Fig. S1 - Simulated reflection coefficient (s₁₁ parameter) for the empty shuttle cavity with a stub coupler as described in the text. The resonance at 9.4 GHz is the desired TM_{110} mode whereas the resonances at 9.0 GHz and 9.5 GHz are spuriously excited TM_{011} and HEM_{111} modes.
Fig. S2 - (A) Signal enhancement of water as function of the sweep field for a microwave pulse with a duration of 1 s and a power of 1.9 W prior to the NMR detection pulse applied to a 10 mM TEMPOL-\textsuperscript{14}N/H\textsubscript{2}O sample. (B) Inverse enhancement plotted over the inverse microwave power. The dotted lines were fitted to the last three data points. Note that here the microwave field is irradiated only at one EPR resonance line and therefore a linear extrapolation towards infinite power can not be used to determine the maximum enhancement. The B\textsubscript{0} field was set to the center line (10 mM) and the up-field (20 mM) line of the TEMPOL-\textsuperscript{14}N EPR spectrum (nominal value in the E-Scan software were 3475.5 G and 3505 G), respectively. The resonance frequency of the cavity with the shuttle container and the sample was measured to be 9.58 GHz. (C) Relaxation of the hyperpolarized signal at function of the post polarization delay \( t_{\text{ppd}} \). (D) Enhancement built-up as the duration of the microwave irradiation was subsequently increased.
Fig. S3 – Normalized low-field signal enhancement of water measured in the high-field position (for 5 mM TEMPONE-D$_{15}$N, 10 mM DSS and 100 mM ethanol in 80/20 H$_2$O/D$_2$O) as function of the $B_0$ field. In this experiment the microwave cavity was tuned to approximately 9.4 GHz and the microwave field was irradiated for 2 s and 15 W for different values of the $B_0$ field. The negative EPR absorption line of TEMPONE-D$_{15}$N is reproduced because the measured initial enhancement depends on the correct irradiation of the EPR lines (note the analogy with Fig. S2A). The shuttle time was $t_{sd} = 40$ ms and $t_{p,td} = 75$ ms. These results imply that the $B_0$ field needs to be adjusted within 2-3 G to obtain the maximum enhancement.
Fig. S4 – Inversion recovery relaxation curves measured at the high-field position. The delay $\tau_1$ is the variable delay that is introduced between the $\pi$ pulse and the $\pi/2$ detection pulse in the 1D inversion recovery pulse sequence. For all signals a spin-lattice relaxation time can be estimated to be in the range 310-500 ms.
Fig. S5 – (A) A variable post-polarisation delay \( t_{ppd} \) was inserted after the microwave pulse, prior to the shuttle process. Here the shuttle time \( t_{sd} = 40 \) ms and the post shuttle delay \( t_{psd} = 70 \) ms were at fixed values. (B) The same experiment but without a post-polarisation of \( t_{ppd} \), a constant shuttle time \( t_{sd} = 40 \) ms and a variable post-shuttle delay \( t_{psd} \).