Supporting Information for:
Reverse dynamic nuclear polarisation for indirect detection of nuclear spins close to unpaired electrons

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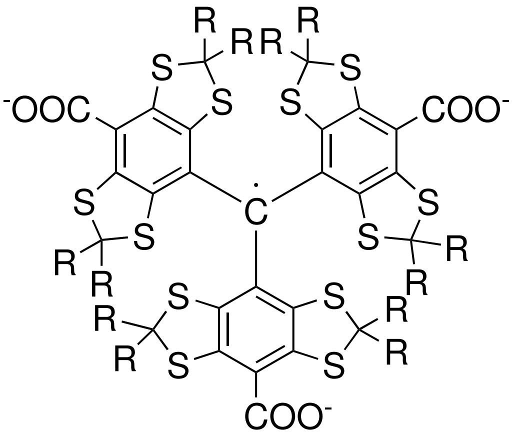
S 1 Structure and EPR spectrum of OX063



OX063 (R = CH_2CH_2OH)

Fig. S1: Chemical structure of the OX063 radical.

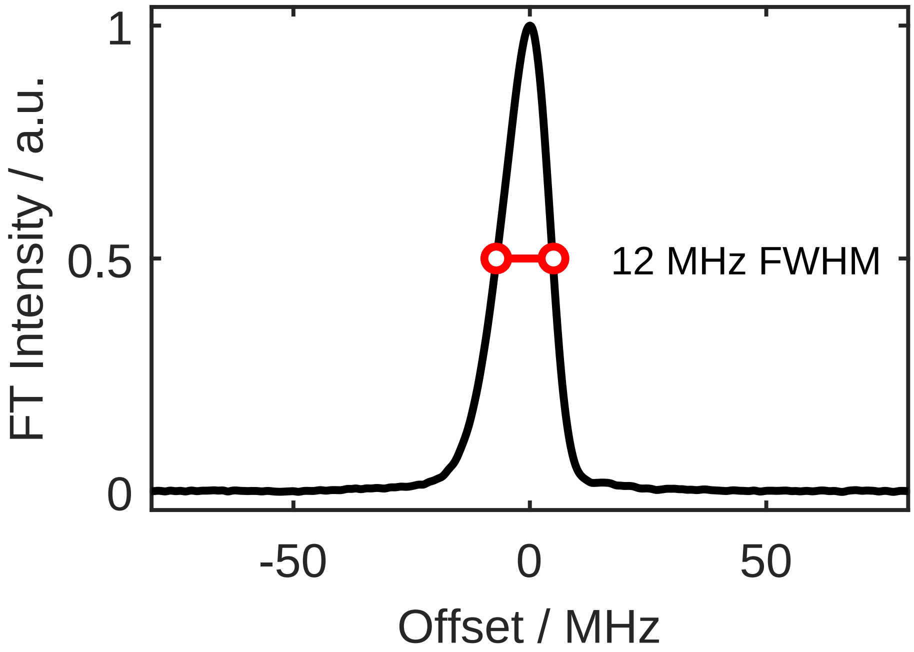


Fig. S2: Chirp echo Fourier transform EPR spectrum of OX063 obtained at a field of 1.2422 T.

S 2 Off-resonance transients in depolarisation curves

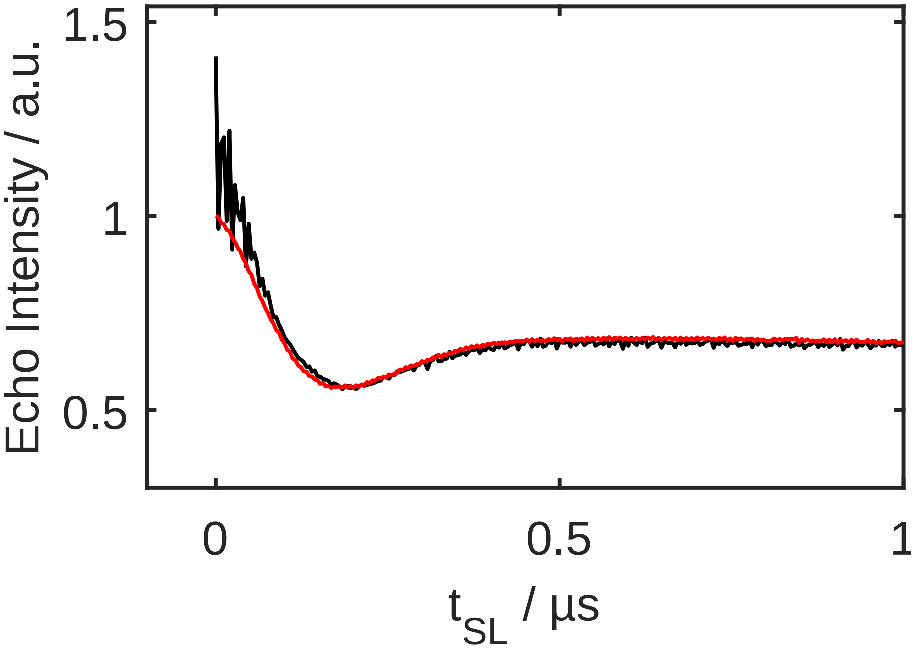


Fig. S3: Comparison of initial part of the depolarisation curve. Black: NOVEL condition fulfilled from the beginning of the spinlock, right after the initial $\pi/2$ pulse. Red: The first 500 ns of the spinlock used the maximum power, then it was dropped to the NOVEL condition ($t = 0$ corresponds to the time where the matching is fulfilled).

S 3 Nutation curves and spectra

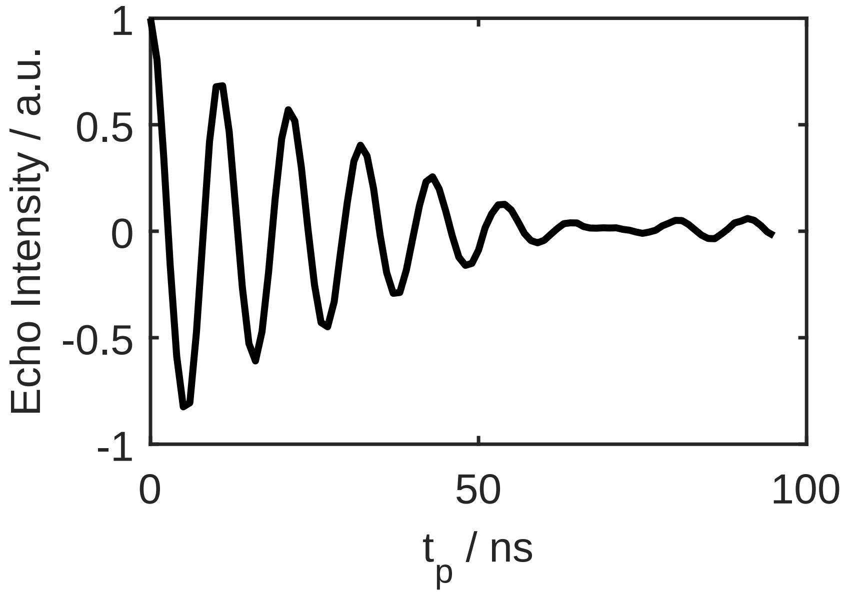


Fig. S4: Nutation curve obtained at the highest power with the sequence $t_\mathrm{p} - T - \pi/2 - \tau - \pi - \tau - echo$.

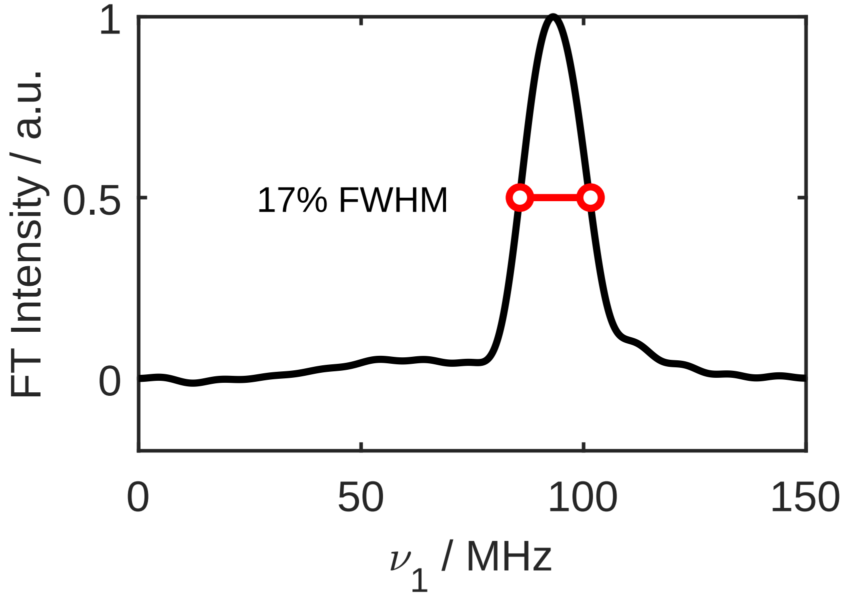


Fig. S5: Nutation spectrum, i.e. the Fourier Transform of Figure S4.

S 4 Resonator Profile

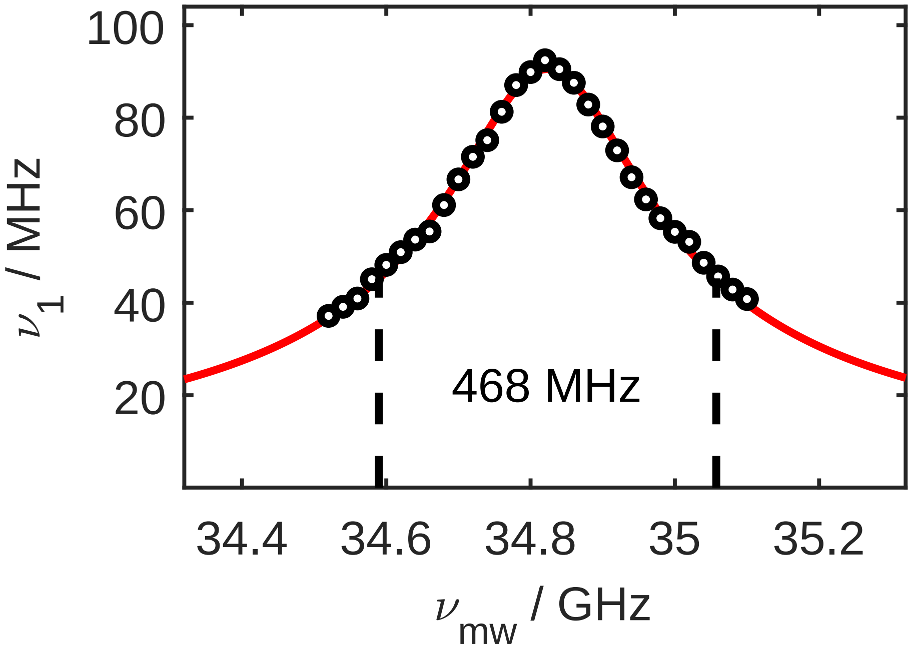


Fig. S6: Resonator profile at full mw power, obtained by measuring nutation spectra at different frequencies. The field was always set on resonance. The plotted value of ν_1 corresponds to the maximum of the nutation spectrum. The FWHM of the resonator profile is 468 MHz.

S 5 Details about RA-NOVEL

The following amplitude modulation function was used:

$$AM(x) = a_0 - \kappa \tan(2 \arctan(\Delta a/\kappa)(0.5 - x)) \tag{1}$$

with $x = t/t_{\max}$, $a_0 = 0.27$, $\Delta a = 0.2$ and $\kappa = 0.025$. The scale corresponds to the digital output of the AWG. $a_0 = 0.265$ corresponded to the normal NOVEL condition. No compensation of the non-linearity of the TWT amplifier was used. When sweeping the pulse length, the waveform was simply stretched.

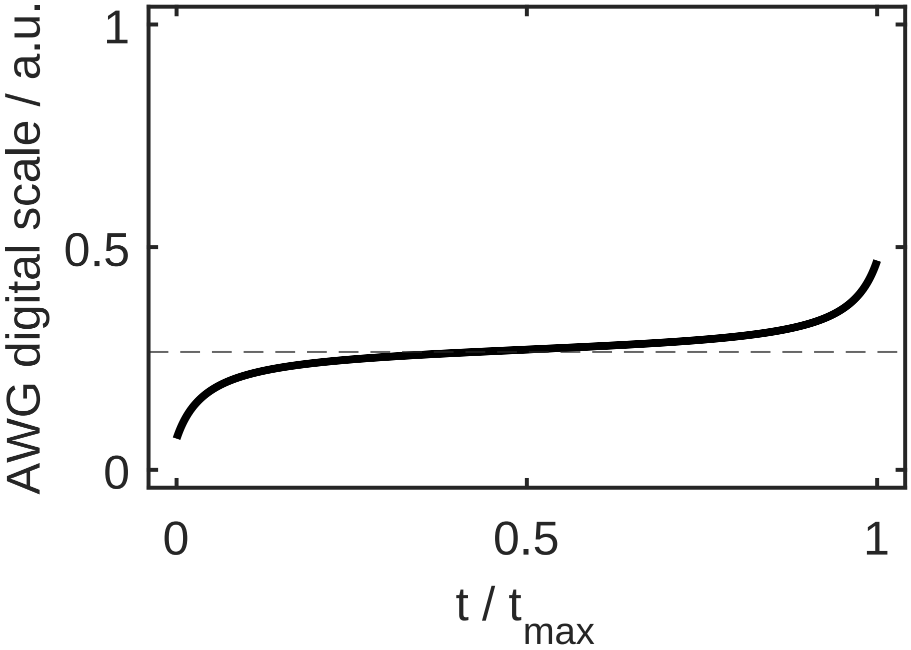


Fig. S7: Waveform used for RA-NOVEL experiments.

S 6 Comparison of $T_{1,e}$

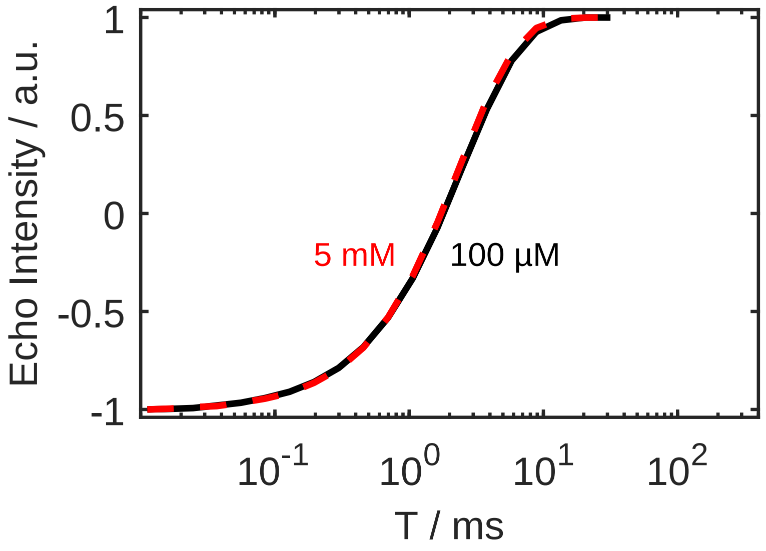


Fig. S8: Inversion recovery curves obtained at 80 K.

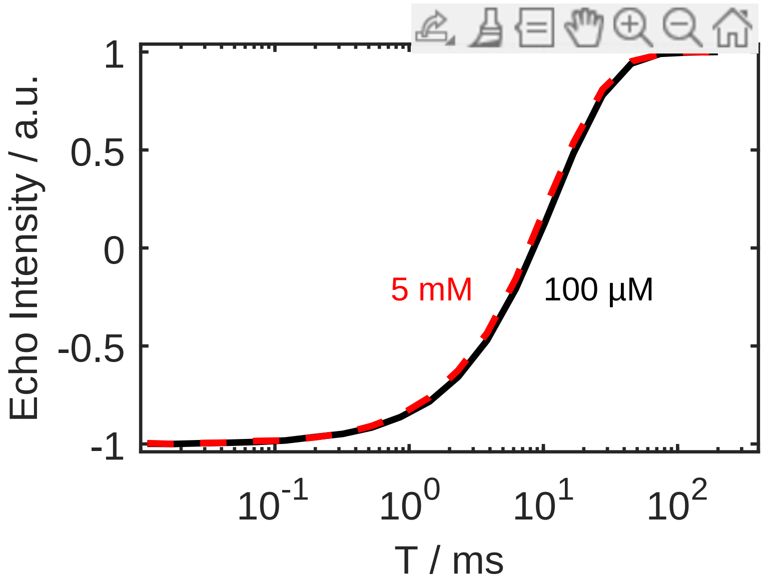


Fig. S9: Inversion recovery curves obtained at 50 K.

S 7 Comparison of $T_{1,\rho}$

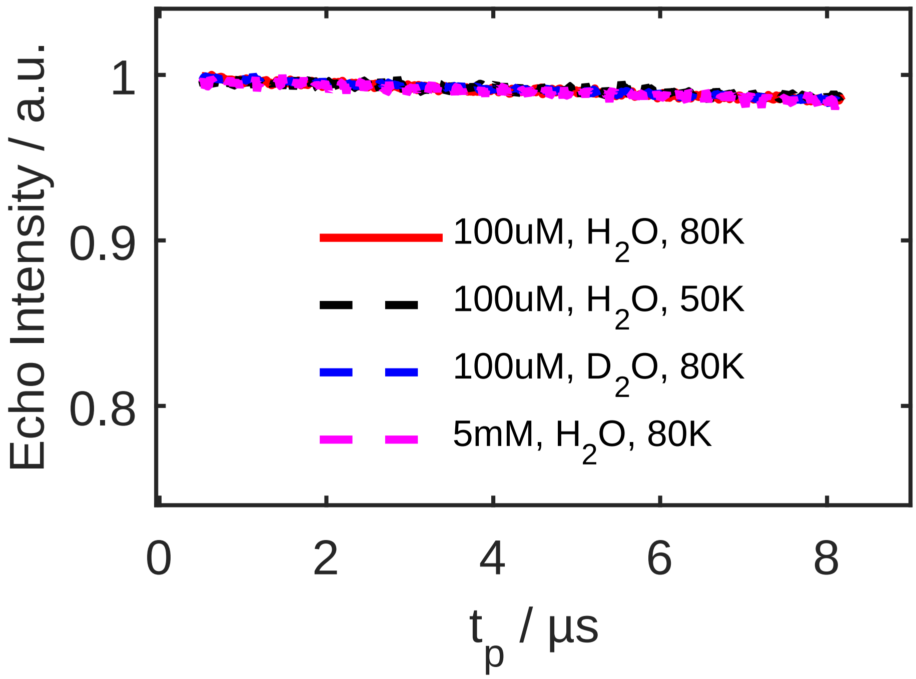


Fig. S10: Measurement of $T_{1\rho}$ for different samples and conditions. The spinlock power was set to the maximum. Since only a few percent of the signal are lost, and there is no difference between samples, the influence of $T_{1,\rho}$ can be neglected for the experiments presented in this work.

S 8 Comparison of T_m

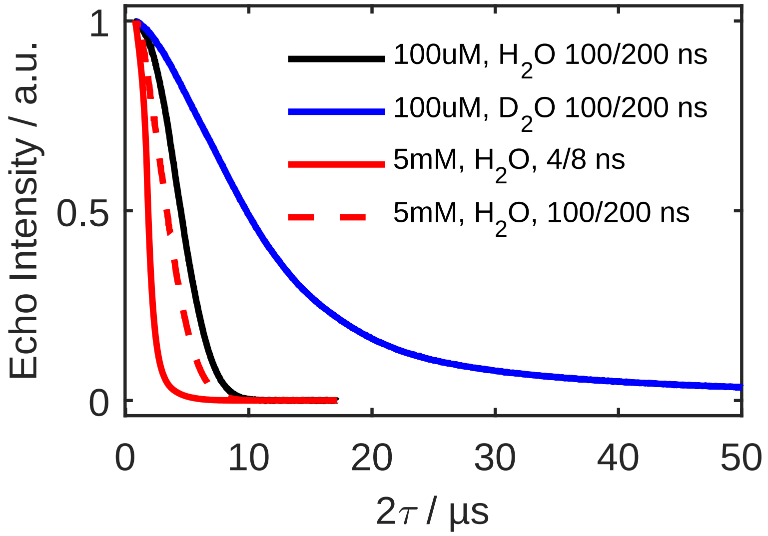


Fig. S11: Hahn echo decays measured at 80 K. the legend indicates the sample and the pulse lengths. As expected, deuteration of the solvent significantly increases the phase memory time. Additionally, the influence of instantaneous diffusion is pronounced at 5 mM. This can be seen because a shortening of the pulses, i.e. an increase in excitation bandwidth, leads to a faster Hahn echo decay.

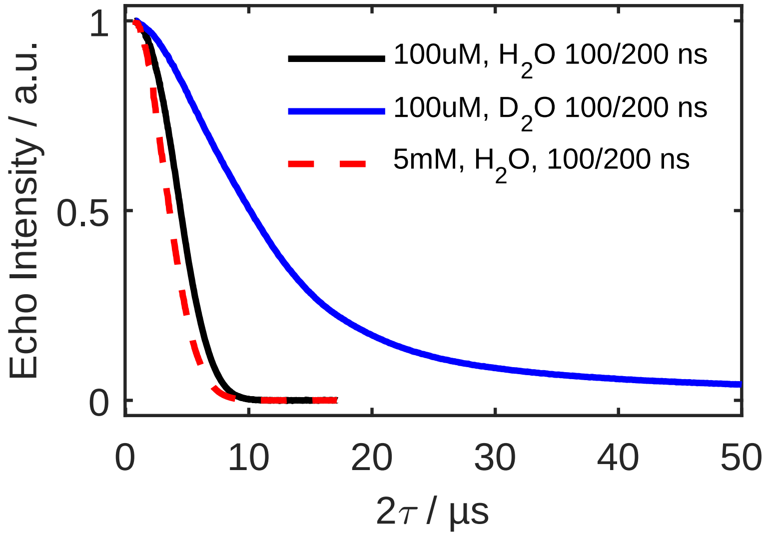


Fig. S12: Hahn echo decays measured at 50 K. There is no significant difference compared to 80 K.

S 9 Saturation behaviour during depolarisation

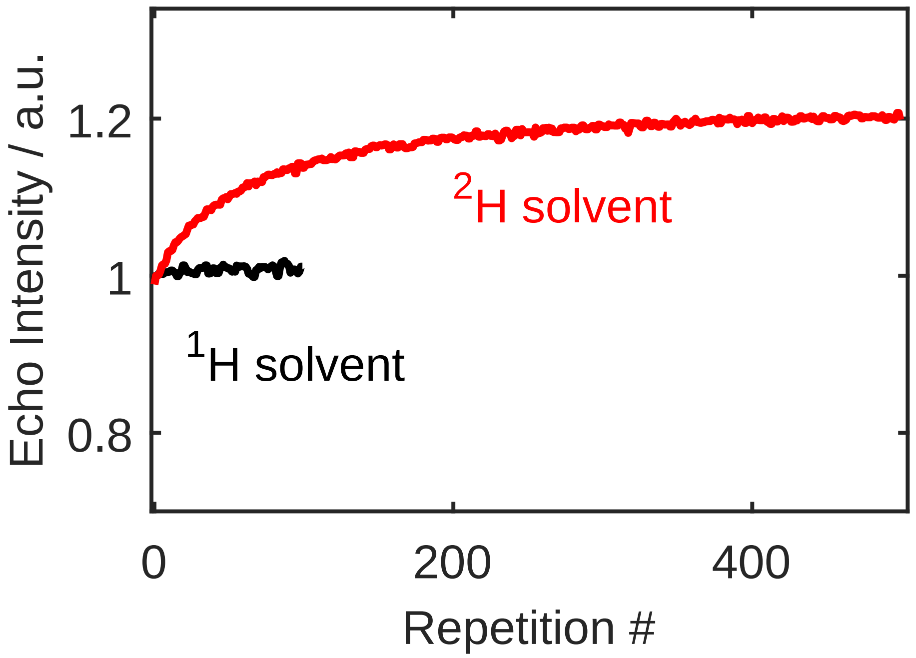


Fig. S13: Echo intensity after 500 ns of a NOVEL-matched spinlock. The pulse sequence was simply repeated without any phase-cycling and a shot-repetition time of 10 ms. Single echoes were detected. Red: deuterated solvent. At the beginning, there is no significant nuclear polarisation on nearby protons. However, after several rounds of transfer, the nuclei acquire an amount of polarisation that slows down the electron-nuclear transfer. This results in an increased electron spin echo after NOVEL matching. Black: protonated solvent. No increase (<2%) in echo intensity is observed over the first 100 repetitions. Note that the experiments shown in the main text were all acquired using phase cycling.

S 10 Saturation behaviour in reverse DNP experiments

A significant nuclear polarisation at the beginning of the measurements might lead to unexpected effects during reverse DNP measurements. We cannot directly saturate the nuclei before, since we are currently using no rf-channel. Even if one would be available, directly coupled nuclei might be unaffected due to significant hyperfine coupling. However, saturating the electrons, then performing reverse DNP several times (see Figure S14) at least partially saturated the nuclei close to the electrons.

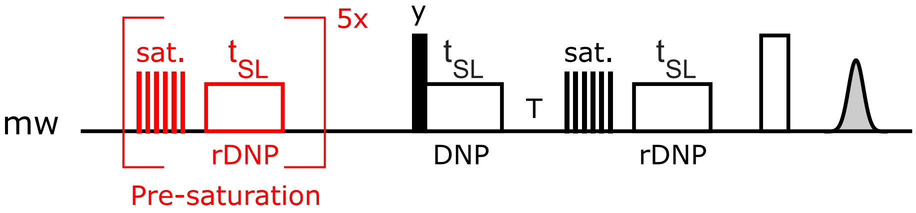


Fig. S14: Electron spin echo intensity after DNP and reverse DNP

The echo intensity after DNP and reverse DNP for the sample with deuterated solvent is shown in Figure S15. If no pre-saturation or phase-cycling is used, the intensity increases with each repetition, indicating an accumulation of nuclear polarisation. Presaturation alone reduces this accumulation, but is not sufficient to completely get rid of it. As expected, phase-cycling also does not lead to an accumulation of nuclear polarisation, because an opposite phase of the $\pi/2$ pulse leads to an opposite sign in nuclear polarisation. However, the first echo was always slightly more intense than the rest. If presaturation and phase-cycling are used together, the echo intensity is constant.

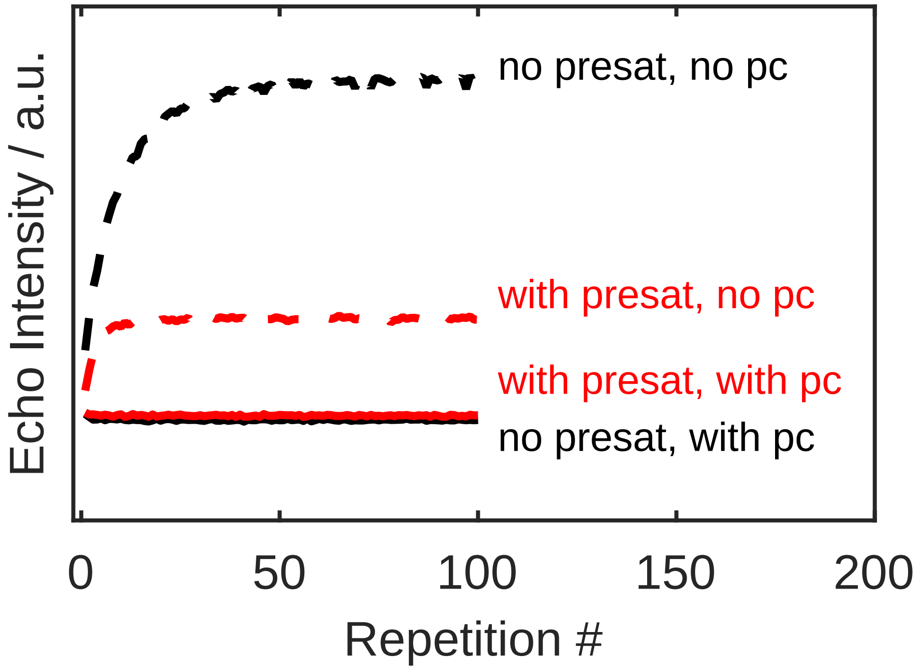


Fig. S15: Electron spin echo intensity after DNP and reverse DNP, using the 100 μM sample in deuterated solvent. The experiment was simply repeated several times, and single two shots were summed up. A combination of presaturation and phase-cycling leads to results without any saturation behaviour from one repetition to the next.