Supporting Information

Adiabatic Solid Effect

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Schematic diagram of the pulsed DNP sequences

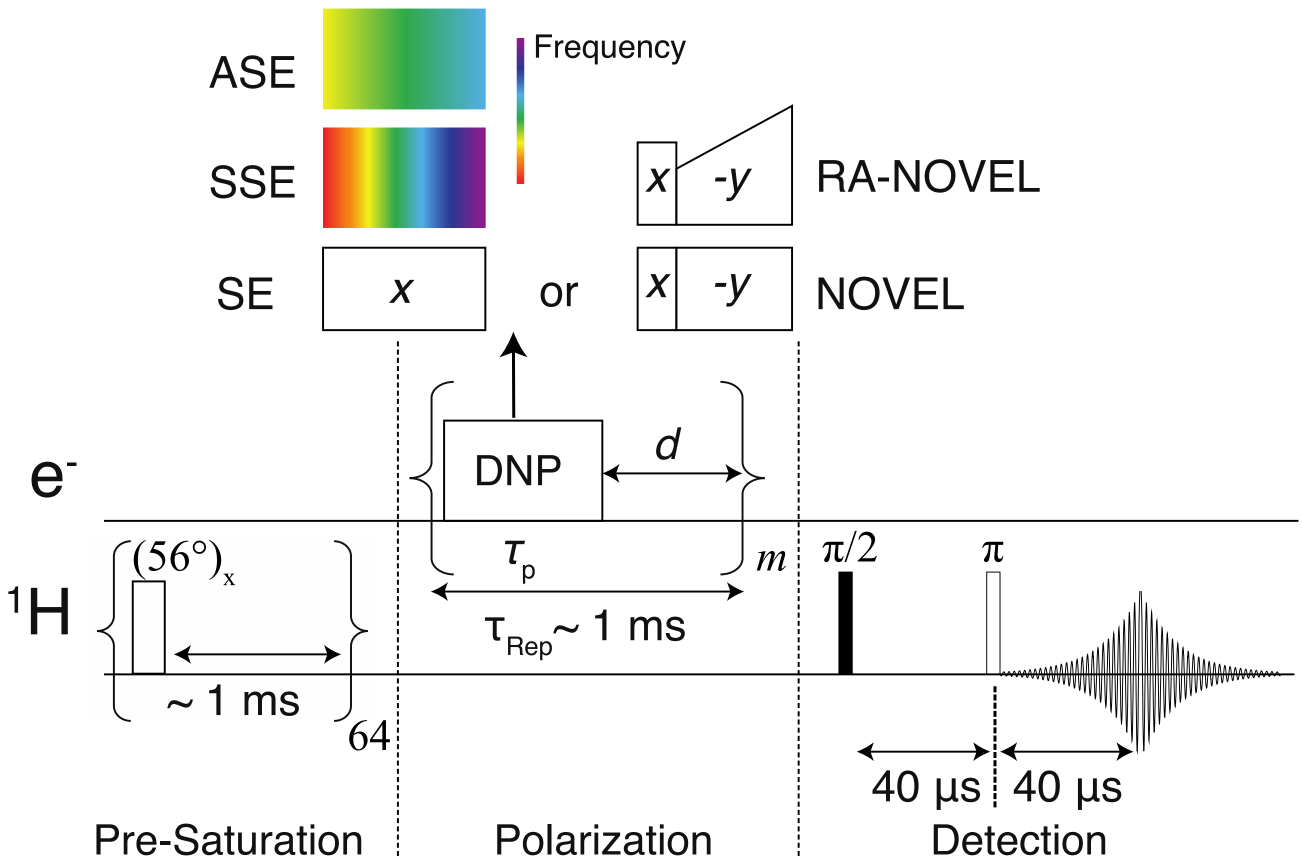

Figure S1. Timing diagrams for the pulse sequences of SE, NOVEL, and their variants performed at Q-band (1.2 T) on static (non-spinning) samples. Pre-Saturation pulses were applied prior to the polarization step to suppress the residual NMR signal from previous acquisition. A spin echo sequence with a 40 μs long delay was used to filter the ^{1}H background signal from the DNP probe. A ^{1}H NMR spectrum without insertion of the sample was acquired and then subtracted from the 'DNP off' spectrum to determine the actual enhancement factor ε.

Experimental details on measuring the quality *Q*-factor of the probe

In order to determine the Q factor of the microwave resonator, the nutation profiles of the EPR at different microwave frequencies were measured. Note that the magnetic field is adjusted for each microwave frequency so that the microwave irradiation is always on resonance with the EPR line ($\Omega = 0$). The maximum intensities of the Fourier-transformed nutation profiles were then assigned to be the Rabi frequencies ω_{1S}. Then, the experimental data was interpolated with a cubic function in MATLAB. The interpolated data was then fitted with a Lorentzian function. We then read out the 3 dB bandwidth, which is equivalent to full width at 0.707 of the maximum ω_{1S}, i.e. the values of microwave frequencies that yield a Rabi frequency of $\omega_{1S} = 76 \times 0.707 \sim 53.7$ MHz. The Q factor can be calculated using the equation $Q = \omega_{\mu w}/(3\text{dB Bandwidth})$. We obtained $Q \sim 1544$ and ~ 1779 for the cubic-interpolated data and fitted Lorentzian function, respectively. Hence, we report an average value of $Q \sim 1650 \pm 100$.

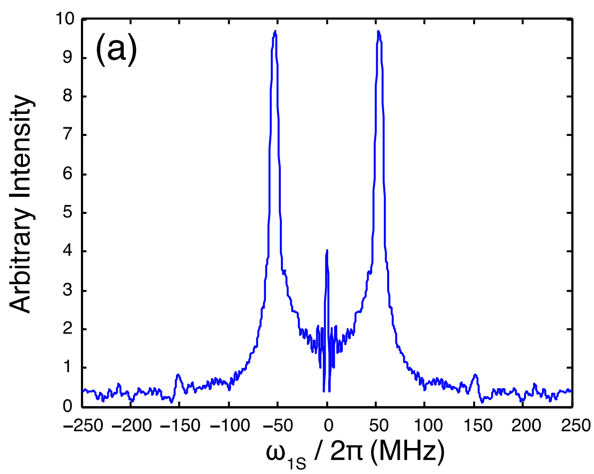

Figure S2. (a) A nutation curve was acquired at the NOVEL condition $\omega_{1S}/2\pi \sim 51$ MHz, and then Fourier-transformed to obtain the nutation profile shown here. The microwave inhomogeneity was characterized to be ~ 6 MHz by determining the FWHM of the peak at the expected $\omega_{1S}/2\pi \sim 51$ MHz position. (b) Measured Rabi frequency as a function of the input pulse's amplitude to the microwave amplifier. The recommended operating regime is at ~ 50 %, where the amplification factor is approximately linear.

<u>Experimental details and parameters used in numerical simulations</u>

The experimental details and parameters used in the numerical simulations are tabulated in Table S1. Note that a pulse length τ_p of 3 μs is used compared to the those used in experiments. This is because one of the limitations of numerical simulations is that it can only be performed on a relatively small spin system, i.e. < 16 spins using a dedicated computer within a reasonable time frame. There are however more than hundreds of proton nuclei per electron spin in an actual DNP sample. Many of the weakly-coupled nuclei require a longer contact time (weaker dipole coupling) to be polarized in experiment. For the numerical simulations shown in Figure 3, the *g*-matrix of the electron in the principal axes frame is given as [2.0015, 2.00319, 2.00319]. The spin trajectories of all three crystallites were calculated at a fixed field position of 1.204 T, which corresponds to the ZQ SE condition. The relaxation parameters are T_{1e}= 2 ms, T_{2e} = 1 μs and T_{1n} = 1 s, T_{2n} = 1 ms for the electron and ^{1}H nuclei, respectively.

	SSE (Expt, Fig. 2b)	SSE (Sim, Fig. 2b)	ASE/SE (Expt, Fig. 2c)	ASE/SE (Sim, Fig. 2c)	RA-NOVEL (Expt, Fig. 4)
$\omega_{1S}/(2\pi)$ (MHz)	25	25	25	25	53
τ_p (μs)	95	3	15	3	20
Δ (MHz)	-90	-90	16/0	16/0	34
m	8192	256	8192	128	350
τ_{rep} (ms)	1	3	1	1	1

Table S1. Values of the parameters used for both the experimental and simulated results.

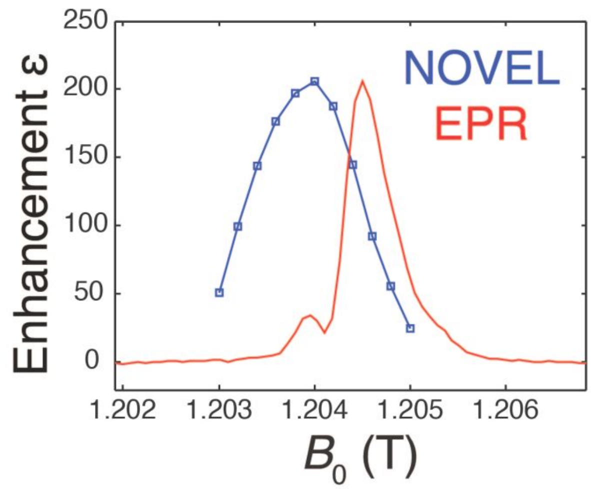

Figure S3. EPR spectrum (red) and DNP field profile of NOVEL (blue) performed with a 5 ns initial $\pi/2$ pulse, followed by a 10.5 μs spin-lock pulse, and another 5 ns $\pi/2$ flip-back pulse to bring the unused electron polarization back to the *z*-axis. The NOVEL sequence was repeated by m = 32768 times with a repetition time $\tau_{\text{rep}} \sim 1$ ms before the NMR acquisition is performed.