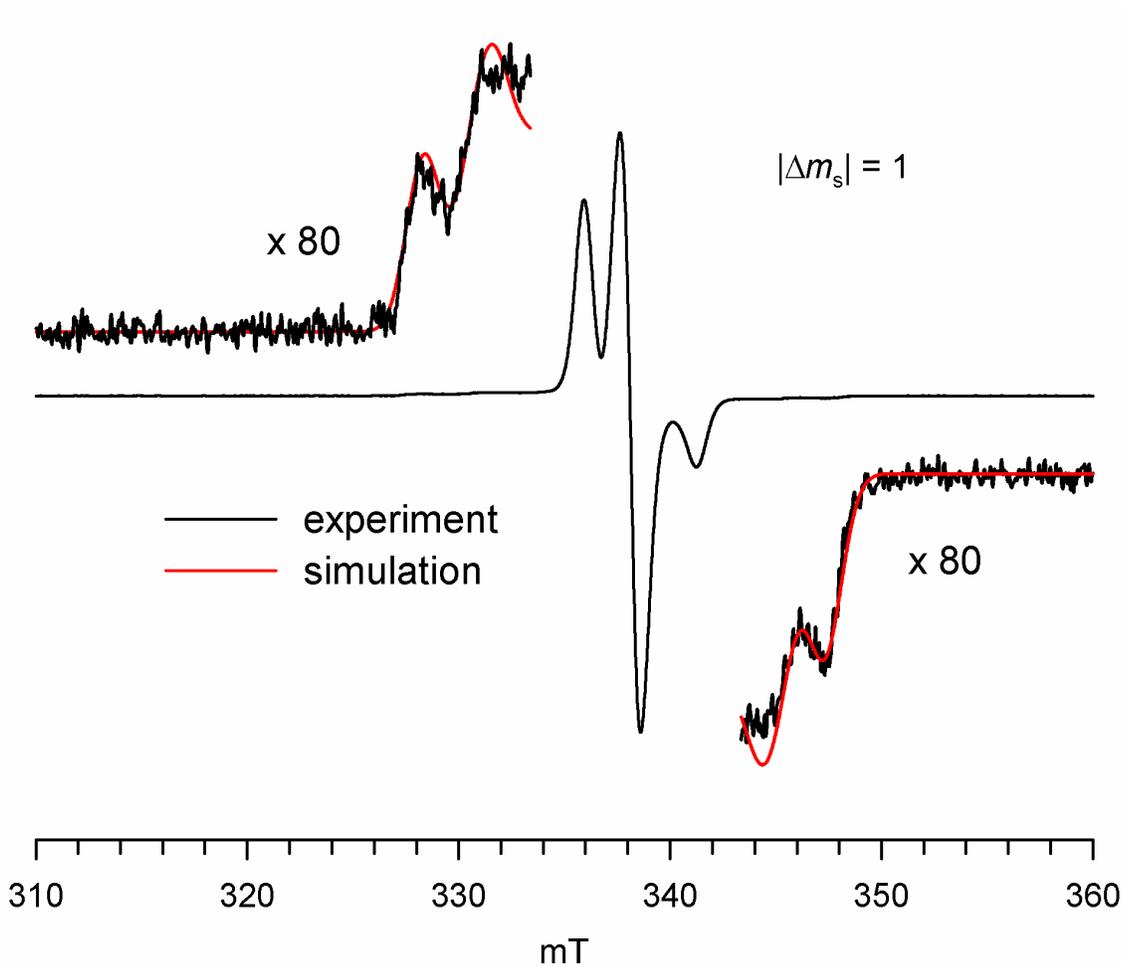


Figure S7. EPR (X-Band, $\nu = 9.4877$ GHz, 140 K) spectra of the reaction mixture of attempted generation of nitroxide tetradical **3** in CH_2Cl_2 . Aza[1₄]metacyclophane **6** was reacted with DMDO (11 equiv) for 290 min at 183 K, and then for 85 min at 193 K (label: MV608-03-7). The side bands were simulated with the following parameters for the $S = 1$ state: $|D/hc| = 8.9 \times 10^{-3} \text{ cm}^{-1}$, $|E/hc| = 1.15 \times 10^{-3} \text{ cm}^{-1}$, $|A_{yy}/2hc| = 0.0 \times 10^{-4} \text{ cm}^{-1}$, $g_x \approx 2.005$, $g_y = 2.0055$, $g_z = 2.0065$, Gaussian line ($L_x = 2.0$, $L_y = 2.2$, $L_z = 1.6$ mT) (label: SM608-7). The center lines correspond to an $S = \frac{1}{2}$ product.

5. Detailed procedure for the ^1H NMR/EPR monitoring of oxidation for diamine **5** and aza[1₄]metacyclophane **6** (Figures S8A-H and S9A-E).

Preparation of diradical 2. Dichloromethane- d_2 (~0.09 mL) and DMDO (~0.11 mL of ~0.32 M solution in dichloromethane, ~5 equiv) were added by vacuum transfer to diamine **5** (3.0 mg, 1 equiv) in a 3-mm NMR sample tube, equipped with high-vacuum stopcock (Kontes or Chemglass). After the tube was flame sealed, the reaction mixture was thoroughly mixed at $-95\text{ }^\circ\text{C}$, and then stored in liquid nitrogen. After 90 min at $-78\text{ }^\circ\text{C}$, the sample tube was inserted to the NMR instrument at $-87\text{ }^\circ\text{C}$, and then series of ^1H NMR spectra at $-87\text{ }^\circ\text{C}$ were obtained, as illustrated in Figure S8A-C (label: MV636-17ex1, MV636-17ex3, MV636-17ex8). After recording the first set of NMR spectra, the sample was ejected cold from the NMR instrument, and then EPR spectrum at 140 K (label: MV636-17-1) was obtained (Figure S8D). Subsequently, the reaction mixture was allowed to attain room temperature, and then immediately, ^1H NMR spectrum (MV637-17-2ex4) was obtained (Figure S8E). After 3 h at room temperature, another ^1H NMR spectrum (MV637-17ex1) was obtained (Figure S8F), followed by EPR spectra at 140 K (MV636-17-4) and 296 K (MV636-17-7) as illustrated in Figures S8G and S8H.

Attempted preparation of tetraradical 1. Dichloromethane (~0.16 mL) and DMDO (~0.32 M solution in dichloromethane, ~0.31 mL, ~10 equiv) were added by vacuum transfer to aza[1₄]metacyclophane **6** (5.9 mg, 1 equiv) in a 5-mm NMR sample tube, equipped with high-vacuum stopcock (Kontes or Chemglass). After stirring for 2 h at $-95\text{ }^\circ\text{C}$, the reaction mixture was concentrated at $-78\text{ }^\circ\text{C}$ for 2 h, to attain about half of the original volume. Subsequently, the volume of the reaction mixture was approximately doubled by vacuum transfer of dichloromethane- d_2 . The NMR sample tube was flame sealed and stored in liquid nitrogen. The sample tube was inserted to the NMR instrument at $-86\text{ }^\circ\text{C}$, and then ^1H NMR spectra at $-86\text{ }^\circ\text{C}$ (MV618-08ex2) were obtained (Figure S9A). After recording the first set of NMR spectra, the sample was ejected cold from the NMR instrument, and then EPR spectrum at 140 K (label: MV618-08-1) was obtained (Figure S9B). Subsequently, the reaction mixture was allowed to attain room temperature for 3 h, and then another ^1H NMR spectrum (MV619-

08-ex1) was obtained (Figure S9C), followed by EPR spectra at 140 K (MV618-08-4) and 296 K (MV618-08-7) as illustrated in Figures S9D and S9E.

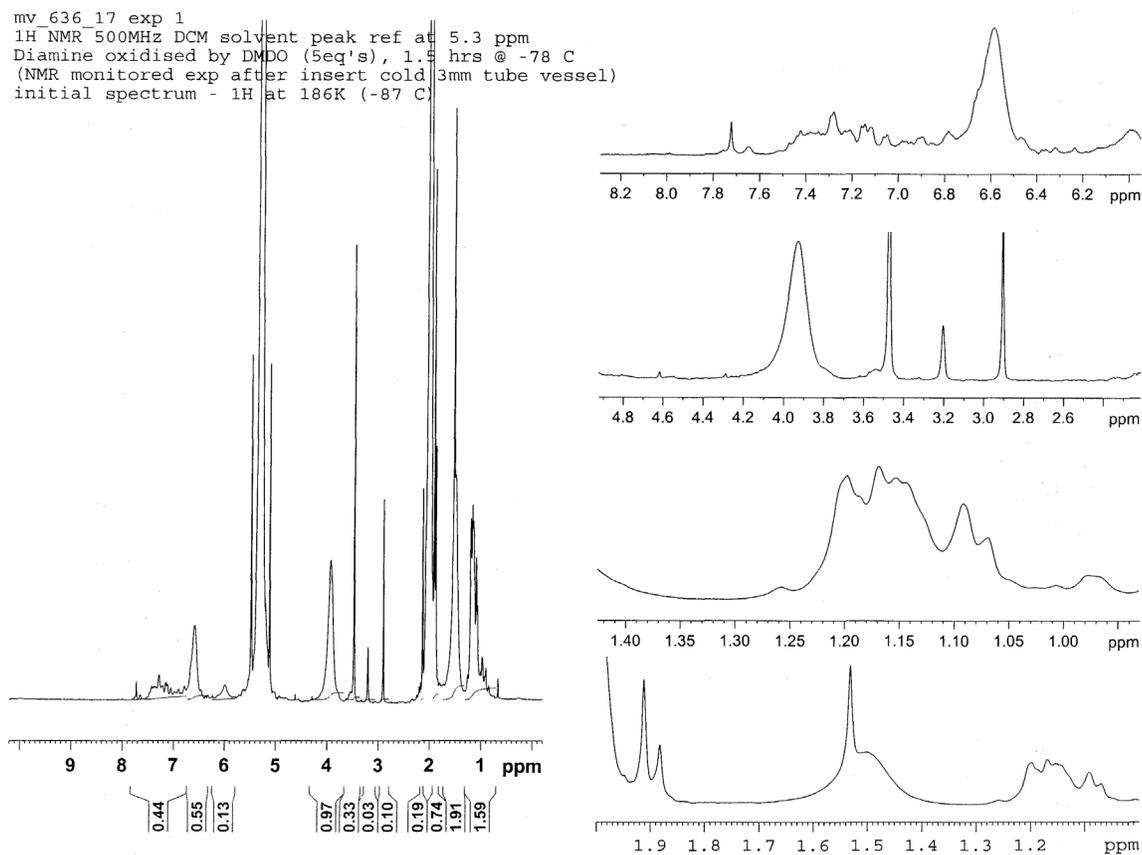


Figure S8A. ^1H NMR (500 MHz, dichloromethane- h_2 /dichloromethane- d_2 , 186 K) spectrum of the reaction mixture for generation of nitroxide diradical **2** (label: MV636-17ex1). The spectrum is obtained after oxidation of diamine **5** with DMDO (~5 equiv) for 90 min at -78°C . The sample was inserted frozen, from liquid nitrogen to the instrument at -87°C (186 K).

exp 2 dual solv sup failed
mv_636_17_exp_3
1H NMR 500MHz DCM solvent peak ref at 5.3 ppm
Diamine oxidised by DMO (5eq's), 1.5 hrs @ -78 C
(NMR monitored exp 20 mins after insert cold 3mm tube vessel)
3rd spectrum - 1H at 186K (-87 C)

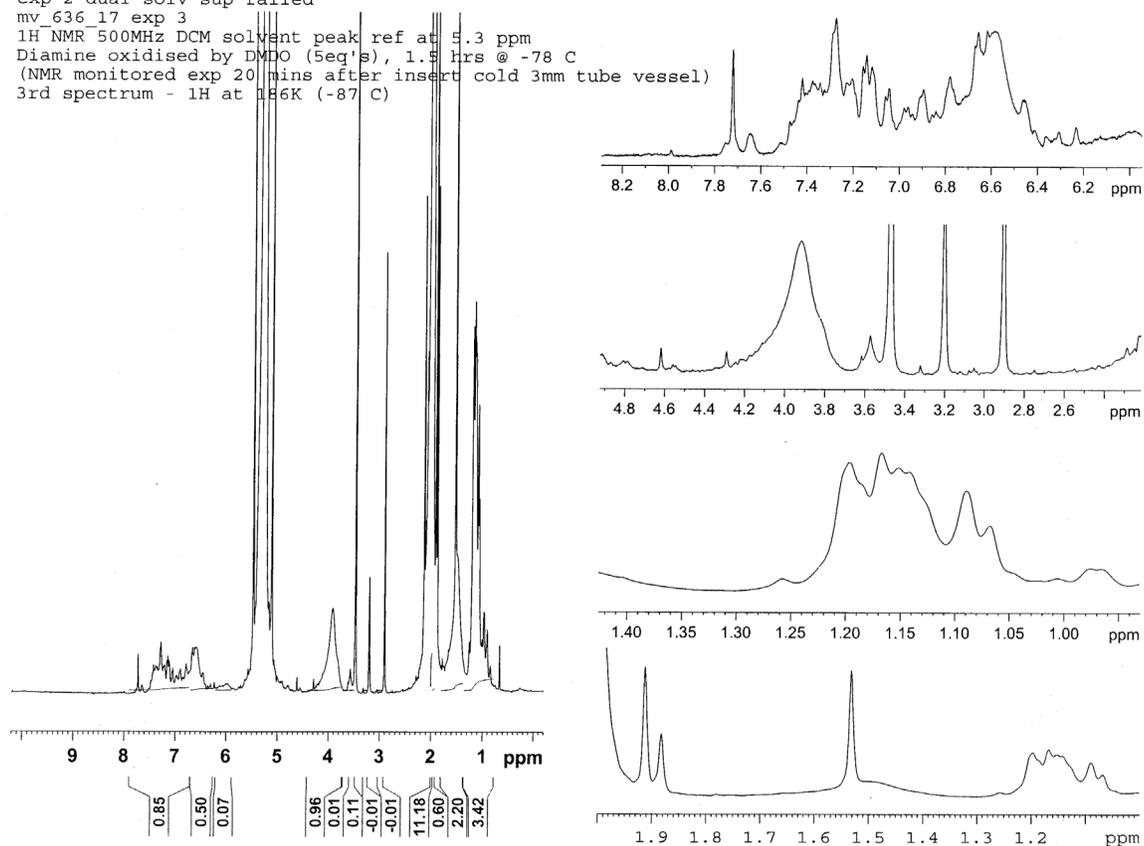


Figure S8B. ^1H NMR (500 MHz, dichloromethane- h_2 /dichloromethane- d_2 , 186 K) spectrum of the reaction mixture for generation of nitroxide diradical **2** (label: MV636-17ex3). The spectrum is obtained 20 min after the initial ^1H spectrum in Figure S8A.

exp 7 multiple solvent suppression failed
mv_636_17 exp 8
1H_NMR_500MHz DCM solvent peak ref at 5.3 ppm
Diamine oxidised by DMO (5eq's), 1.5 hrs @ -78 C
(NMR monitored exp 60 mins after insert cold 3mm tube vessel)
1H at 186K (-87 C)

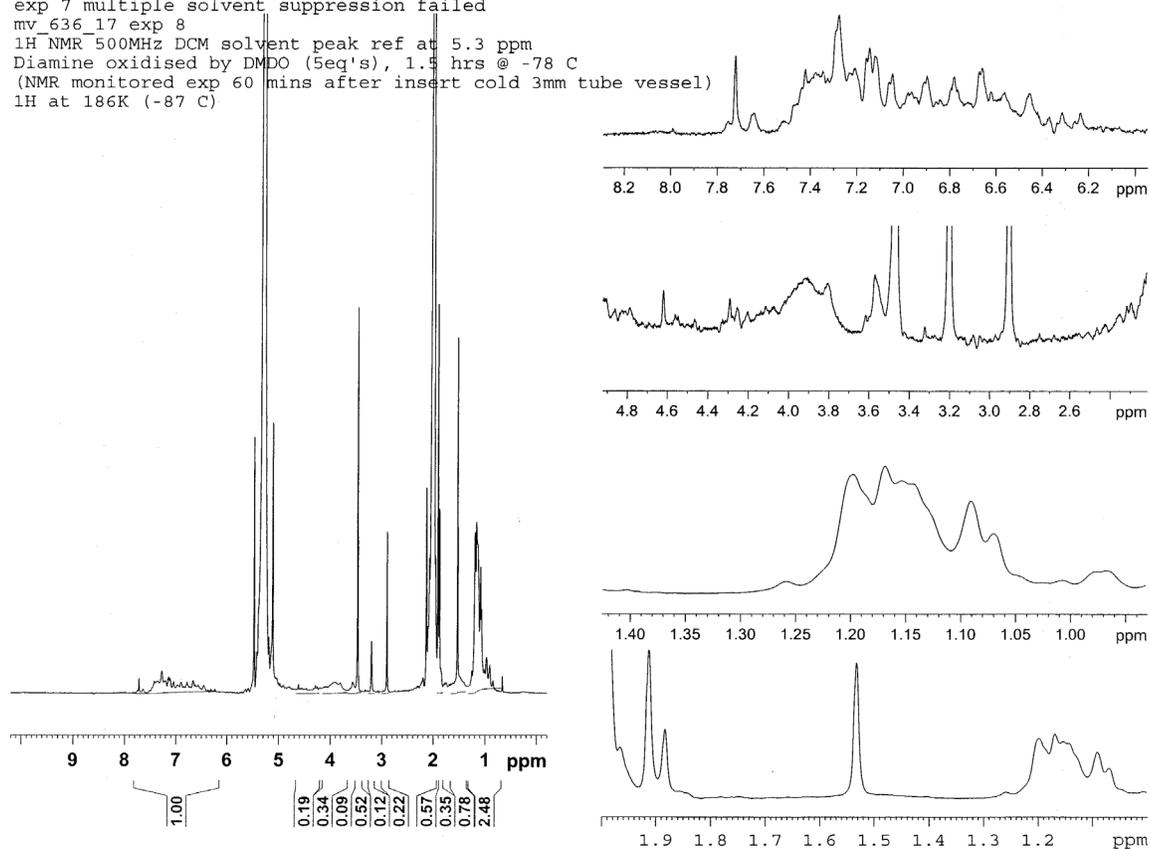


Figure S8C. ¹H NMR (500 MHz, dichloromethane-*h*₂/dichloromethane-*d*₂, 186 K) spectrum of the reaction mixture for generation of nitroxide diradical **2** (label: MV636-17ex8). The spectrum is obtained 60 min after the initial ¹H spectrum in Figure S8A.

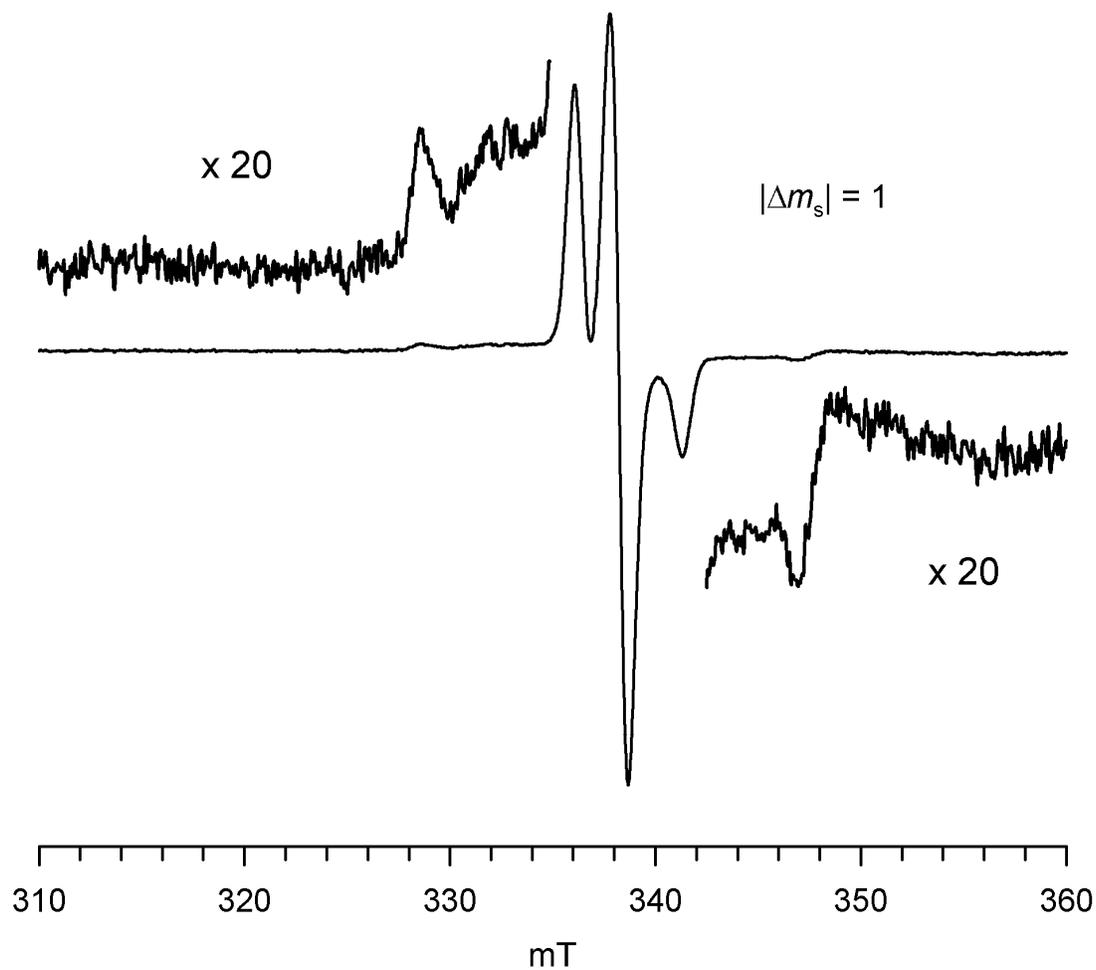


Figure S8D. EPR (X-Band, $\nu = 9.4908$ GHz, 140 K) spectrum of the reaction mixture of attempted generation of nitroxide diradical **2** (label: MV636-17-1), following the ^1H NMR spectrum in Figure S8C.

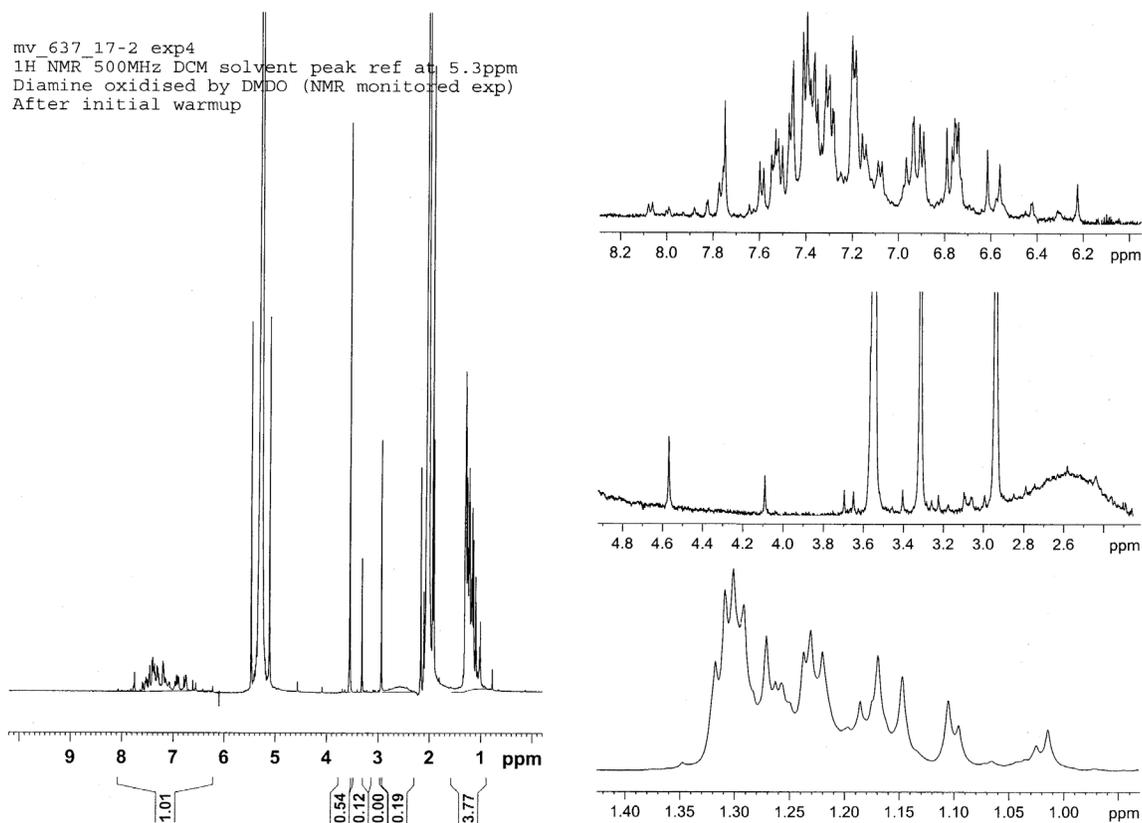


Figure S8E. ^1H NMR (500 MHz, dichloromethane- h_2 /dichloromethane- d_2 , 295 K) spectrum of the reaction mixture for generation of nitroxide diradical **2** (label: MV637-17-2ex4). The spectrum is obtained following the EPR spectrum in Figure S8D and after the reaction mixture is allowed to attain room temperature for about 5 min.

mv_637_17 exp 1
1H NMR 500MHz DCM solvent peak ref at 5.3 ppm
Diamine oxidised by DMDO (NMR monitored exp)
after 3hrs at RT, prior to EPR spectrum

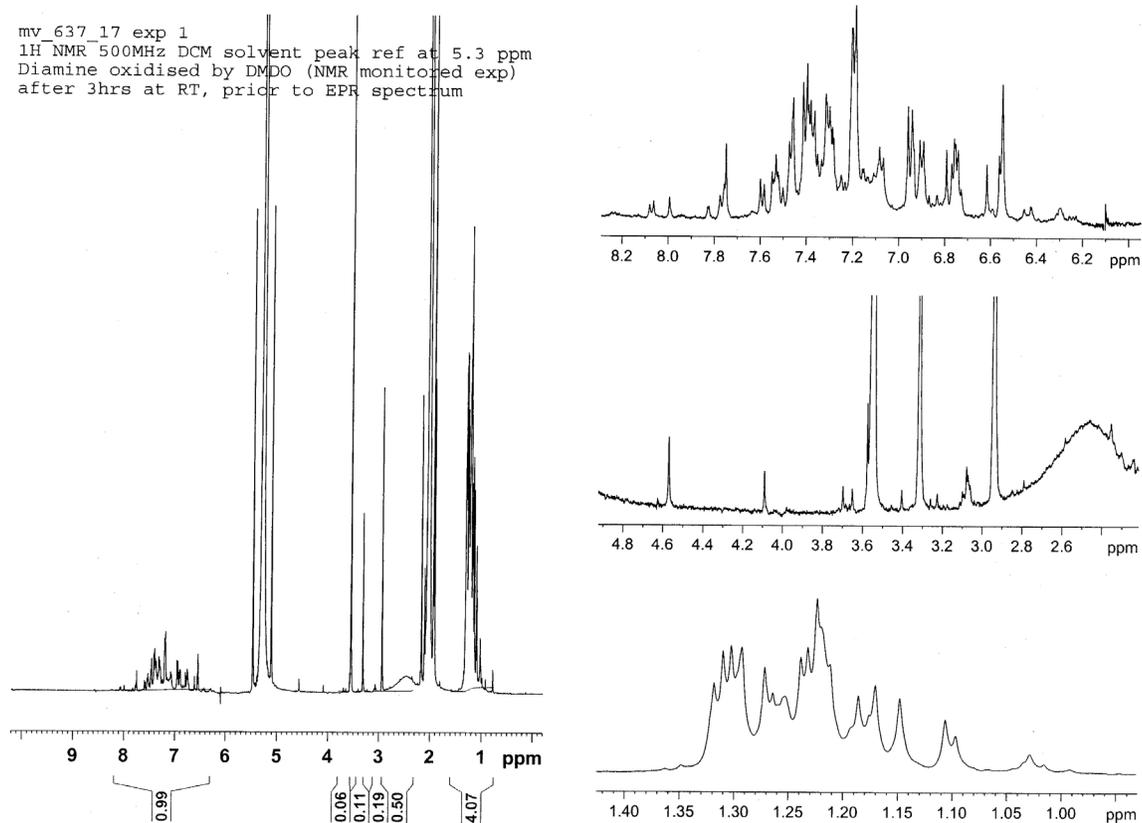


Figure S8F. ¹H NMR (500 MHz, dichloromethane-*h*₂/dichloromethane-*d*₂, 295 K) spectrum of the reaction mixture for generation of nitroxide diradical **2** (label: MV637-17ex1). The spectrum is obtained following the ¹H NMR spectrum in Figure S8E and after the reaction mixture is allowed to attain room temperature for about 3 h.

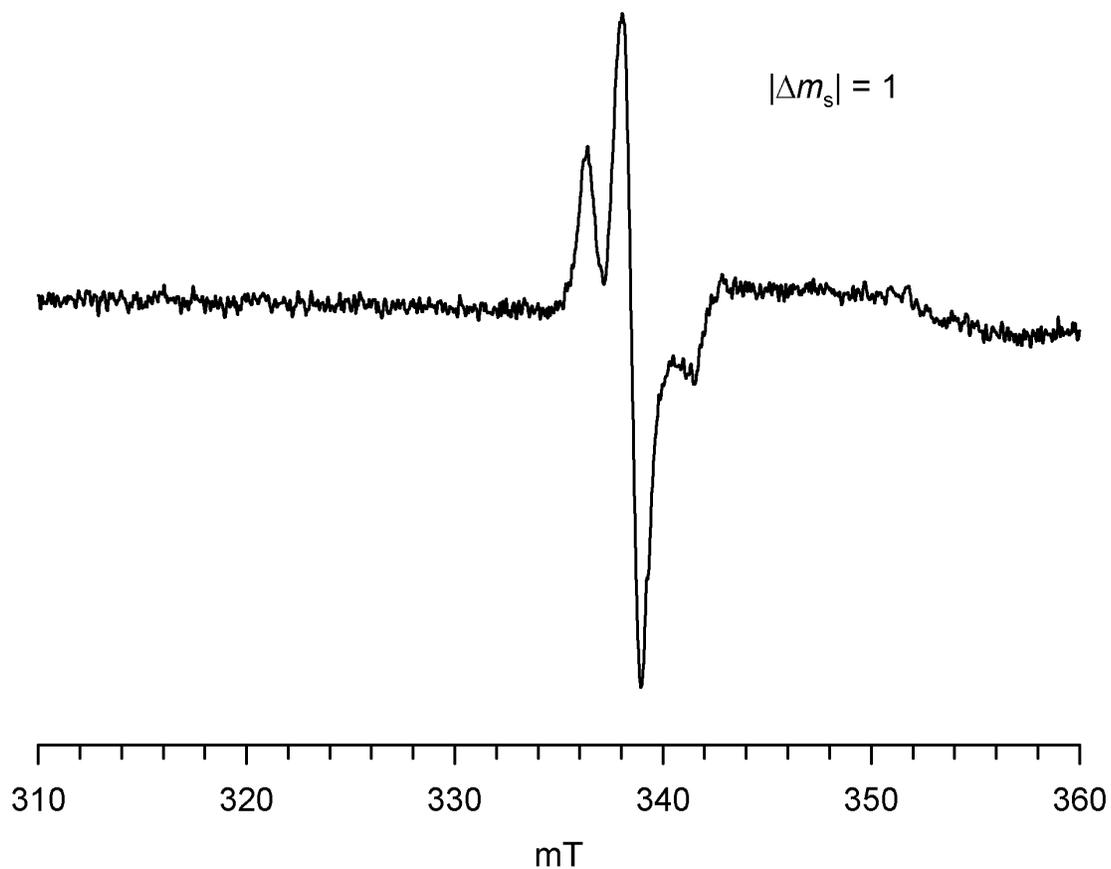


Figure S8G. EPR (X-Band, $\nu = 9.4938$ GHz, 140 K) spectrum of the reaction mixture for generation of nitroxide diradical **2** (label: MV636-17-4), following the ^1H NMR spectrum in Figure S8F. (The reaction mixture was already at room temperature for 4 h.)

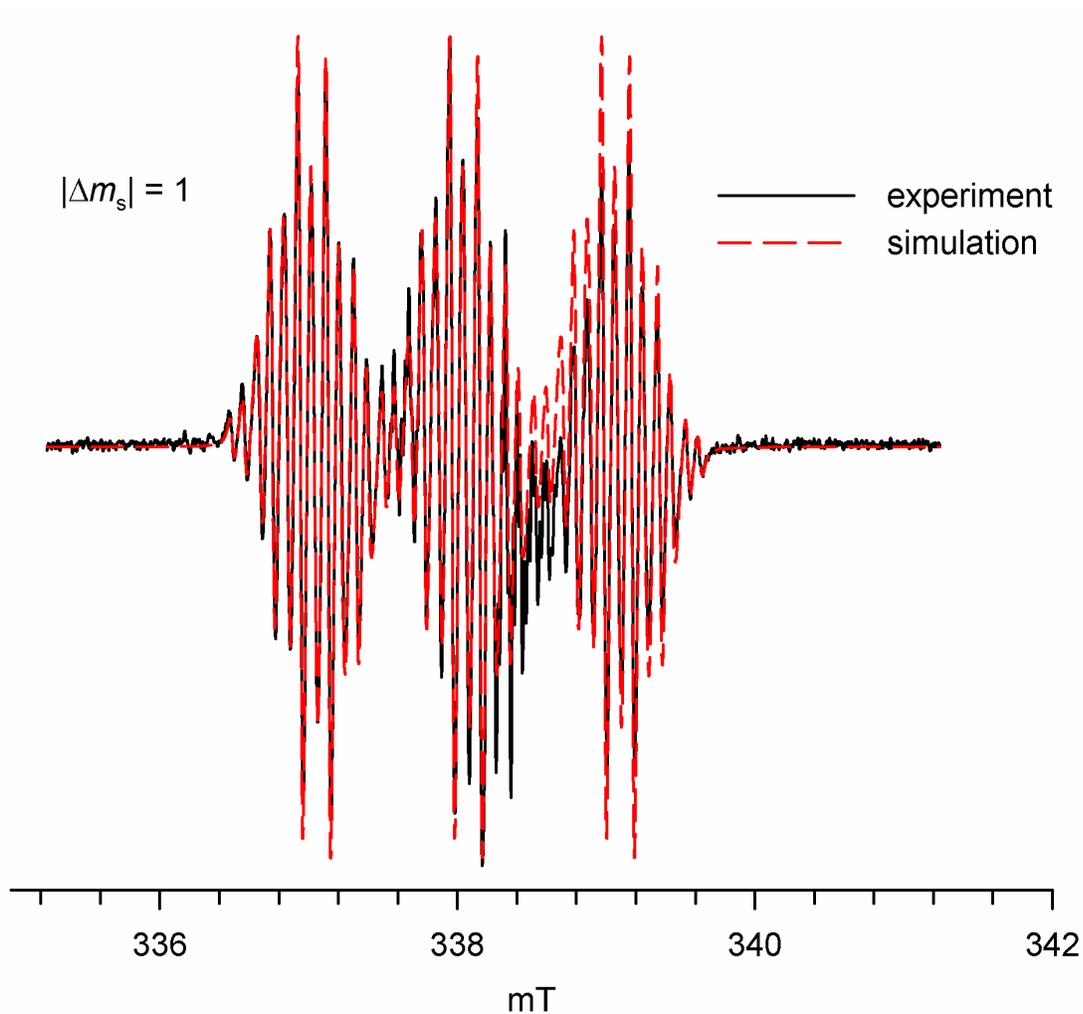


Figure S8H. EPR (X-Band, $\nu = 9.4896$ GHz, modulation amplitude of 0.01 mT, 297 K) spectrum of the reaction mixture for generation of nitroxide diradical **2** (label: MV636-17-7), following the ^1H NMR spectrum in Figure S8F and the EPR spectrum in Figure S8G. (The reaction mixture was already at room temperature for 4 h.) Spectral simulation parameters: hyperfine splitting in mT (number of nuclei), $a_{\text{N}} = 1.020$ (1), $a_{\text{H}} = 0.185$ (2), $a_{\text{H}} = 0.082$ (2), $a_{\text{H}} = 0.189$ (1), $a_{\text{H}} = 0.188$ (1), $a_{\text{H}} = 0.190$ (1), 100% Lorentzian linewidth = 0.028 mT, $g \approx 2.005$, $R = 0.957$ (label: simdata3_dirad).

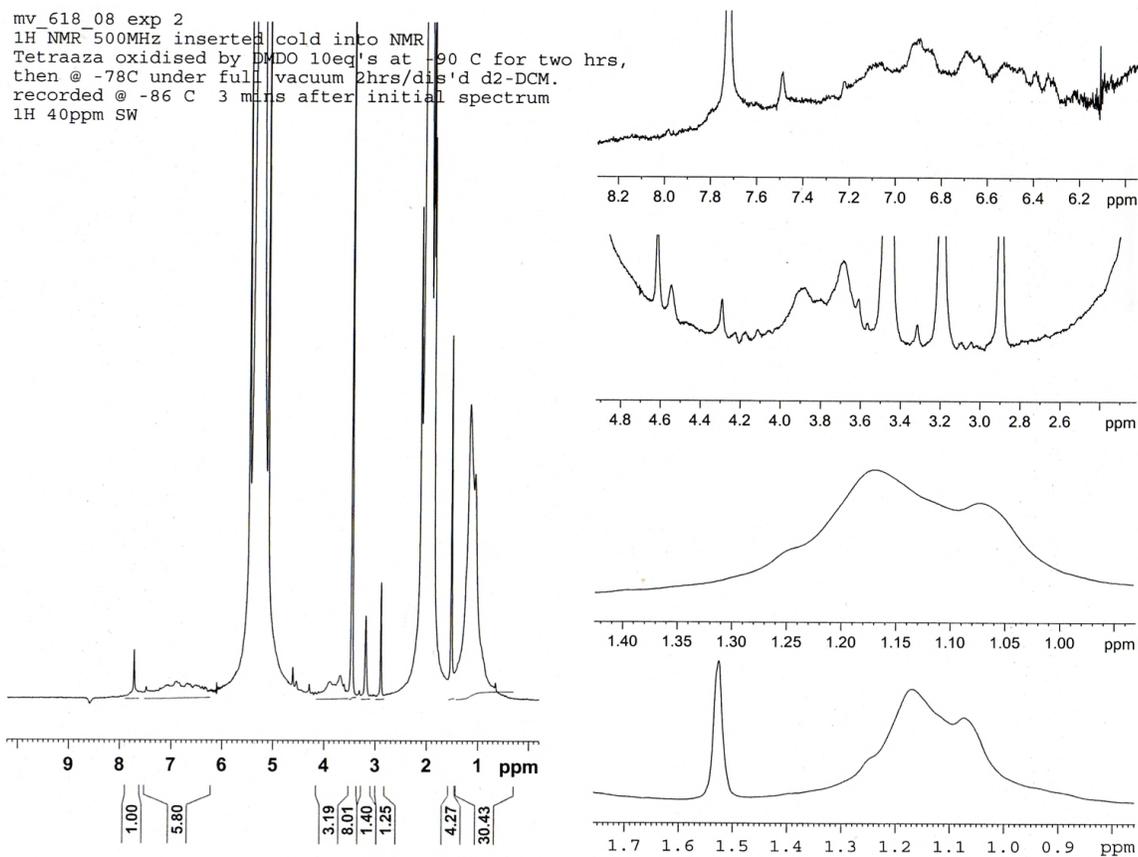


Figure S9A. ¹H NMR (500 MHz, dichloromethane-*h*₂/dichloromethane-*d*₂, 187 K) spectrum of the reaction mixture of attempted generation of nitroxide tetradical **3** (label: MV618-08ex2). The spectrum is obtained after oxidation of aza[1₄]metacyclophane **6** with DMDO (10 equiv) for 2 h at -90 °C and 2 h at -78 °C. The sample was inserted frozen, from liquid nitrogen to the instrument at -86 °C (187 K).

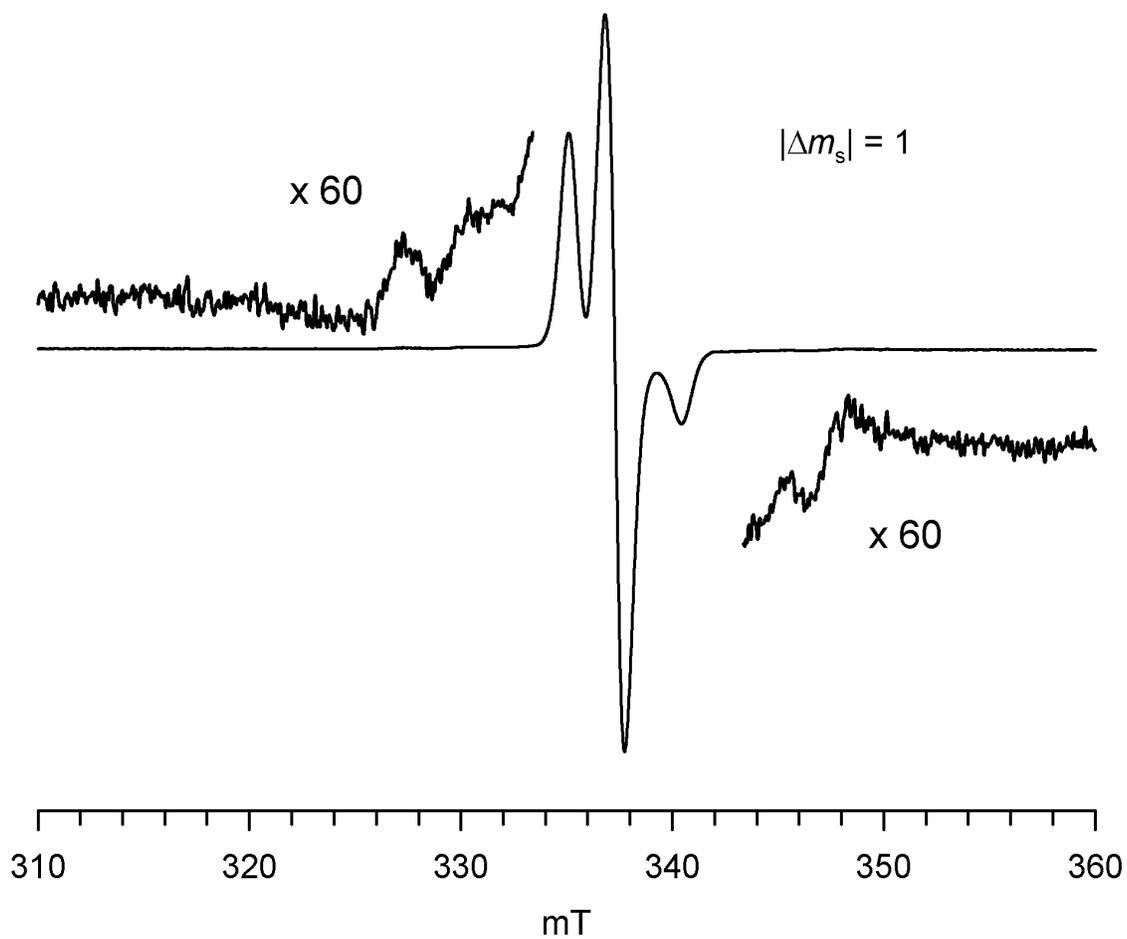


Figure S9B. EPR (X-Band, $\nu = 9.4640$ GHz, 140 K) spectra of the reaction mixture of attempted generation of nitroxide tetraradical **3** (label: MV618-08-1), following the ^1H NMR spectrum in Figure S9A.

mv_619_08_exp_1
 500MHz inserted cold into NMR
 Tetraaza oxidised by DMDO 10eq's at -90 C for two hrs,
 then @ -78C under full vacuum 2hrs/diss'd d2-DCM.
 recorded @ RT after 2nd warm up
 1H 500NMR 128scans no solvent suppression
 @RT for 3hrs then lq N2 then RT for 5mins

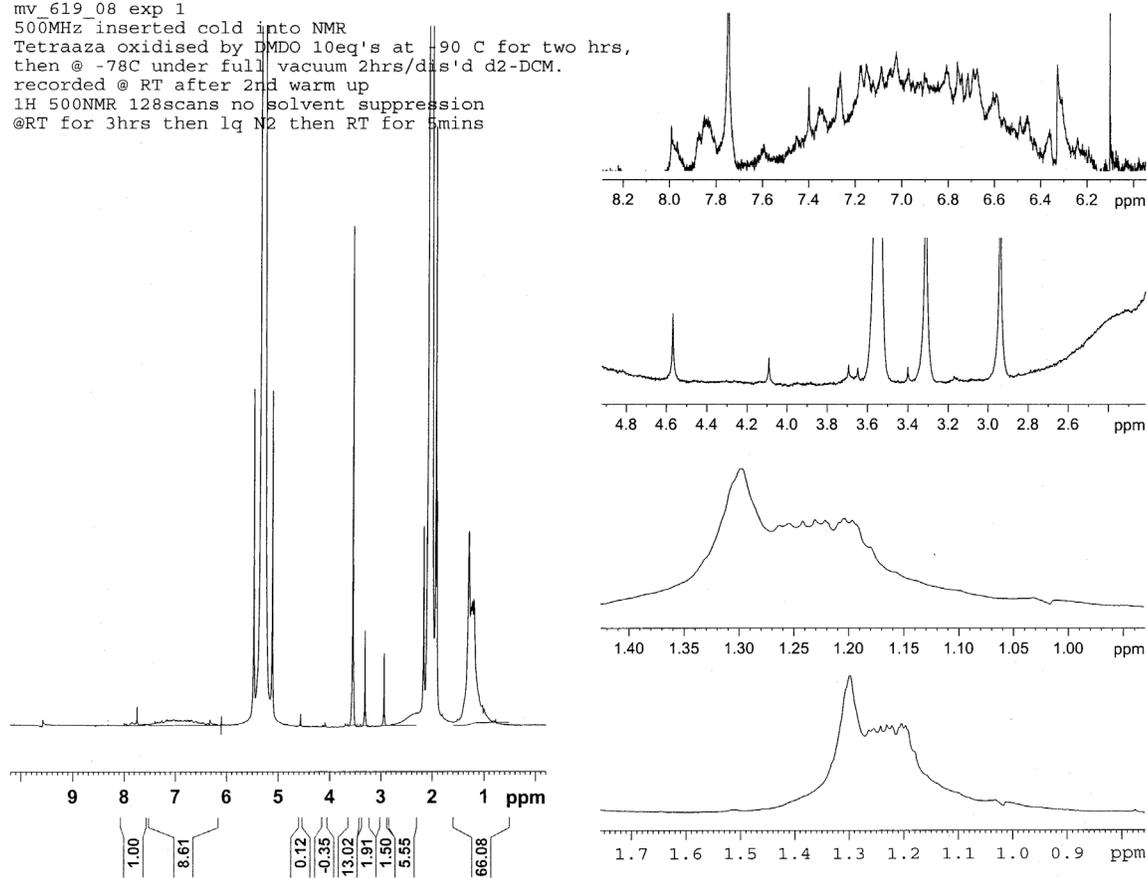


Figure S9C. ¹H NMR (500 MHz, dichloromethane-*h*₂/dichloromethane-*d*₂, 187 K) spectrum of the reaction mixture of attempted generation of nitroxide tetradical **3** (label: MV619-08ex1). The spectrum is obtained following the EPR spectrum in Figure S9B and after the reaction mixture is allowed to attain room temperature for 3 h.

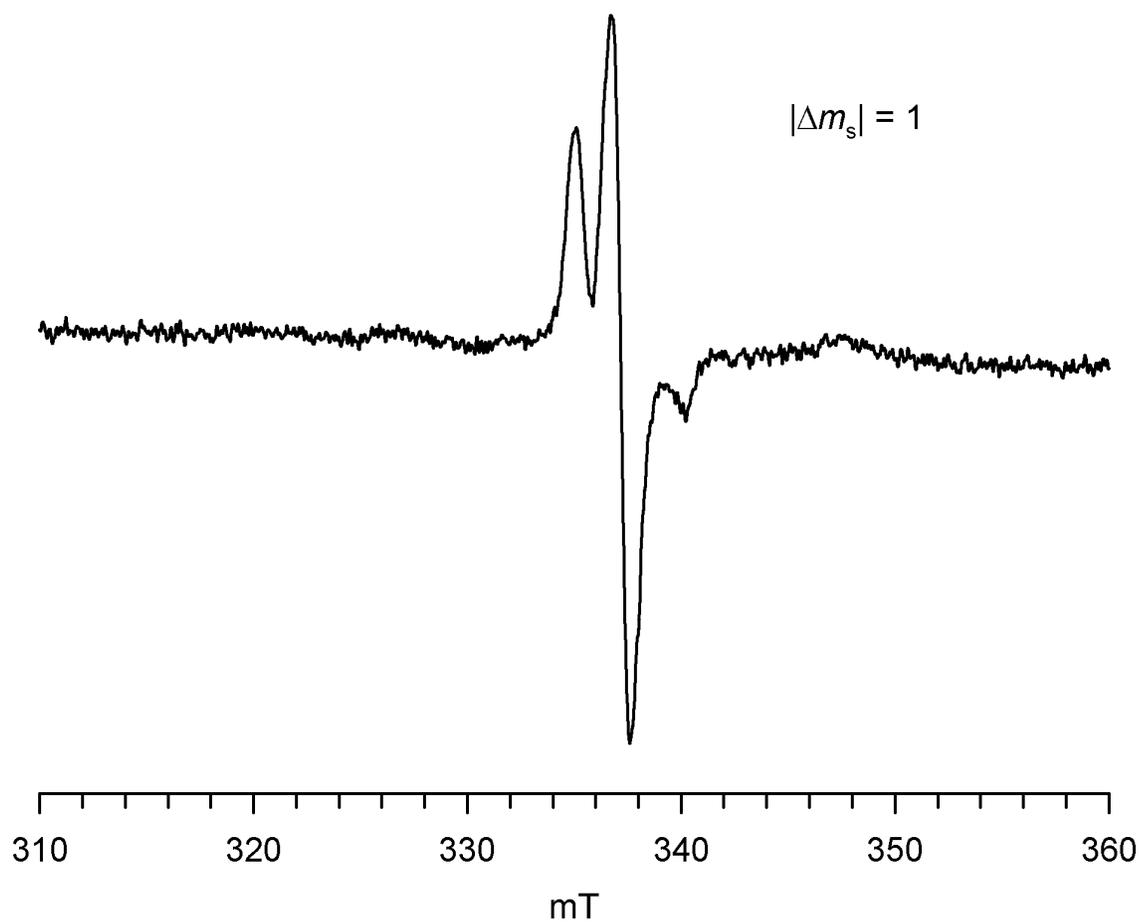


Figure S9D. EPR (X-Band, $\nu = 9.4604$ GHz, 140 K) spectrum of the reaction mixture of attempted generation of nitroxide tetraradical **3** (label: MV618-08-4), following the ^1H NMR spectrum in Figure S9C. (The reaction mixture was already at room temperature for 3 h.)

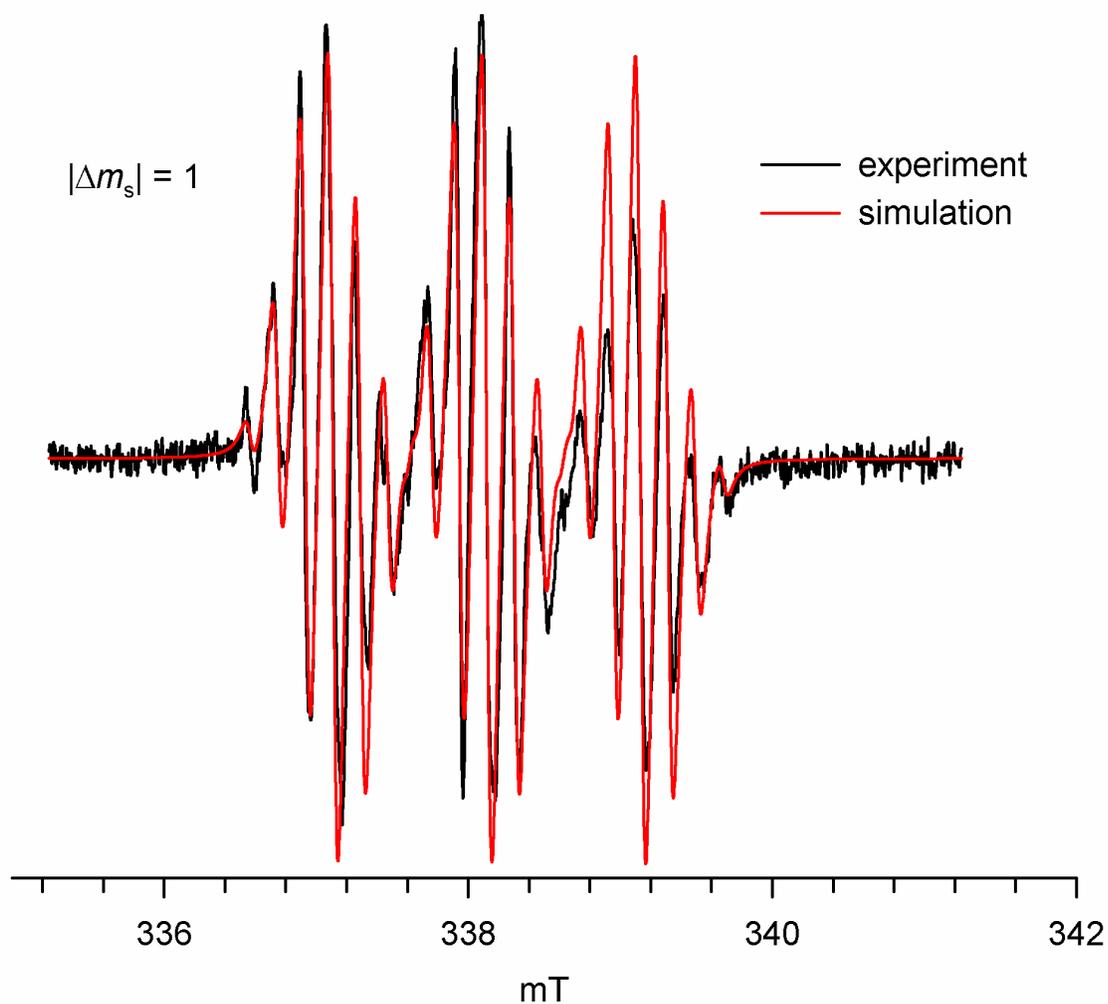


Figure S9E. EPR (X-Band, $\nu = 9.4920$ GHz, modulation amplitude of 0.05 mT, 297 K) spectrum of the reaction mixture of attempted generation of nitroxide tetraradical **3** (label: MV618-08-7), following the ^1H NMR spectrum in Figure S9C and the EPR spectrum in Figure S9D. (The reaction mixture was already at room temperature for 3 h.) Spectral simulation parameters: hyperfine splitting in mT (number of nuclei), $a_{\text{N}} = 1.011$ (1), $a_{\text{H}} = 0.1798$ (2), $a_{\text{H}} = 0.182$ (2), $a_{\text{H}} = 0.1800$ (2), 100% Lorentzian linewidth = 0.062 mT, $g \approx 2.005$, $R = 0.919$ (label: simdata3_tetra2).

6. NMR spectra for synthetic intermediates (Figures S10 – S15).

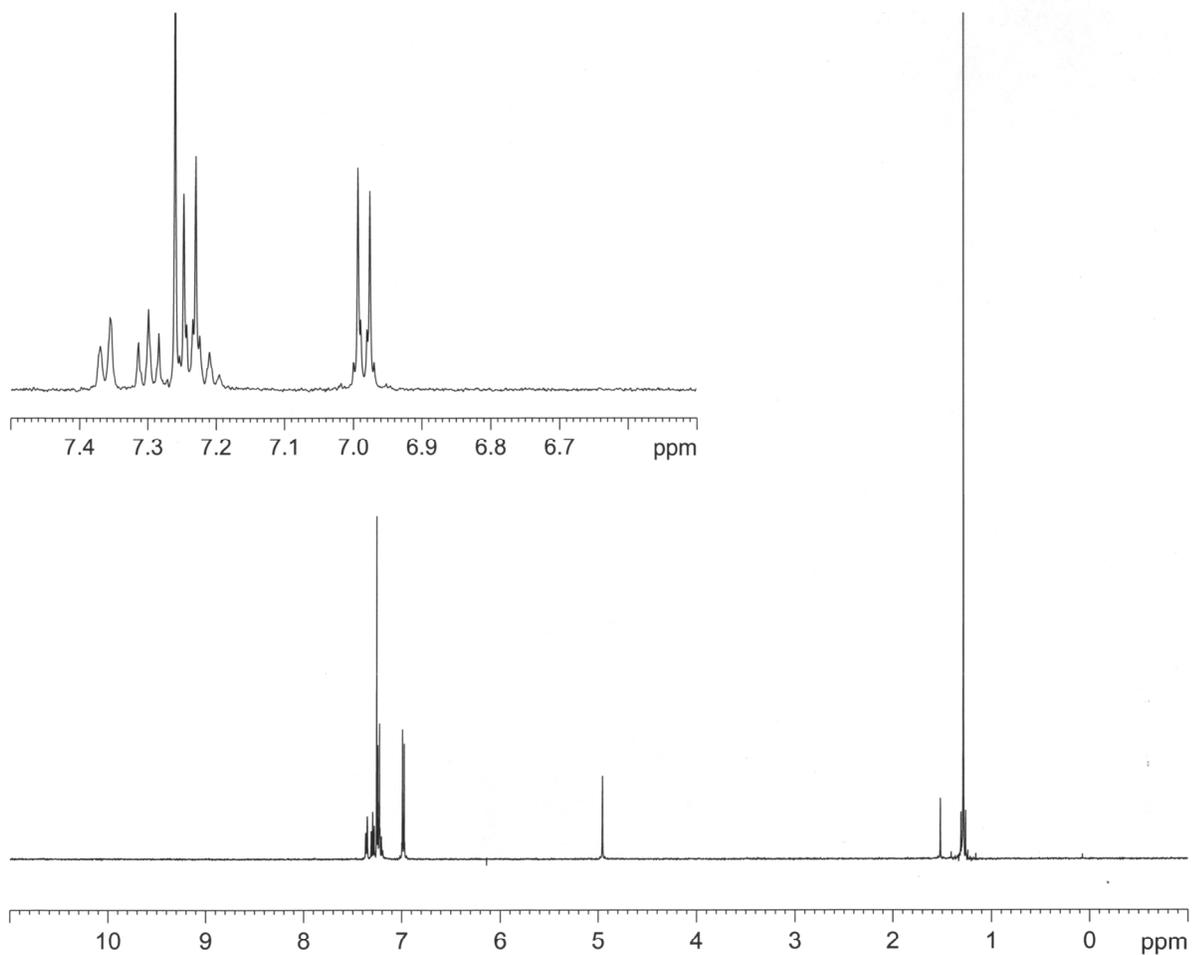


Figure S10. ¹H NMR (500 MHz, chloroform-*d*) spectrum of *N*-benzylated amine **8** (label: mv_113_05).

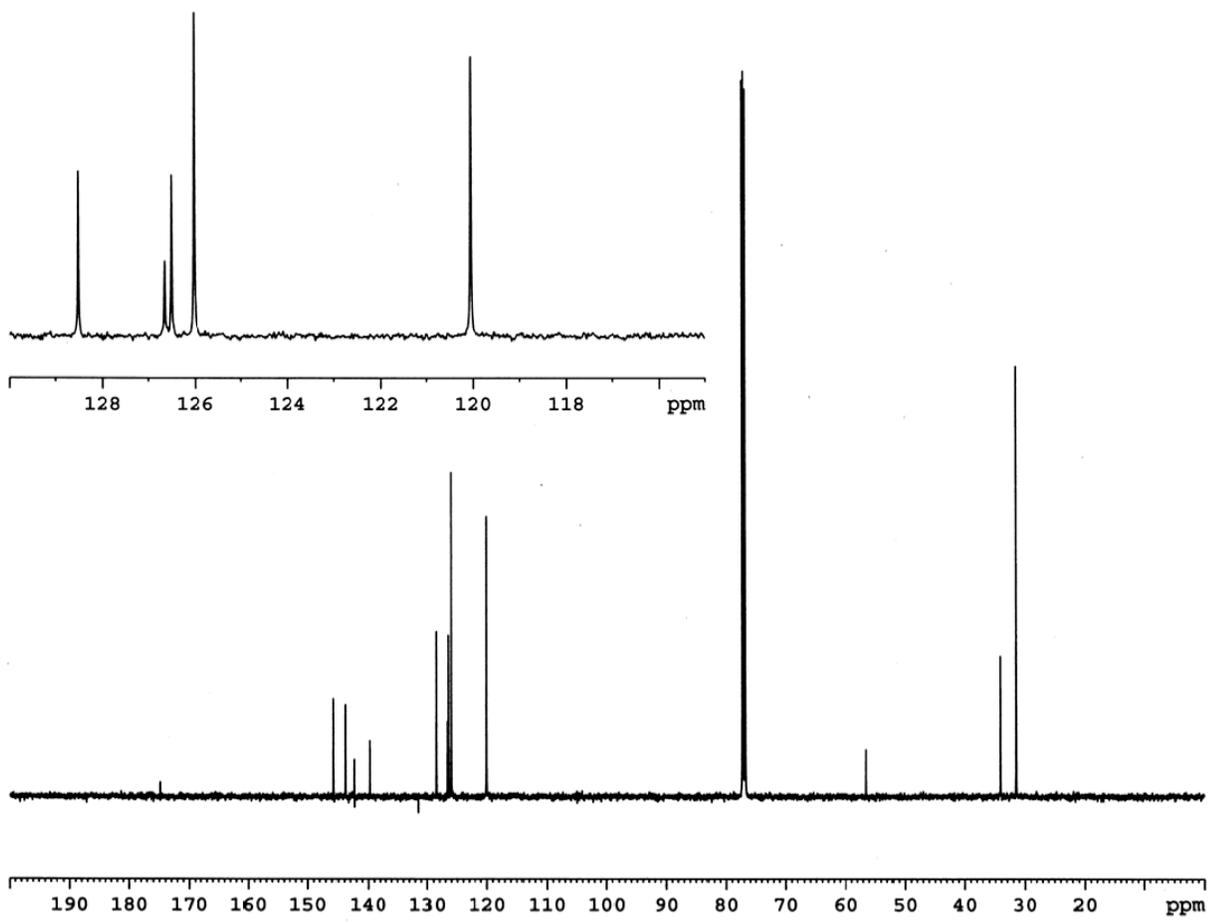


Figure S11. ^{13}C NMR (125 MHz, chloroform-*h*) spectrum of *N*-benzylated amine **8** (label: mv_113_05-Carbon).

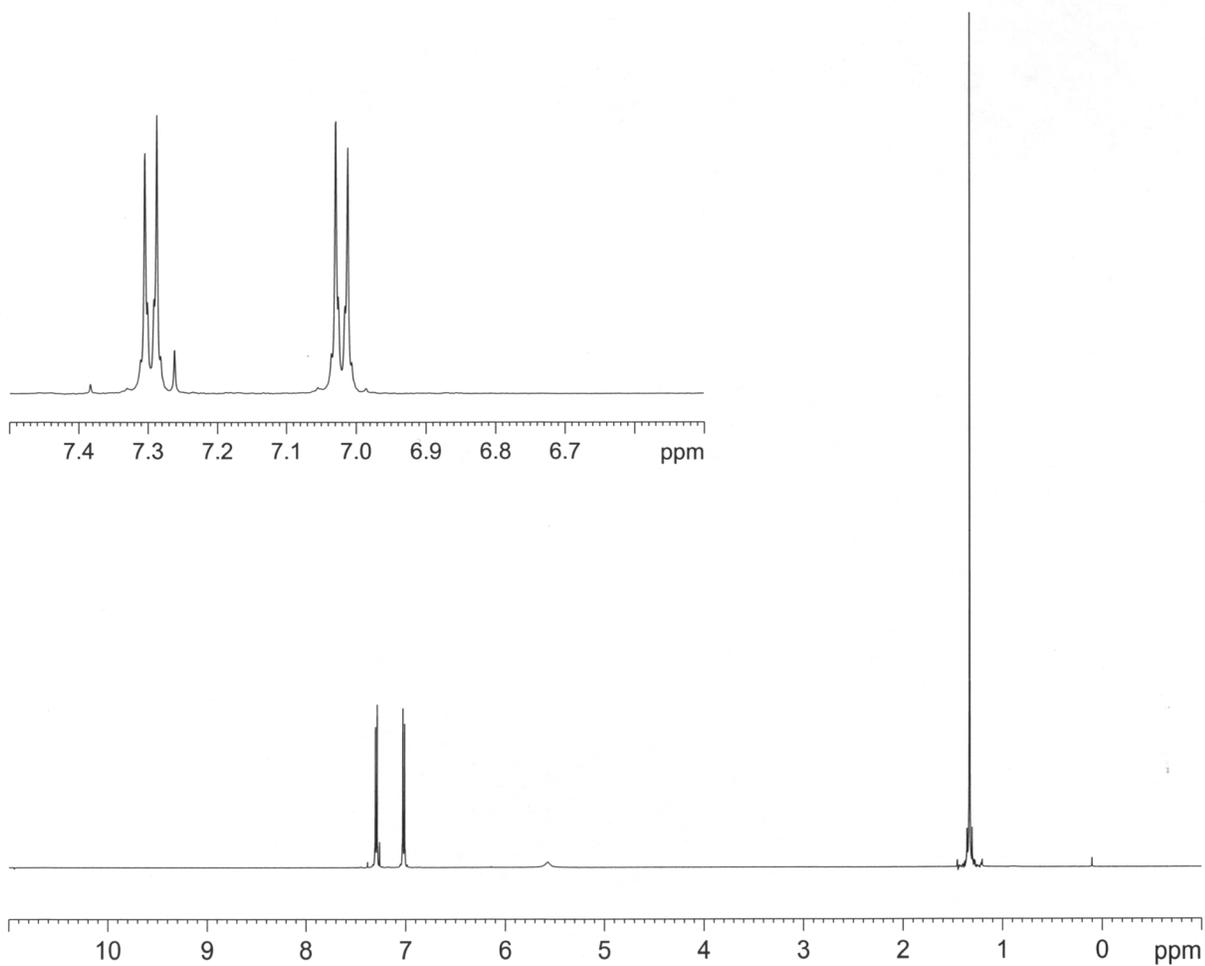


Figure S12. ^1H NMR (500 MHz, chloroform-*h*) spectrum of secondary diarylamine **4** for generation of nitroxide radical **1**.

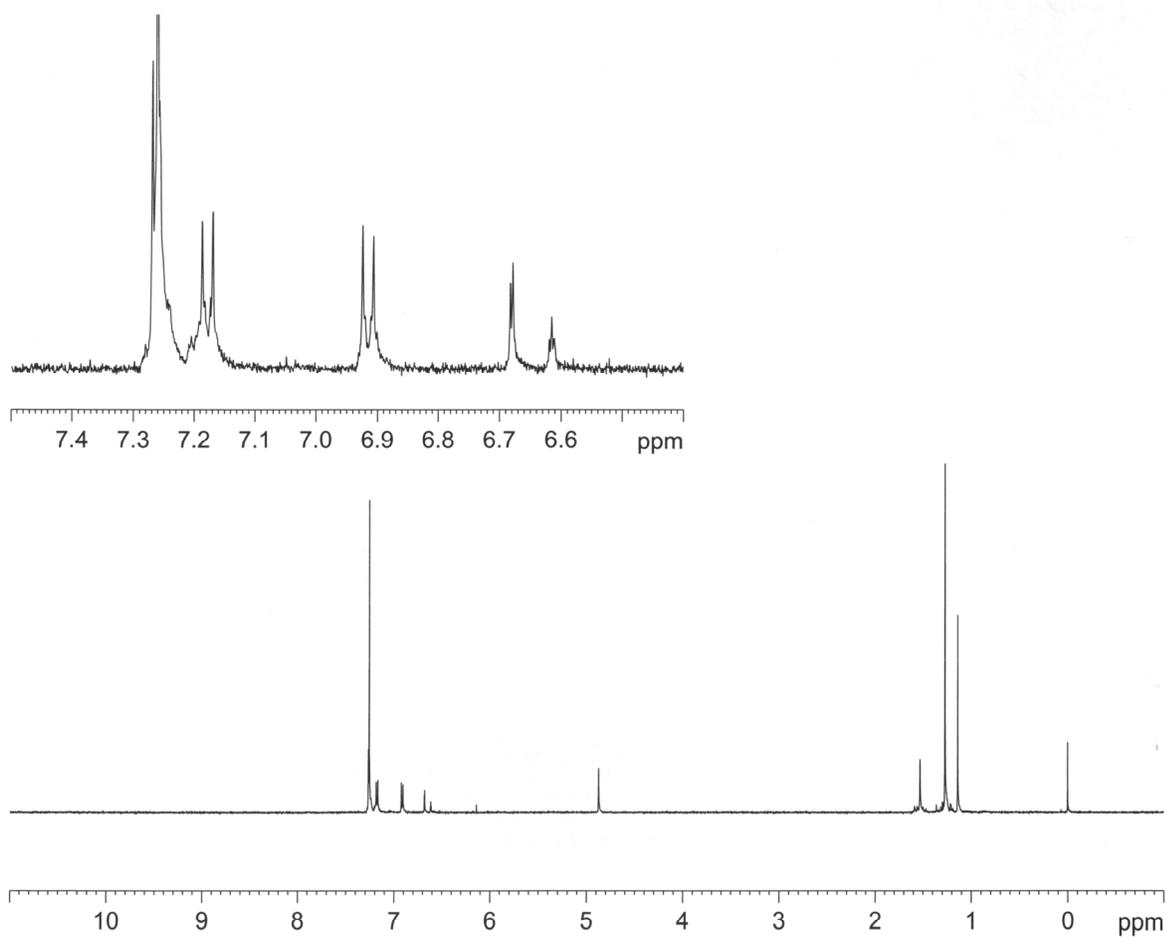


Figure S13. ^1H NMR (500 MHz, chloroform-*h*) spectrum of *N*-benzylated diamine **10** for generation of nitroxide diradical **2** (label: mv_148_31-cr2).

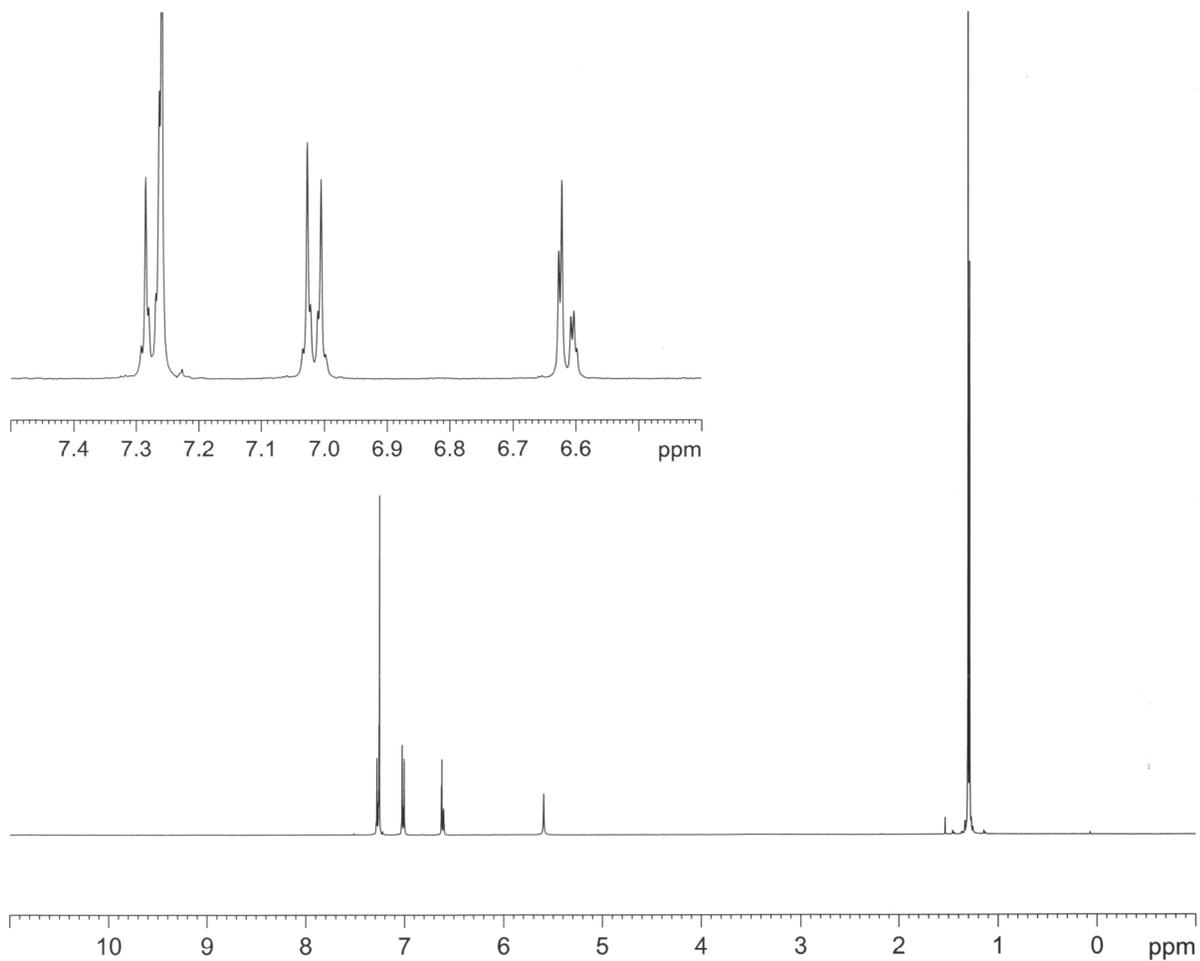


Figure S14. ¹H NMR (400 MHz, chloroform-*h*) spectrum of secondary diamine **5** for generation of nitroxide diradical **2** (label: mv_157_37_xst1).

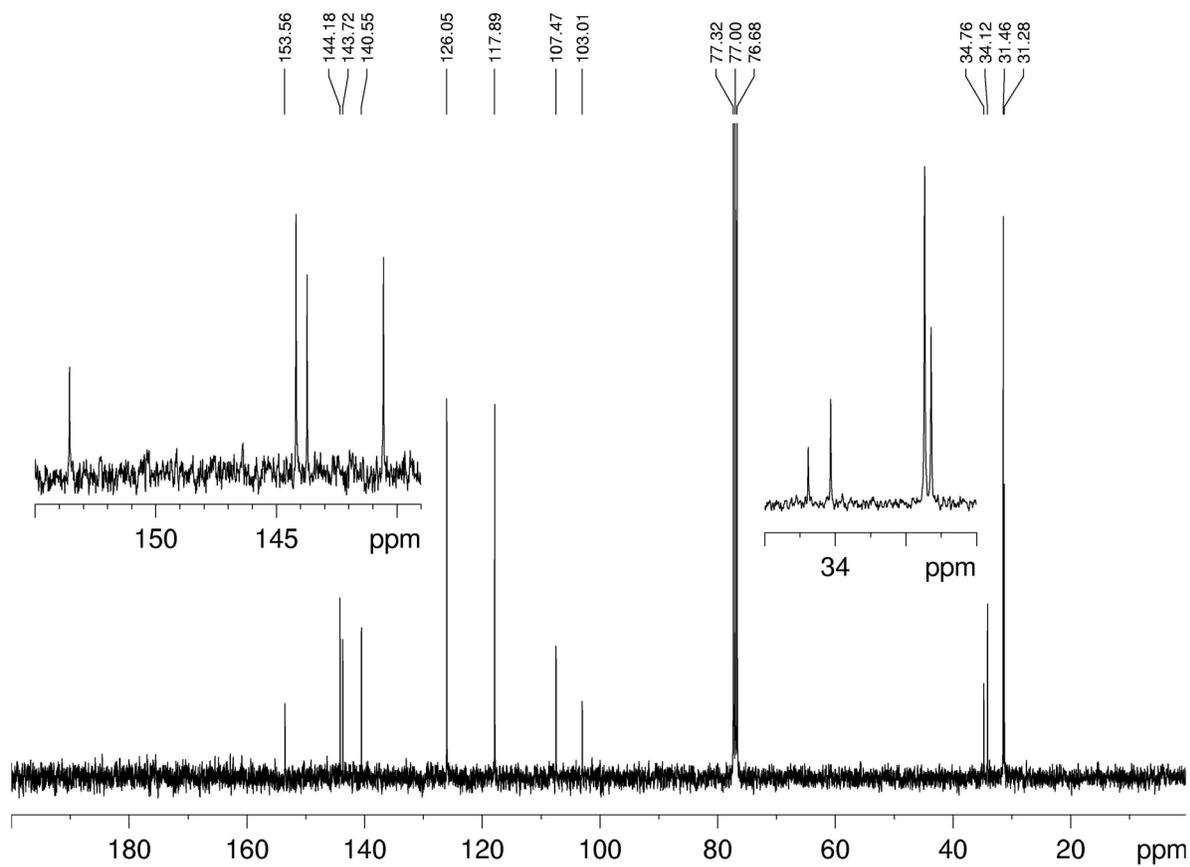


Figure S15. ^{13}C NMR (100 MHz, chloroform-*h*) spectrum of secondary diamine **5** for generation of nitroxide diradical **2** (label: mv_157_37_xst1-C).

7. Complete reference 47 and DFT calculations on diarylnitroxide diradical 2.

Complete Ref. 47, “More Frisch et. al.”

(47) Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

DFT Calculations. Triplet states of diarylnitroxide diradical **2** were subjected to full geometry optimization using the UB3LYP/6-31G(d) level of theory. At the fully optimized geometries for the triplet states, the single-point energies for open-shell singlet states were calculated using the broken-symmetry approximation. As the broken-symmetry singlets are approximately 1:1 mixtures of singlet and triplet states, the singlet-triplet energy gap ($2J$) is given by equation S1, in which ${}^S E_{BS}$ and ${}^T E$ correspond to the energy of the lowest energy broken symmetry singlet and triplet states, respectively.

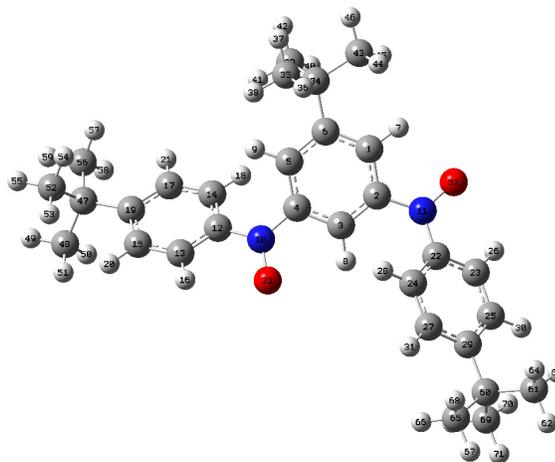
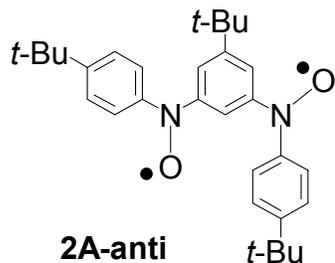
$$2J = 2({}^S E_{BS} - {}^T E) \quad (S1)$$

Table S1. UB3LYP/6-31G(d) calculations for conformers of diradical **2**.

	2A-anti	2B-endo	2C-exo
Optimized geometry for triplets			
N...N, O...O distances (Å) for triplets	4.9, 6.2	4.8, 4.9	4.9, 7.0
α , β torsion angles (°) for triplets	25.2, 154.3	26.6, 26.3	-151.5, -151.7
Dipole moment ^a for triplets	2.87	5.51	3.42
Total energy for triplets (¹ E) ^b	-1425.92486953	-1425.92309079	-1425.92419925
Relative energy for triplets ^c	0	1.11	0.42
Zero-point-energy (ZPE) for triplets ^c	388.646	388.589	388.656
Relative energy with ZPE for triplets ^c	0	1.05	0.43
Electronic and thermal free energy for triplets ^b	-1425.373211	-1425.371473	-1425.372801
Relative free energy for triplets ^c	0	1.09	0.26
Total energy for BS singlets (^S E _{BS}) ^{b,d,e}	-1425.92343452	-1425.92187961	-1425.92287864
Singlet-triplet energy gap, 2(^S E _{BS} - ¹ E) ^{c,e}	1.8	1.5	1.7

^a Dipole moment in Debye. ^b in Hartree/molecule. ^c in kcal mol⁻¹. ^d Broken-symmetry singlet with $S(S+1) \approx 1.0$ at the geometry optimized for the triplet.⁴⁸⁻⁵⁰ ^e Full geometry optimization of the broken-symmetry singlet for **2A-anti** lowers the energy by 0.08 kcal mol⁻¹ only. ^c The UB3LYP (broken symmetry with $S(S+1) \approx 1.0$ singlets and $S(S+1) \approx 2.0$ triplets) level of theory usually overestimates the singlet-triplet gaps, $2(\text{}^S E_{\text{BS}} - \text{}^1 E)$, for the triplet ground state organic diradicals, and underestimates such gaps for the singlet ground state diradicals.^{49,50}

(a) Diarylnitroxide diradical, conformer 2A-anti: full geometry optimization of the triplet followed by frequency calculation of the triplet and by the energy calculation of broken symmetry singlet at the geometry of the triplet (UB3LYP/6-31G(d) level). For reference, full geometry optimization of the broken symmetry singlet was included.



Full geometry optimization of the triplet

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.650516	2.862194	-0.101779
2	6	0	1.371600	1.665747	-0.270484
3	6	0	0.739555	0.428689	-0.146172
4	6	0	-0.623032	0.402728	0.172952
5	6	0	-1.335041	1.591255	0.375441
6	6	0	-0.704369	2.838698	0.230181
7	1	0	1.189648	3.788457	-0.238004
8	1	0	1.257348	-0.506920	-0.301706
9	1	0	-2.375893	1.540543	0.669356
10	7	0	-1.226654	-0.876107	0.340207
11	7	0	2.743519	1.771490	-0.630591
12	6	0	-2.618518	-1.133144	0.165439
13	6	0	-3.194431	-2.179128	0.899490
14	6	0	-3.402767	-0.429851	-0.755010
15	6	0	-4.537920	-2.483253	0.730499
16	1	0	-2.572447	-2.738533	1.588146
17	6	0	-4.751426	-0.753142	-0.910014
18	1	0	-2.963522	0.350076	-1.367088
19	6	0	-5.357583	-1.778757	-0.171709
20	1	0	-4.957536	-3.293045	1.320478
21	1	0	-5.326090	-0.190949	-1.637443
22	6	0	3.711740	0.745775	-0.407431
23	6	0	4.795197	0.659255	-1.292241
24	6	0	3.652828	-0.119102	0.689819
25	6	0	5.777837	-0.299733	-1.089537
26	1	0	4.847923	1.351696	-2.124010
27	6	0	4.652514	-1.074667	0.875424
28	1	0	2.845281	-0.044931	1.409361
29	6	0	5.735062	-1.197222	-0.005685
30	1	0	6.598689	-0.348276	-1.799546
31	1	0	4.573334	-1.725316	1.738868
32	8	0	3.138708	2.851022	-1.207369
33	8	0	-0.472377	-1.861257	0.680638
34	6	0	-1.519408	4.126189	0.458321

35	6	0	-2.062980	4.141461	1.906834
36	1	0	-1.243231	4.117266	2.633651
37	1	0	-2.646422	5.053294	2.082573
38	1	0	-2.715556	3.285679	2.109749
39	6	0	-2.705131	4.165597	-0.534805
40	1	0	-2.348929	4.163467	-1.571280
41	1	0	-3.375257	3.308495	-0.407363
42	1	0	-3.297274	5.075728	-0.381420
43	6	0	-0.674446	5.396688	0.247272
44	1	0	0.166768	5.449866	0.947278
45	1	0	-0.275206	5.457169	-0.771233
46	1	0	-1.297394	6.282938	0.412015
47	6	0	-6.842826	-2.152561	-0.314972
48	6	0	-6.961669	-3.626885	-0.770236
49	1	0	-8.016568	-3.910637	-0.868483
50	1	0	-6.476776	-3.778325	-1.741244
51	1	0	-6.497745	-4.313832	-0.054846
52	6	0	-7.549490	-1.980458	1.051126
53	1	0	-7.105557	-2.616819	1.823809
54	1	0	-7.487872	-0.942240	1.396840
55	1	0	-8.609722	-2.248449	0.967813
56	6	0	-7.571754	-1.271202	-1.346755
57	1	0	-7.548702	-0.211436	-1.068021
58	1	0	-7.139221	-1.372115	-2.348674
59	1	0	-8.623326	-1.572186	-1.410814
60	6	0	6.844464	-2.247746	0.170713
61	6	0	8.211303	-1.536542	0.313606
62	1	0	9.013724	-2.274649	0.433543
63	1	0	8.448836	-0.927008	-0.564412
64	1	0	8.221024	-0.878301	1.189778
65	6	0	6.626727	-3.124209	1.418930
66	1	0	5.684766	-3.681952	1.367580
67	1	0	7.438707	-3.855301	1.501736
68	1	0	6.623462	-2.529763	2.339753
69	6	0	6.874822	-3.172501	-1.069777
70	1	0	7.069990	-2.612764	-1.990572
71	1	0	7.664375	-3.926591	-0.964058
72	1	0	5.919416	-3.695158	-1.192201

Rotational constants (GHZ): 0.1659127 0.0508247 0.0410491
SCF Done: E(UB+HF-LYP) = -1425.92486952 A.U. after 8 cycles
Conv = 0.6621D-08 -V/T = 2.0097
S**2 = 2.0296

Annihilation of the first spin contaminant:

S**2 before annihilation 2.0296, after 2.0006

Item	Value	Threshold	Converged?
Maximum Force	0.000004	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.003439	0.001800	NO
RMS Displacement	0.000570	0.001200	YES

Predicted change in Energy=-2.133882D-08

Optimization completed on the basis of negligible forces.

■ Stationary point found.

■ **Frequency calculation of the triplet**

SCF Done: E(UB+HF-LYP) = -1425.92486953 A.U. after 21 cycles
Conv = 0.4355D-08 -V/T = 2.0097
S**2 = 2.0296

Annihilation of the first spin contaminant:

S**2 before annihilation 2.0296, after 2.0006

Dipole moment (field-independent basis, Debye):

X = -2.7440 Y = -0.5811 Z = 0.6167 Tot = 2.8719

Three lowest frequencies:

	1	2	3
	A	A	A
Frequencies --	13.0590	20.1519	25.4154

This molecule is an asymmetric top.

Rotational symmetry number 1.

Warning -- assumption of classical behavior for rotation
may cause significant error

Rotational temperatures (Kelvin) 0.00796 0.00244 0.00197

Rotational constants (GHZ): 0.16591 0.05082 0.04105

Zero-point vibrational energy 1626095.0 (Joules/Mol)
388.64602 (Kcal/Mol)

Warning -- explicit consideration of 60 degrees of freedom as
vibrations may cause significant error

Zero-point correction= 0.619347 (Hartree/Particle)

Thermal correction to Energy= 0.653496

Thermal correction to Enthalpy= 0.654440

Thermal correction to Gibbs Free Energy= 0.551658

Sum of electronic and zero-point Energies= -1425.305523

Sum of electronic and thermal Energies= -1425.271374

Sum of electronic and thermal Enthalpies= -1425.270430

Sum of electronic and thermal Free Energies= -1425.373211

Energy Calculation of the Broken-Symmetry Singlet

Linear equations converged to 1.378D-10 1.378D-09 after 19 iterations.

SCF Done: E(UB+HF-LYP) = -1425.92343452 a.u. after 12 cycles

Convg = 0.7617D-06 91 Fock formations.

S**2 = 1.0150 -V/T = 2.0097

Annihilation of the first spin contaminant:

S**2 before annihilation 1.0150, after 0.1219

Full Geometry Optimization of the Broken-Symmetry Singlet

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.659697	2.836028	-0.126608
2	6	0	1.356944	1.631876	-0.317956
3	6	0	0.715275	0.403827	-0.170923
4	6	0	-0.634155	0.396966	0.196206
5	6	0	-1.323354	1.591526	0.419726
6	6	0	-0.683693	2.831517	0.250492
7	1	0	1.205256	3.755408	-0.284319
8	1	0	1.218731	-0.537729	-0.339775
9	1	0	-2.355397	1.552201	0.745798
10	7	0	-1.251327	-0.877114	0.393528
11	7	0	2.721489	1.718635	-0.728559
12	6	0	-2.637769	-1.131603	0.197518
13	6	0	-3.225220	-2.187007	0.910141
14	6	0	-3.411773	-0.412220	-0.720394
15	6	0	-4.567413	-2.484755	0.721980
16	1	0	-2.612643	-2.757274	1.598154
17	6	0	-4.759147	-0.730049	-0.894291
18	1	0	-2.965655	0.376609	-1.315737
19	6	0	-5.376193	-1.765012	-0.178231
20	1	0	-4.995019	-3.301864	1.296051
21	1	0	-5.324533	-0.154612	-1.618712
22	6	0	3.699534	0.713946	-0.472809
23	6	0	4.791609	0.618781	-1.347370

24	6	0	3.642267	-0.127581	0.643645
25	6	0	5.784222	-0.322489	-1.113987
26	1	0	4.842026	1.290943	-2.195564
27	6	0	4.652259	-1.065588	0.858990
28	1	0	2.827969	-0.048906	1.354906
29	6	0	5.744132	-1.194970	-0.009716
30	1	0	6.611361	-0.376896	-1.816319
31	1	0	4.573572	-1.697656	1.736207
32	8	0	3.085345	2.766444	-1.380231
33	8	0	-0.502333	-1.848187	0.783430
34	6	0	-1.475736	4.129285	0.499219
35	6	0	-1.986379	4.150465	1.959558
36	1	0	-1.151313	4.113195	2.668138
37	1	0	-2.552294	5.070520	2.148995
38	1	0	-2.647210	3.304460	2.176215
39	6	0	-2.682903	4.184398	-0.467012
40	1	0	-2.350016	4.179338	-1.511178
41	1	0	-3.359871	3.334922	-0.325232
42	1	0	-3.260729	5.101221	-0.299433
43	6	0	-0.618774	5.388500	0.269982
44	1	0	0.240417	5.427850	0.948839
45	1	0	-0.244503	5.446556	-0.758100
46	1	0	-1.224912	6.282869	0.452355
47	6	0	-6.861017	-2.131406	-0.342203
48	6	0	-6.980725	-3.598447	-0.819981
49	1	0	-8.035656	-3.877234	-0.931389
50	1	0	-6.487938	-3.737171	-1.788918
51	1	0	-6.525094	-4.297279	-0.110819
52	6	0	-7.581177	-1.976193	1.018900
53	1	0	-7.147847	-2.625561	1.786767
54	1	0	-7.518715	-0.943366	1.380297
55	1	0	-8.641675	-2.238259	0.920969
56	6	0	-7.575933	-1.232363	-1.368563
57	1	0	-7.551967	-0.176882	-1.074095
58	1	0	-7.133032	-1.320202	-2.367185
59	1	0	-8.627868	-1.528394	-1.448107
60	6	0	6.865498	-2.225991	0.201811
61	6	0	8.220949	-1.492979	0.342883
62	1	0	9.032070	-2.216877	0.488314
63	1	0	8.459601	-0.900349	-0.546352
64	1	0	8.212112	-0.814737	1.203682
65	6	0	6.646091	-3.077195	1.467097
66	1	0	5.712208	-3.648586	1.418224
67	1	0	7.466802	-3.795176	1.574994
68	1	0	6.624829	-2.462460	2.374241
69	6	0	6.922183	-3.178322	-1.016701
70	1	0	7.118368	-2.637015	-1.948180
71	1	0	7.721629	-3.917998	-0.886092
72	1	0	5.975912	-3.717980	-1.136443

Rotational constants (GHZ): 0.1663548 0.0505754 0.0410419

SCF Done: E(UB+HF-LYP) = -1425.92355948 a.u. after 4 cycles

Conv = 0.1459D-06 49 Fock formations.

S**2 = 1.0162 -V/T = 2.0097

Annihilation of the first spin contaminant:

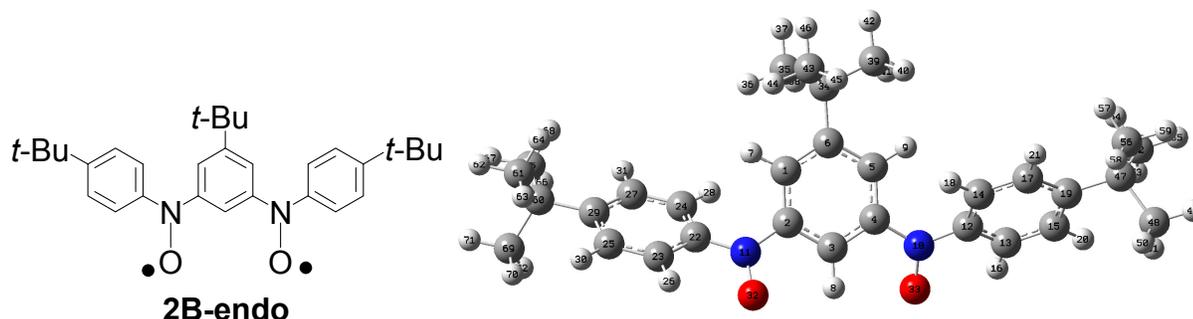
S**2 before annihilation 1.0162, after 0.1314

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.000908	0.001800	YES
RMS Displacement	0.000146	0.001200	YES

Predicted change in Energy=-6.959201D-09

Optimization completed.
 -- Stationary point found.

(b) Diarylnitroxide diradical, conformer 2B-endo: full geometry optimization of the triplet followed by frequency calculation of the triplet and by the energy calculation of broken symmetry singlet at the geometry of the triplet (UB3LYP/6-31G(d) level).



Full geometry optimization of the triplet

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.158868	0.611461	0.285312
2	6	0	-1.161013	-0.790290	0.274279
3	6	0	0.009055	-1.504338	0.004596
4	6	0	1.176359	-0.792739	-0.267782
5	6	0	1.177296	0.613709	-0.287635
6	6	0	0.010681	1.330739	-0.004346
7	1	0	-2.070007	1.137657	0.541668
8	1	0	0.008653	-2.584948	0.007255
9	1	0	2.090023	1.131723	-0.547096
10	7	0	2.342536	-1.540247	-0.598313
11	7	0	-2.326947	-1.537858	0.607164
12	6	0	3.674228	-1.078764	-0.379974
13	6	0	4.686265	-1.556103	-1.223950
14	6	0	4.010600	-0.233715	0.682640
15	6	0	6.001315	-1.164967	-1.014738
16	1	0	4.420562	-2.233362	-2.026975
17	6	0	5.339690	0.144696	0.876654
18	1	0	3.247935	0.108358	1.373604
19	6	0	6.368153	-0.303016	0.036229
20	1	0	6.761655	-1.544138	-1.691445
21	1	0	5.563985	0.793040	1.716254
22	6	0	-3.658764	-1.079900	0.383566
23	6	0	-4.672247	-1.556971	1.226028
24	6	0	-3.993940	-0.238401	-0.682404
25	6	0	-5.987579	-1.169531	1.011710
26	1	0	-4.407360	-2.231192	2.031854
27	6	0	-5.323393	0.136161	-0.881472
28	1	0	-3.230337	0.103505	-1.372392
29	6	0	-6.353383	-0.311640	-0.042905
30	1	0	-6.749019	-1.548604	1.687242
31	1	0	-5.546619	0.781516	-1.723666
32	8	0	-2.170697	-2.696017	1.142981
33	8	0	2.188433	-2.703485	-1.123506
34	6	0	-0.028149	2.871356	0.002724
35	6	0	-1.074626	3.366939	-1.023369
36	1	0	-2.080780	3.002084	-0.791291
37	1	0	-1.112151	4.463005	-1.027829

38	1	0	-0.820771	3.031855	-2.035596
39	6	0	1.332902	3.493222	-0.363322
40	1	0	2.118034	3.206802	0.345550
41	1	0	1.657635	3.204757	-1.369528
42	1	0	1.254775	4.585888	-0.343341
43	6	0	-0.420208	3.367291	1.415027
44	1	0	-1.403082	2.994525	1.721847
45	1	0	0.310221	3.039203	2.163302
46	1	0	-0.458435	4.463122	1.434897
47	6	0	7.841095	0.098847	0.224245
48	6	0	8.696104	-1.169677	0.457726
49	1	0	9.750875	-0.898377	0.587658
50	1	0	8.368726	-1.703222	1.357188
51	1	0	8.633611	-1.866417	-0.384661
52	6	0	8.341725	0.826314	-1.046784
53	1	0	8.264491	0.193203	-1.936911
54	1	0	7.760651	1.736788	-1.232962
55	1	0	9.394348	1.112243	-0.931813
56	6	0	8.042153	1.040060	1.426822
57	1	0	7.481509	1.974903	1.312448
58	1	0	7.737043	0.569756	2.368545
59	1	0	9.102415	1.301180	1.517474
60	6	0	-7.826775	0.085715	-0.236752
61	6	0	-8.333403	0.815630	1.030489
62	1	0	-9.386464	1.098224	0.911390
63	1	0	-8.257129	0.185462	1.922785
64	1	0	-7.755516	1.728335	1.215695
65	6	0	-8.026473	1.022732	-1.442826
66	1	0	-7.717168	0.550331	-2.382123
67	1	0	-9.087105	1.280866	-1.537617
68	1	0	-7.468568	1.959351	-1.329586
69	6	0	-8.677636	-1.185809	-0.469115
70	1	0	-8.616036	-1.879851	0.375572
71	1	0	-9.732682	-0.917684	-0.603292
72	1	0	-8.345915	-1.721189	-1.365889

Rotational constants (GHZ): 0.3134598 0.0402246 0.0374879
SCF Done: E(UB+HF-LYP) = -1425.92309079 A.U. after 6 cycles
Conv = 0.7383D-08 -V/T = 2.0097
S**2 = 2.0281

Annihilation of the first spin contaminant:

S**2 before annihilation 2.0281, after 2.0005

Item	Value	Threshold	Converged?
Maximum Force	0.000009	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.000441	0.001800	YES
RMS Displacement	0.000102	0.001200	YES

Predicted change in Energy=-1.876023D-09

Optimization completed.

-- Stationary point found.

Dipole moment (field-independent basis, Debye):

X= -0.0155 Y= 5.5085 Z= -0.0203 Tot= 5.5086

■ *Frequency calculation of the triplet*

Initial convergence to 1.0D-05 achieved. Increase integral accuracy.

SCF Done: E(UB+HF-LYP) = -1425.92309080 A.U. after 20 cycles
Conv = 0.8214D-08 -V/T = 2.0097
S**2 = 2.0281

Annihilation of the first spin contaminant:

S**2 before annihilation 2.0281, after 2.0005

Three lowest frequencies:

	1	2	3
	A	A	A
Frequencies --	9.9849	17.7796	31.7608

This molecule is an asymmetric top.

Rotational symmetry number 1.

Warning -- assumption of classical behavior for rotation
may cause significant error

Rotational temperatures (Kelvin) 0.01504 0.00193 0.00180

Rotational constants (GHZ): 0.31346 0.04022 0.03749

Zero-point vibrational energy 1625856.0 (Joules/Mol)
388.58891 (Kcal/Mol)

Warning -- explicit consideration of 60 degrees of freedom as
vibrations may cause significant error

Zero-point correction= 0.619256 (Hartree/Particle)

Thermal correction to Energy= 0.653415

Thermal correction to Enthalpy= 0.654359

Thermal correction to Gibbs Free Energy= 0.551618

Sum of electronic and zero-point Energies= -1425.303835

Sum of electronic and thermal Energies= -1425.269676

Sum of electronic and thermal Enthalpies= -1425.268732

Sum of electronic and thermal Free Energies= -1425.371473

Energy Calculation of the Broken-Symmetry Singlet

SCF Done: E(UB+HF-LYP) = -1425.92187961 a.u. after 12 cycles

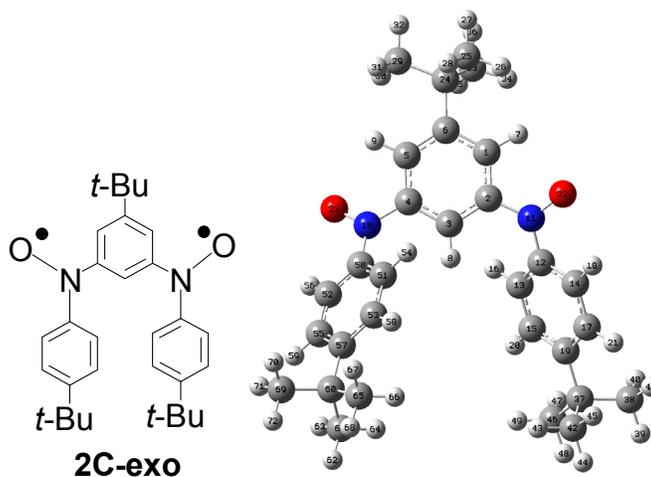
Convg = 0.7220D-06 91 Fock formations.

S**2 = 1.0145 -V/T = 2.0097

Annihilation of the first spin contaminant:

S**2 before annihilation 1.0145, after 0.1228

(c) Diarylnitroxide diradical, conformer 2C-exo: full geometry optimization of the triplet followed by frequency calculation of the triplet and by the energy calculation of broken symmetry singlet at the geometry of the triplet (UB3LYP/6-31G(d) level).



Full geometry optimization of the triplet

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.535854	1.053824	0.440870
2	6	0	-2.136664	1.082938	0.426535
3	6	0	-1.401478	-0.029348	-0.003050
4	6	0	-2.100668	-1.159614	-0.435770
5	6	0	-3.504750	-1.173695	-0.459406

6	6	0	-4.238511	-0.072055	-0.012140
7	1	0	-4.049226	1.931871	0.811795
8	1	0	-0.320382	-0.013044	0.000142
9	1	0	-3.984260	-2.066748	-0.834109
10	7	0	-1.423027	-2.316123	-0.917753
11	7	0	-1.493191	2.257075	0.914262
12	6	0	-0.194322	2.684388	0.508692
13	6	0	0.313012	2.435105	-0.770743
14	6	0	0.563341	3.444471	1.410619
15	6	0	1.572858	2.918523	-1.126138
16	1	0	-0.276288	1.889103	-1.499060
17	6	0	1.814424	3.914573	1.036729
18	1	0	0.150870	3.658013	2.389580
19	6	0	2.358762	3.664217	-0.237304
20	1	0	1.929286	2.710297	-2.128570
21	1	0	2.381167	4.493596	1.760349
22	8	0	-2.121617	2.979097	1.773624
23	8	0	-2.027554	-3.058444	-1.777021
24	6	0	-5.778534	-0.058961	0.000130
25	6	0	-6.274301	0.131543	1.453199
26	1	0	-5.909466	1.066723	1.889987
27	1	0	-7.370474	0.154909	1.479822
28	1	0	-5.936855	-0.691562	2.093384
29	6	0	-6.378337	-1.366985	-0.548597
30	1	0	-6.080690	-1.549272	-1.587275
31	1	0	-6.081614	-2.235668	0.049816
32	1	0	-7.472046	-1.307237	-0.523280
33	6	0	-6.287972	1.111543	-0.873962
34	1	0	-5.934842	2.080368	-0.506055
35	1	0	-5.951055	1.002643	-1.911137
36	1	0	-7.384387	1.134489	-0.873738
37	6	0	3.750876	4.208847	-0.600485
38	6	0	3.744299	5.752244	-0.488932
39	1	0	4.733104	6.155813	-0.738858
40	1	0	3.013631	6.191770	-1.177322
41	1	0	3.493875	6.087851	0.522873
42	6	0	4.800057	3.629228	0.378452
43	1	0	4.830017	2.535293	0.318698
44	1	0	5.799297	4.010580	0.135579
45	1	0	4.583598	3.901684	1.416763
46	6	0	4.171764	3.832973	-2.033780
47	1	0	3.484502	4.243242	-2.782412
48	1	0	5.167370	4.239623	-2.243363
49	1	0	4.222865	2.747109	-2.173595
50	6	0	-0.111987	-2.703790	-0.510502
51	6	0	0.386553	-2.439157	0.769267
52	6	0	0.668820	-3.441102	-1.411523
53	6	0	1.660099	-2.884482	1.125794
54	1	0	-0.219492	-1.911095	1.497045
55	6	0	1.933052	-3.873581	-1.036486
56	1	0	0.263668	-3.667147	-2.390723
57	6	0	2.468612	-3.606716	0.237847
58	1	0	2.009327	-2.665476	2.128492
59	1	0	2.517343	-4.435850	-1.759330
60	6	0	3.875847	-4.110040	0.602041
61	6	0	4.908495	-3.499771	-0.375851
62	1	0	5.918016	-3.852856	-0.132661
63	1	0	4.700486	-3.777456	-1.414523
64	1	0	4.907261	-2.405488	-0.315243
65	6	0	4.284273	-3.722562	2.035889
66	1	0	4.304953	-2.635711	2.175852
67	1	0	3.607718	-4.151890	2.783583

68	1	0	5.290522	-4.101290	2.246829
69	6	0	3.915065	-5.652941	0.489804
70	1	0	3.199032	-6.114436	1.179193
71	1	0	3.673101	-5.995429	-0.521760
72	1	0	4.915951	-6.026918	0.737660

Rotational constants (GHZ): 0.1037608 0.0844256 0.0513663
SCF Done: E(UB+HF-LYP) = -1425.92419925 A.U. after 7 cycles
Conv = 0.7053D-08 -V/T = 2.0097
S**2 = 2.0291

Annihilation of the first spin contaminant:

S**2 before annihilation 2.0291, after 2.0005

Item	Value	Threshold	Converged?
Maximum Force	0.000010	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.000578	0.001800	YES
RMS Displacement	0.000145	0.001200	YES

Predicted change in Energy=-3.375205D-09

Optimization completed.

-- Stationary point found.

Dipole moment (field-independent basis, Debye):

X= 3.4144 Y= 0.0780 Z= 0.0033 Tot= 3.4153

Frequency calculation of the triplet

Initial convergence to 1.0D-05 achieved. Increase integral accuracy.

SCF Done: E(UB+HF-LYP) = -1425.92419926 A.U. after 20 cycles
Conv = 0.7605D-08 -V/T = 2.0097
S**2 = 2.0291

Annihilation of the first spin contaminant:

S**2 before annihilation 2.0291, after 2.0005

Three lowest frequencies:

	1	2	3
	A	A	A
Frequencies --	9.3913	19.6789	26.1438
Red. masses --	4.5874	4.4056	3.4259
Frc consts --	0.0002	0.0010	0.0014
IR Inten --	0.1528	0.5328	0.0439

This molecule is an asymmetric top.

Rotational symmetry number 1.

Warning -- assumption of classical behavior for rotation
may cause significant error

Rotational temperatures (Kelvin) 0.00498 0.00405 0.00247

Rotational constants (GHZ): 0.10376 0.08443 0.05137

Zero-point vibrational energy 1626135.9 (Joules/Mol)

388.65581 (Kcal/Mol)

Warning -- explicit consideration of 60 degrees of freedom as
vibrations may cause significant error

Zero-point correction= 0.619362 (Hartree/Particle)

Thermal correction to Energy= 0.653522

Thermal correction to Enthalpy= 0.654466

Thermal correction to Gibbs Free Energy= 0.551398

Sum of electronic and zero-point Energies= -1425.304837

Sum of electronic and thermal Energies= -1425.270677

Sum of electronic and thermal Enthalpies= -1425.269733

Sum of electronic and thermal Free Energies= -1425.372801

Energy Calculation of the Broken-Symmetry Singlet

Linear equations converged to 1.311D-10 1.311D-09 after 18 iterations.

SCF Done: E(UB+HF-LYP) = -1425.92287864 a.u. after 12 cycles
Conv = 0.7346D-06 87 Fock formations.

$S^{*2} = 1.0139$ $-V/T = 2.0097$
Annihilation of the first spin contaminant:
 S^{*2} before annihilation 1.0139, after 0.1226

8. References for supporting information.

- S1. Adam, W.; Bialas, J.; Hadjiarapoglou, L. *Chem. Ber.* **1991**, *124*, 2377.
- S2. Gilbert, M.; Ferrer, M.; Sanchez-Baeza, F.; Messeguer, A. *Tetrahedron* **1997**, *53*, 8643–8650.
- S3. Vale, M.; Pink, M.; Rajca, S.; Rajca, A. *J. Org. Chem.* **2008**, *73*, 27–35.
- S4. Ivanov, Y. A.; Kokorin, A. I.; Shapiro, A. B.; Rozantsev, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, *10*, 2217–2222.