Supporting Information for:

Electron Decoupling with Dynamic Nuclear Polarization in Rotating Solids

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1. Electron γB_1 estimation

The intensity of the magnetic field oscillating at the electron Zeeman frequency of 198 GHz, and the resulting nutation frequency of the electron spins ($\gamma_S B_{1S} = \omega_{1S} / 2\pi,$ also known as the Rabi frequency) is an important factor in understanding DNP and also electron decoupling. We computed the $\omega_{1S} / 2\pi$ across the sample using a finite element analysis program, High Frequency Structural Simulator (HFSS, available from Ansys, PA). HFSS solves the Maxwell equations with a given electromagnetic intensity and input profile. We estimate an input power of 5 W into the MAS stator (shown in Figure S1a) based on power measurements of the microwave beam outside of the magnet bore and losses in the transmission line. A peak electric field intensity of 15 kV/m corresponds to 5 W and is introduced into the stator as a Gaussian profile emitted from the aperture of a 4.8 mm inner diameter corrugated waveguide. The Gaussian profile of the microwave beam irradiating the sample was confirmed using a pyro-electric camera (Ophir-Spiricon, Israel). The simulation models the sample as a frozen glycerol and water mixture, with the real part of the dielectric constant (ε'_r) as 3.5 and the loss tangent as 0.007. The simulation yields the magnetic field intensity transverse to the polarizing superconducting magnetic field, B_0.

A phase dependent magnetic field is plotted in Figure S1c and shows the instantaneous intensity of the 198 GHz electromagnetic wave. However, it is the phase independent average of the magnetic field intensity over the 5 picosecond period of the wave, which is used to calculate the electron nutation frequency. Also, the microwave power emitted from the gyrotron is linearly polarized, and the electron spins only interact with one of the counter-rotating circular polarizations, so only half the power contributes to the $\omega_{1S}/2\pi$. This $\omega_{1S}/2\pi$ intensity in the MAS stator is shown in Figure S1b and expanded in the area of the sample in Figure S1d. As calculated previously, the $\omega_{1S}/2\pi$ frequency is inhomogeneous across the sample, and we calculate an average $\omega_{1S}/2\pi$ of 0.38 MHz. Further details of the $\omega_{1S}/2\pi$ calculation can be found in a similar treatment in our previous study.

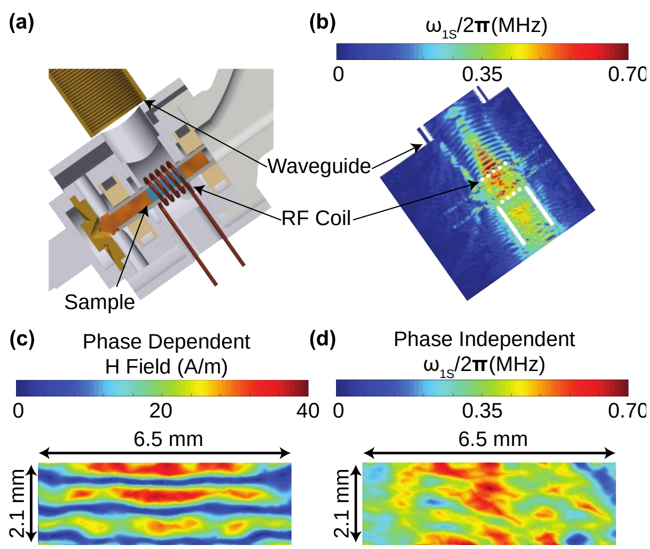


Figure S1: (a) Computer assisted design of stator, coil, sample and waveguide. **(b)** Colormap representation of $\omega_{1S}/2\pi$ inside the stator and surrounding areas. **(c)** Phase dependent H field across the sample area. **(d)** $\omega_{1S}/2\pi$ across the sample area. The average $\omega_{1S}/2\pi$ is 0.38 MHz with 5 W of linearly polarized microwave power entering the stator.

2. Homogeneous T_2 measurements with CPMG

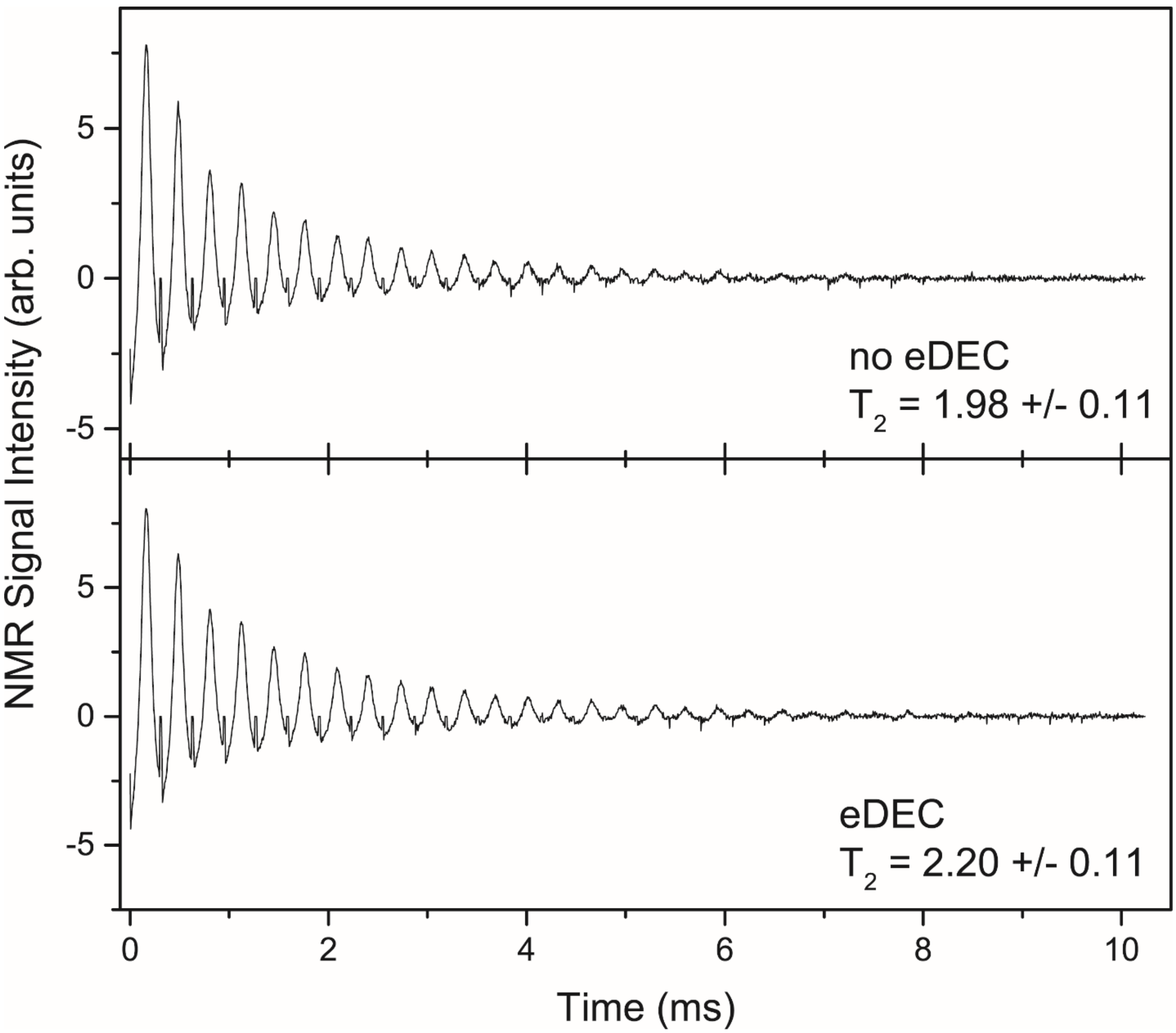


Figure S2. CPMG echoes used to measure homogeneous T_2 relaxation times. Homogeneous T_2 lengthened by 0.12 ms with electron decoupling. CPMG experimental parameters: ${}^{13}C_{\pi/2} = 3\mu s,$ ${}^{13}C_{\pi} = 6\ \mu s,\ \omega_{{}^1H\ \mathrm{TPPM}} = 77kHz,\ \tau_{CPMG} = 242\mu s,\ \tau_{pol} = 7\mu s,$ Spinning Frequency = $4kHz,$ 8 transients.

3. Gyrotron Frequency Agility

In order to sweep microwave frequency for electron decoupling, the acceleration voltage of the gyrotron was varied using a Trek Model 5/80 amplifier utilizing an input from the Redstone Tecmag arbitrary waveform generator (awg). The following plots provide examples of how the data in Figure 3 of the main text was obtained.

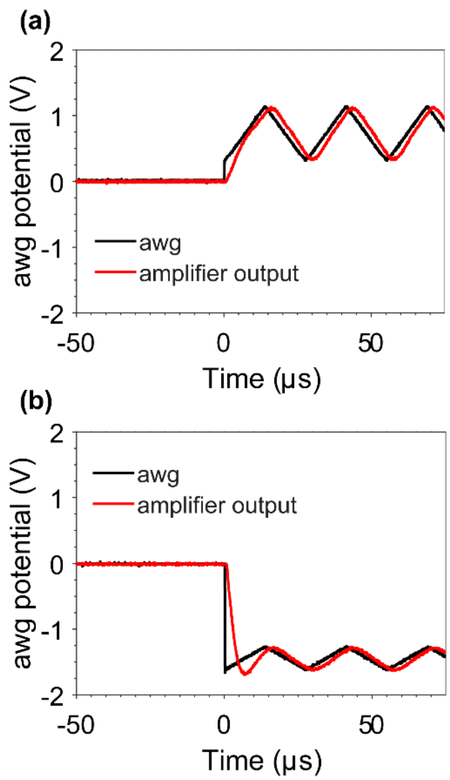


Figure S3: Comparison of awg input waveform to the output of the amplifier. It can be seen that the amplifier cannot sweep as fast as the awg and therefore shapes the waveform to a small extent. **(a)** The oscilloscope outputs of the awg and amplifier for a sweep time of 13.75 μs and a sweep width of 87 MHz at a center frequency of 197.640 GHz, which are close to the found optimal decoupling conditions. **(b)** The oscilloscope outputs of the awg and amplifier for a sweep time of 13.75 μs and a sweep width of 35 MHz at a center frequency of 197.863 GHz. These parameters were used as the off resonance conditions so that microwave heating was still present in the undecoupled spectra.

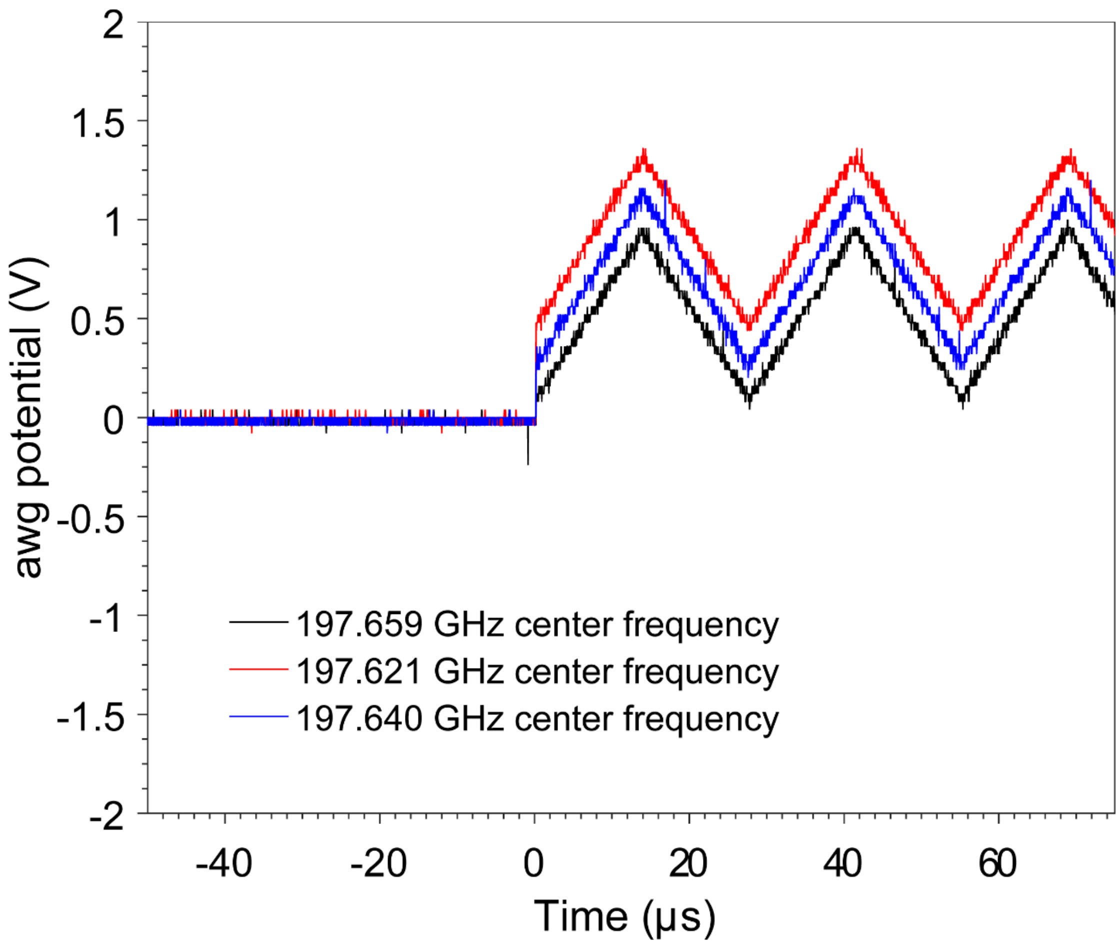


Figure S4: The center of the voltage sweeps of the awg are changed in order to change the center frequency of the gyrotron. Pictured are the oscilloscope outputs for 87 MHz sweeps over 13.75 µs at varying center frequencies. This was the technique used to produce Figure 3b.

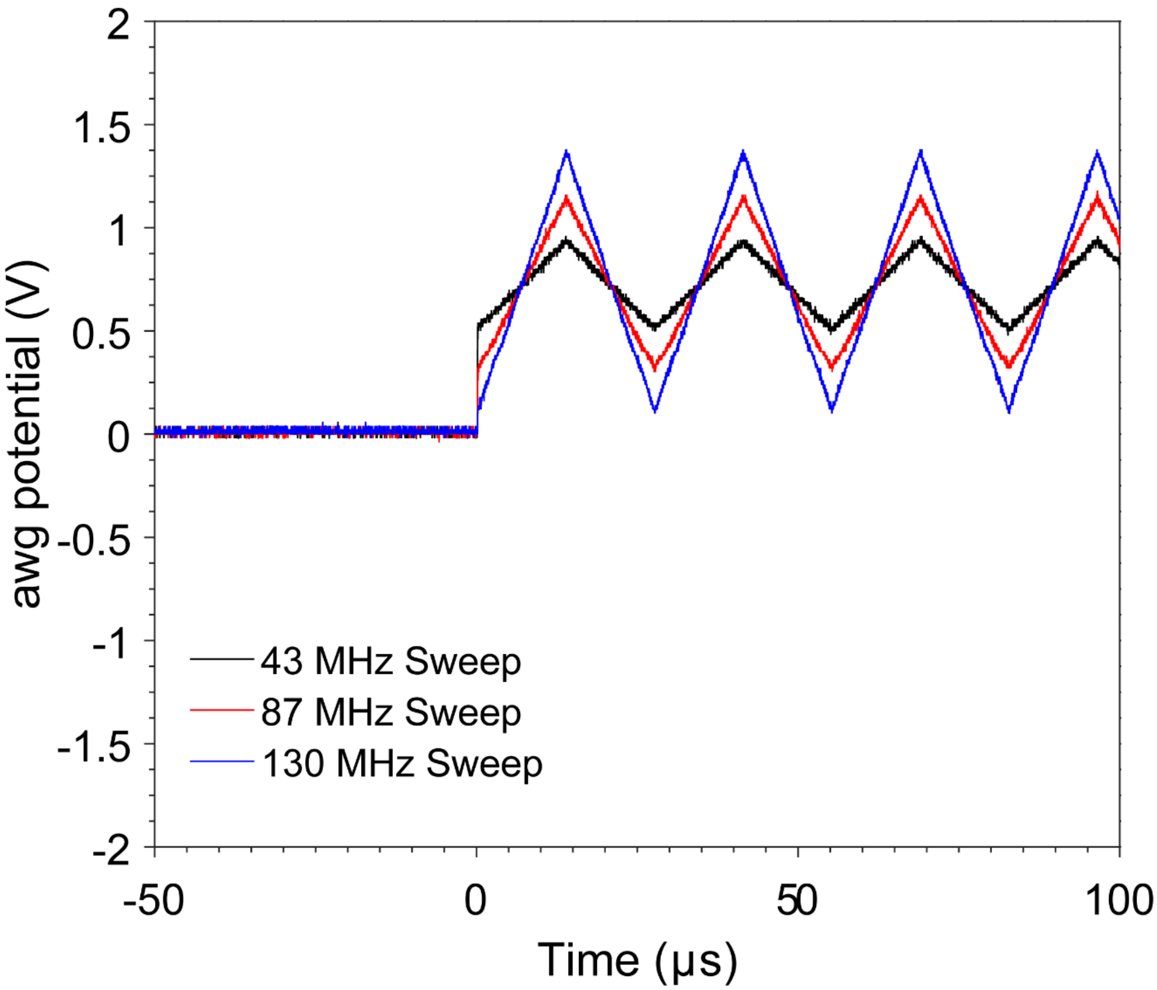


Figure S5: The voltage sweep sizes are changed at constant sweep time in order to vary the sweep width of the gyrotron output frequencies. Pictured are the oscilloscope outputs for several sweep widths for a 13.75 μs sweep time centered at 197.640 GHz. This was the technique used to produce Figure 3c.

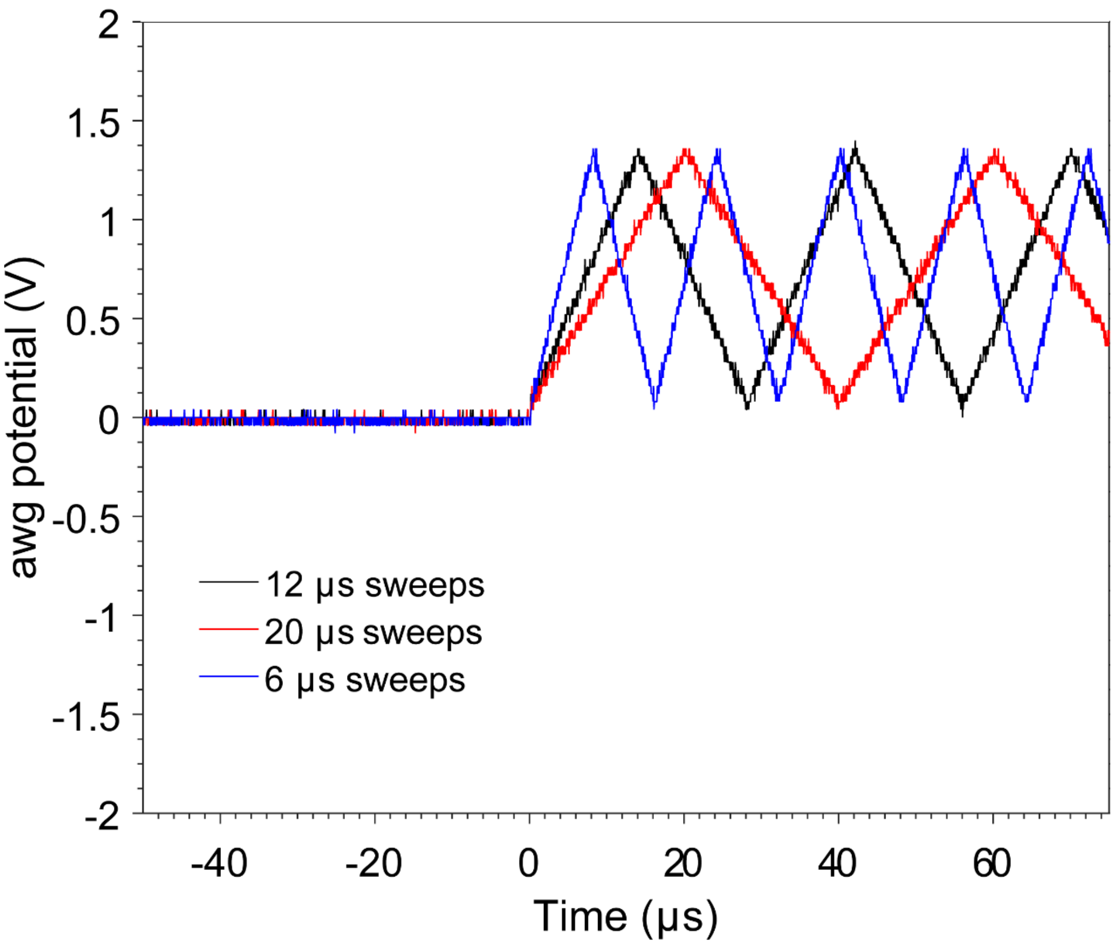


Figure S6: The voltage sweep time (τ_{sw}) of the awg is varied holding the center voltage and sweep width constant in order to produce frequency sweeps of varying τ_{sw}. Pictured are 130 MHz sweep widths with a center frequency of 197.640 GHz. This is the technique that was used to produce Figure 3d.

4. Direct ^{13}C Linewidths with and without Radical

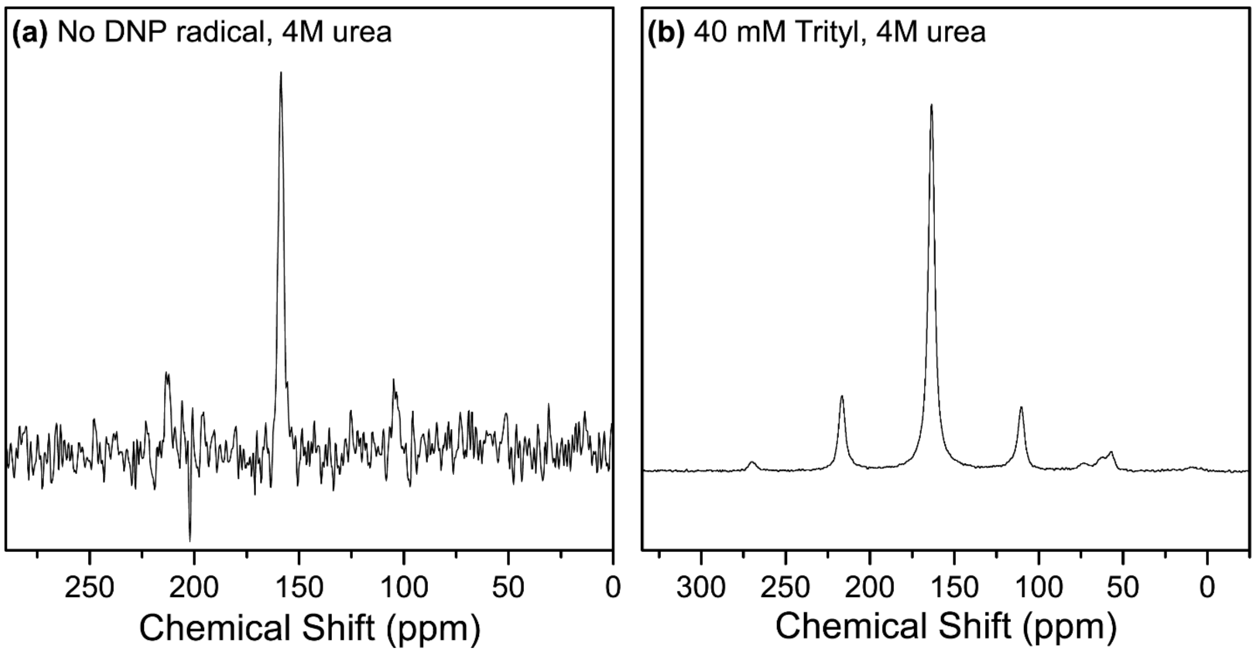


Figure S7: Spectra were taken of samples with and without radical present under direct carbon spectra (no CP). The polarization time used was 7 s. **(a)** A spectrum taken with no radical present in 4 M [^{13}C, ^{15}N]-urea with a 7 second polarization time. The linewidth obtained is 233 Hz, demonstrating the lack of paramagnetic broadening. **(b)** Paramagnetic broadening increases the peak widths with no electron decoupling to 339 Hz when 40 mM of Trityl OX063 is present.

5. T_{1_DNP} Buildup Curve

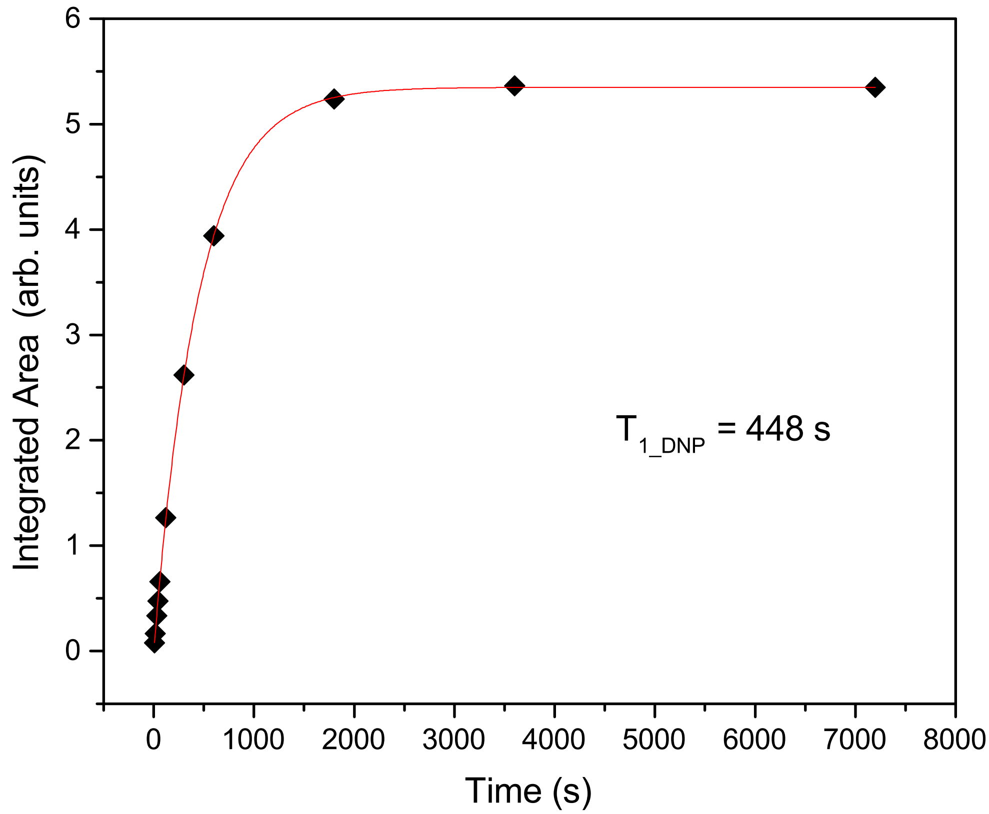


Figure S8: A T_{1_DNP} buildup curve. A T_{1_DNP} of 448 seconds was measured. The red line is a fit of the experimentally determined data.

6. Error Analysis

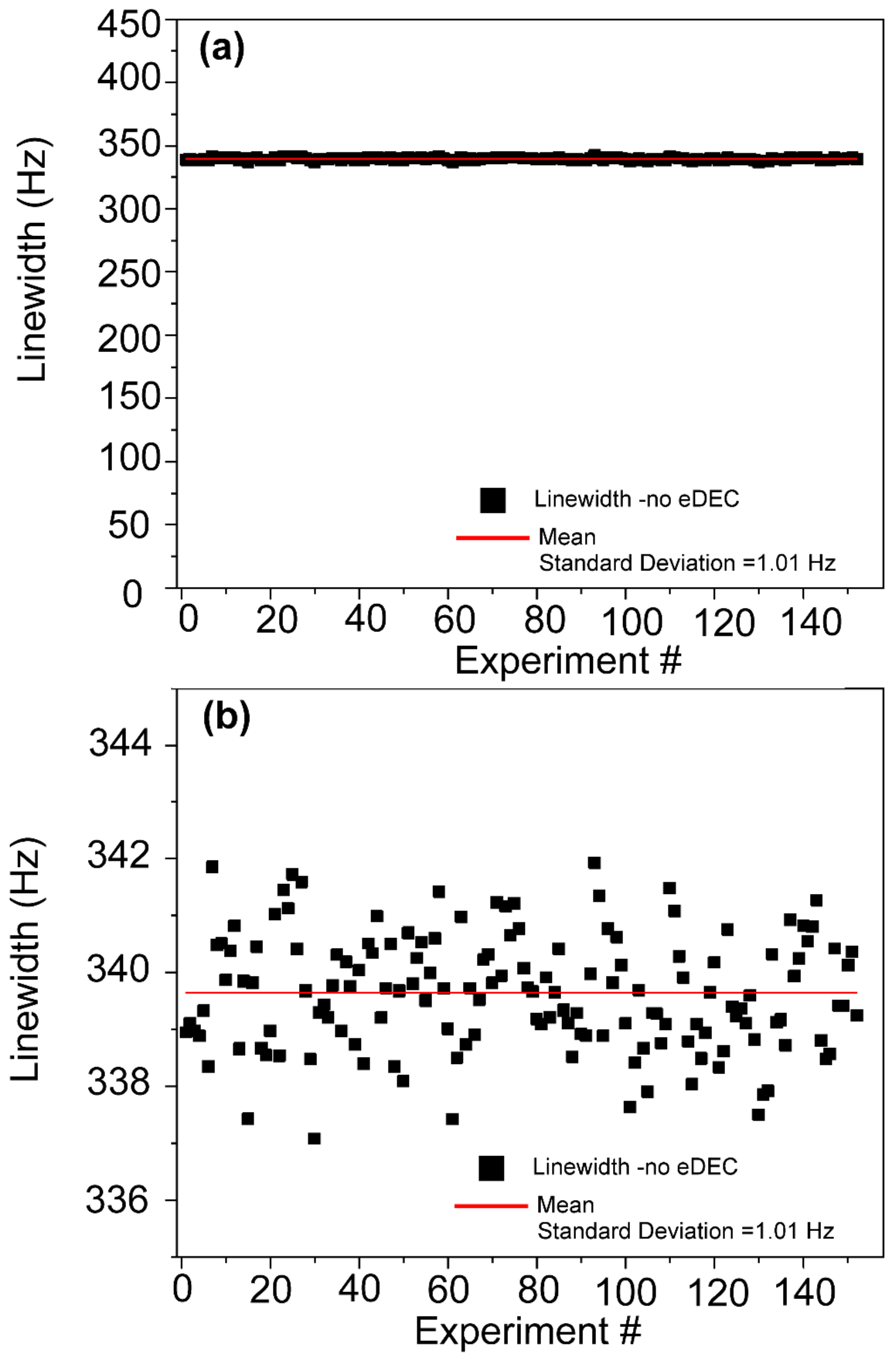


Figure S9: **(a)** Repeated experiments with no electron decoupling. The standard deviation of the fitted linewidths was 1.01 Hz. **(b)** An expansion of (a) about the mean.

Note: The data from Figure S9 was used to calculate the standard deviations in the linewidths of Figure 3 of the main text. Each data point consists of 8 transients for Figure 3a. All spectra taken to produce Figure 3b,c,d are assumed to have the same error in their linewidth. Because the data points in Figure 3 represent a *difference* in two linewidths, the error of the difference needs to be propagated accordingly. The standard deviations were calculated according to Equation (1) below:

$$\sigma = \sqrt{\frac{\Sigma\left(LW_i - \overline{LW}\right)^2}{N}} \tag{1}$$

LW_i is the linewidth of the i^{th} spectrum, $\overline{LW}$ is the mean linewidth, N is the number of linewidths measured, and σ is the standard deviation. To propagate the error, the variances (the squares of the calculated standard deviations) need to be added to obtain the variance in the difference. Taking the square root of this yields the standard deviation in the difference. Equation (2) demonstrates this below:

$$\sigma_{\Delta\omega_{eDEC}/2\pi} = \sqrt{\sigma^2_{no\ eDEC} + \sigma^2_{eDEC}} \tag{2}$$

Under the assumption that $\sigma_{no\ eDEC} = \sigma_{eDEC}$, we have the following:

$$\sigma_{\Delta\omega_{eDEC}/2\pi} = \sqrt{2\sigma^2_{no\ eDEC}} = \sigma_{no\ eDEC}\sqrt{2} \tag{3}$$

In order to calculate the error in the percent change in linewidth, we begin with the formula for the percent change in linewidth shown below, where P is the percent difference in the linewidths, $LW_{no\ eDEC}$ is the linewidth with no electron decoupling, and LW_{eDEC} is the linewidth with electron decoupling:

$$P = \frac{LW_{no\ eDEC} - LW_{eDEC}}{LW_{no\ eDEC}} \times 100 \tag{4}$$

In order to propagate the error for this quantity correctly, we use Equation (5):

$$\sigma_P = \overline{P}\sqrt{\left(\frac{\sigma_{\Delta\omega_{eDEC}/2\pi}}{LW_{no\ eDEC} - LW_{eDEC}}\right)^2 + \left(\frac{\sigma_{no\ eDEC}}{LW_{no\ eDEC}}\right)^2} \qquad (5)$$

7. Electron decoupling performance dependence on polarization time as indicated by transverse relaxation

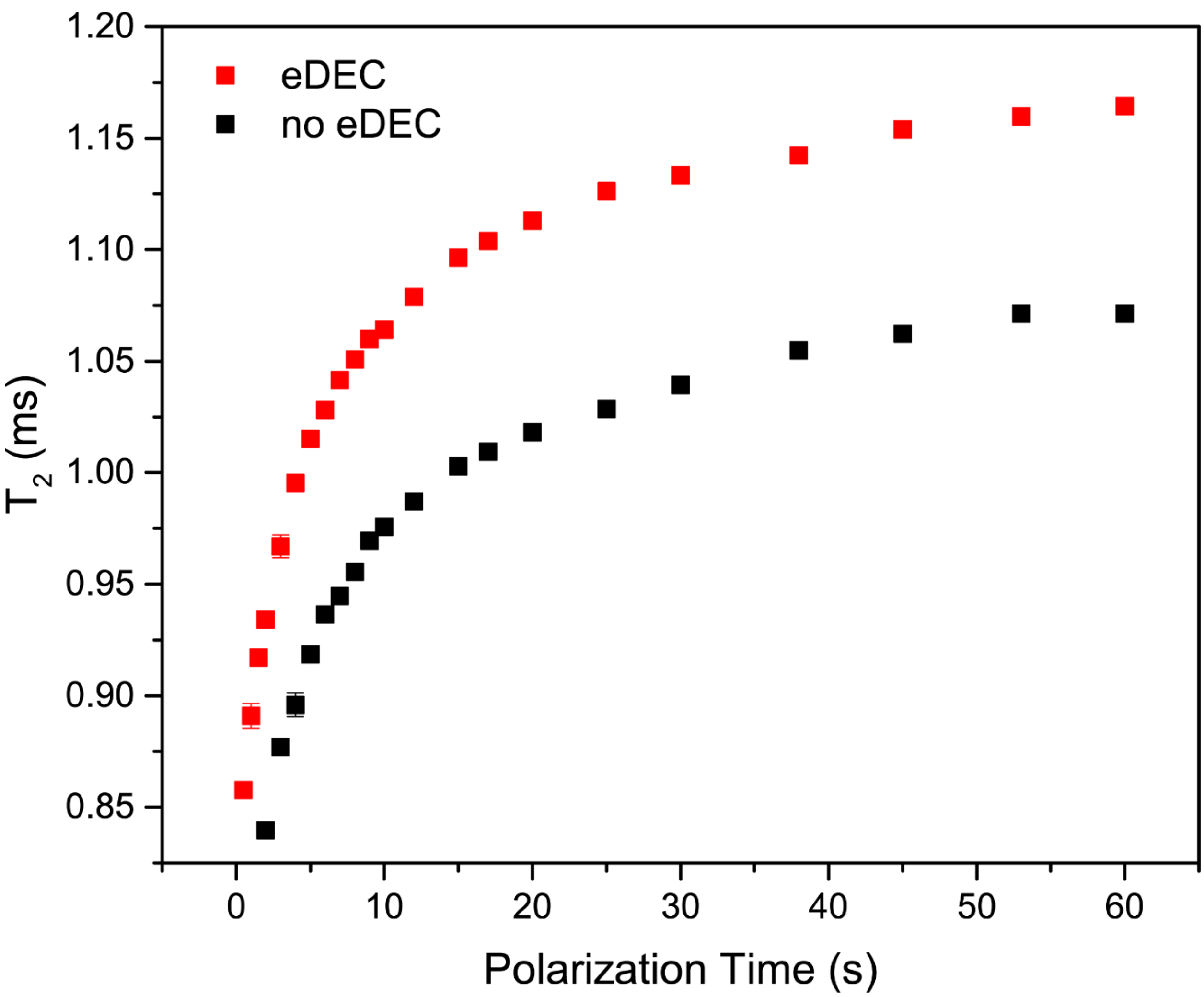


Figure S10: The total T_2 as a function of polarization time. Performing electron decoupling lengthens the overall T_2. The total T_2 was estimated from the linewidth of the peaks.

8. Difference in Integrated Area with and without Electron Decoupling

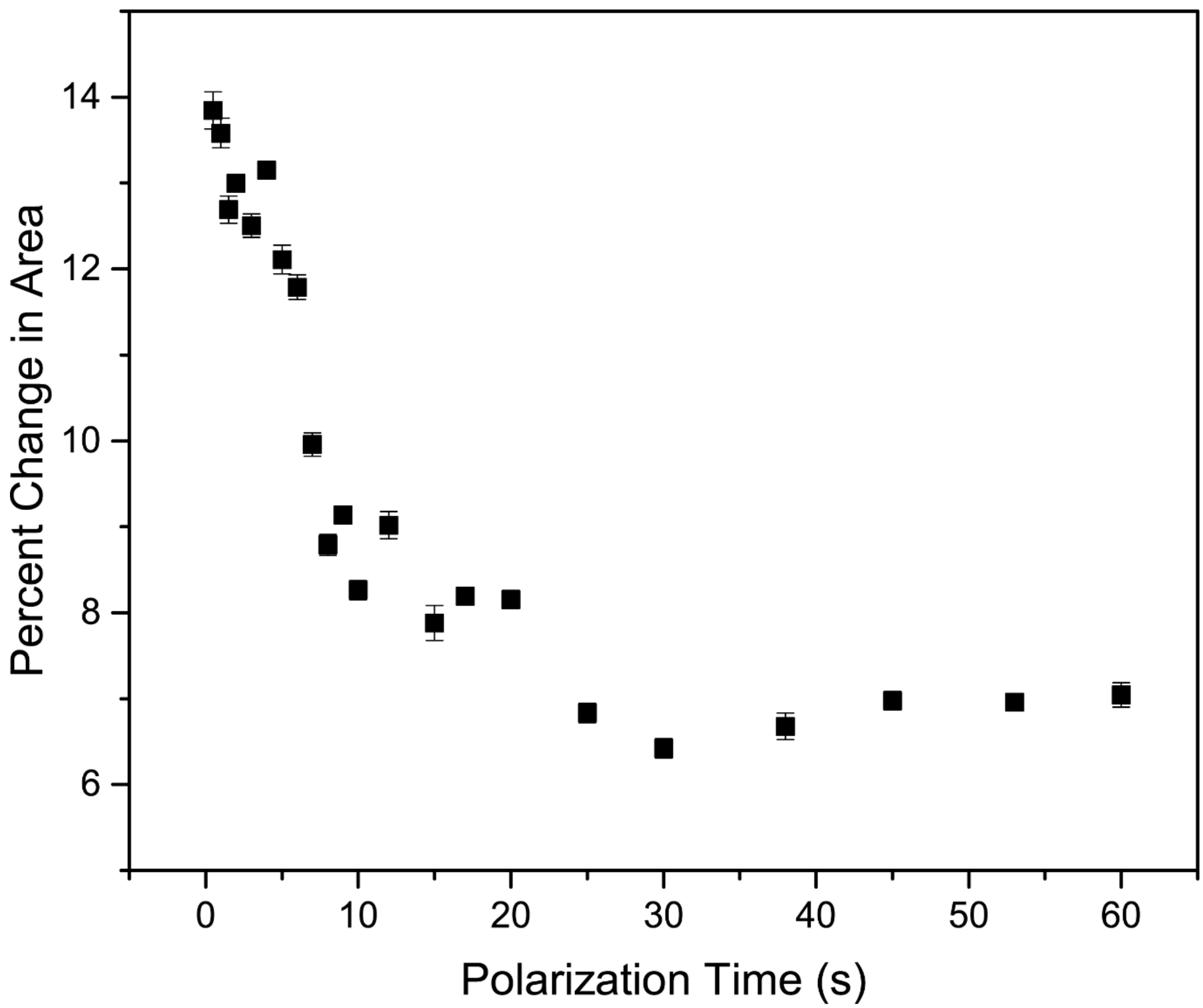


Figure S11: A larger integrated area was observed for spectra taken with electron decoupling versus those that were taken without. Error bars represent one standard deviation in the percent area. It can be seen that the majority of the error bars are within the data points. In agreement with the linewidth data, the decoupling has a larger effect at shorter polarization times before those electrons that are strongly coupled to carbons are swamped by those that are not.

9. Linewidth Summary

Table S1: Linewidths of central carbon resonance from [^{13}C, ^{15}N]-urea under various NMR experimental conditions. Unless specified, the linewidths were a result of a ^{13}C Hahn echo experiment. Parameters for ^{1}H-^{13}C cross-polarization with Hahn echo: $^{1}H_{\pi/2} = 3.625\mu s,\ ^{13}C_{\pi/2} = 3\mu s,\ ^{13}C_{\pi} = 6\ \mu s,$ Mixing Time $= 1\ ms,\ \omega_{^1H\ \mathrm{TPPM}} = 77kHz,$ Recycle delay $= 7s.$

Condition	Linewidth (Hz)
0.5 sec, w/o eDEC	419
0.5 sec, w/ eDEC	371
7 sec, w/o eDEC	339
7 sec, w/ eDEC	306
7 sec, w/o eDEC & DNP	315
7 sec, CP w/o eDEC	261
7 sec, CP no electrons/radical	228
7 sec, no electrons/radical	233

10. Adiabaticity Factor Calculation

HFSS, along with the design of the stator and waveguide used in the experiments as drawn in Autodesk Inventor, were used to estimate an average γB_1 of $380\ kHz$ over the sample. This calculation was performed assuming $5\ W$ of microwave power made it into the sample. Most of the experiments performed were done with a $\frac{\Delta\omega}{2\pi}$ (sweep width) of $87\ MHz.$ Most of the t_{sw}'s (sweep times) were $13.75\ \mu s$. The equation for the adiabaticity (Q) of a linear sweep is given below:

$$Q = \frac{\omega_1^2 * t_{sw}}{\Delta\omega} \tag{6}$$

Or defining $\frac{\Delta\omega}{t_{sw}}$ as k, we have the following:

$$Q = \frac{\omega_1^2}{k} \tag{7}$$

Converting this to accept MHz as an input, the adiabaticity factor becomes the following for a linear sweep:

$$Q = \frac{2\pi \nu_1^2 t_{sw}}{\Delta \nu} \tag{8}$$

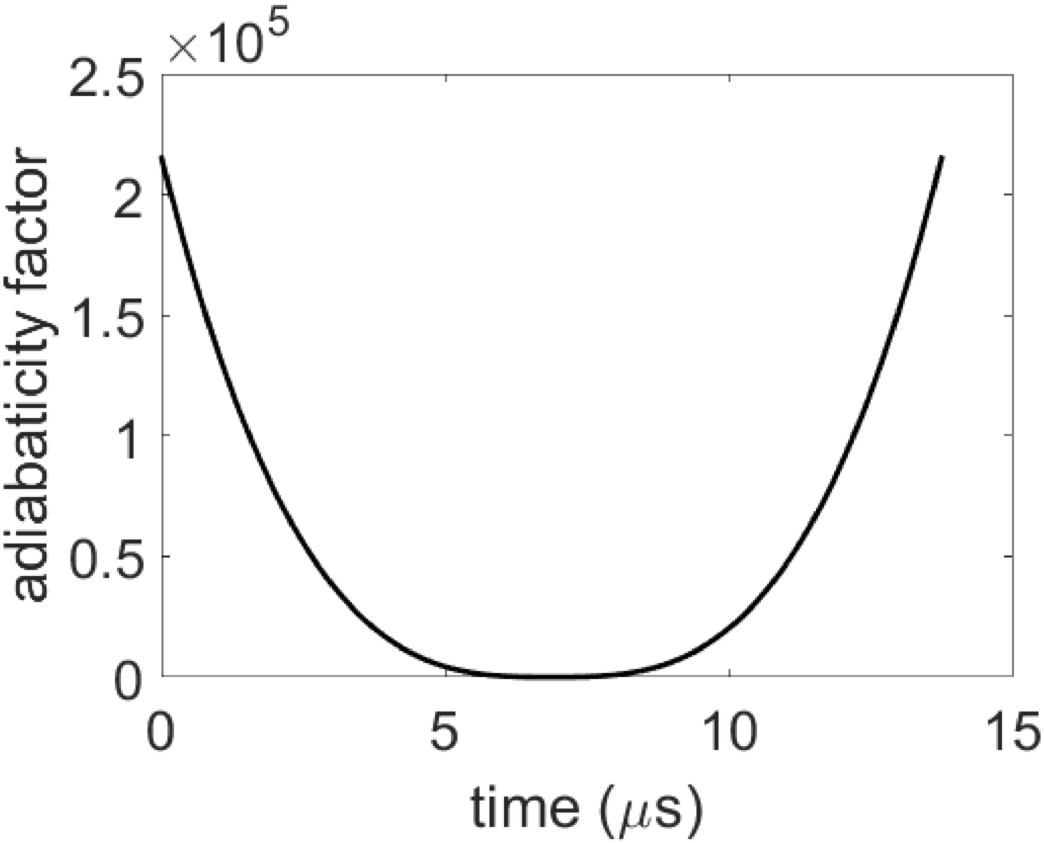
The ν 's here are then in terms of Hz , rather than $\frac{rad}{s}$. Plugging in the numbers given above, the adiabaticity factor comes out to the following:

$$Q = \frac{2\pi \left(380 \times 10^3\, Hz\right)\left(13.75 \times 10^{-6}\, s\right)}{\left(87 \times 10^6\, Hz\right)} = 0.14 \tag{9}$$

The adiabaticity factor, however, is time dependent and this calculation is of the minimum that it attains during the sweep. The equation for this is the following for a linear sweep:

$$Q(t) = \frac{\left[k^2\left(t - \frac{t_{sw}}{2}\right)^2 + \omega_1^2\right]^{\frac{3}{2}}}{\omega_1 k} \tag{10}$$

Plotting this function for the values given yield the following plot:



According to the Landau-Zener equation, the probability that the states follow an adiabatic path and does not undergo a diabatic transition under the sweep is given by equation (11) below:

$$P = 1 - e^{-\frac{\pi\omega_1^2}{2k}} \tag{11}$$

We see the factor $\frac{\omega_1^2}{k}$ in the numerator though, which we have already defined as Q, so if we substitute in for $\frac{\omega_1^2}{k}$ the value of 0.14 that we determined for Q earlier, then we obtain the following for P :

$$P = 1 - e^{-\frac{\pi}{2}*0.14} = 0.20 \tag{12}$$

The flip angle that would produce the same probability of a spin flip can be calculated in the following manner. The probability that a spin changes from one spin state to another under a pulse is given by equation (13) below, which can be determined by solving s:

$$P_{flip} = \sin^2\left(\frac{\theta}{2}\right) \tag{13}$$

If we set P equal to P_{flip} then we obtain the following:

$$\sin^2\left(\frac{\theta}{2}\right) = 0.20 \tag{14}$$

Here, θ is the flip angle of the pulse. Solving this for θ yields:

$$\theta = 2\arcsin\left(\sqrt{0.20}\right) = 53^\circ \tag{15}$$

This means that the "effective flip angle" of the sweeps is about 53°.