Supplementary Material (ESI) for Chemical Communications

Triplet ground state ($S = 1$) pegylated bis(aminoxyl) diradical: synthesis and the effect of water on magnetic properties.

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Electronic Supporting Information

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Experimental Section

General procedures and materials. Ether and tetrahydrofuran (THF) were freshly distilled from sodium/benzophenone prior to use. *n*-BuLi (hexane) was obtained from either Aldrich or Acros and added by drops. Prior to use, concentration of *n*-BuLi was determined by titration with *N*-pivaloyl-*o*-toluidine (Suffert, J. *J. Org. Chem.*, **1989**, *54*, 509–510). Per-deuterated solvents for NMR spectroscopy were obtained from Cambridge Isotope Laboratories. All other commercially available chemicals were obtained from Aldrich or Acros. Column chromatography was carried out on TLC grade silica gel (Aldrich), using 0–20 psig pressure. Reverse phase chromatography (RP) was carried out on C18 Ultra-Clean^{TM} Columns (Alltech). Preparative TLC (PTLC) was carried out using Analtech silica plates (tapered with a preadsorbent zone). PTLC plates with deactivated silica were prepared by treatment with pentane/triethylamine, 99:1, followed by drying under low vacuum (diaphragm pump, <10 Torr) for 2 h. Standard Schlenk techniques for synthesis under inert atmosphere, were employed.

NMR spectra were obtained using Bruker Avance (^{1}H, 400 MHz and 600 MHz) using $CDCl_3$ or D_2O as solvent. The chemical shift references were as follows: (^{1}H) TMS, 0.0 ppm ($CDCl_3$), (^{1}H) HDO, 4.80 ppm (D_2O), (^{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 ^{1}H) and 1.0–2.0 Hz (for ^{13}C). Selected spectra were resolution enhanced or broadened, using exponential and Gaussian multiplications; the corresponding parameters, LB and GB (in units of Hz), were included in the spectral listings.

Values of the magnetic moment and χT were obtained in water (D_2O/H_2O, ~1:1) using the ^{1}H NMR-based Evans method (Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005. Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791–792). Concentric NMR tubes (Wilmad, cat. No. WGS-5BL) were used. Diamagnetic susceptibility of H_2O at 20 °C, $\chi_{dia} = -0.7218\times10^{-6}$ emu g^{-1}, and Pascal constant correction for aminoxyls were used (*Handbook of Chemistry and Physics*, CRC Press, INC, Florida, 1983–1984, 64th Ed., E-119).

T_1 measurements were made on a 200 MHz Varian Gemini 2000 NMR using a standard inversion recovery sequence (180–t–90), at 25 °C. Proton relaxivity measurement were performed in H_2O, using water as probe and aminoxyls as paramagnetic relaxation enhancers. Solutions of aminoxyls in water were prepared at specified concentrations. These solutions are contained in a thin-wall, 0.8-mm O.D. glass capillary, which is mounted in a 5-mm NMR tube with a teflon support. The T_1 for each solution and for pure water (or buffer) were calculated using a standard Varian program VNMR6.1C.

IR spectra were obtained using a Nicolet Avatar 360 FT-IR instrument, equipped with an ATR sampling accessory (Spectra Tech, Inc.). A few drops of the compound in CH_2Cl_2 were applied to the surface of a ZnSe ATR plate horizontal parallelogram (45°, Wilmad). After the solvent evaporated, the spectrum was acquired (128 scans, 4-cm^{-1} resolution).

MS analyses were carried out at the Nebraska Center for Mass Spectrometry.

EPR spectroscopy. CW X-band EPR spectra were acquired on Bruker EMX instrument, equipped with a frequency counter and nitrogen flow temperature control (130–300 K). All spectra were obtained using dual-mode cavity, with the oscillating magnetic field perpendicular (TE_{102}) to the swept magnetic field. Parallel (TE_{012}) mode was not used.

SQUID Magnetometry. Quantum Design (San Diego, CA) MPMS5S (with continuous temperature control) was used. The SQUID sample tubes (S. Rajca, A. Rajca, J. Wongsriratanakul, P. Butler, S. Choi, *J. Am. Chem. Soc.* **2004**, *126*, 6972–6986), containing **1** in degassed D_2O, were carefully inserted to the magnetometer, with the sample chamber at 290–300 K. The sequence of measurements started with a cooling mode from 300 K to 1.8 K, and then followed with the other sequences of measurements below the melting point of D_2O (1.8–260 K). After the measurements, each SQUID sample tube was opened and cleaned, and then identical sequences of measurements was carried out for the point-by-point correction for diamagnetism. For solid (neat) samples, additional correction was used based upon Pascal constants ($\chi_{dia} = 3.2\times10^{-4}$ emu mol^{-1} for **1**). For samples in D_2O, the following procedure was employed: (1) the mass of D_2O was determined and ^1H NMR spectrum of **1** was obtained to verify its purity, (2) correction for diamagnetism was obtained using the empty SQUID tube (as described above), χ_{dia} =

3.2×10^{-4} emu mol^{-1} for **1**, and $\chi_{dia} = 12.41\times10^{-6}$ emu mol^{-1} for D_2O at 213 K (CRC Handbook, 64th Ed., CRC Press, 1983–1984, E-113). Accurate correction for diamagnetism for samples in D_2O was difficult to attain, probably because residual amounts of D_2O remained outside the sample measurement space.

EPR Spectral Simulations and Numerical Curve Fitting for SQUID Magnetic Data. The WINEPR SimFonia program (Version 1.25, Bruker) was used for spectral simulations of **1** in glassy matrices. WinSIM program (Public EPR Software Tools, D. A. O'Brien, D. R. Duling, Y. C. Fann) was used for numerical fitting of EPR spectra of **2** in solution.

The SigmaPlot for Windows software package was used for numerical curve fitting. The reliability of a fit is measured by the parameter dependence, which is defined as follows: *dependence = 1 – ((variance of the parameter, other parameters constant)/(variance of the parameter, other parameters changing))*. Values close to 1 indicate overparametrized fit.

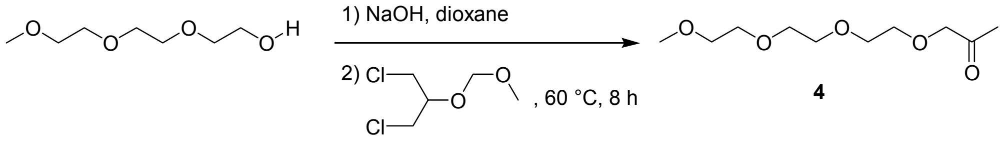
M vs. *T* data were plotted as χT vs. *T*, and then numerically fit to the model of diradical (eq. 1S), with the three variable parameters (J/k, θ, and w), as described in the text. This model accounts for paramagnetic saturation:

$$\chi T = 2wNg\mu_B T \sinh(g\mu_B H/k(T-\theta))/\{H[\exp(-2J/kT) + 1 + 2\cosh(g\mu_B H/k(T-\theta))]\} \quad (1S)$$

For neat **1** at $H = 30000$ Oe, typical values of optimized parameters (parameter dependence and standard error) were as follows: $J/k = 326$ K (0.39 and 3.2%), $\theta = -2.1$ K (0.49 and 0.9%), and $w = 0.93$ (0.63 and 0.1%); norm was 0.0454.

Attempts to include residual monoradical in the model (4th variable parameter) led to the fits showing negligible amounts (<1%) of monoradical, though such fits were very close to over parametrization.

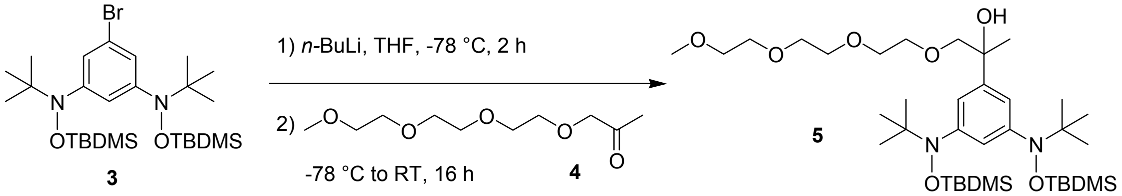
Ketone 4



1-{2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxy}-propan-2-one 4. To a solution of triethyleneglycol monomethyl ether (3.28 g, 0.02 mol, 1 equiv) in dioxane (30 mL) was added sodium hydroxide (3.20 g, 0.0800 mol, 4 equiv) and the 2-chloro-1-(chloromethyl)ethyl methoxymethyl ether (X.-P. Gu., I. Ikeda, S. Komada, A. Masuyama, M. Okahara, *J. Org. Chem.* **1986**, *51*, 5425–5427) (3.80 g, 0.02 mol, 1.1 equiv). After 8 h at 60 °C, the reaction mixture was filtered and evaporated under reduced pressure. The crude mixture was then stirred for 2 h at room temperature with 5 mL of a 1 % H_2SO_4 aqueous solution. After neutralization (pH = 7) with NaOH, the organic layer was diluted and extracted with dichloromethane, to give a crude product (6.7 g). Distillation under high vacuum provide a mixture of target and starting material (2.4 g); the 859 mg portion of the mixture was purified by flash chromatography (dichloromethane/methanol, 99:1) to yield a pale yellow oil (249 mg, 16 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (s, 2H), 3.69 (s, 4H), 3.66 (s, 4H), 3.67 – 3.61 (m, 6H, overlapped with 3.66 (s, 4H)), 3.57 – 3.52 (m, 2H), 3.37 (s, 3H), 2.16 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 206.9, 76.5, 71.7, 70.6, 70.4, 70.3, 70.3, 70.2, 58.75, 26.0. HR FAB-MS (3-NBA + Li matrix): m/z (ion type, %RA or m/z = 225–230, deviation for the formula): 229.1544 (2%, impurity), 228.1516

([M+1]$^+$, 11%, –5.1 ppm for $^{12}C_9{}^{13}C_1H_{20}O_5Li_1$), 227.1475 ([M]$^+$, 100%, –2.0 ppm for $^{12}C_{10}H_{20}O_5Li_1$), 225.1308 ([M–2H]$^+$, 2%, 2.7 ppm for $^{12}C_{10}H_{18}O_5Li_1$). IR (cm^{-1}): 2872 (CH$_2$, br), 1728 (C=O), 1108 (C–O).

Alcohol 5.

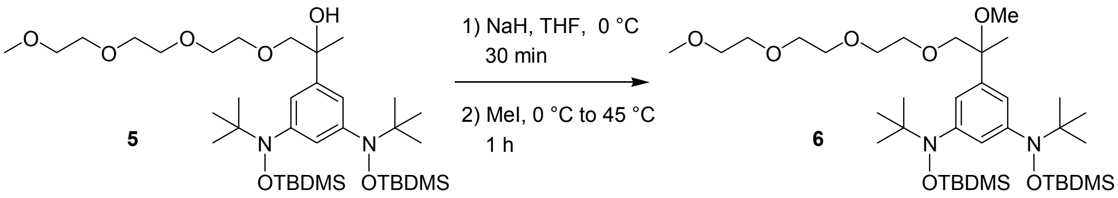


Experiment	**3**	*n*-BuLi equiv	Yield %
GS0124	20 mg (0.036 mmol)	1.1 (0.42M, 0.04 mmol)	41%
GS0125	30 mg (0.054 mmol)	1.2 (2.32M, 0.06 mmol)	combined purification 65%
GS0127	125 mg (0.22 mmol)	1.2 (2.47M, 0.27 mmol)	

GS0127 **2-{3,5-Bis-[*tert*-butyl-(*tert*-butyl-dimethyl-silanyl)-amino]-phenyl}-1-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-propan-2-ol 5.** *n*-BuLi (2.47 M, 109 μL, 0.268 mmol, 1.2 equiv) was added to a solution of **3** (125 mg, 0.223 mmol, 1 equiv) in THF (4.2 mL) stirred at –78 °C. After 2.5 h at –78 °C, the ketone **4** (73.8 mg, 0.335 mmol, 1.5 equiv) in solution in THF (2.1 mL) was added. The reaction mixture was slowly warmed to room temperature, and then kept stirring for another 16 h. The usual aqueous workup gave a crude product (132 mg). This crude and the other one from a 30-mg scale reaction were purified by flash chromatography (dichloromethane/methanol, 98:2) to give the product (125 mg, 65%) as a pale yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.16 (br, 2H), 6.95 (br, 1H), 3.69 – 3.52 (m, 14H), 3.38 (s, 3H), 1.46 (s, 3H), 1.06 (s, 18H), 0.89 (s, 18H), –

0.13 (br, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 150.0, 143.6, 121.0, 118.8, 79.6, 73.9, 71.9, 71.1, 70.6, 70.6, 70.5, 70.4, 70.0, 59.0, 26.3, 26.2, 17.9, –4.6. IR (cm^{-1}): 3489 (O-H, v. br), 2928 (CH_2, v. br), 1589 (Ar C–H) 1112 (C–O, br), 835.

Methyl ether 6.

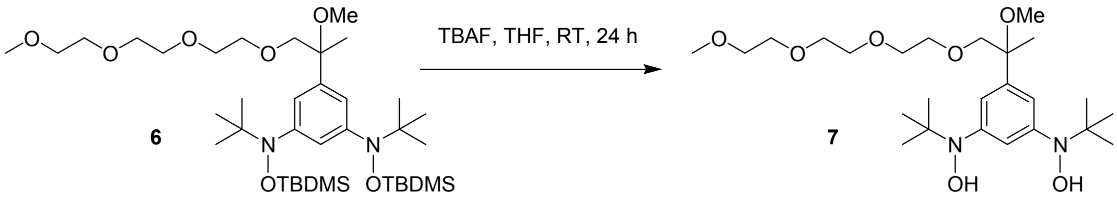


Experiment	**5**	Temperature	Yield %
GS 01-26	7 mg (0.01 mmol)	RT	34%
GS 01-29	10 mg (0.014 mmol)	40/45 °C	Combined purification 90%
GS 01-32	78 mg (0.11 mmol)	40/45 °C	

GS0132 **N,N'-Di-*tert*-butyl-N,N'-bis-(*tert*-butyl-dimethyl-silanyl)-5-(1-methoxy-2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-1-methyl-ethyl)-benzene-1,3-diamine 6.** Sodium hydride (22.3 mg, 0.557 mmol, 60% dispersion in mineral oil, 5 equiv) was added to a solution of alcohol **5** (78.0 mg, 0.111 mmol, 1 equiv) in dry THF (5 mL) at 0 °C. After the reaction mixture was stirred at 0 °C for 30 min, methyl iodide (42 μL, 0.668 mmol, 6 equiv) was added. The reaction was stirred at 0 °C for 30 min, and then at 45 °C for 1 h. The usual aqueous workup gave a crude product (92 mg). This crude and the other one from a 10-mg scale reaction were purified by flash chromatography (pentane/ether, 7:3) to give the product (72 mg, 90%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.22 – 6.80 (m, 3H), 3.69 – 3.49 (m, 13H), 3.40 – 3.34 (m, 4H), 3.04 (s, 3H), 1.56 (s, 3H), 1.06

(s, 18H), 0.90 (s, 18H), –0.11 (br, 12H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 150.1, 140.5, 121.9, 120.6, 79.5, 79.3, 71.9, 71.2, 70.5, 61.0, 59.0, 50.4, 26.3, 26.1, 19.9, 17.9, –4.5. HR FAB-MS (3-NBA + Na matrix): m/z (ion type, %RA or m/z = 735–740, deviation for the formula): 738.4925 ($[M+1]^+$, 48%, 5.6 ppm for $^{12}C_{36}{}^{13}C_1H_{74}N_2O_7Na_1Si_2$), 737.4923 ($[M]^+$, 100%, 1.2 ppm for $^{12}C_{37}H_{74}N_2O_7Na_1Si_2$), 736.4853 ($[M–H]^+$, 3%, 0.2 ppm for $^{12}C_{37}H_{73}N_2O_7Na_1Si_2$), 735.4821 ($[M–2H]^+$, 4%, –6.2 ppm for $^{12}C_{37}H_{72}N_2O_7Na_1Si_2$). IR ($cm^{-1}$): 2928 ($CH_2$, v. br), 1589 (Ar C–H), 1115 (C–O, br), 835.

Dihydroxylamine 7.



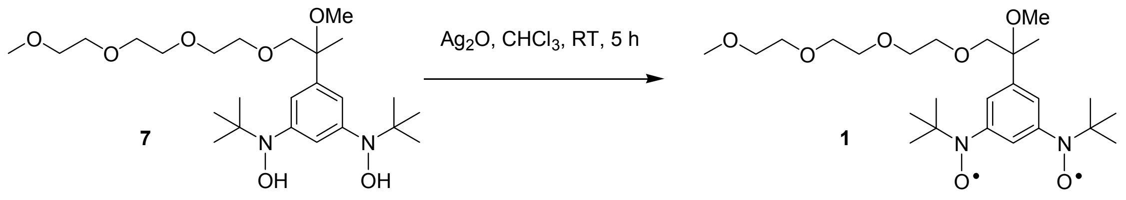
Experiment	**6**	Yield %
GS 01-35	7 mg (0.01 mmol)	90%
GS 01-42	69.5 mg (0.10 mmol)	95%

GS0142 **N,N'-Di-*tert*-butyl-N,N'-bis-(hydroxyl)-5-(1-methoxy-2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-1-methyl-ethyl)-benzene-1,3-diamine 7.** TBAF (0.46 mL, 0.456 mmol, 4.6 equiv) was added dropwise to a solution of methyl ether **6** (69.5 mg, 0.099 mmol, 1 equiv) in dry THF (0.6 mL) at RT. The reaction mixture, protected from UV, was stirred at room temperature for 12 h. The crude mixture was rapidly filtered through a pad of silica using ether (100 mL). Concentration under reduced pressure and drying under high vacuum for 24 h gave the product (44 mg, 95%) as a colorless oil. ^1H NMR (400

MHz, $CDCl_3$): δ = 7.83 (br, 1.5H), 7.14 (s, 1H), 6.87 (s, 2H), 3.69 – 3.43 (m, 13H), 3.36 (s, 3H), 3.26 (d, J = 10.4 Hz, 1H), 3.00 (s, 3H), 1.46 (s, 3H), 1.11 (s, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 148.2, 140.7, 120.0, 119.6, 79.1, 71.8, 71.1, 70.5, 70.4, 60.5, 58.9, 26.0, 25.9, 19.9. HR EI-MS cluster: m/z (ion type, %RA or m/z = 450–505, deviation for the formula): 486.3285 ($[M]^+$, 15%, 4.1 ppm for $^{12}C_{25}H_{46}N_2O_7$), 470.3355 ($[M–O]^+$, 21%, 0.3 ppm for $^{12}C_{25}H_{46}N_2O_6$), 469.3277 ($[M–OH]^+$, 19%, 0.2 ppm for $^{12}C_{25}H_{45}N_2O_6$), 455.3437 ($[M–O_2+1]^+$, 32%, 0.8 ppm for $^{12}C_{24}{}^{13}C_1H_{46}N_2O_5$), 454.3396 ($[M–O_2]^+$, 100%, 2.4 ppm for $^{12}C_{25}H_{46}N_2O_5$), 453.3323 ($[M–O_2H]^+$, 23%, 1.1 ppm for $^{12}C_{25}H_{45}N_2O_5$). IR (cm^{-1}): 3374 (O-H, v. br), 2923 (CH_2, v. br), 1589 (Ar C–H), 1101 (C–O, br).

Ag_2O. A concentrated aqueous solution of sodium hydroxide (5.40 M, 500 µL, 2.34 mmol, 1.5 equiv) was added to an aqueous solution (5.5 mL) of silver nitrate (530 mg, 3.12 mmol, 2 equiv). A brown precipitate of silver oxide was obtained instantaneously. The reaction mixture was kept stirring for 30 min at RT, and then the precipitate was filtered and washed successively with water, acetone and ether, followed by drying under high vacuum overnight, protected from UV.

Diradical 1.



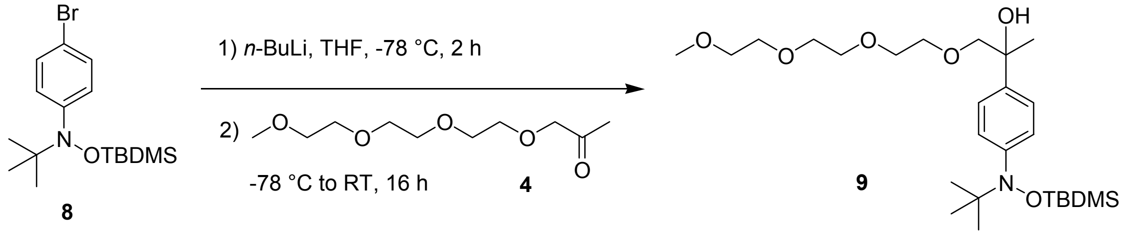
Experiment	**7**	Purification	Yield %
GS0139	5.4 mg (0.009 mmol)	Silica + RP	1.8 mg, 42%
GS0147	40 mg (0.08 mmol)	Silica + RP×2	17.4 mg, 44%

GS0168 (from GS0147)	15 mg (0.03 mmol)	Silica + RP×2	12 mg, 80%
GS0332 (combined)	13 mg	Silica	9.8 mg, 75%

GS0147 **N,N'-Di-*tert*-butyl-N,N'-bis-(nitroxide)-5-(1-methoxy-2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-1-methyl-ethyl)-benzene-1,3-diamine 1.** A solution of the dihydroxylamine **7** (40.0 mg, 0.0821 mmol, 1 equiv) in degassed chloroform (3.5 mL) was added onto freshly prepared silver oxide (190 mg, 0.821 mmol, 10 equiv). The reaction mixture, protected from UV, was stirred under N_2 at room temperature for ~5 h. Subsequently, the reaction mixture was filtered through a pad of cotton, using chloroform (5 mL), and then concentrated under reduced pressure, to give a dark orange-red oil (29 mg). Flash chromatography (silica, ether) gave the product (21.3 mg). Further purification employed reverse phase chromatography (Ultra-Clean^{TM} C18 catridge). The cartridge was washed successively with 5 mL of methanol, chloroform, hexane, chloroform, methanol and water before application of the diradical. Elution by methanol/water (7:3, v/v) gave a dark orange-red oil (17.4 mg, 44%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.54 (v. br, 2–3H), 4.41 (v. br, 2–3H), 4.0 – 3.2 (m, 3.85 (sh), 3.73, 3.62, 3.44 (with sh), 17–19H), –2.27 (v. br, 18H). ^{1}H NMR (400 MHz, D_2O): δ = 12.0 – (–2.0) (m, 5.96, 3.73, 3.47, 23.5–25.5H), –6.87 (v. br, 18H). HR EI-MS cluster: m/z (ion type, %RA or m/z = 450–505, deviation for the formula): 485.3226 ($[M+H]^+$, 8%, 0.2 ppm for $^{12}C_{25}H_{45}N_2O_7$), 484.3157 ($[M]^+$, 8%, –1.8 ppm for $^{12}C_{25}H_{44}N_2O_7$), 472.3320 (impurity, 9%), 470.3331 ($[M–O+2H]^+$, 11%, 5.4 ppm for $^{12}C_{25}H_{46}N_2O_6$), 469.3276 ($[M–O+H]^+$, 16%, 0.4 ppm for $^{12}C_{25}H_{45}N_2O_6$), 455.3432 ($[M–O_2+2H+1]^+$, 35%, 1.9 ppm for $^{12}C_{24}{}^{13}C_1H_{46}N_2O_5$), 454.3406 ($[M–O_2+2H]^+$, 100%, 0.2

ppm for $^{12}C_{25}H_{46}N_2O_5$) 453.3366 ($[M–O_2+H]^+$, 19%, –8.4 ppm for $^{12}C_{25}H_{45}N_2O_5$), 453.2951 (impurity, 8%). IR (cm^{-1}): 2936 (CH_2, v. br), 1112 (C–O, br).

Alcohol 9.

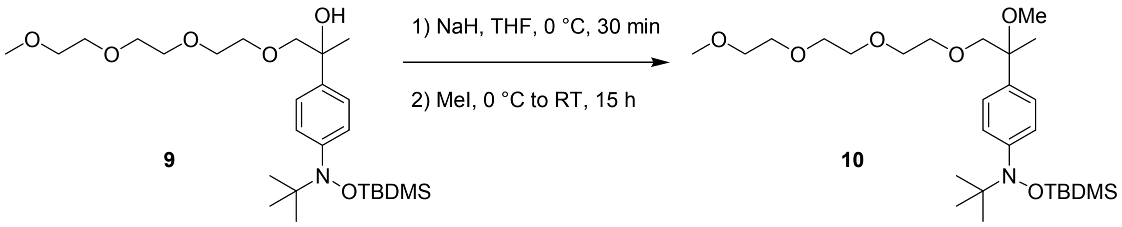


Experiment	**8**	*n*-BuLi equiv	Yield %
GS0258	5 mg (0.014 mmol)	1.2	not purified
GS0262	162 mg (0.45 mmol)	1.2	80%

GS0262 **2-[4-tert-butyl-(tert-butyl-dimethyl-silanyl)-amino]-1-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-propan-2-ol 9.** *n*-BuLi (3.11 M, 0.175 mL, 0.534 mmol, 1.2 equiv) was added to a solution of **8** (162 mg, 0.453 mmol, 1 equiv) in THF (8.0 mL) stirred at –78 °C. After 2 h at –78 °C, the ketone **4** (150 mg, 0.679 mmol, 1.5 equiv) in solution in THF (4.0 mL) was added. The reaction mixture was slowly warmed to room temperature, and then kept stirring for another 16 h. The usual aqueous workup gave a crude product (269 mg), which was purified by flash chromatography (dichloromethane/methanol, 98:2), to yield the product (178 mg, 80%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30, 7.18 (AB, J = 9 Hz, 4H), 3.72 – 3.53 (m, 14H), 3.38 (s, 3H), 3.25 (br, 0.7H), 1.52 (s, 3H), 1.08 (s, 9H), 0.89 (s, 9H), –0.15 (br, 6H). HR FAB-MS (3-NBA + Na matrix): m/z (ion type, %RA or m/z = 520–525, deviation for the formula): 523.3265 ($[M+1]^+$, 33%, –

0.8 ppm for ${}^{12}C_{25}{}^{13}C_1H_{49}N_1O_6Na_1Si_1$), 522.3234 ([M]$^+$, 100%, –1.4 ppm for ${}^{12}C_{26}H_{49}N_1O_6Na_1Si_1$), 521.3130 ([M–H]$^+$, 2%, 3.6 ppm for ${}^{12}C_{26}H_{48}N_1O_6Na_1Si_1$), 520.3069 ([M–2H]$^+$, 3%, 0.2 ppm for ${}^{12}C_{26}H_{47}N_1O_6Na_1Si_1$). IR (cm^{-1}): 3454 (O-H, br), 2928 (CH$_2$, v. br), 1110 (C–O, br).

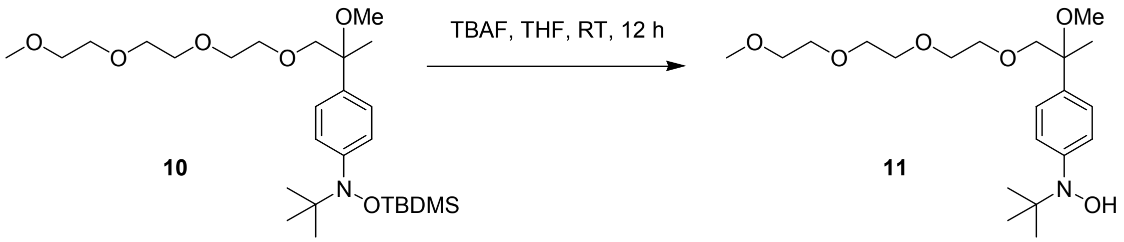
Methyl ether 10.



Experiment	**9**	Yield %
GS0264	5 mg (0.01 mmol)	Combined purification 92%
GS0268	80 mg (0.16 mmol)	

GS0268 **N-*tert*-Butyl-N-(*tert*-butyl-dimethyl-silanyl)-[4-(1-methoxy-2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-1-methyl-ethyl)-phenyl]-amine 10.** Sodium hydride (32.0 mg, 0.802 mmol, 60% dispersion in mineral oil, 5.0 equiv) was added to a solution of alcohol **9** (80.0 mg, 0.160 mmol, 1.0 equiv) in dry THF (5 mL) at 0 °C. After the reaction mixture was stirred at 0 °C for 30 min, and then methyl iodide (60 µL, 0.96 mmol, 6 equiv) was added. The reaction mixture was allowed to attain room temperature over 1 h, and then was stirred for additional 15 h. The usual aqueous workup gave a crude product (110 mg). This crude and the other one from a 5-mg scale reaction were purified by flash chromatography (dichloromethane/methanol, 98:2), to give the product (81 mg, 92%) as a pale yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.23, 7.20 (AB, J = 9 Hz, 4H), 3.69 – 3.43 (m, 14H), 3.37 (m, 3H), 3.07 (s, 3H), 1.59 (s, 3H), 1.09 (s, 9H), 0.89 (s, 9H), –0.15 (br, 6H). HR FAB-MS (3-NBA + Na matrix): m/z (ion type, %RA or m/z = 534–539, deviation for the formula): 538.4046 (impurity, 1%), 537.3420 ([M+1]$^+$, 30%, –0.6 ppm for $^{12}C_{26}{}^{13}C_1H_{51}N_1O_6Na_1Si_1$), 536.3379 ([M]$^+$, 100%, 0.8 ppm for $^{12}C_{27}H_{51}N_1O_6Na_1Si_1$), 534.3228 ([M–2H]$^+$, 2%, –0.3 ppm for $^{12}C_{27}H_{49}N_1O_6Na_1Si_1$). IR (cm^{-1}): 2928 (CH$_2$, v. br), 1110 (C–O, br).

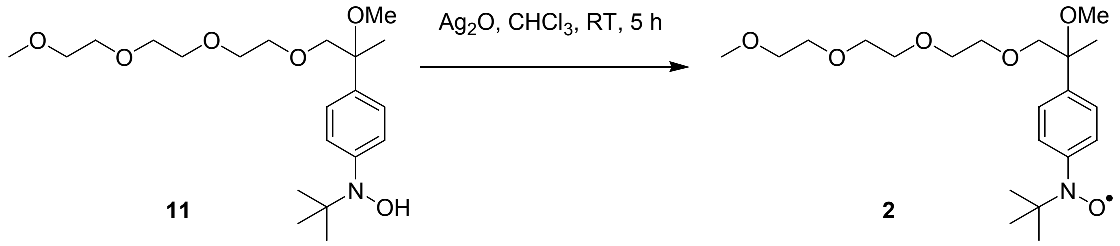
Hydroxylamine 11.



Experiment	Scale	Yield %
GS0271	5 mg (0.01 mmol)	82%
GS0273	40 mg (0.08 mmol)	67%
GS0308	25 mg (0.05 mmol)	92%

GS0308 **N-*tert*-Butyl-N-[4-(1-methoxy-2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-1-methyl-ethyl)-phenyl]-hydroxylamine 11.** TBAF (0.11 mL, 0.112 mmol, 2.3 equiv) was added dropwise to a solution of methyl ether **10** (25 mg, 0.049 mmol, 1 equiv) in dry THF (0.3 mL) at RT. The reaction mixture protected from UV was stirred at room temperature for 12 h. The crude mixture was quickly filtered through a pad of silica, using ether. Concentration under reduced pressure gave the product (18 mg, 92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28, 7.22 (AB, J = 8.4 Hz, 4H), 5.87 (br, 1H), 3.68 – 3.44 (m, 14H), 3.37 (s, 3H), 3.10 (s, 3H), 1.59 (s, 3H), 1.15 (s, 9H).

Monoradical 2.



Experiment	**11**	Purification	Yield %
GS0303	21 mg (0.05 mmol)	(1) Silica, (2) RP (degradation), (3) Silica (decomposition)	
GS0311	18 mg (0.045 mmol)	Deactivated PTLC	48%

GS0311 **N-*tert*-Butyl-N-[4-(1-methoxy-2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-1-methyl-ethyl)-phenyl]-nitroxide 2.** The hydroxylamine **11** (18 mg, 0.045 mmol, 1 equiv) and the freshly prepared silver oxide (52 mg, 0.226 mmol, 5 equiv) were stirred in degassed chloroform (2 mL), protected from UV and under N_2, at room temperature for 2 h. The reaction was stopped by rapid filtration through a pad of cotton, washed with chloroform (5 mL). Concentration under reduced pressure gave a crude product (18 mg). Purification by PTLC with deactivated silica (pentane/acetone, 85:15) gave the product

(8.6 mg, 48%) as dark orange-red oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.5 – 2.8$ (m, 4.26, 4.02, 3.85, 3.78, 3.67, 3.59, 3.42, ~20H), 1.90 (br, ~3H), –4.50 (v. br, 9H). IR (cm^{-1}): 2879 (CH_2, v. br), 1107 (C–O, br). EPR (toluene, rt, numerical fit ($R = 0.995$)): Lorentzian line width (0.039), *g*-shift (–0.10), and hyperfine^{14}N- or ^{1}H-splitting (spin, number): 1.22 (1, 1), 0.20 (0.5, 2), 0.087 (0.5, 2). The line widths and hyperfine splittings were converted to milliTesla.

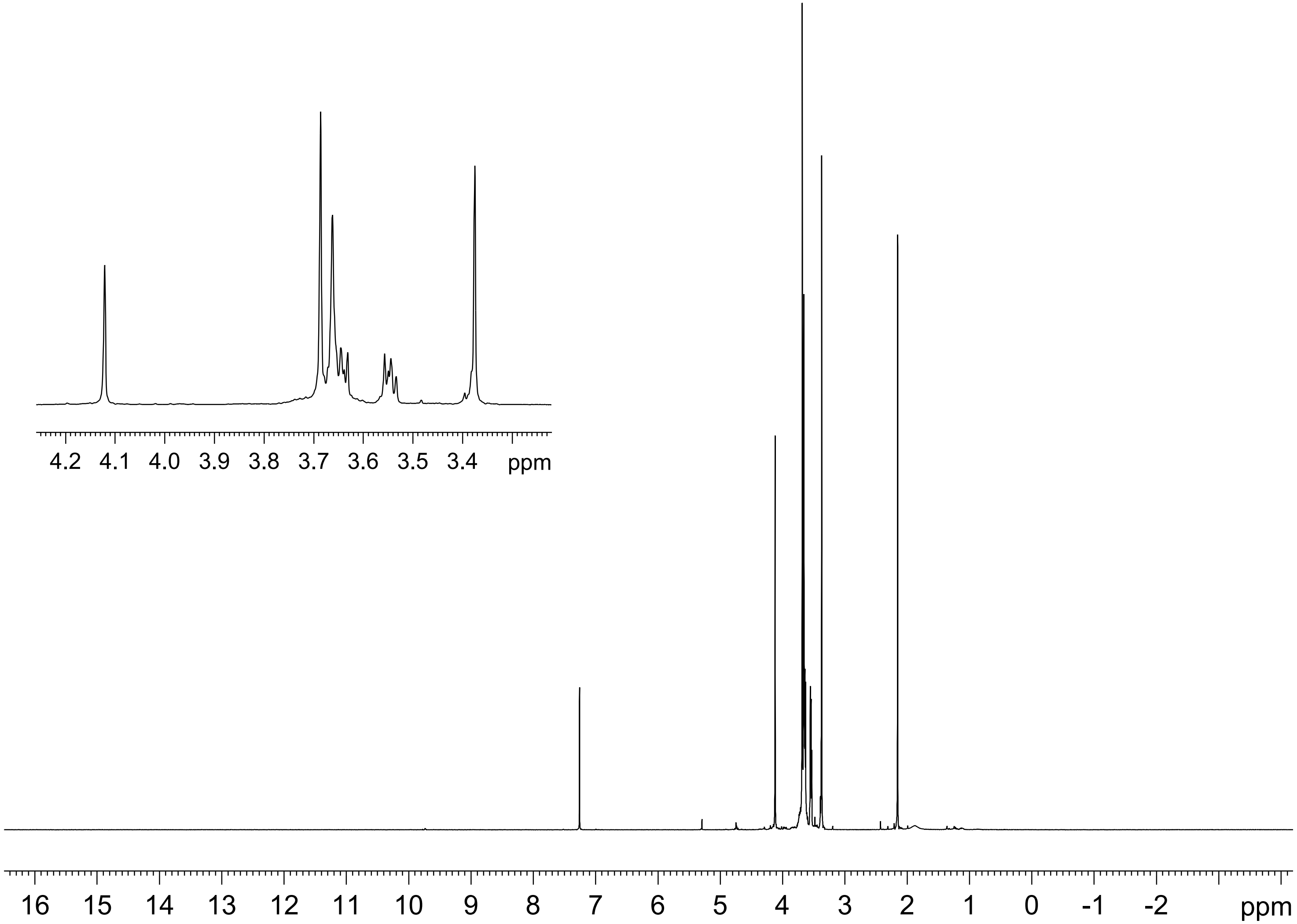


Figure 1S ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of ketone **4** (NMR file: gs0261fp).

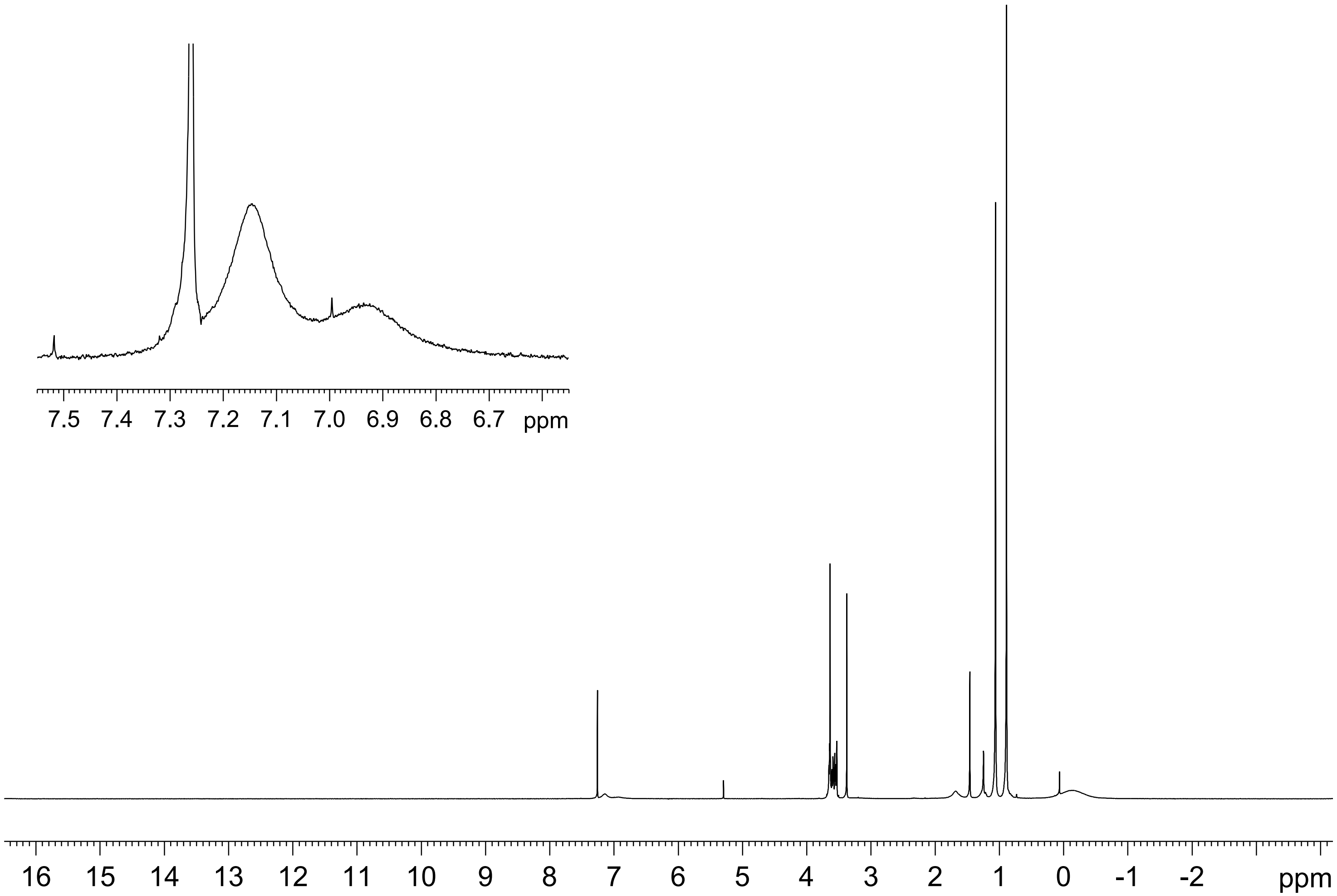


Figure 2S ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of alcohol **5** (NMR file: gs0124f2).

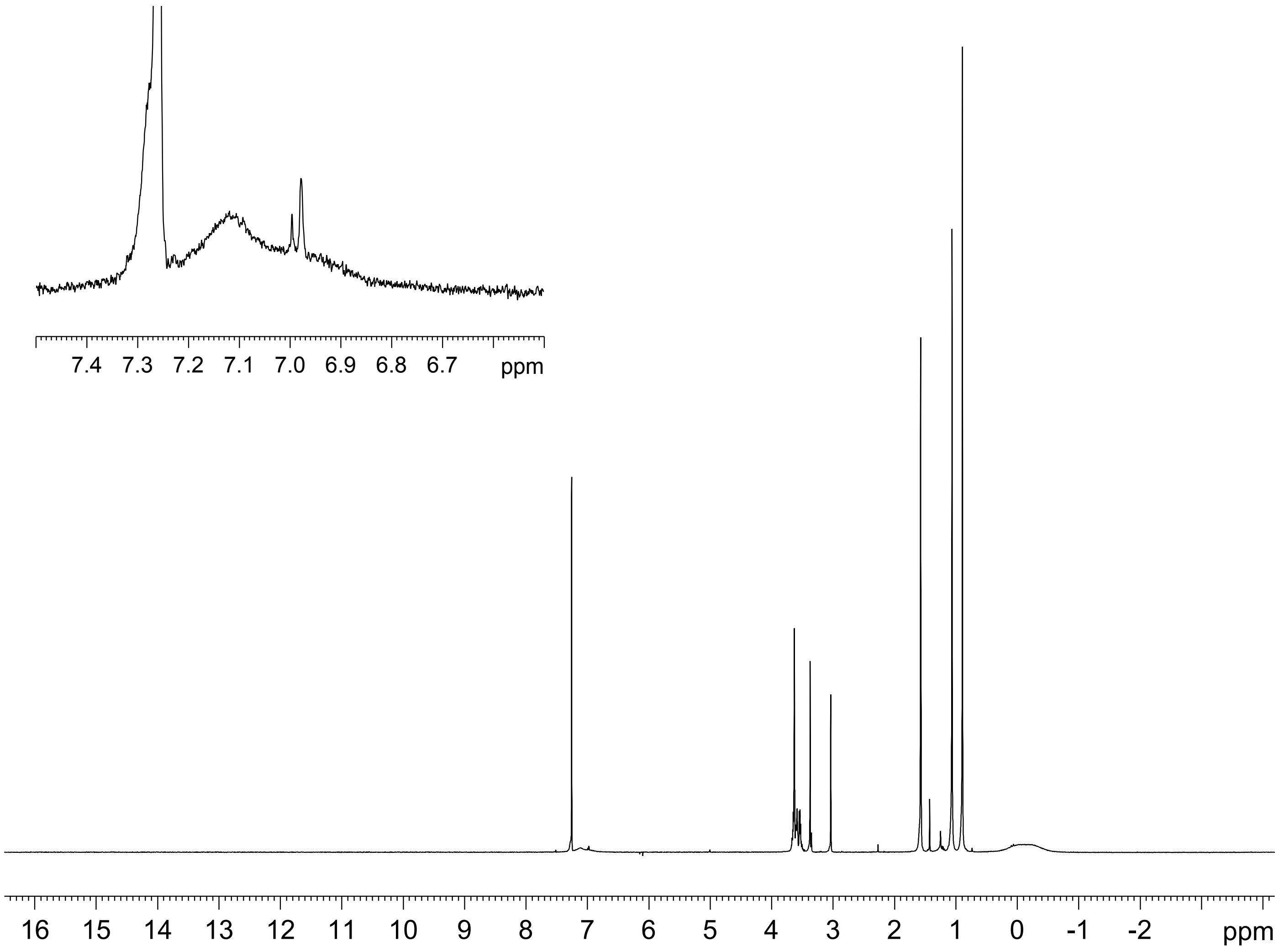


Figure 3S ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of methyl ether **6** (NMR file: gs0126f1).

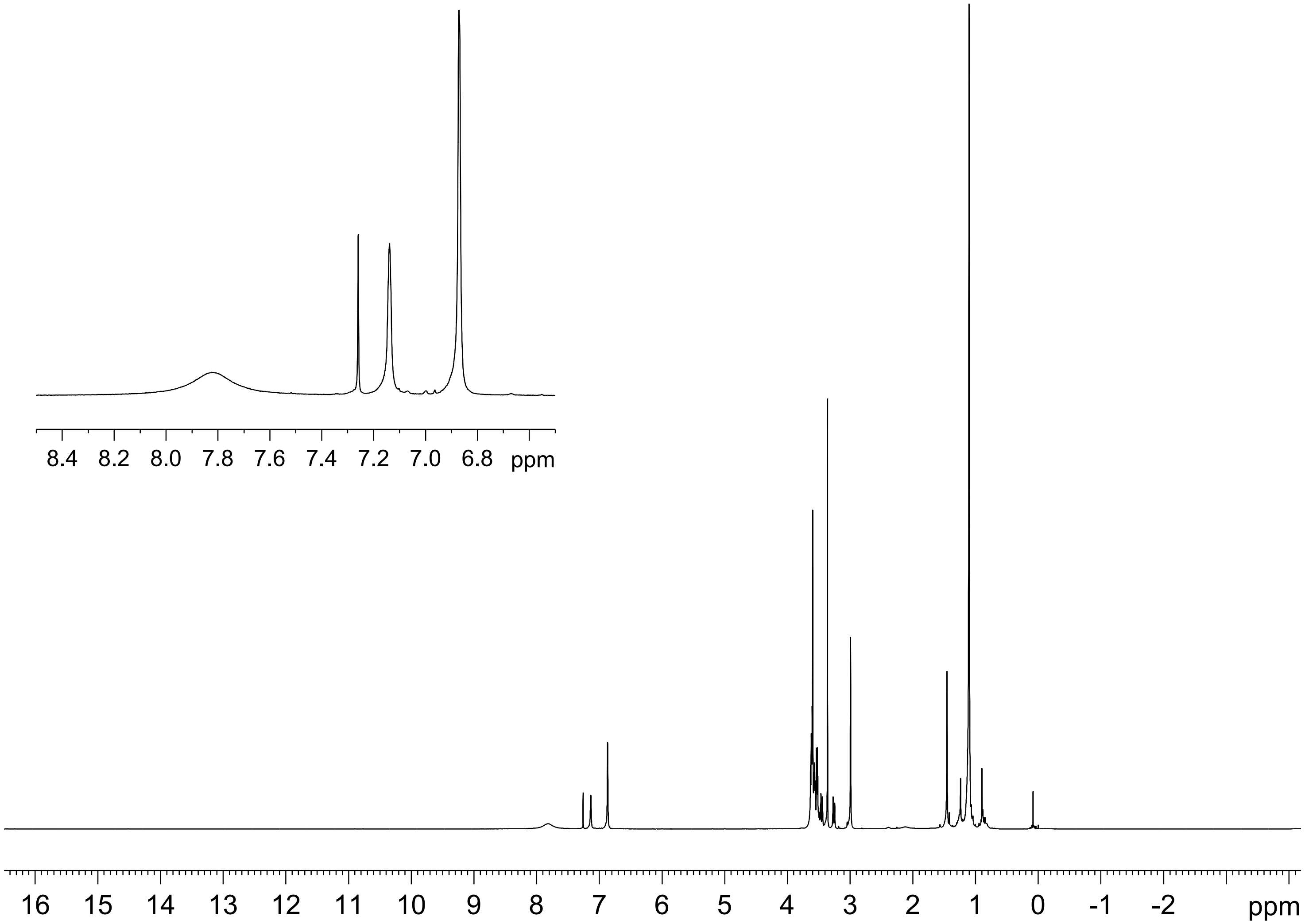


Figure 4S ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the dihydroxylamine **7** (NMR file: gs0142crude3).

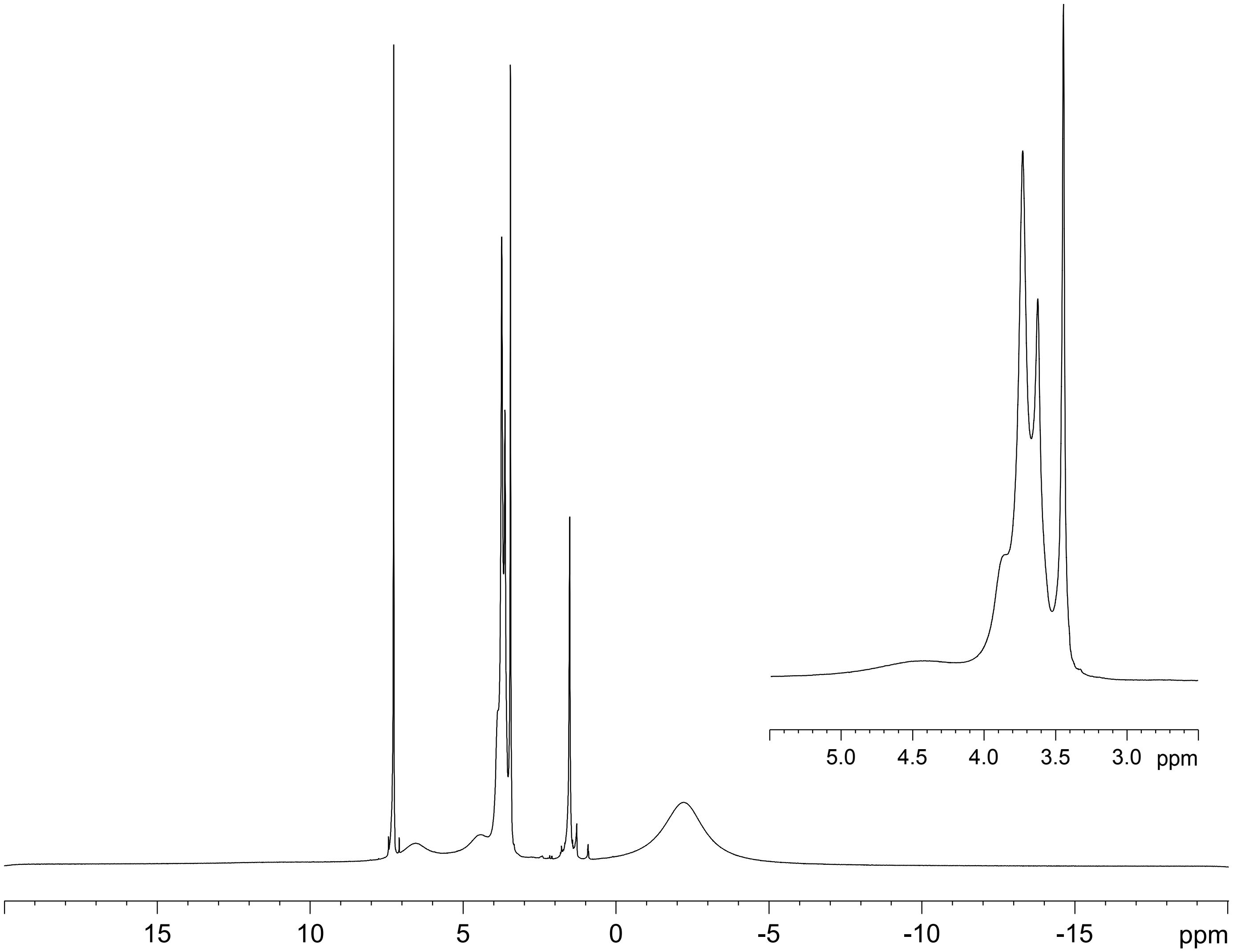


Figure 5S ^{1}H NMR (600 MHz, $CDCl_3$, LB = 1.0) spectrum of diradical **1** (conc = 0.01 M) (NMR file: gs0155p2).

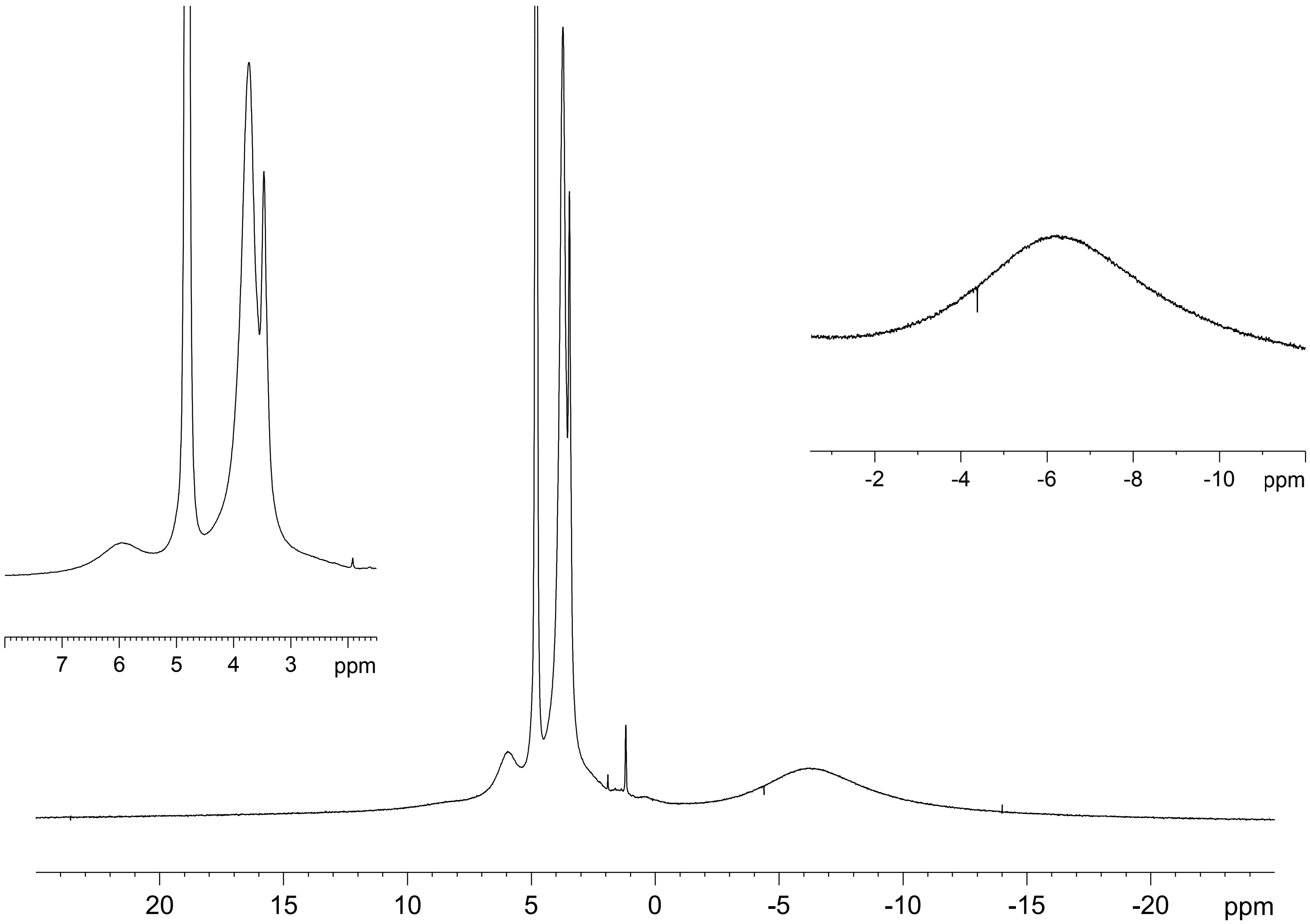


Figure 6S ^{1}H NMR (400 MHz, D_2O, LB = 2) spectrum of the diradical **1** (conc = 0.01 M) (NMR file: gs0147d2o2).

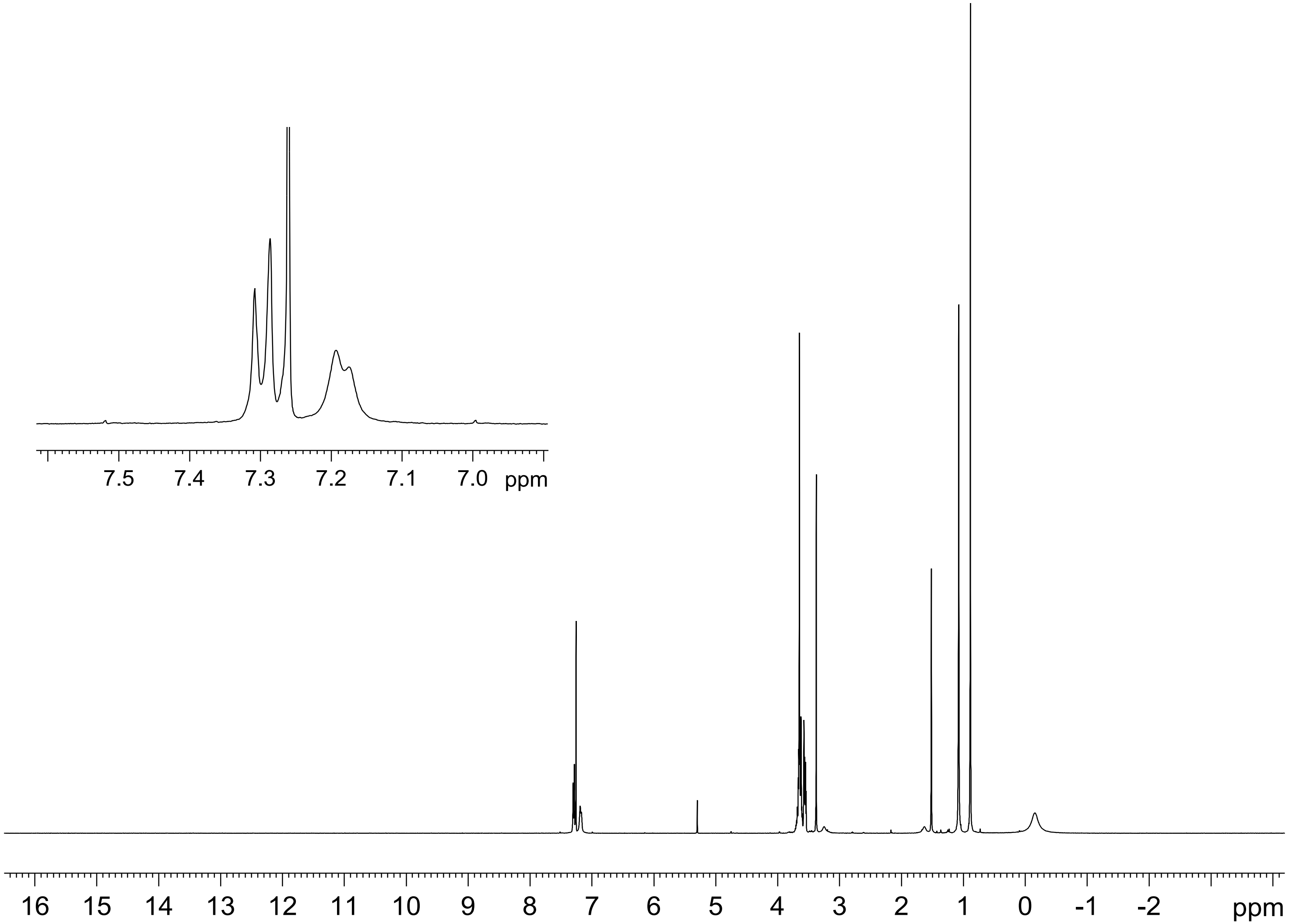


Figure 7S ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the alcohol **9** (NMR file: gs0262fp).

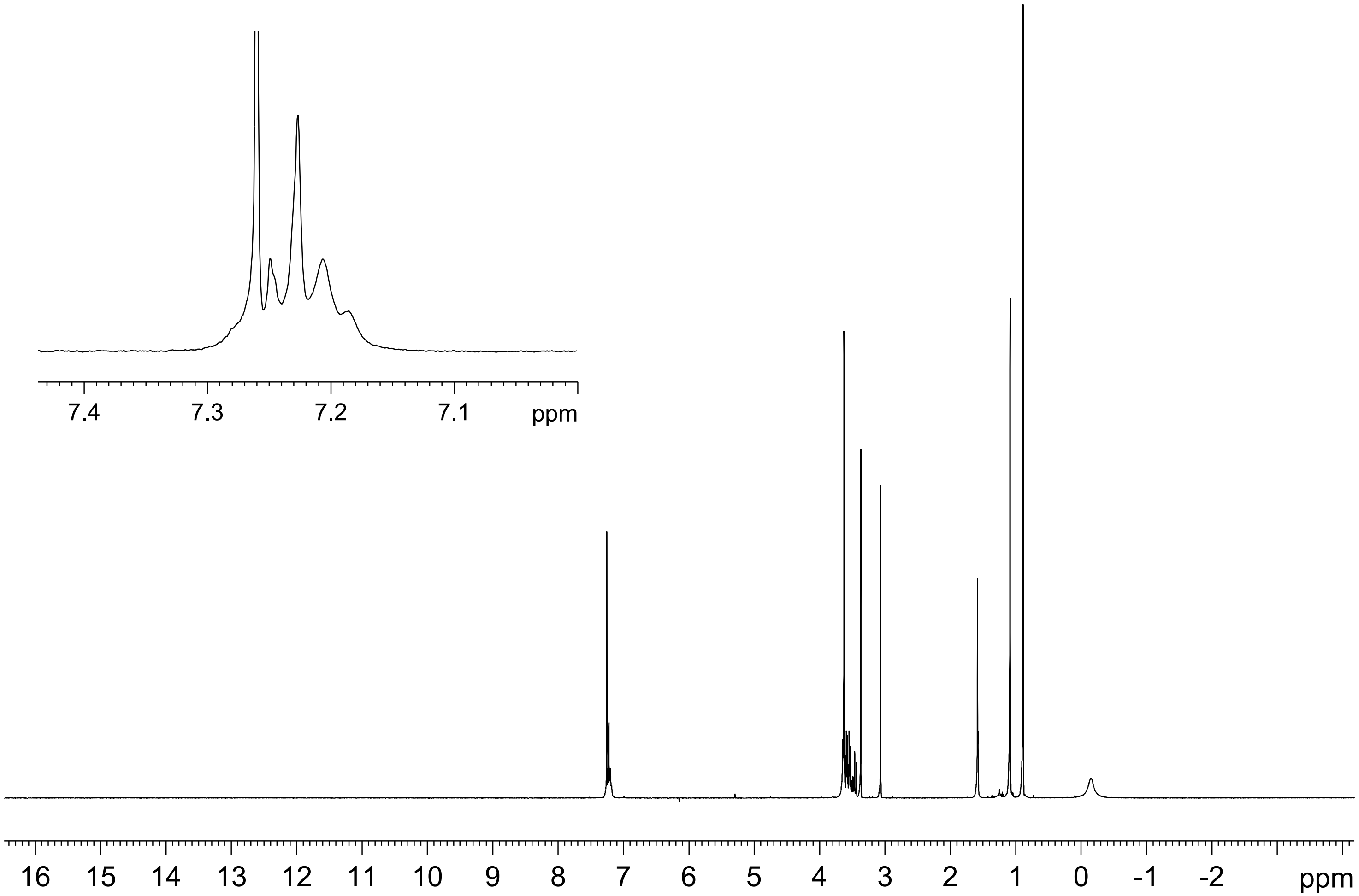


Figure 8S ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the methyl ether **10** (NMR file: gs0268fp).

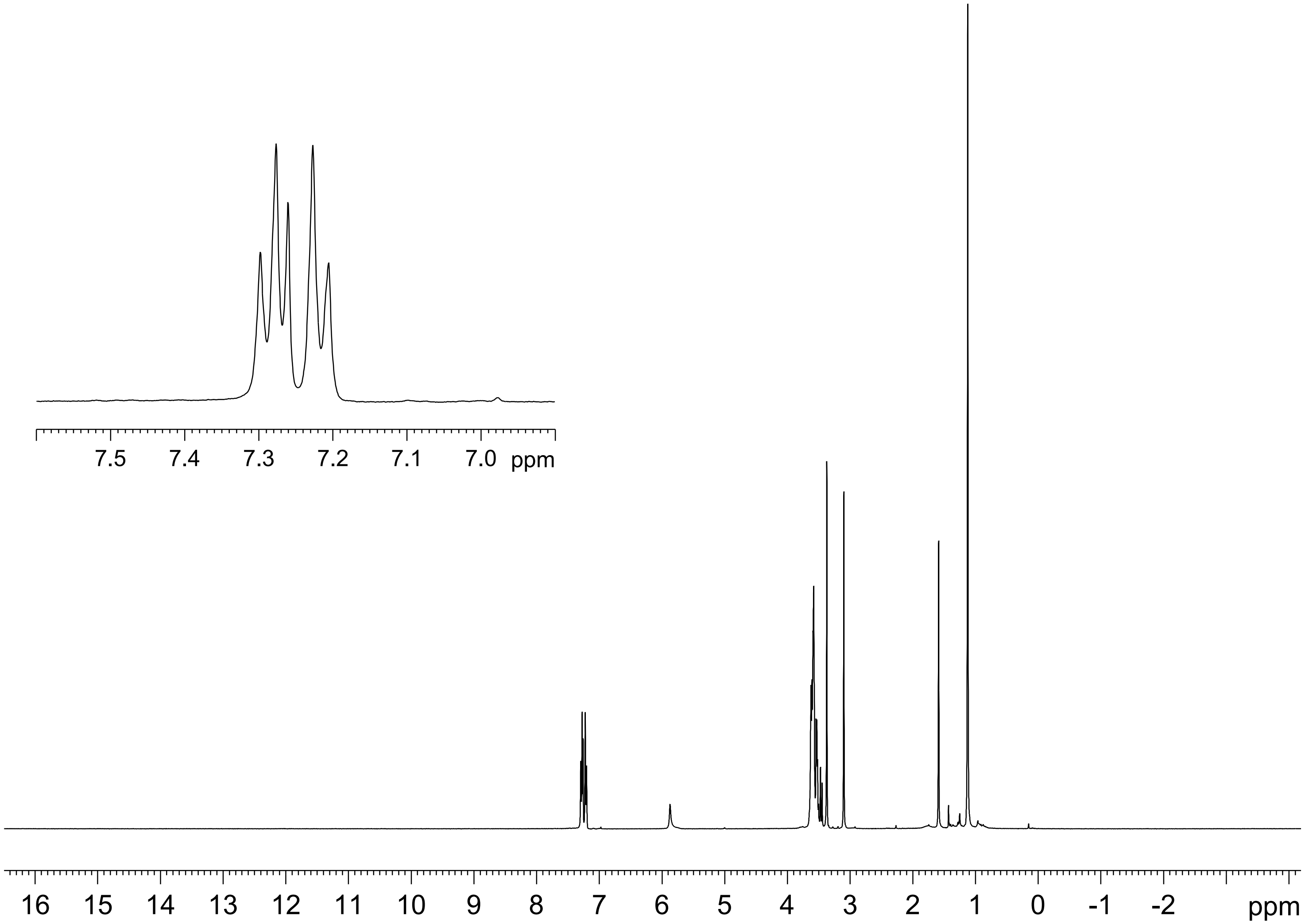


Figure 9S ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the hydroxylamine **11** (NMR file: gs0268fp).

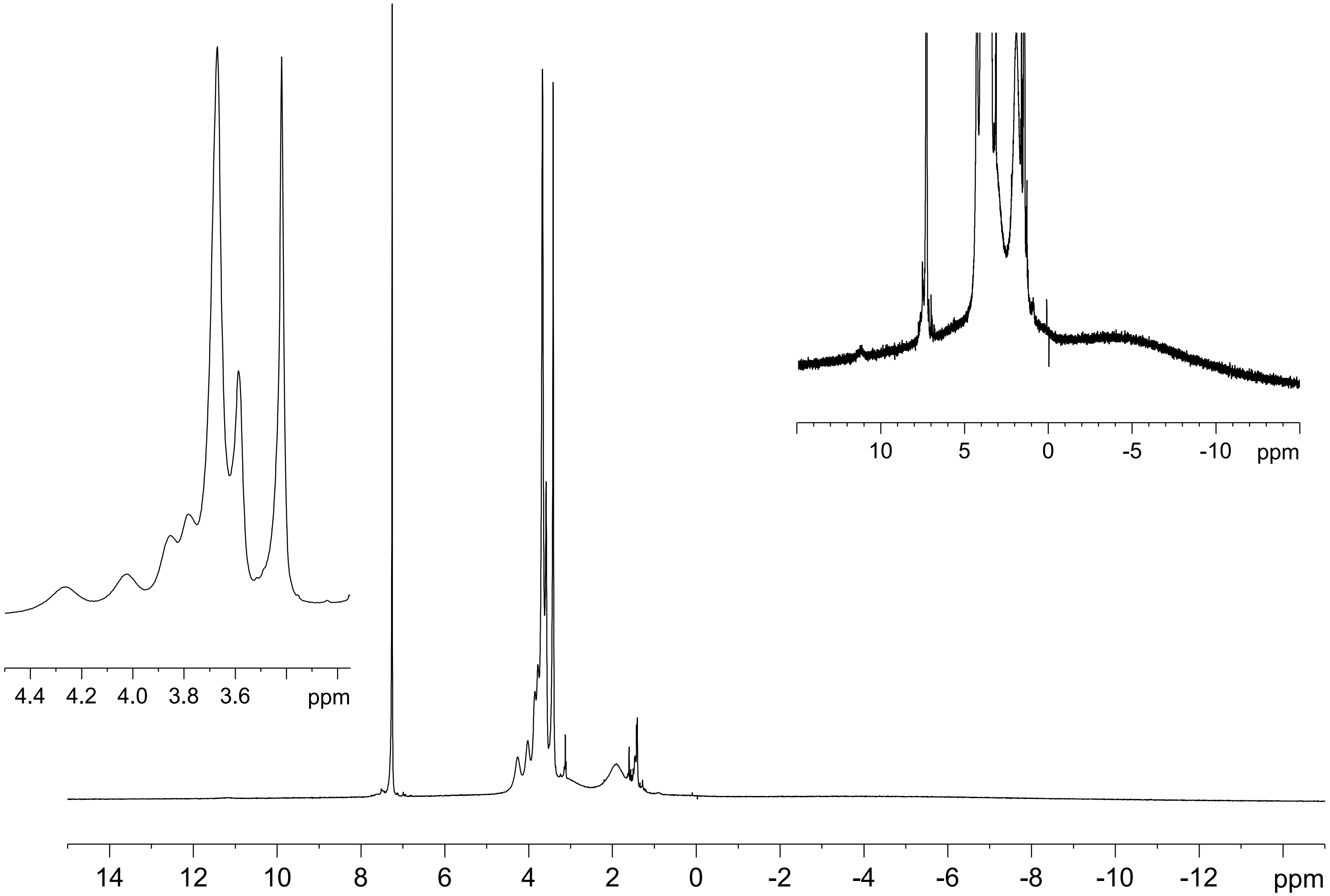


Figure 10S ^{1}H NMR (400 MHz, $CDCl_3$, LB = 0.3) spectrum of the monoradical **2** (conc = 0.02M) (NMR file: gs0311fp2bis).

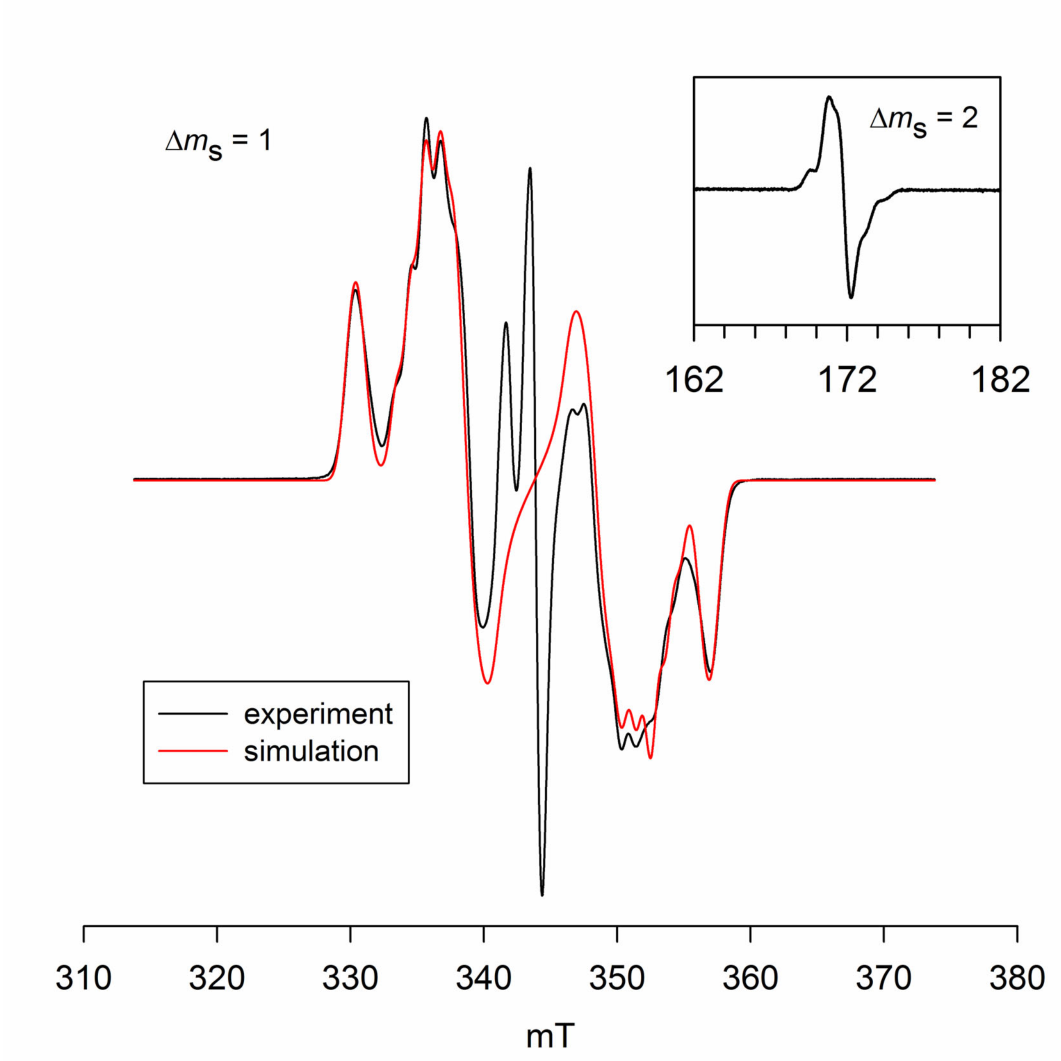


Figure 11S EPR (X-Band, 9.6522 GHz) spectrum of 1 mM diradical **1** in toluene at 140 K (KS1038r5&r7, GS161, SIM3_GS). The sample was slowly cooled from room temperature to 140 K in the EPR cavity. The fitting parameters for the spectral simulation to the $S = 1$ state are as follows: $|D/hc| = 1.24\times10^{-2}$ cm^{-1}, $|E/hc| = 1.13\times10^{-3}$ cm^{-1}, $g_x = 2.0066$, $g_y = 2.0040$, $g_z = 2.0068$, $A_{xx} = 7\times10^{-4}$ cm^{-1}, $A_{yy} = 10\times10^{-4}$ cm^{-1}, $A_{zz} = 4\times10^{-4}$ cm^{-1}, Gaussian line ($L_x = 10$ G, $L_y = L_z = 9$ G). The center lines correspond to an $S = ½$ (monoradical) impurity.

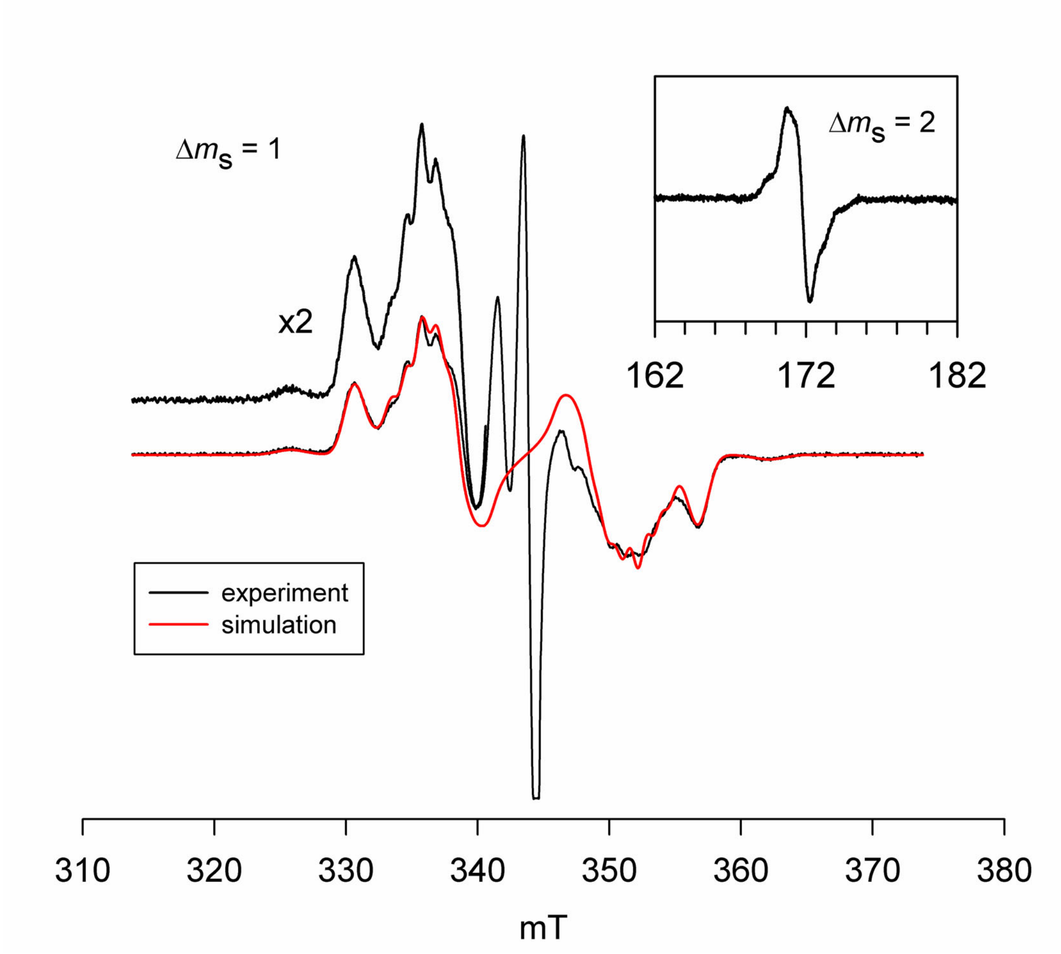


Figure 12S EPR (X-Band, 9.650 GHz) spectrum of ~1 mM diradical **1** in water/ethanol (1:2) at 135 K (GS343r2&r4, GS332PS, GS343r2_EtOH_SIM7). The sample was rapidly quenched from room temperature. The fitting parameters for the spectral simulation of the mixture of two $S = 1$ states are as follows: **the $S = 1$ state with 87 % content**, $|D/hc| = 1.22\times10^{-2}$ cm^{-1}, $|E/hc| = 1.05\times10^{-3}$ cm^{-1}, $g_x = 2.0066$, $g_y = 2.0040$, $g_z = 2.0060$, $A_{xx} = 8\times10^{-4}$ cm^{-1}, $A_{yy} = 10.5\times10^{-4}$ cm^{-1}, $A_{zz} = 4\times10^{-4}$ cm^{-1}, Gaussian line ($L_x = 10$ G, $L_y = 9$ G, $L_z = 11$ G); **the $S = 1$ state with 13 % content**, $|D/hc| = 1.70\times10^{-2}$ cm^{-1}, $|E/hc| = 1.00\times10^{-3}$ cm^{-1}, $g_x = 2.0066$, $g_y = 2.0054$, $g_z = 2.0044$, $A_{xx} = 10\times10^{-4}$ cm^{-1}, $A_{yy} = 4\times10^{-4}$ cm^{-1}, $A_{zz} = 7\times10^{-4}$ cm^{-1}, Gaussian line ($L_x = L_y = 15$ G, $L_z = 12$ G). The center lines correspond to an $S = ½$ (monoradical) impurity.

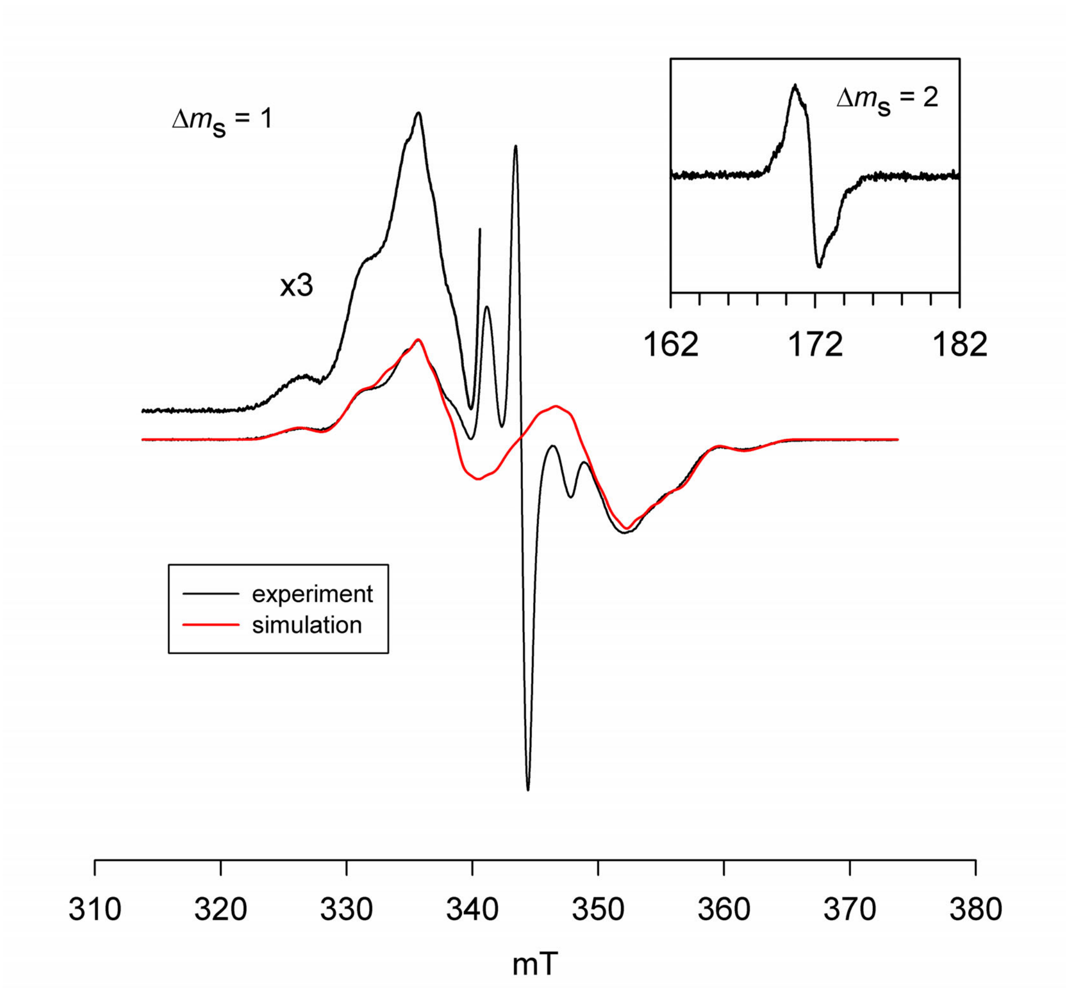


Figure 13S EPR (X-Band, 9.651 GHz) spectrum of 1 mM diradical **1** in water/glycerol (2:1) at 140 K (KS1029r3&r4, GS355, KS1029r3_Gly_SIM8). The sample was rapidly quenched from room temperature. The fitting parameters for the spectral simulation of the mixture of two $S = 1$ states are as follows: **the $S = 1$ state with 69% content**, $|D/hc| = 1.22\times10^{-2}$ cm^{-1}, $|E/hc| = 1.10\times10^{-3}$ cm^{-1}, $g_x = 2.0066$, $g_y = 2.0040$, $g_z = 2.0055$, $A_{xx} = 10\times10^{-4}$ cm^{-1}, $A_{yy} = 10\times10^{-4}$ cm^{-1}, $A_{zz} = 8\times10^{-4}$ cm^{-1}, Gaussian line ($L_x = L_y = 11$ G, $L_z = 12$ G); **the $S = 1$ state with 31% content**, $|D/hc| = 1.655\times10^{-2}$ cm^{-1}, $|E/hc| = 1.20\times10^{-3}$ cm^{-1}, $g_x = 2.0066$, $g_y = 2.0044$, $g_z = 2.0048$, $A_{xx} = 10\times10^{-4}$ cm^{-1}, $A_{yy} = 8\times10^{-4}$ cm^{-1}, $A_{zz} = 10\times10^{-4}$ cm^{-1}, Gaussian line ($L_x = L_y = 15$ G, $L_z = 13.5$ G). The center lines correspond to an $S = ½$ (monoradical) impurity.