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Supporting information for: A Transition from Solid Effect to Indirect Cross Effect with Broadband Microwave Irradiation

D. Shimon[a] and I. Kaminker[b]

[a] Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

[b] School of Chemistry, Faculty of Exact Sciences, Tel Aviv University, Tel Aviv, Israel

S1 DNP SPECTRA AND ENHANCEMENTS

Here, we show non-normalized DNP spectra, so it's possible to compare the enhancements. As described in the main text, frequency modulation improves the enhancement when compared to cw irradiation ($\Delta\omega_{chirp} = 0$), in all cases. In addition, each sample has a different value of $\Delta\omega_{chirp}$ that results in maximal enhancement. We also notice that when the modulation is turned on, there is a slight "smoothing" effect on the DNP spectra, and sharp features that were resolved under cw irradiation are less and less visible as $\Delta\omega_{chirp}$ is increased. For the DNP spectra at 3.4 T the frequency separation between the maximum and minimum enhancement increases as $\Delta\omega_{chirp}$ increases. This is much less prominent at 7 T.

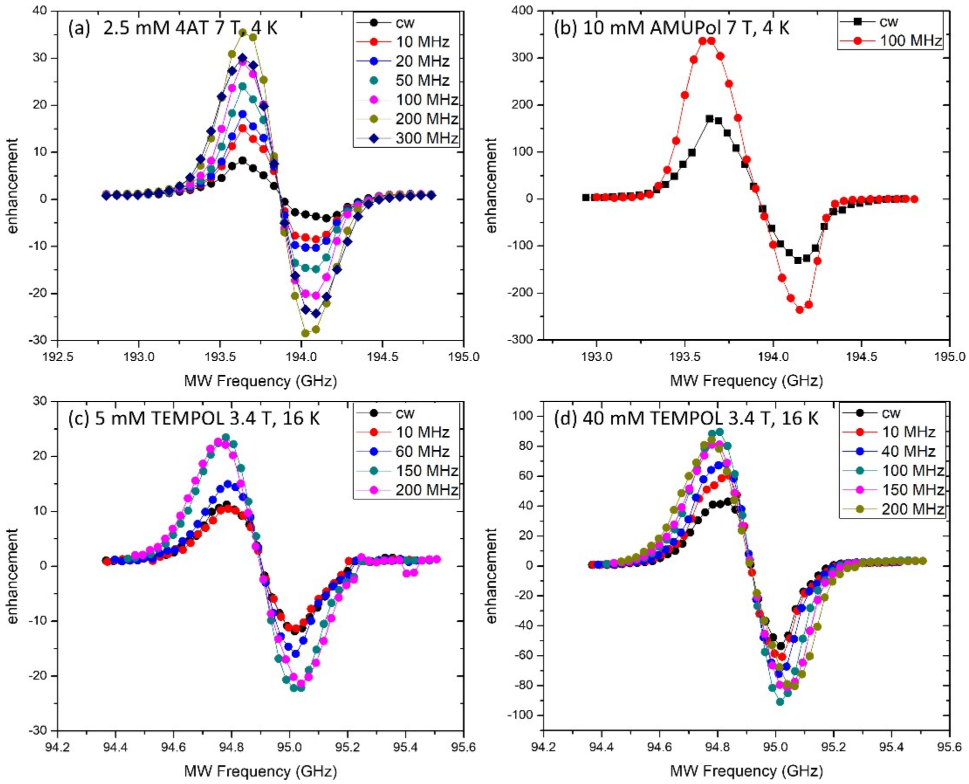

Figure S1: [1]H-DNP enhancement as a function of the MW irradiation frequency (DNP spectra), for several values as function of $\Delta\omega_{chirp}$. The radical type, radical concentration, temperature, and experimental magnetic field are indicated on the figure.

S2 ELDOR AND DNP SPECTRA AT 7 T

The ELDOR spectra measured at 7 T for the 2.5 mM 4AT sample are plotted in Figure S2. Also, in that figure are the fits of the ELDOR spectra.

The DNP spectra measured at 7 T for the 2.5 mM 4AT sample are plotted in Figure S3. The fits of the DNP spectra are also plotted, in addition to the difference between the experimental spectra and the fits.

The DNP spectra measured at 7 T for the 2.5 mM 4AT sample are plotted in Figure S4. The fits of the DNP spectra are also plotted, in addition to the difference between the experimental spectra and the fits. Here, we added SE to the fit, to show that the quality of the fit decreases as compared to when only the iCE is used for fitting.

The ELDOR spectra measured at 7 T for the 10 mM AMUPol sample are plotted in Figure S5. Also, in that figure are the fits of the ELDOR spectra.

The DNP spectra measured at 7 T for the 10 mM AMUPol sample are plotted in Figure S6. The fits of the DNP spectra are also plotted, in addition to the difference between the experimental spectra and the fits

The DNP spectra measured at 7 T for the 10 mM AMUPol sample are plotted in Figure S7. The fits of the DNP spectra are also plotted, in addition to the difference between the experimental spectra and the fits. Here, we added SE to the fit, to show that the quality of the fit decreases as compared to when only the iCE is used for fitting.

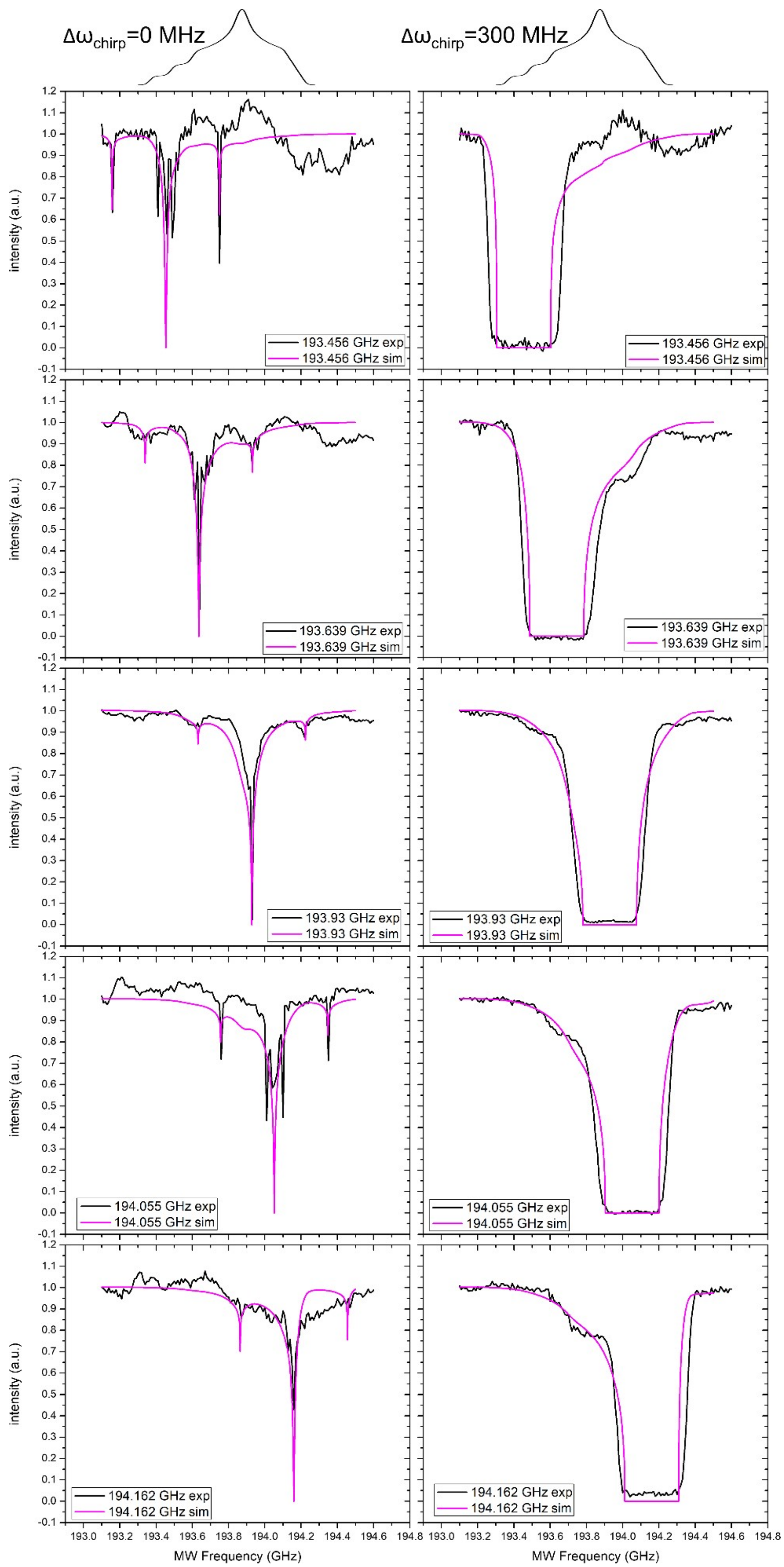

Figure S2: ELDOR spectra for the 2.5 mM 4AT sample with $\Delta\omega_{chirp} = 0$ MHz (left column) and $\Delta\omega_{chirp} = 300$ MHz (right column) plotted at several detection frequencies, ω_{detect}, given in the legends. The EPR line is plotted above the ELDOR spectra for comparison. Overlaid are the simulated ELDOR spectra (magenta). The parameters used for the fits are given in Table A1, in the main text. The experiments were performed at 4 K.

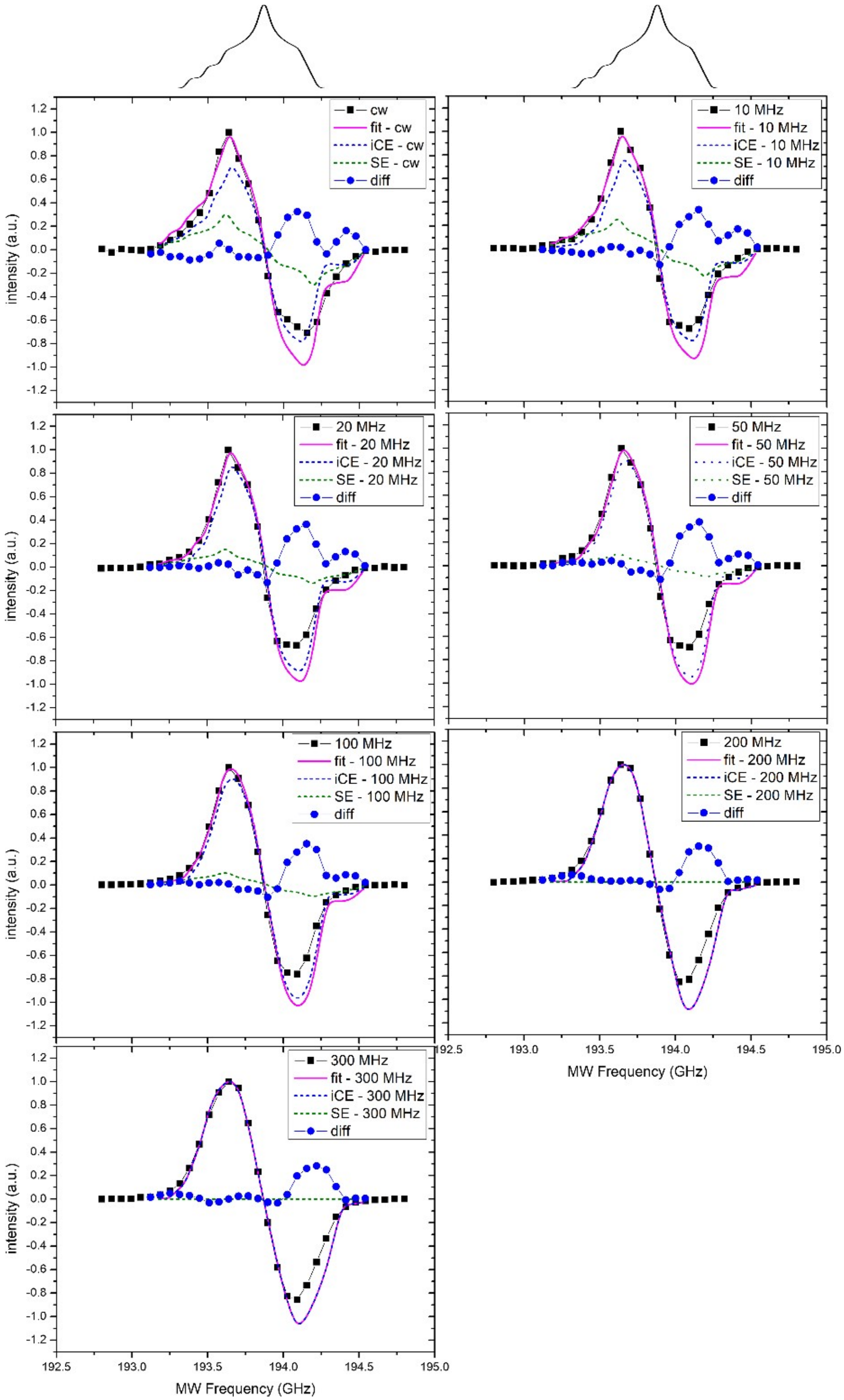

Figure S3: DNP spectra for the 2.5 mM 4AT sample plotted at several $\Delta\omega_{chirp}$ values. The chirp pulse bandwidth is given in the legend. The EPR line is plotted above the DNP spectra for comparison. Overlaid are the fits of the DNP spectra (magenta), which is the sum of the iCE (dashed blue) and SE (dashed green) DNP spectra with the ratios given Table 1. Also overlaid is the difference between the experiment and the fit (blue symbols). The experiments were performed at 4 K.

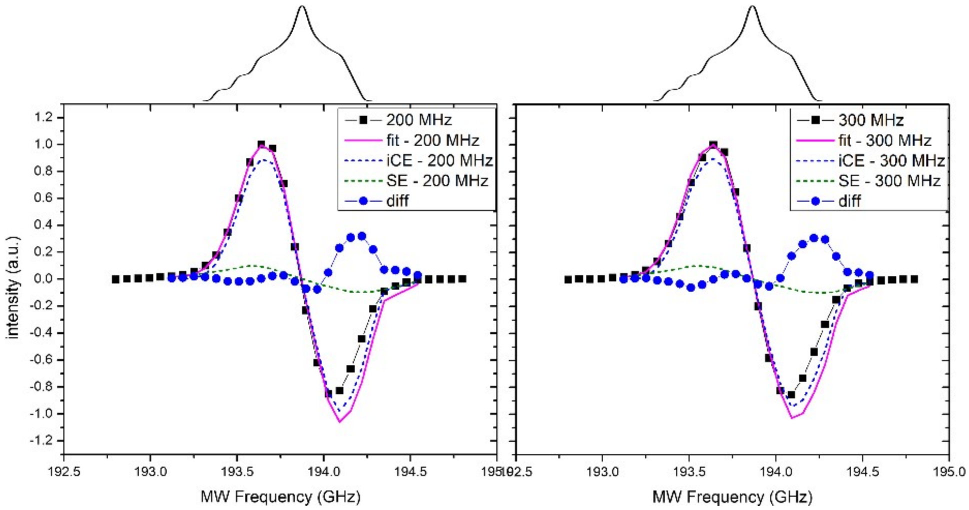

Figure S4: DNP spectra and fits for the 2.5 mM 4AT sample plotted at several $\Delta\omega_{chirp}$ values, with $k_{iCE}(\Delta\omega_{chirp}) = 0.9$ and $k_{SE}(\Delta\omega_{chirp}) = 0.1$ to show that the fits do not improve with the addition of the SE. The chirp pulse bandwidth is given in the legend. The EPR line is plotted above the DNP spectra for comparison. Overlaid are the fits of the DNP spectra (magenta), which is the sum of the iCE (dashed blue) and SE (dashed green) DNP spectra. Also overlaid is the difference between the experiment and the fit (blue symbols). The experiments were performed at 4 K.

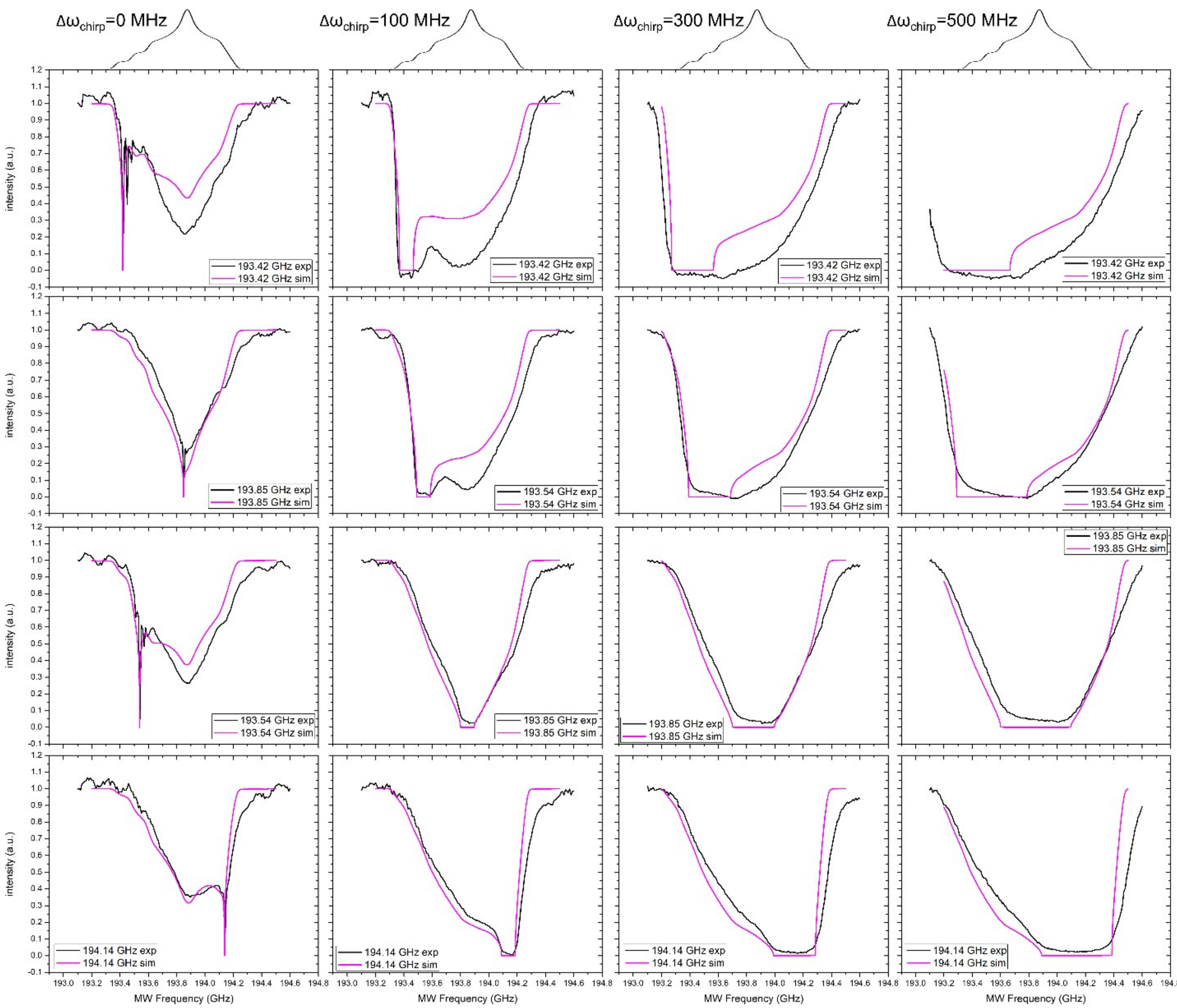

Figure S5: ELDOR spectra for the 10 mM AMUPol sample with (from left to right) $\Delta\omega_{chirp} = 0$ MHz, $\Delta\omega_{chirp} = 100$ MHz, $\Delta\omega_{chirp} = 300$ MHz $\Delta\omega_{chirp} = 500$ MHZ, plotted at several detection frequencies, ω_{detect}, given in the legends. The EPR line is plotted above the ELDOR spectra for comparison. Overlaid are the simulated ELDOR spectra (magenta). The parameters used for the fits are given in Table A1, in the main text. The experiments were performed at 4 K.

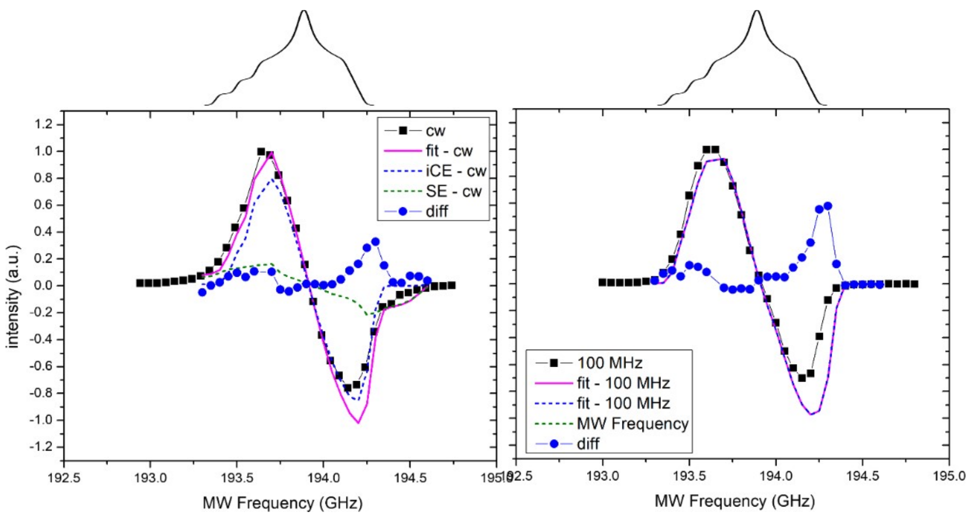

Figure S6: DNP spectra for the 10 mM AMUPol sample plotted at several $\Delta\omega_{chirp}$values. The chirp pulse bandwidth is given in the legend. The EPR line is plotted above the DNP spectra for comparison. Overlaid are the simulated DNP spectra (magenta), which is the sum of the iCE (dashed blue) and SE (dashed green) DNP spectra with the ratios given Table 1. Also overlaid is the difference between the experiment and the fit (blue symbols). The experiments were performed at 4 K.

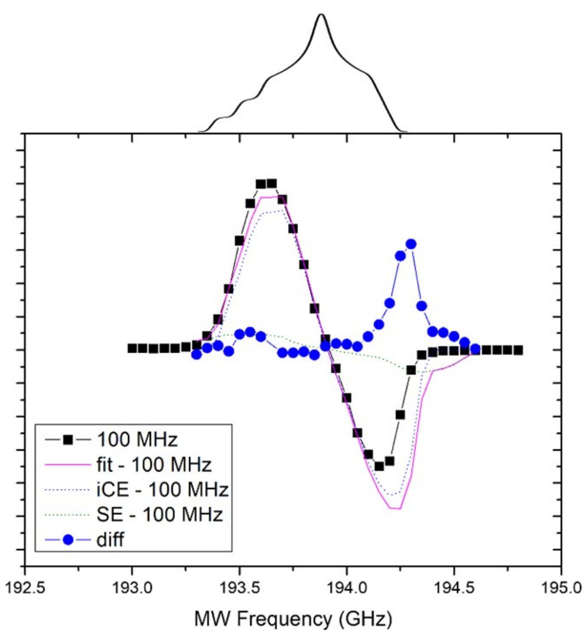

Figure S7: DNP spectrum and fit for the 10 mM AMUPol sample plotted at several $\Delta\omega_{chirp}$ values, with $k_{iCE}(\Delta\omega_{chirp}) = 0.9$ and $k_{SE}(\Delta\omega_{chirp}) = 0.1$ to show that the fit does not improve with the addition of the SE. The chirp pulse bandwidth is given in the legend. The EPR line is plotted above the DNP spectum for comparison. Overlaid is the fit of the DNP spectra (magenta), which is the sum of the iCE (dashed blue) and SE (dashed green) DNP spectra. Also overlaid is the difference between the experiment and the fit (blue symbols). Also overlaid is the difference between the experiment and the fit (blue symbols). The experiments were performed at 4 K.

S3 ELDOR AND DNP SPECTRA AT 3.4 T

The ELDOR spectra measured at 3.4 T for the 40 mM TEMPOL sample are plotted in Figure S8 before baseline correction. Also, in that figure are the spline functions used for the baseline correction.

The ELDOR spectra measured at 3.4 T for the 5 mM TEMPOL sample are plotted in Figure S9. Also, in that figure are the fits of the ELDOR spectra.

The DNP spectra measured at 3.4 T for the 5 mM TEMPOL sample are plotted in Figure S10. The fits of the DNP spectra are also plotted, in addition to the difference between the experimental spectra and the fits.

The DNP spectra measured at 3.4 T for the 5 mM TEMPOL sample are plotted in Figure S11. The fits of the DNP spectra are also plotted, in addition to the difference between the experimental spectra and the fits. Here, we added SE to the fit, to show that the quality of the fit decreases as compared to when only the iCE is used for fitting.

The ELDOR spectra measured at 3.4 T for the 40 mM TEMPOL sample are plotted in Figure S12 before baseline correction. Also, in that figure are the spline functions used for the baseline correction.

The ELDOR spectra measured at 3.4 T for the 40 mM TEMPOL sample are plotted in Figure S13. Also, in that figure are the fits of the ELDOR spectra.

The DNP spectra measured at 3.4 T for the 40 mM TEMPOL sample are plotted in Figure S14. The fits of the DNP spectra are also plotted, in addition to the difference between the experimental spectra and the fits.

The DNP spectra measured at 3.4 T for the 40 mM TEMPOL sample are plotted in Figure S15. The fits of the DNP spectra are also plotted, in addition to the difference between the experimental spectra and the fits. Here, we added SE to the fit, to show that the quality of the fit decreases as compared to when only the iCE is used for fitting.

DNP enhancement as a function of $\Delta\omega_{chirp}$ curves measured at 3.4 T for the 40 mM TEMPOL sample are plotted in Figure S16.

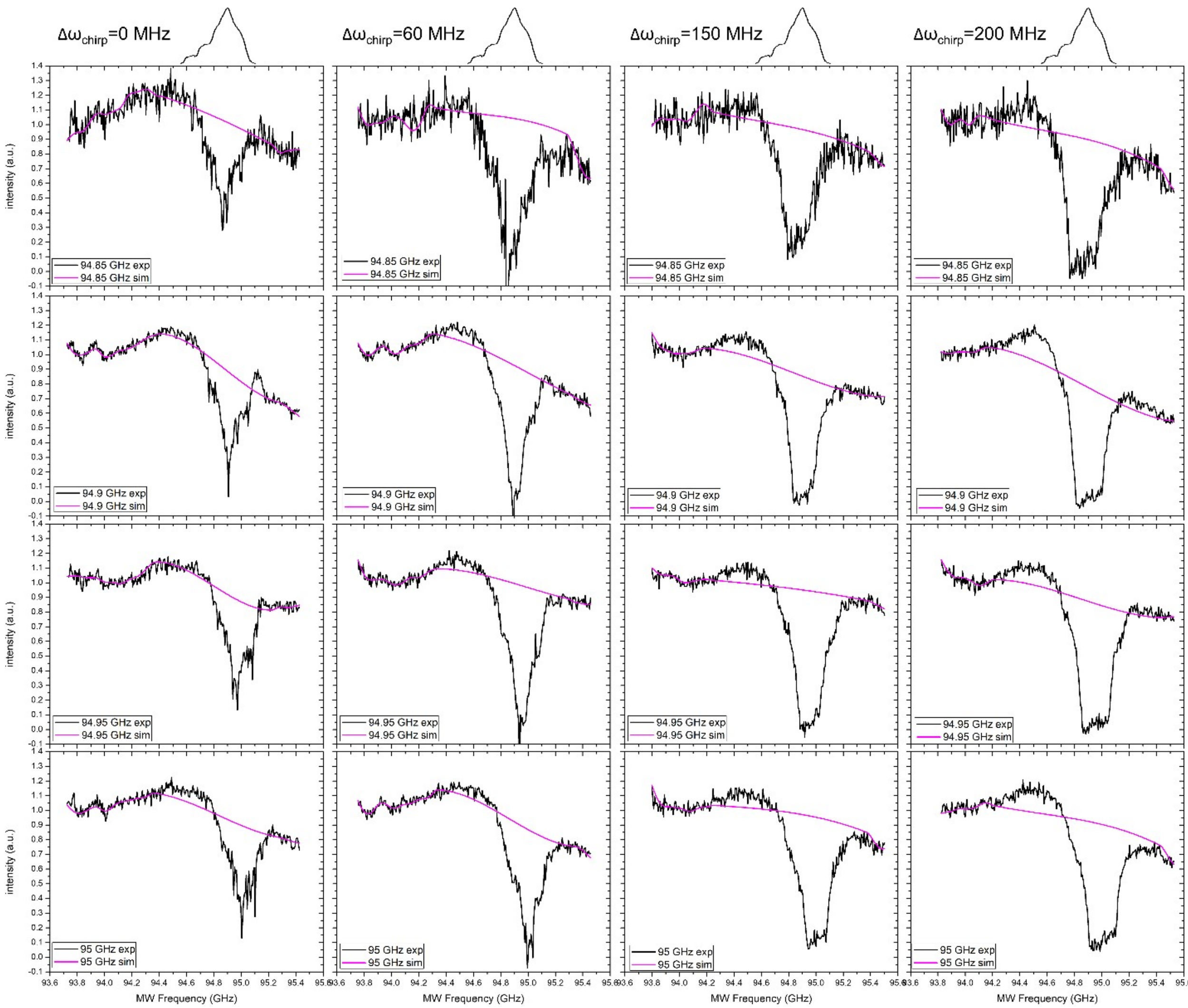

Figure S8: ELDOR spectra for the 5 mM TEMPOL sample with (from left to right) $\Delta\omega_{chirp} = 0$, $\Delta\omega_{chirp} = 60$ MHz, $\Delta\omega_{chirp} = 150$ MHz and $\Delta\omega_{chirp} = 200$ MHz, plotted at several detection frequencies, ω_{detect}, given in the legends. The EPR line is plotted above the ELDOR spectra for comparison. Overlaid are the spline functions used to baseline correct the ELDOR spectra (magenta). The experiments were performed at 16 K.

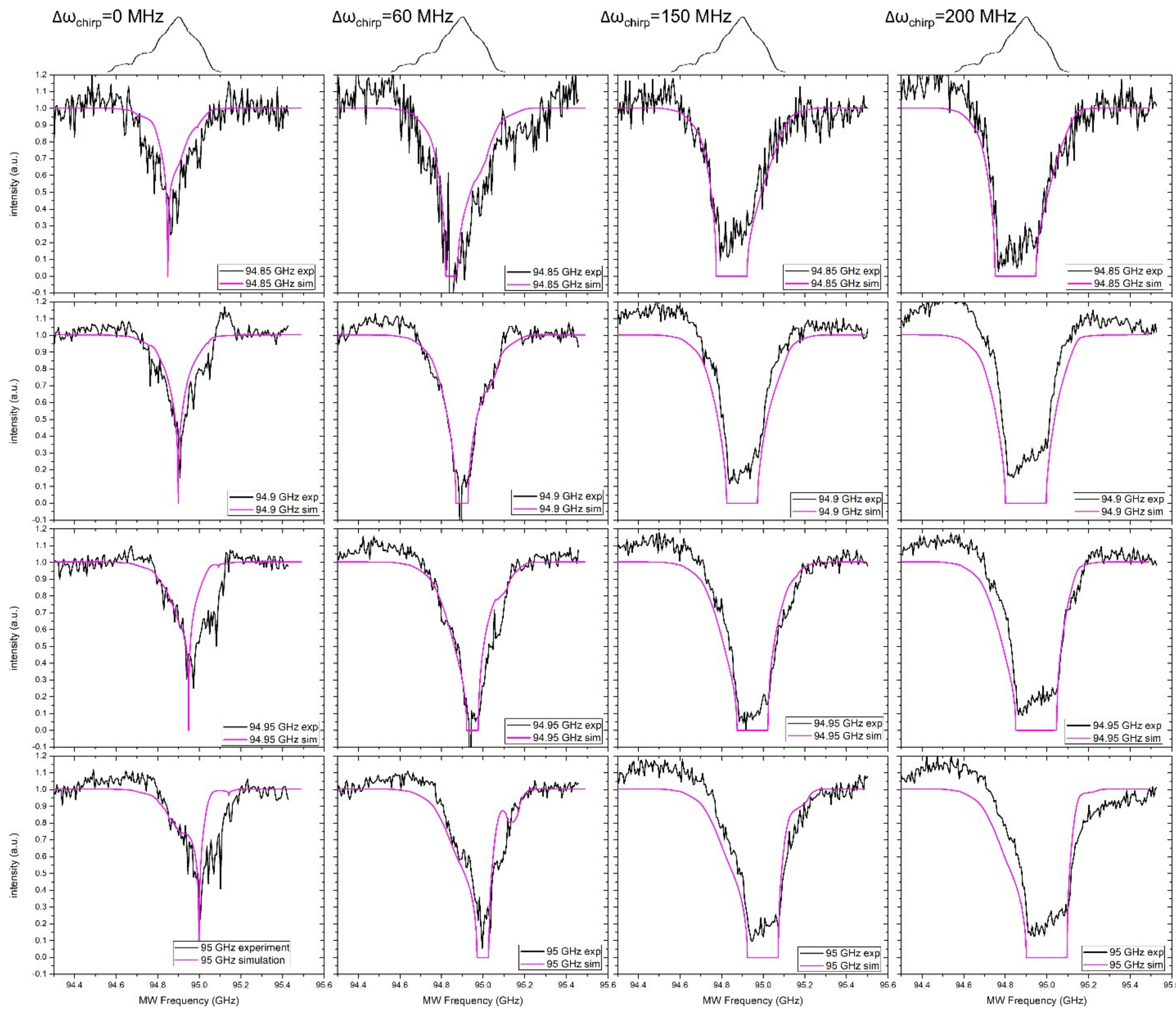

Figure S9: ELDOR spectra for the 5 mM TEMPOL sample (from left to right $\Delta\omega_{chirp} = 0$, $\Delta\omega_{chirp} = 60$ MHz, $\Delta\omega_{chirp} = 150$ MHz and $\Delta\omega_{chirp} = 200$ MHz, plotted at several detection frequencies, ω_{detect}, given in the legends. The EPR line is plotted above the ELDOR spectra for comparison. Overlaid are the simulated ELDOR spectra (magenta). The parameters used for the fits are given in Table A1, in the main text. The experiments were performed at 16 K.

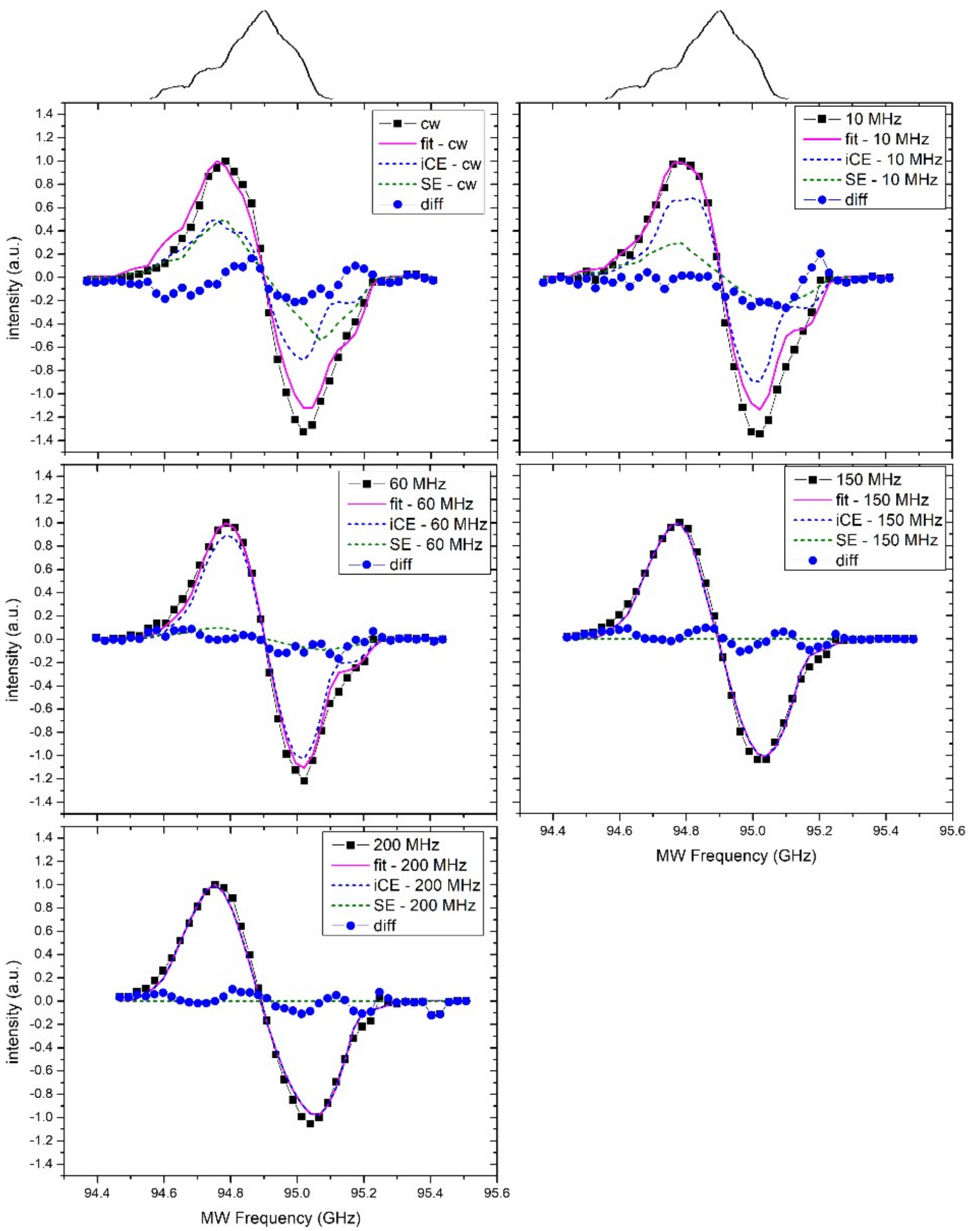

Figure S10: DNP spectra for the 5 mM TEMPOL sample plotted at several $\Delta\omega_{chirp}$ values. The chirp pulse bandwidth is given in the legend. The EPR line is plotted above the DNP spectra for comparison. Overlaid is the fit of the DNP spectra (magenta), which is the sum of the iCE (dashed blue) and SE (dashed green) DNP spectra with the ratios given Table 1. Also overlaid is the difference between the experiment and the fit (blue symbols). The experiments were performed at 16 K.

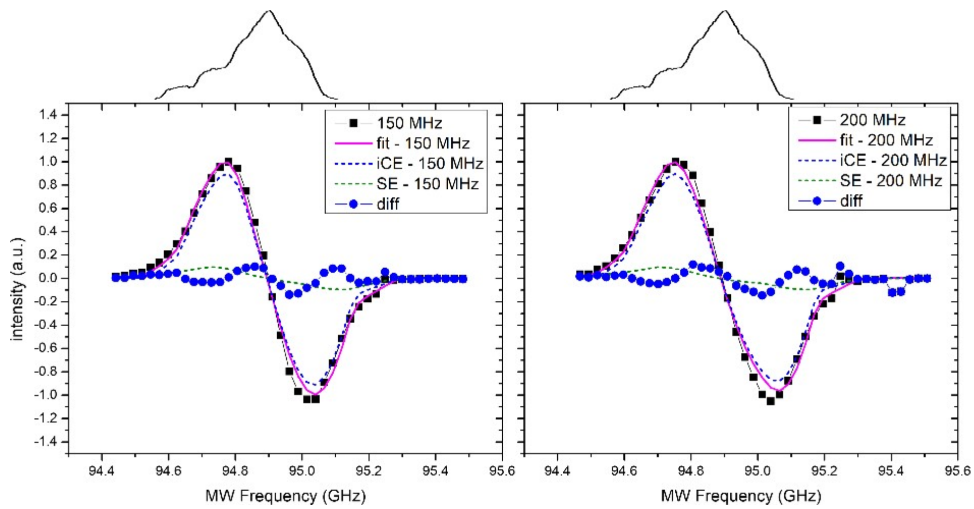

Figure S11: DNP spectra and fits for the 5 mM TEMPOL sample plotted at several $\Delta\omega_{chirp}$values, with $k_{iCE}(\Delta\omega_{chirp}) = 0.9$ and $k_{SE}(\Delta\omega_{chirp}) = 0.1$ to show that the fits do not improve with the addition of the SE. The modulation amplitude is given in the legend. The EPR line is plotted above the DNP spectra for comparison. Overlaid are the fits of the DNP spectra (magenta), which is the sum of the iCE (dashed blue) and SE (dashed green) DNP spectra. Also overlaid is the difference between the experiment and the fit (blue symbols). The experiments were performed at 16 K.

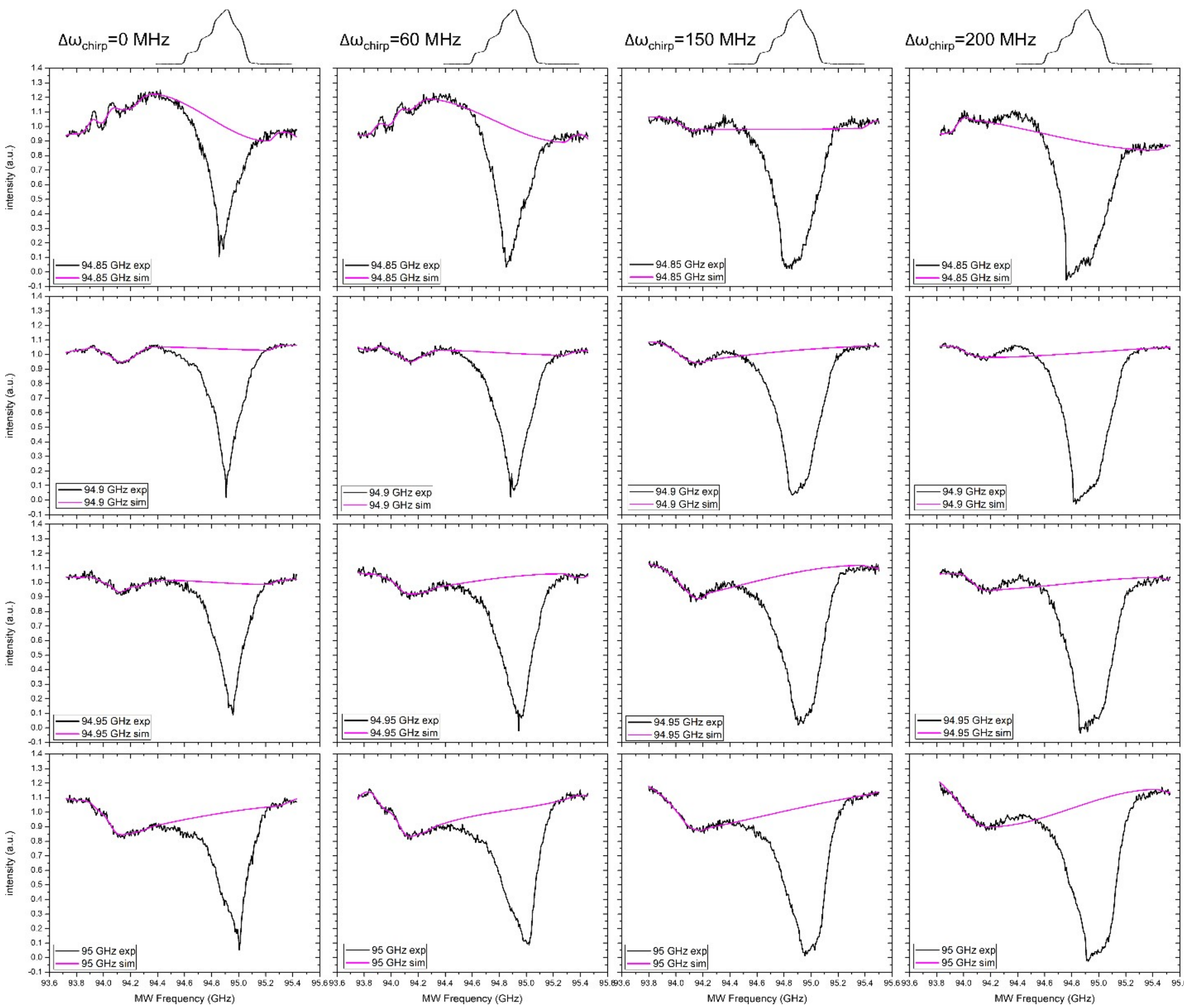

Figure S12: ELDOR spectra for the 40 mM TEMPOL sample with (from left to right) $\Delta\omega_{chirp} = 0$, $\Delta\omega_{chirp} = 60$ MHz, $\Delta\omega_{chirp} = 150$ MHz and $\Delta\omega_{chirp} = 200$ MHz, plotted at several detection frequencies, ω_{detect}, given in the legends. The EPR line is plotted above the ELDOR spectra for comparison. Overlaid are the spline functions used to baseline correct the ELDOR spectra (magenta). The experiments were performed at 16 K.

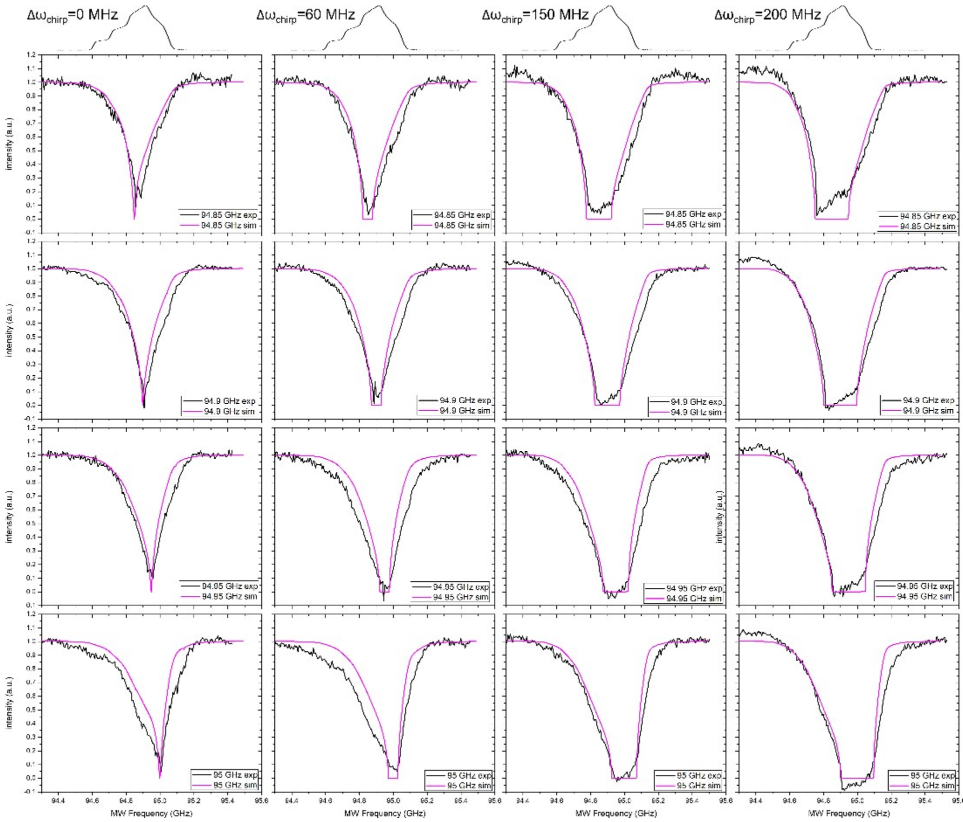

Figure S13: ELDOR spectra for the 40 mM TEMPOL sample with (from left to right) $\Delta\omega_{chirp} = 0$, $\Delta\omega_{chirp} = 60$ MHz, $\Delta\omega_{chirp} = 150$ MHz and $\Delta\omega_{chirp} = 200$ MHz, plotted at several detection frequencies, ω_{detect}, given in the legends. The EPR line is plotted above the ELDOR spectra for comparison. Overlaid are the simulated ELDOR spectra (magenta). The parameters used for the fits are given in Table 1, in the main text. The experiments were performed at 16 K.

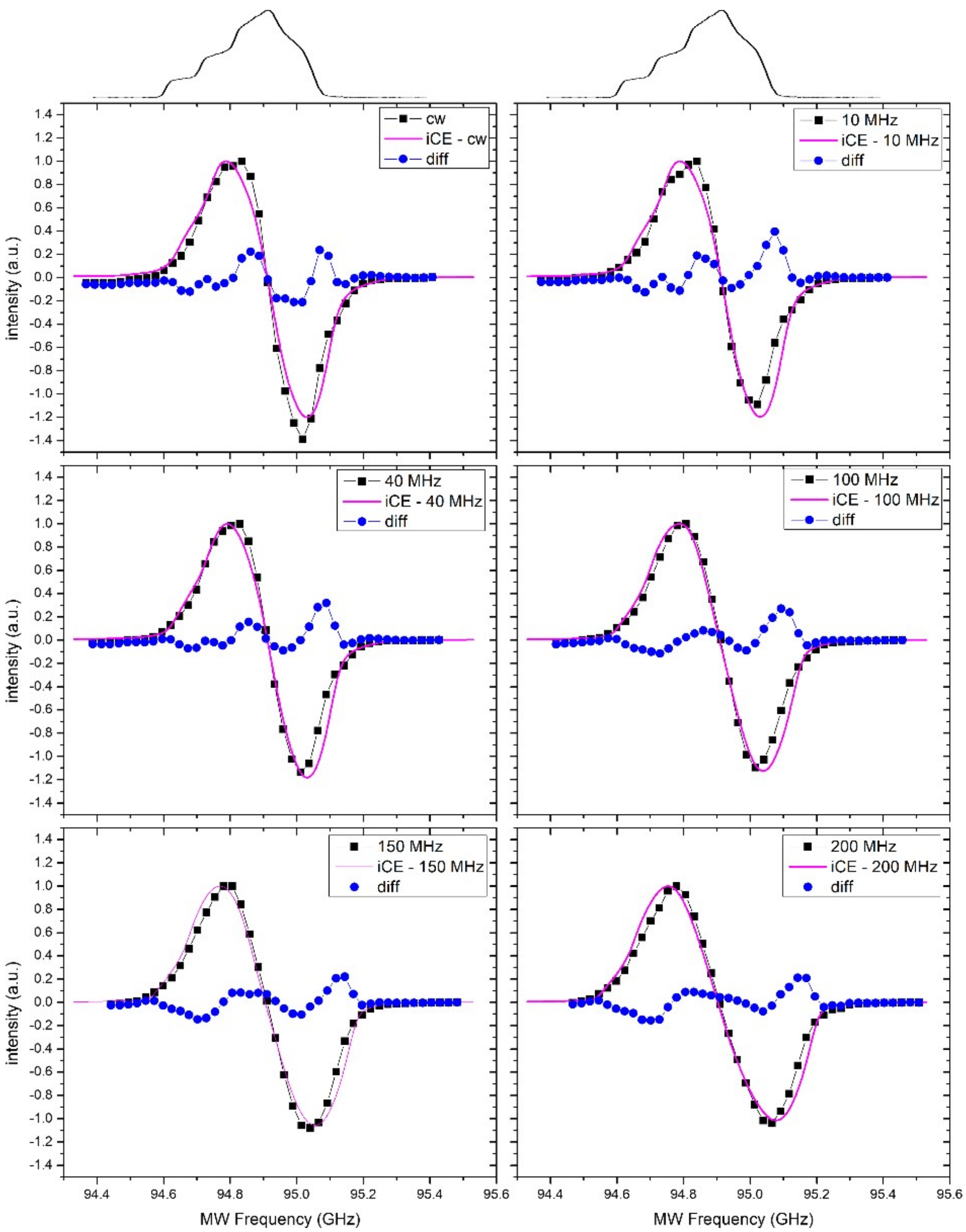

Figure S14: DNP spectra for the 40 mM TEMPOL sample plotted at several $\Delta\omega_{chirp}$ values. The chirp pulse bandwidth is given in the legend. The EPR line is plotted above the DNP spectra for comparison. Overlaid are the fits of the DNP spectra (magenta), which is the sum of the iCE (dashed blue) and SE (dashed green) DNP spectra with the ratios given Table 1. Also overlaid is the difference between the experiment and the fit (blue symbols). The experiments were performed at 16 K.

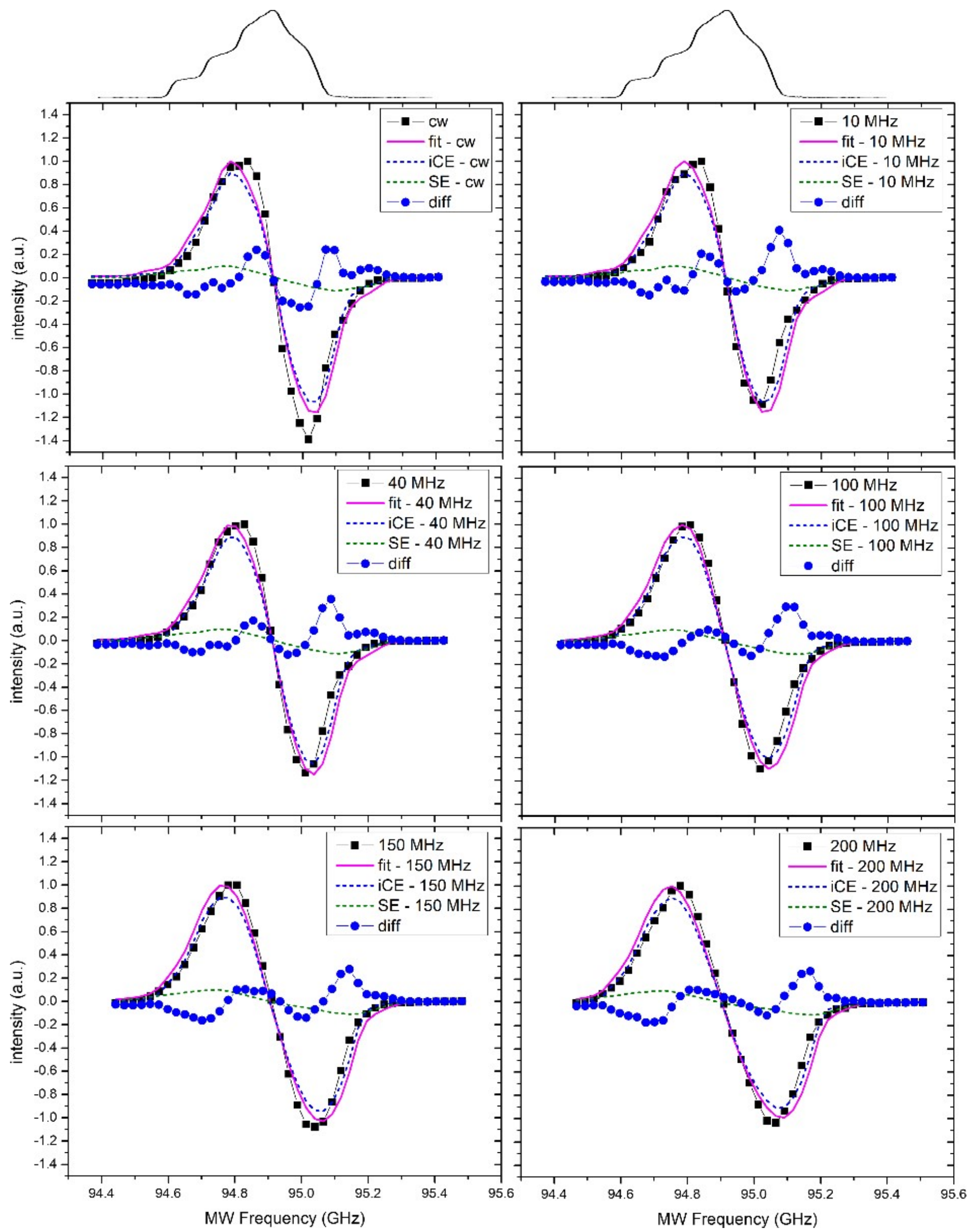

Figure S15: DNP spectra and fits for the 40 mM TEMPOL sample plotted at several $\Delta\omega_{chirp}$ values, with $k_{iCE}(\Delta\omega_{chirp}) = 0.9$ and $k_{SE}(\Delta\omega_{chirp}) = 0.1$ to show that the fits do not improve with the addition of the SE. The chirp pulse bandwidth is given in the legend. The EPR line is plotted above the DNP spectra for comparison. Overlaid are the fits of the DNP spectra (magenta), which is the sum of the iCE (dashed blue) and SE (dashed green) DNP spectra. Also overlaid is the difference between the experiment and the fit (blue symbols). The experiments were performed at 16 K.

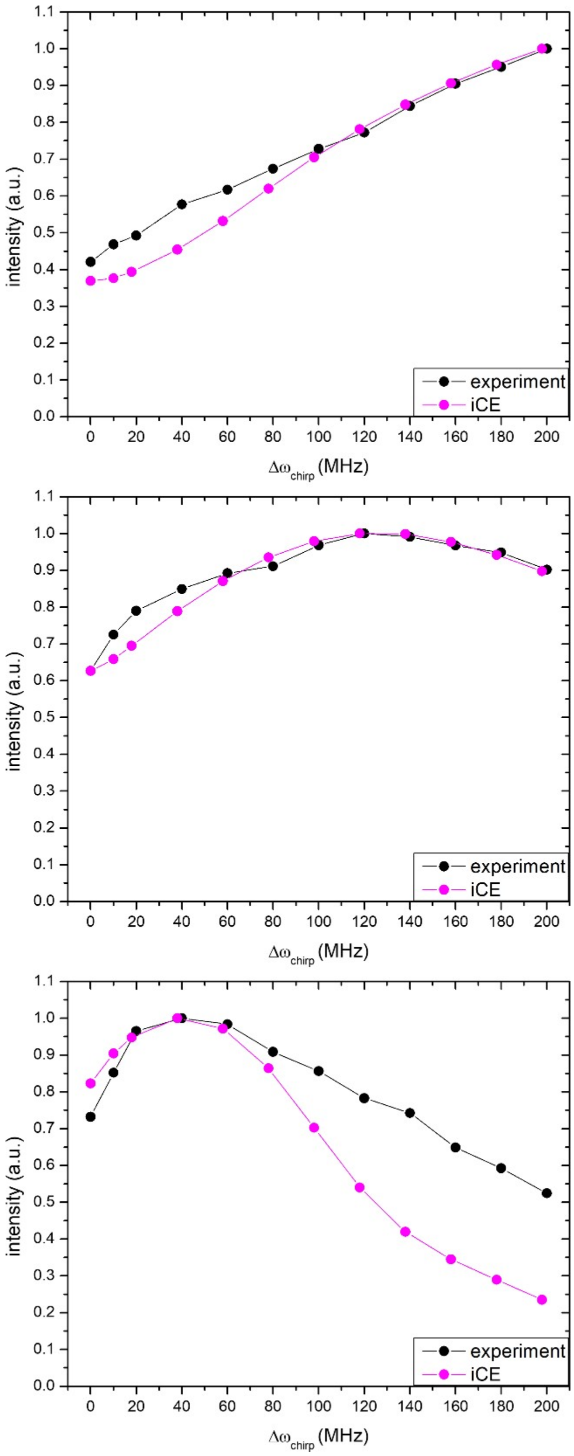

Figure S16: DNP enhancement as a function of $\Delta\omega_{chirp}$for the 40 mM TEMPOL sample Each plot compares the experimental DNP enhancement with the curve for the iCE (magneta). The curves were measured at the following frequencies: 94.679 GHz (top), 94. 783 GHz (middle) and 94.861 GHz (bottom). The experiments were performed at 16 K.

S4 Quality of DNP Fits

We define a parameter for the quality of the fitting of the experimental DNP spectra as:

$$\sigma_{DNP} = \sqrt{\frac{\sum_{\omega_{excite}} \left[S_{exp}(\omega_{excite}) - S_{sim}(\omega_{excite})\right]^2}{n_{\omega_{excite}}}}$$

where $n_{\omega_{excite}}$ is the number of points measured in the experimental DNP spectrum. The values of $k_{iCE}(\Delta\omega_{chirp})$ and $k_{SE}(\Delta\omega_{chirp})$ are chosen such that σ_{DNP} is minimal, and ensuring that $k_{iCE}(\Delta\omega_{chirp}) + k_{SE}(\Delta\omega_{chirp}) = 1$, for each DNP spectrum. The values of the sum squares of the difference are given in the Supporting Information (Table S1), for cases where it isn't obvious if SE should be included or not.

As described in the main text, the amount of SE needed to fit the experimental spectra decreases as $\Delta\omega_{chirp}$ increases. In fact, for all samples, the fits of the spectra with higher $\Delta\omega_{chirp}$ values used $k_{SE}(\Delta\omega_{chirp} > 150) = 0$. The 40 mM TEMPOL DNP spectra also used $k_{SE}(\Delta\omega_{chirp}) = 0$ for all values of $\Delta\omega_{chirp}$. In order to check if adding SE will improve the quality of the fits, we compared σ_{DNP} when $k_{SE}(\Delta\omega_{chirp}) = 0$ and $k_{SiCE}(\Delta\omega_{chirp}) = 1$ with $k_{SE}(\Delta\omega_{chirp}) = 0.1$ and $k_{SiCE}(\Delta\omega_{chirp}) = 0.9$. The values are given in Table S2. In all cases, the fits with $k_{SE}(\Delta\omega_{chirp}) = 0$ and $k_{SiCE}(\Delta\omega_{chirp}) = 1$ were of higher quality, proving that no SE is necessary in those cases.

Table S1: The values of by $k_{iCE}(\Delta\omega_{chirp})$ and $k_{SE}(\Delta\omega_{chirp})$ used to fit the DNP spectra for different values of $\Delta\omega_{chirp}$, and the fit quality σ_{DNP}, both for the optimal fits, and for fits where the addition of the SE lowers the quality of the fit (highlighted in yellow).

Sample	$\Delta\omega_{chirp}$ (MHz)	$k_{iCE}(\Delta\omega_{chirp})$	$k_{SE}(\Delta\omega_{chirp})$	σ_{DNP}
2.5 mM 4AT 7 T, 4 K	200	1	0	0.024
	300	1	0	0.023
	200	0.9	0.1	0.025
	300	0.9	0.1	0.025
10 mM AMUPol 7 T, 4 K	100	1	0	0.036
	100	0.9	0.1	0.038
5 mM TEMPOL 3.4 T, 16 K	150	1	0	0.008
	200	1	0	0.009
	150	0.9	0.1	0.008
	200	0.9	0.1	0.010
40 mM TEMPOL 3.4 T, 16 K	0 (cw)	1	0	0.016
	10	1	0	0.016
	40	1	0	0.013
	100	1	0	0.012
	150	1	0	0.012
	200	1	0	0.012

	0 (cw)	0.9	0.1	0.019
	10	0.9	0.1	0.018
	40	0.9	0.1	0.016
	100	0.9	0.1	0.015
	150	0.9	0.1	0.015
	200	0.9	0.1	0.015

S5 RELAXATION TIMES AND DNP BUILDUP

T_{1n} and T_{bu} at 7 T are plotted in Figure S17 and Figure S18, for 7 T and 3.4 T, respectively. The relaxation times are given in Table S2.

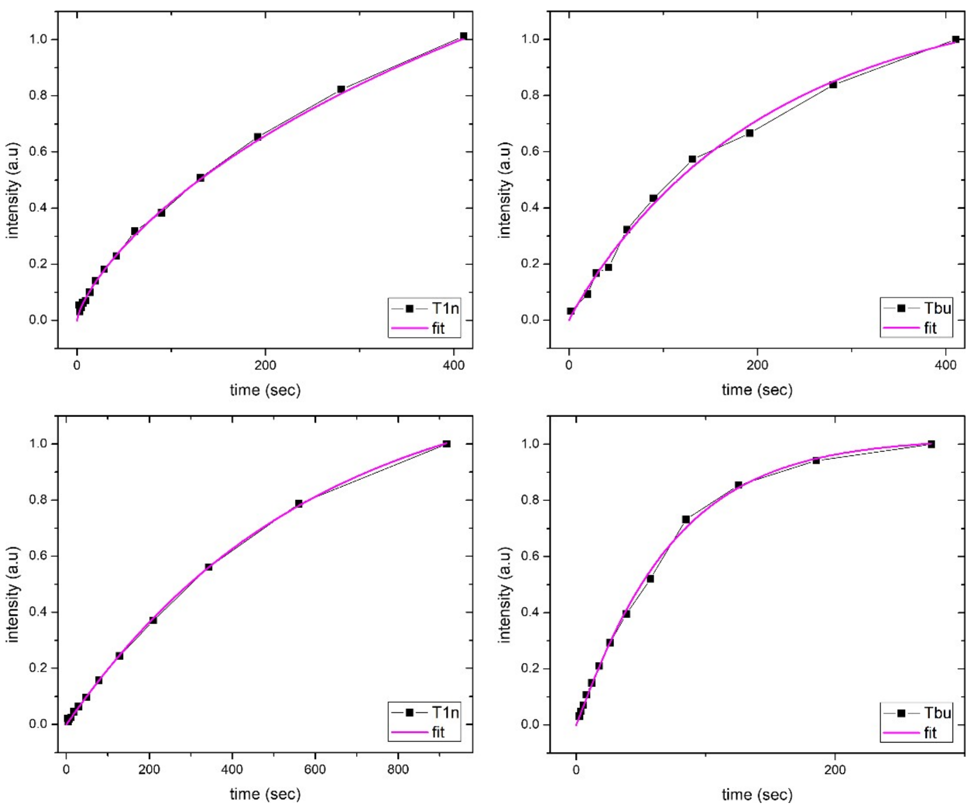

Figure S17: T_{1n} and T_{bu} relaxation curves for the 2.5 mM 4AT sample (top row) and the 10 mM AMUPol (bottom row). The T_{bu} curves are measured at the maximum of the corresponding DNP spectra. The experiments were performed at 4 K.

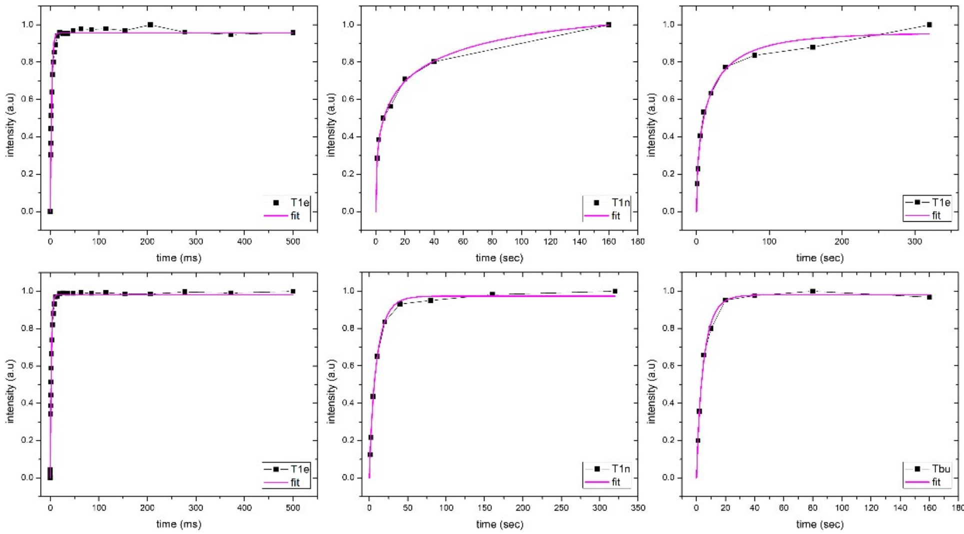

Figure S18: T_{1e}, T_{1n} and T_{bu} relaxation curves for the 5 mM TEMPOL sample (top row) and the 40 mM TEMPOL (bottom row). The T1e curve is measured at 94.9 GHz for both samples. The T_{bu} curve is measured at 94.783 GHz for the 5 mM sample, and at 94.835 GHz for the 40 mM sample. The experiments were performed at 16 K.

Table S2: Relaxation times for the electron, T_{1e}, the ^{1}H nucei, T_{1n}, the DNP buildup, T_{bu}, and the stretched exponential stretch factor α. The errors represent the 95 % confidence interval, given from the fit.

Sample	T_{1e}		T_{1n}		T_{bu}	
	T_{1e} (ms)	α	T_{1n} (s)	α	T_{1e} (s)	α
2.5 mM 4AT 7 T, 4 K	x	x				
10 mM AMUPol 7 T, 4 K	x	x	585 ± 83	1.01 ± 0.05	73 ± 7	1.05 ± 0.08
5 mM TEMPOL 3.4 T, 16 K	3 ± 0.4	1.07 ± 0.17	24 ±	0.38 ± 0.08	17 ± 7	0.55 ± 0.13
40 mM TEMPOL 3.4 T, 16 K	2 ± 0.3	1.05 ± 0.17	9 ± 0.9	0.87 ± 0.09	5 ± 0.7	0.88 ± 0.14

S6 SE OF A SINGLE ELECTRON BIN

As described in the main text, we expect the SE to decrease as the chirp pulse bandwidth increases. This can be understood if we consider the enhancement of a single electron bin as a function of the chirp pulse bandwidth, as shown in simulations in Figure 3 in the main text, and in Figure S19, below. As explained in the main text, the SE enhancement drops off when the single quantum (SQ) transition of the electron is saturated. In the absence of spectral diffusion, there is a sharp drop off around $\Delta\omega_{chirp} \approx 2\omega_n$. When spectral diffusion is active, the SE enhancement starts to decrease at $\Delta\omega_{chirp} < 2\omega_n$.

Note that in cases where the spectral diffusion is low, $\Lambda \leq 100\ (\mu s^{-3})$, there is an increase in the enhancement from a single bin at low chirp pulse bandwidths ($\Delta\omega_{chirp} < 10\ MHz$). In these cases, the irradiation on the double quantum (DQ) or zero quantum (ZQ) transition results in partial saturation of the SQ transition. This saturation does not occur once the chirp pulse bandwidth increases ($\Delta\omega_{chirp} > 10\ MHz$), and the irradiation exactly at the DQ/ZQ is weaker. Nor does it occur once the spectral diffusion distributes the electron polarization throughout the EPR line ($\Lambda > 100\ (\mu s^{-3})$)

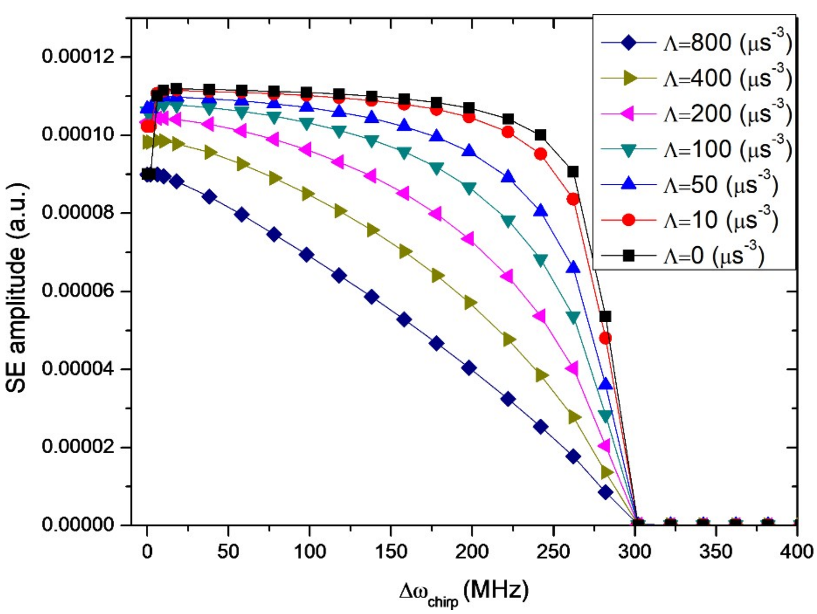

Figure S19: The SE enhancement of a single electron bin as a function of the chirp pulse bandwidth, for various electron spectral diffusion values. The simulation parameters match those given in Table A1 in the main text, for the 40 mM TEMPOL sample, at 3.4 T, with spectral diffusion values given in the legend. The simulations show how the SE enhancement of a single electron spin packet decreases as a function of the chirp pulse bandwidth.