Supplementary Information

**High DNP efficiency of TEMPONE radical in liquid toluene at low concentrations**

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**SI1: Experimental set up for DNP**

The low-field DNP spectrometer consists of a commercial Bruker ElexSys E500 CW/transient EPR spectrometer equipped with a Bruker AmpX CW amplifier (5 W) and a Bruker Minispec for NMR (2-65 MHz). EPR excitation and NMR detection is accomplished in a Bruker FlexLine dielectric microwave resonator (EN 4118X-MD-4) with ENDOR coils matched for proton NMR at 14 MHz. For DNP, a liquid sample is continuously irradiated for several seconds by microwave (X-band, 9.7 GHz) on-resonant with one EPR transition of the radical. Subsequently, the nuclear magnetization is detected by FID. To avoid heating of the resonator, a constant flow of N₂ gas inside the cavity is applied.
SI2: Evaluation of enhancements

The different enhancements of two types of protons were obtained as following. Firstly, the amplitude ratios of DNP vs Boltzmann signal were calculated for the two individual peaks in the spectra and related to the DNP enhancement $\varepsilon$ according to:

\[ \varepsilon_{\text{ring}} = \frac{I_{\text{ring}, \text{DNP}}}{I_{\text{ring}, \text{Bol}}} = \frac{\Delta v_{\text{ring, DNP}} \cdot h_{\text{ring}, \text{DNP}}}{\Delta v_{\text{ring, Bol}} \cdot h_{\text{ring, Bol}}} = k_{\text{ring}} \cdot E_{\text{ring}} \]  

\[ \varepsilon_{\text{methyl}} = \frac{I_{\text{methyl, DNP}}}{I_{\text{methyl, Bol}}} = \frac{\Delta v_{\text{methyl, DNP}} \cdot h_{\text{methyl, DNP}}}{\Delta v_{\text{methyl, Bol}} \cdot h_{\text{methyl, Bol}}} = k_{\text{methyl}} \cdot E_{\text{methyl}} \]  

where $I$ is the area of the NMR Lorentzian line given by $I = 1.57 \cdot h \cdot \Delta v_{1/2}$ (C. P. Poole, *Electron Spin Resonance*, John Wiley & Sons, New York, 1983, p. 783), $h$ is the maximum of the absorption line, $\Delta v$ is the width at half height and $E = h_{\text{DNP}} / h_{\text{Bol}}$ is the ratio of the amplitudes. The factor $k = \Delta v_{\text{DNP}} / \Delta v_{\text{Bol}}$ is introduced to account for the artificial broadening observed during signal averaging. This broadening is due to field instability caused by the electromagnet (no shimming is available in our set up). Assuming that line broadening is similar after same number of accumulations, we set $k_{\text{ring}} \approx k_{\text{methyl}} \approx k$ and therefore $\varepsilon_{\text{ring}} = k \cdot E_{\text{ring}}$, $\varepsilon_{\text{methyl}} = k \cdot E_{\text{methyl}}$. The factor $k$ was calculated for each individual concentration/sample.

Subsequently the enhancement is measured again and calibrated with the first point of the FID, for which the line broadening effect can be neglected. The first point of the FID reflects the DNP signal enhancement $\varepsilon_{\text{FID}}$ according to:

\[ \frac{5 \varepsilon_{\text{ring}} + 3 \varepsilon_{\text{methyl}}}{8} = \varepsilon_{\text{FID}} \]  

In this expression, the Boltzmann FID signal is normalized to unity considering an intensity ratio of the two proton groups (ring : methyl) of 5:3.

By substituting $\varepsilon_{\text{ring}} = k \cdot E_{\text{ring}}$, $\varepsilon_{\text{methyl}} = k \cdot E_{\text{methyl}}$ in eq. (2) we obtain:

\[ \frac{(5 \cdot E_{\text{ring}} + 3 \cdot E_{\text{methyl}}) \cdot k}{8} = \varepsilon_{\text{FID}} \]  

From the observed FID enhancement and the enhancement of the amplitudes $E$ we can calculate with eq. 3 the factor $k$, which is then inserted in eq. (1) to obtain the absolute enhancement $\varepsilon_{\text{ring}}$ and $\varepsilon_{\text{methyl}}$ of each type of protons.
Fig. S1 Calculated concentration dependence of the leakage factor $f$ in toluene and water doped with TEMPONE-D-$^{15}$N using:

$$f = \frac{n}{R_{\text{dia}}} \frac{1}{R + n}$$  \hspace{1cm} (4)

Where $n$ is the radical concentration and $R$ the relaxivity. In toluene, $R_{\text{dia}}$ and $R$ amount to 0.077 s$^{-1}$ and 0.133 s$^{-1}$ mM$^{-1}$, respectively; in water, $R_{\text{dia}}$ and $R$ are 0.33 s$^{-1}$ and 0.284 s$^{-1}$ mM$^{-1}$, respectively (from Ref.24).
Fig. S2 Peak-to-trough intensity power dependence of the low field EPR line (the derivative of Lorentzian line) for TEMPONE-D$_{15}$N in toluene at different concentrations. The solid lines represent fitting curves with (C. P. Poole, *Electron Spin Resonance*, John Wiley & Sons, New York, 1983):

\[ y' = \frac{y_0 c \sqrt{QP}}{\left(1 + \gamma_s^2 T_1 T_2 c^2 QP\right)^{3/2}} \]  \hspace{1cm} (5)

where \( P \) is the microwave power, \( \gamma_s \) is gyromagnetic ratio of the electron, \( T_1 \) and \( T_2 \) are the longitudinal and transversal electronic relaxation times, respectively, \( y_0 c \sqrt{Q} \) is the slope of the curve below saturation as deduced from the linear range of the curve, \( c^2 Q \) is a conversion factor in \( B_1^2 = c^2 QP \) (where \( B_1 \) is a microwave field strength).

Based on the fitting results, the saturation factor \( s_1 \) could be calculated according to:

\[ s_1 = \frac{\gamma_s^2 T_1 T_2 c^2 QP}{1 + \gamma_s^2 T_1 T_2 c^2 QP} \]  \hspace{1cm} (6)

The saturation factor reaches the maximal value of unity for all concentrations at \( P = 3 \text{W} \), which is the power used in our DNP experiments.
**Fig. S3** CW-EPR spectra for TEMPONE-D$_{15}$N in toluene at different concentrations ($P = 2$ mW). Peak-to-peak line widths were used to extract $T_2$, as reported in Table 1 of main text. Exp. Parameters were: 1 G modulation amplitude, 100 kHz modulation frequency, 5.12 ms conversion time, 1024 points.
Fig. S4 Recovery curves of the EPR FID in polarization recovery EPR and ELDOR experiments for a) 0.1 mM and b) 3 mM TEMPONE in toluene. The time evolution of the FID signals ($i_1$ EPR and $i_2$ ELDOR) after a saturating pulse is described by eq. 4 in the main text. The relaxation times $T_{1e} = (2w_e)^{-1}$ determined from the fitting of both curves (EPR and ELDOR) are 480 ns and 441 ns, respectively. The normalized amplitudes values from the fit were: $A_1 = 0.77$, $B_1 = 0.25$, $A_2 = 0.58$, $B_2 = -0.27$ (for 0.1 mM); $A_1 = 0.69$, $B_1 = 0.3$, $A_2 = 0.84$, $B_2 = -0.26$ (for 3 mM).

Fig. S5 Estimate of exchange coupling rate from the EPR line width as a function of radical concentration.

$$\Delta B_{pp}(\omega_{ex}) - \Delta B_{pp}(0) = \frac{4 \omega_{ex}}{3\sqrt{3} \gamma_s}$$

(8)

where $\omega_{ex} = n \cdot K_s$ is the Heisenberg exchange rate ($K_s$ is normalized rate per mole, $n$ is the radical concentration), $\gamma_s$ is electron gyromagnetic ratio. By fitting the concentration dependence with a straight line, we obtained $K_s$ of $(4.3 \pm 0.5) \times 10^9$ s$^{-1}$ M$^{-1}$ and $\Delta B_{pp}(0)$ of 0.32 G.