Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplemental Materials

The *Supplemental Materials* section contains plots of the trityl echo-detected EPR spectra (Fig. S1). It also shows the plots that can be found in the main text (**Fig. 2**, **Fig. 4** and **Fig. 5)** with the addition of a fourth sample, p-Gd-Pure (Fig. S2, Fig. S3, and Fig. S4, respectively). The sample p-Gd-Pure is simply p-Pure with the addition of 2mM Gd595. Lastly, Fig. S5 shows the DNP enhancement and the DNP build-up time as a function of forward

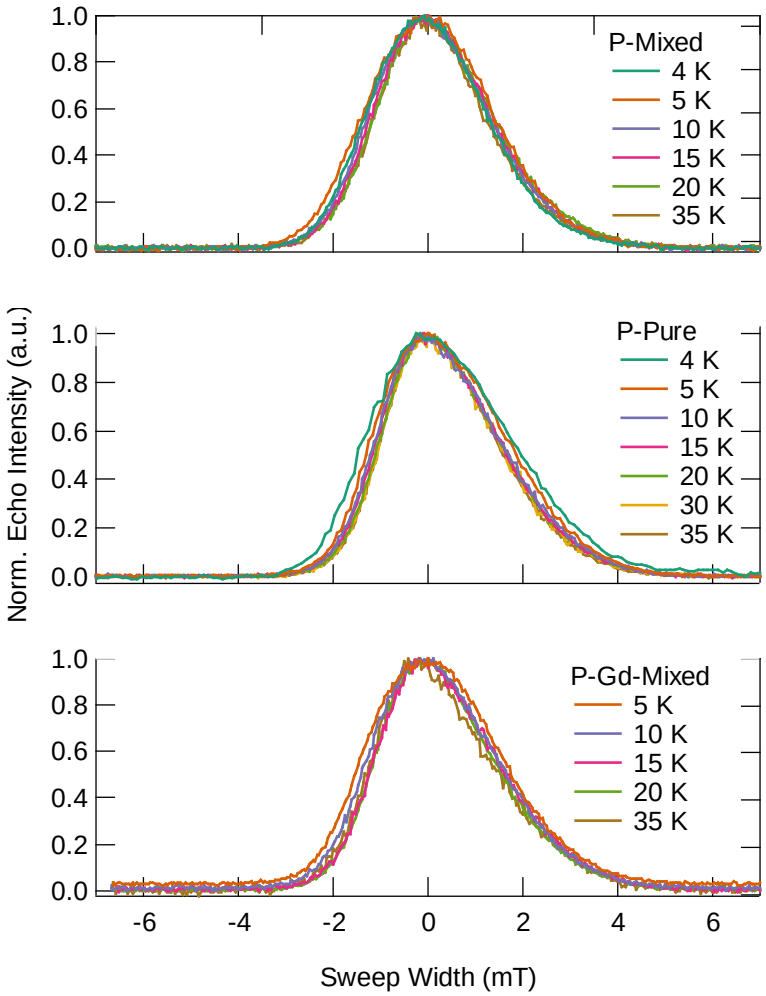

Figure S1. Echo-detected trityl EPR at 240 GHz of P-Mixed plotted at varying lattice temperatures. The spectra at FWHM broadens at low temperatures while no significant changes in lineshape are seen.

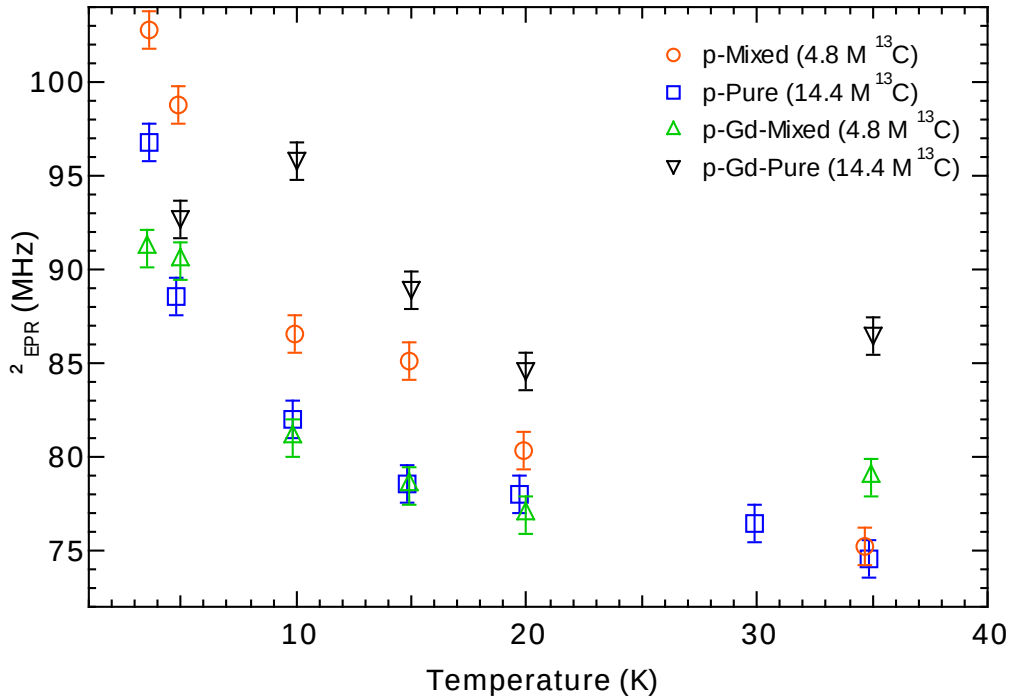

Figure S2. Inhomogeneously broadened echo-detected trityl EPR FWHM (Δ_{EPR}) plotted as a function of lattice temperature for four samples at 8.5 T. The p-Mixed, p-Pure, p-Gd-Mixed, and p-Gd-Pure all have the same trityl concentration of 15 mM. Interestingly, the trityl Δ_{EPR} increases at lower temperature.

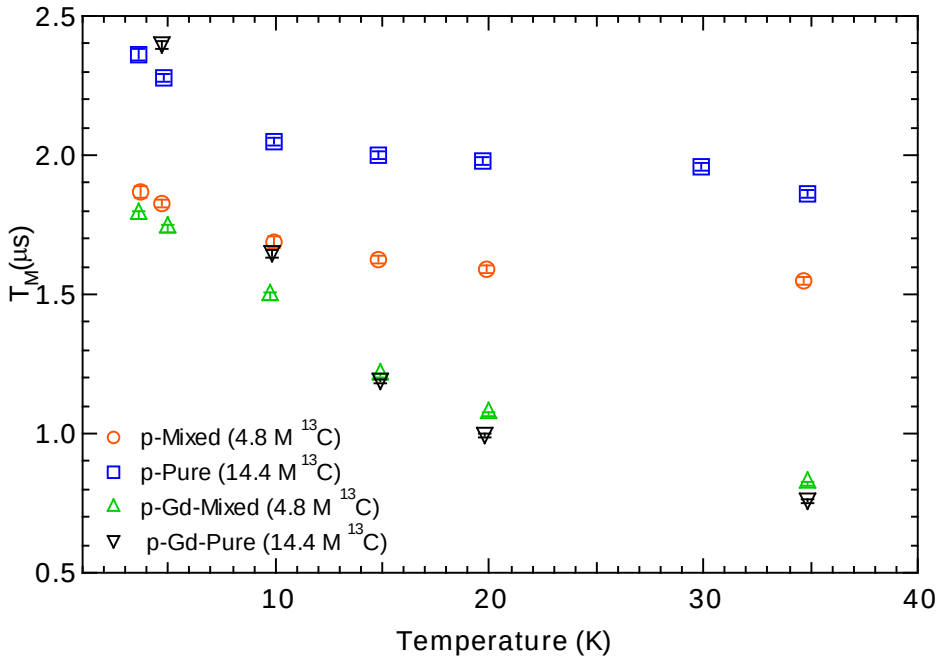

Figure S3. Electron spin phase memory time (T_M) constants as a function of lattice temperature for four different samples. The p-Mixed, p-Pure, p-Gd-Mixed, and p-Gd-Pure samples all have the same trityl concentration of 15 mM. Interestingly, the same trend of the T_M values matching up with their non-Gd doped counterpart at low temperatures is seen. This again suggests a solvent induced T_M relaxation at low lattice temperatures.

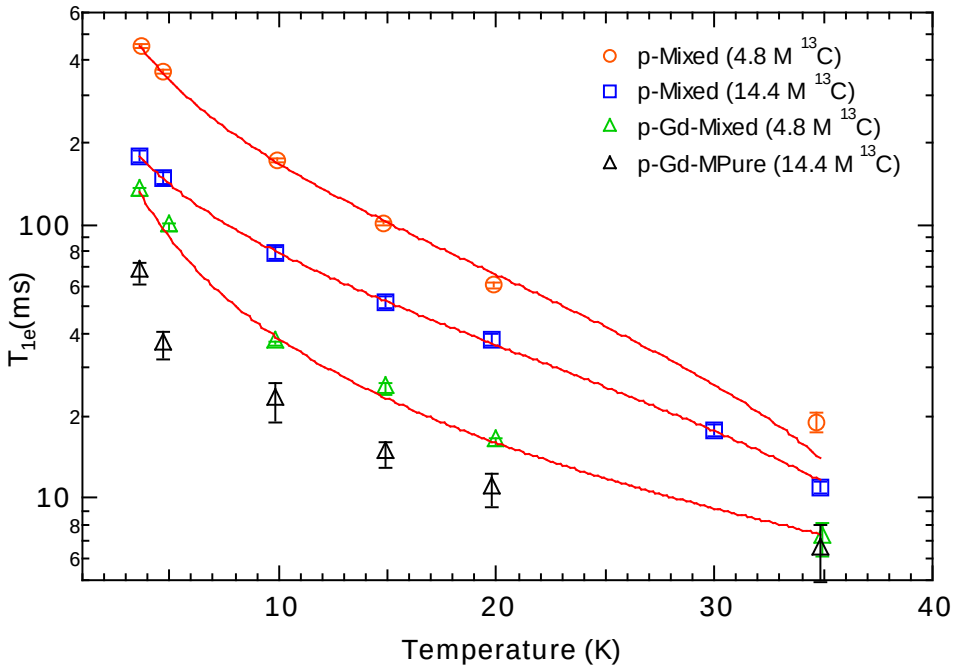

Figure S4. The electron spin-lattice relaxation time (T_{1e}) constants as a function of lattice temperature for four different samples. The p-Mixed, p-Pure, p-Gd-Mixed, and p-Gd-Pure samples all have the same trityl concentration of 15 mM. The p-Gd-Pure sample have the lowest T_{1e} of all the samples. Power law fits are shown in red.

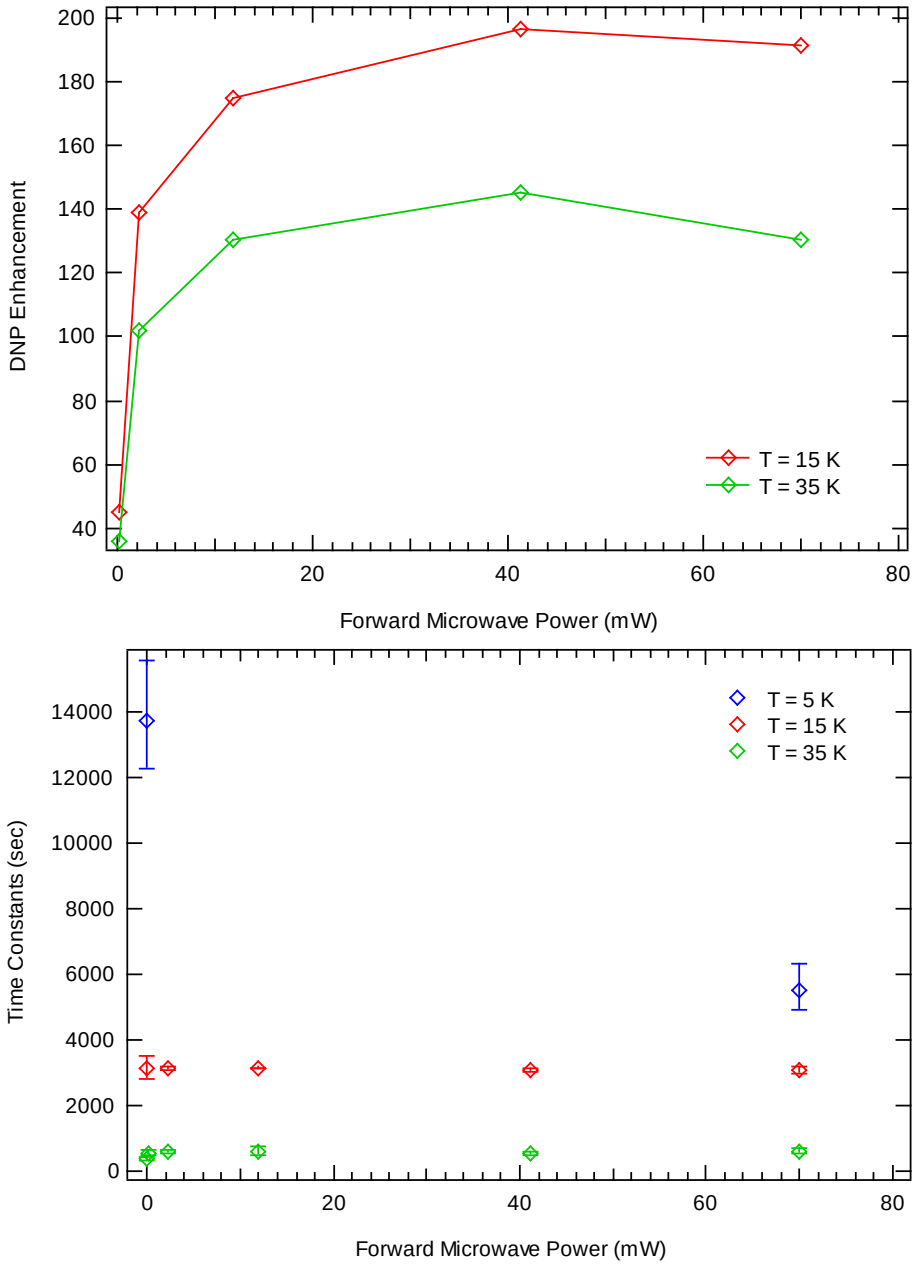

Figure S5. *Top*: DNP enhancement of p-Mixed as a function of μW forward power at two different lattice temperatures. This shows that OX063Me trityl radical EPR is easily saturated even down to 10 mW of forward power (which is actually much less when talking about the actual power at the sample). The percentage change between each data point is roughly equal for both lattice temperatures. Lines are drawn to guide the eye.
Bottom: DNP build-up time (T_{DNP}) of p-Mixed as a function of μW forward power at various lattice temperatures. When the μW power goes to zero the associated time constant is T_{1n}. At temperatures above 15 K it is clear that T_{DNP} stays roughly constant with μW forward power. It is implied that when the forward MW power is 0, the time constant is T_{1n} rather than T_{DNP}.