Supporting information

Full optimization of dynamic nuclear polarization on a 1 tesla benchtop polarizer with hyperpolarizing solids

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1.   Supporting data
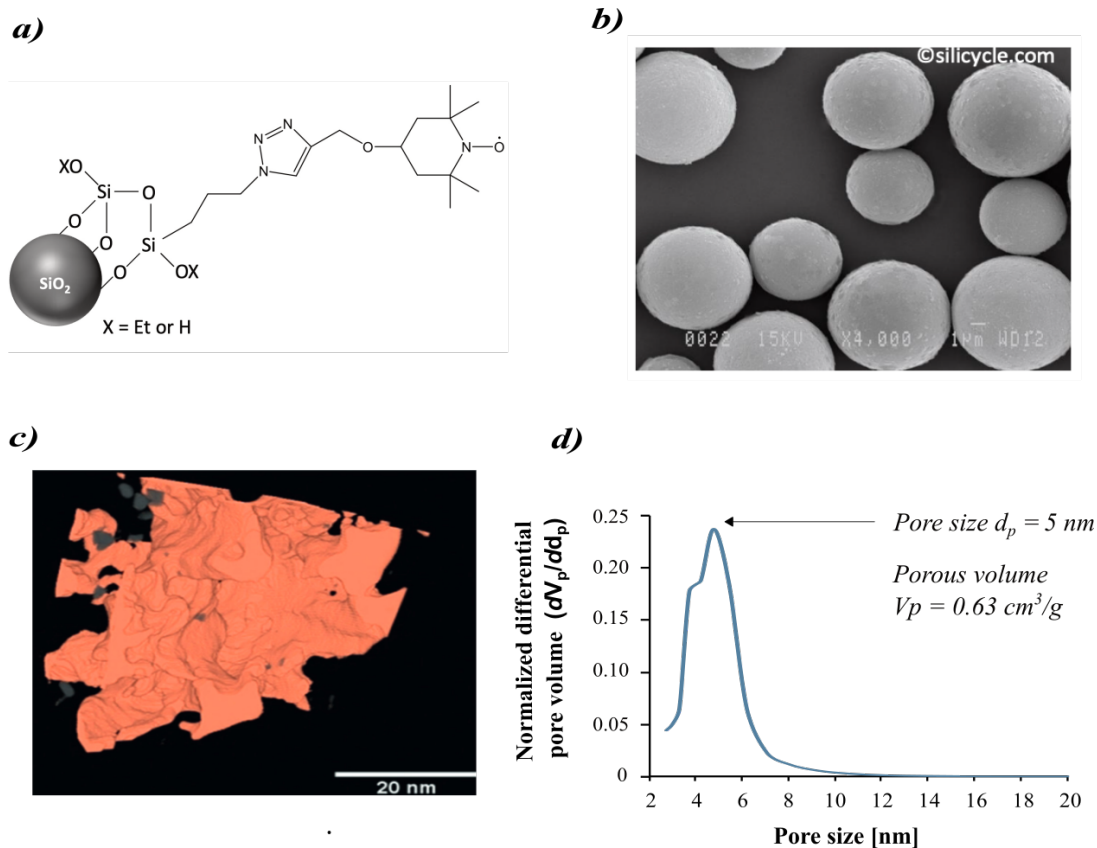
1.1.   HYPSO-5 material properties

Figure S 1. Material properties of HYPSO-5, the hyperpolarizing solid used for performing DNP at 1 T and 77 K. a) Lewis structure of the immobilized TEMPOL derivatives on the silica surface of commercially available mesoporous silica beads by Silia*Sphere*[TM]. **b)** SEM image (provided by Silicycle) of silica beads exhibiting a mean particle size of 7 µm. Note that that the silica beads used for preparing HYPSO-5 in this work have monodisperse size of 15 µm. **c)** Electron tomography image of HYPSO-5 material reproduced from Cavaillès *et al.*[1] using the same porous structure **d)** BJH pore size distribution determined from nitrogen adsorption-desorption data (desorption data, specifically) of the HYPSO-5 material with 43 µmol.cm⁻³ nitroxide radicals immobilized. The detailed synthesis procedure for preparing this family of hyperpolarizing solids can be found in Cavaillès *et al.* [1]

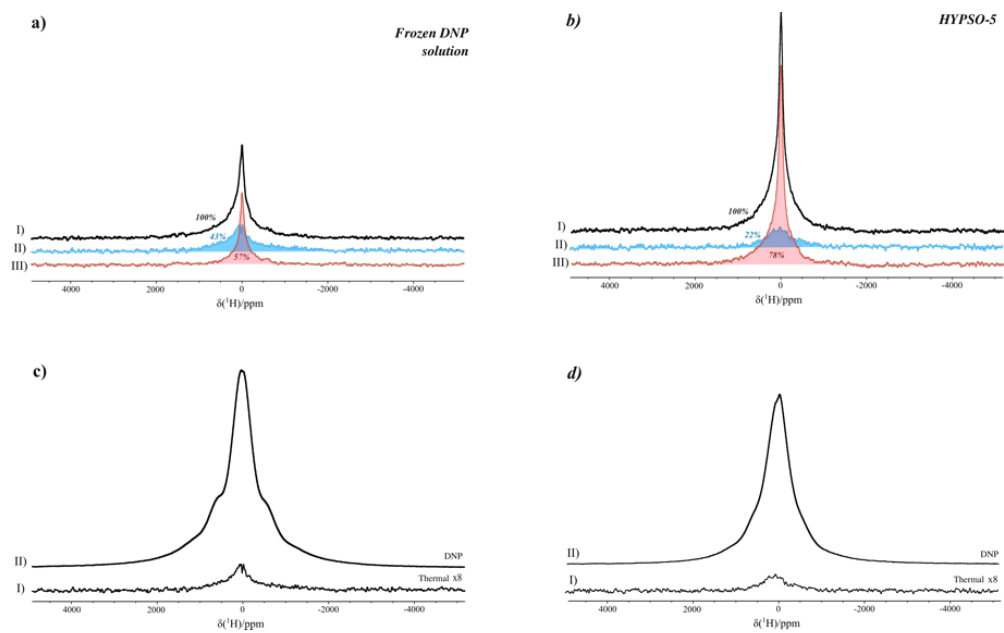## 1.2.　　Probe background quantification

Figure S 2. a) ^{1}H-NMR thermal background signal of the probe at 77 K (red, III) subtracted from the total ^{1}H-NMR thermal measurement (black, I) on a 2:2:6 H_2O:D_2O:DMSO-d_6 (*v:v:v*) frozen TEMPOL (50mM) solution provides the percentage of the signal originating from only the sample (blue, II). b) Analogous procedure was employed to extract the background contribution when performing DNP using HYPSO-5 powder impregnated with a 2:8 H_2O:D_2O (*v:v*) solution. c) The ^{1}H-NMR signal with microwave on (II) and the thermal signal (I) originating solely from the frozen DNP solution sample (corrected from background) provides us with the hyperpolarization enhancement factors which are reported in the main manuscript using equation 2. d) An analogous procedure as in (c) was performed for calculating the hyperpolarization enhancement factors in case of the HYPSO-5 powders.

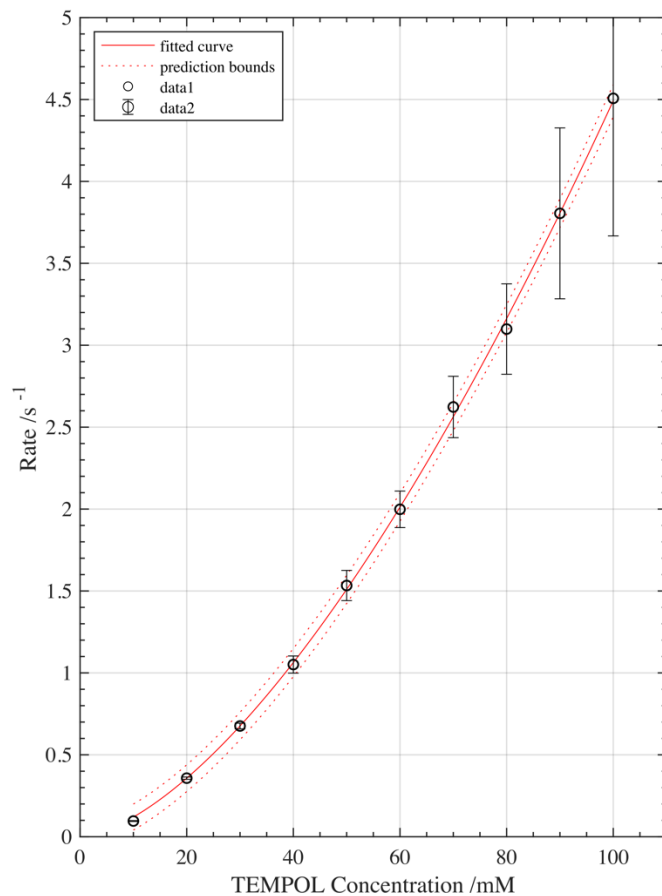## 1.3.   DNP build-up rate versus radical concentration

Figure S 3. DNP build-up rates $\left(\tau_{\mathrm{dnp}}^{-1}\right)$ in the frozen DNP solution plotted for the negative DNP optima for each TEMPOL concentrations at 1 T and 77 K. The non-linear relation between τ_{dnp}^{-1} and radical concentration was fitted with the non-linear model $\tau_{\mathrm{dnp}}^{-1} = \alpha C_{\mathrm{e}}^{\lambda}$ *with* $D_{\mathrm{ee}} \propto C_{\mathrm{e}}$, (equation 1 in the main manuscript). Here C_{e} represents the concentration of TEMPOL, D_{ee} the e-e dipolar interaction strength, α the proportionality constant and λ the exponent that empirically describes the relationship between τ_{dnp}^{-1} and C_{e}. The fitted value for λ exponent was found to be 1.58 ± 0.03. The striped lines are the fits representing the 95% confidence interval boundaries.
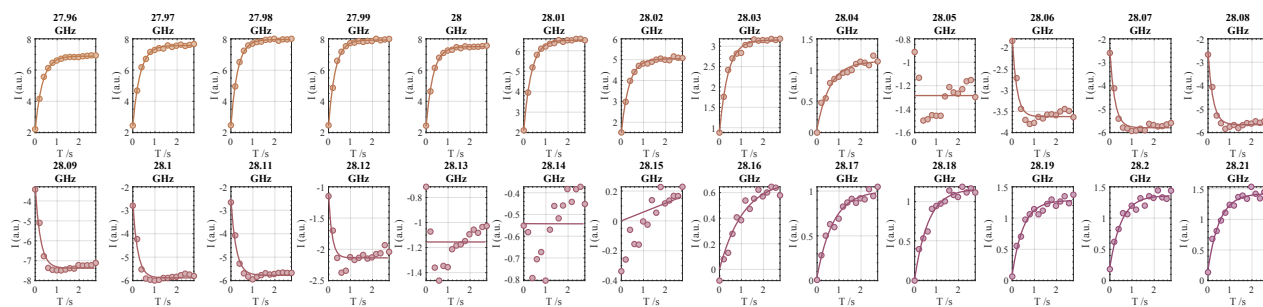
Figure S 4. ^{1}H-DNP build-up plots and fitted build-up rates for 50 mM TEMPOL contructed by integration of the total hyperpolarized ^{1}H-NMR signal without taking into account the presence of the background signal.
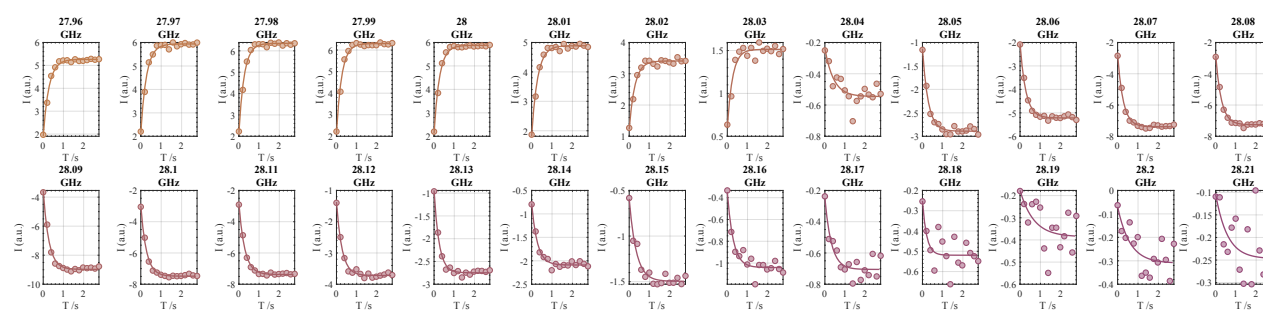

Figure S 5. ^{1}H-DNP build-up plots and fitted build-up rates for 50 mM TEMPOL contructed by integration the background corrected hyperpolarized ^{1}H-NMR signal. This is a more robust procedure to analyze and compare the hyperpolarization build-up rates since only the polarization induced by DNP is taken into account.
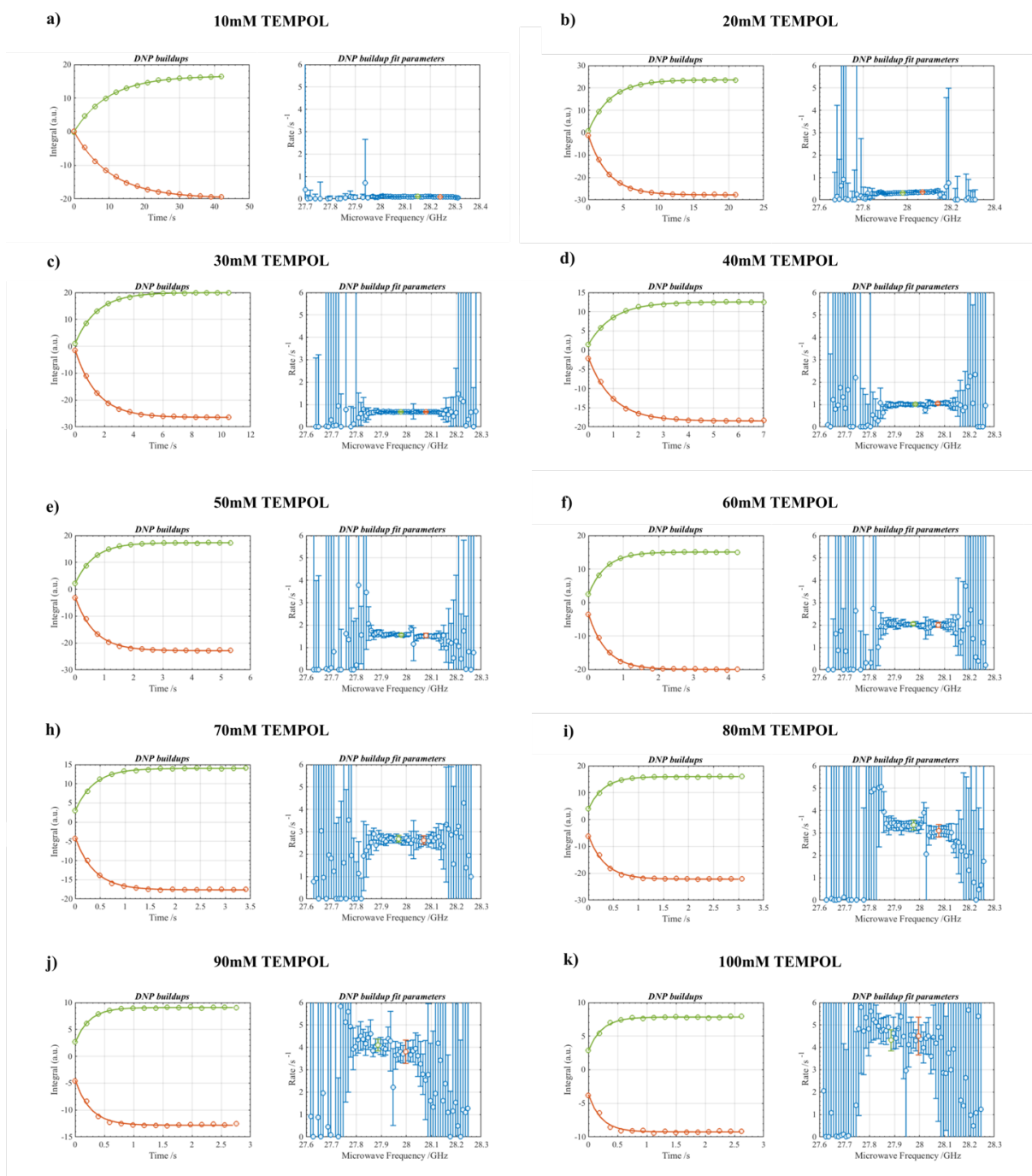
Figure S 6. The DNP build-up rates (corrected for the background as shown in **Figure S7 and S8**) at each corresponding $f_{\mu w}$ are extracted using the MATLAB processing pipeline and plotted for each of the TEMPOL radical concentration used in the glassy frozen solutions to benchmark DNP performance at 1 T and 77 K.
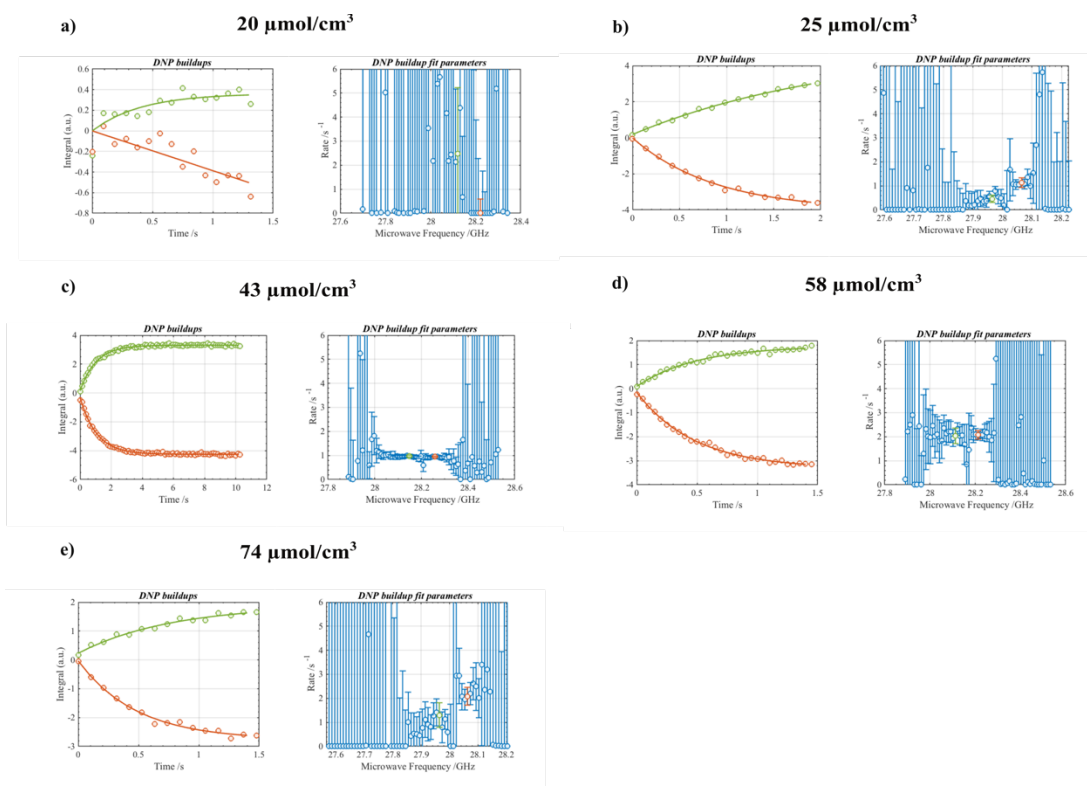
a)   **20 µmol/cm³**   b)   **25 µmol/cm³**

c)   **43 µmol/cm³**   d)   **58 µmol/cm³**

e)   **74 µmol/cm³**

Figure S 7. The background corrected DNP build-up rates (see Figure S5) at each corresponding $f_{\mu w}$ are extracted using the MATLAB processing pipeline and plotted for each of the immobilized nitroxide radical concentration used in the HYPSO-5 powders to benchmark DNP performance at 1 T and 77 K.

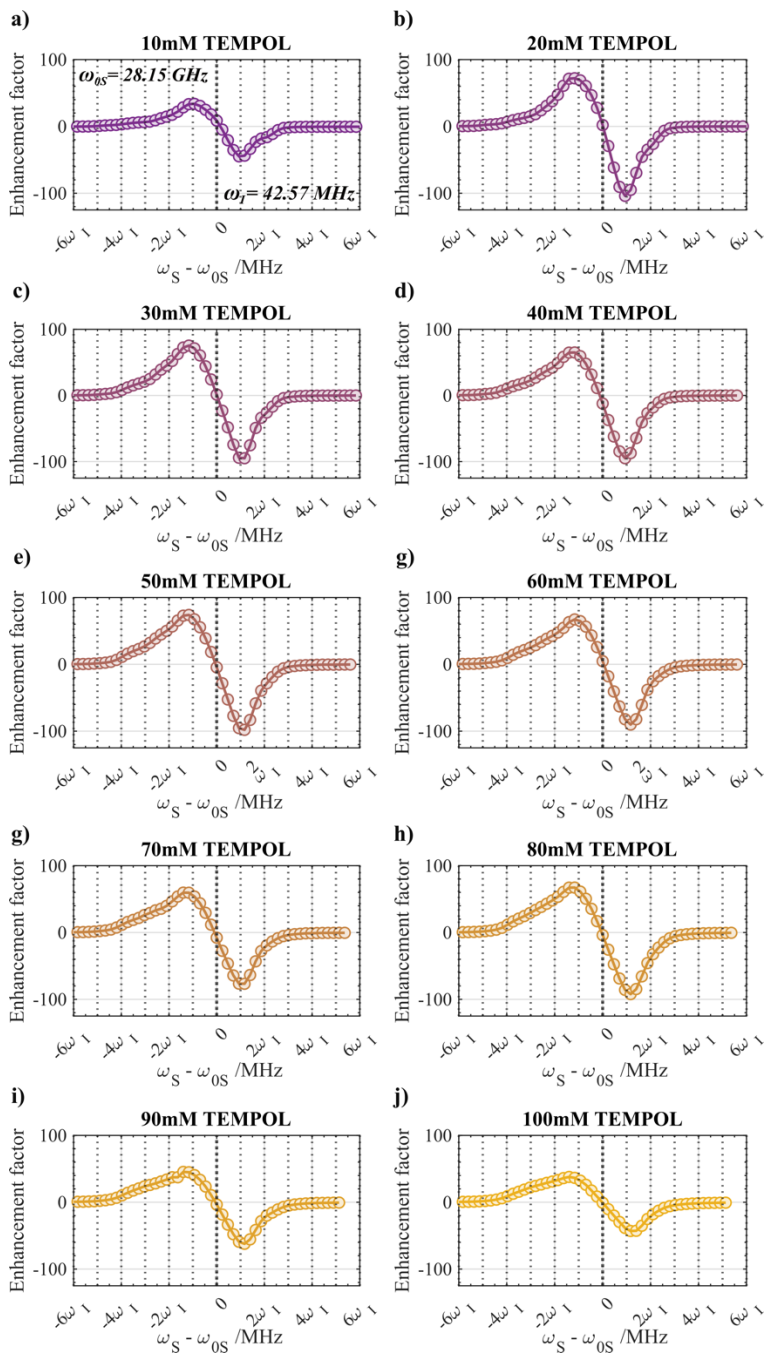## 1.4.   DNP spectra for free and immobilized nitroxide radicals

Figure S 8. Separate representation of the DNP spectra for each of the TEMPOL radical concentration used in the glassy frozen solutions to study the DNP mechanisms occurring at 1 T (ω_I of 42.57 MHz) and 77 K with broad-line radicals.
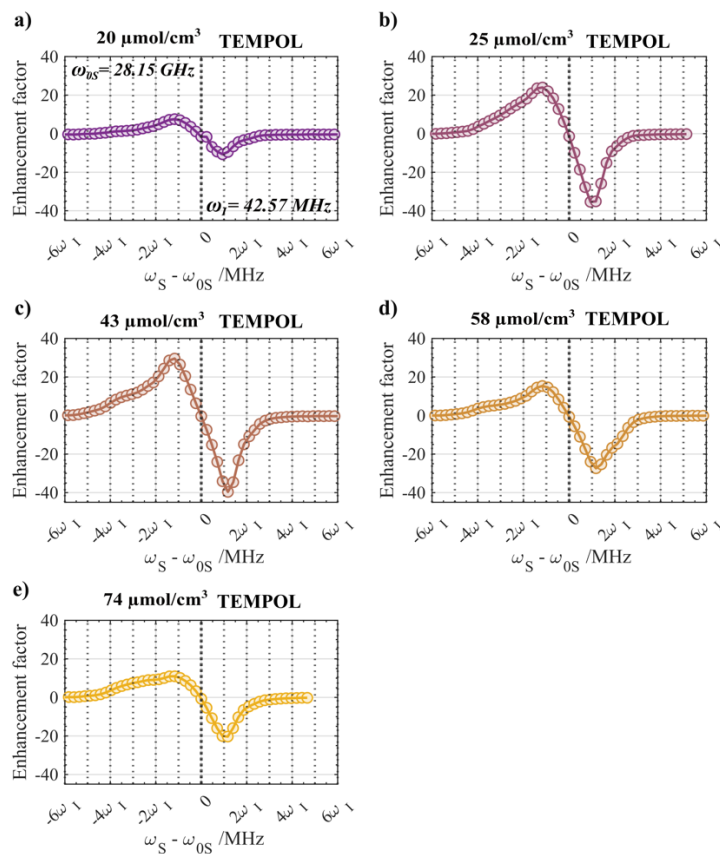
Figure S 9. Separate representation of the DNP spectra for each of the immobilized nitroxide concentration used in the HYPSO-5 powders to study the DNP mechanisms occurring at 1 T (ω_I of 42.57 MHz) and 77 K with immobilized broad-line radicals.
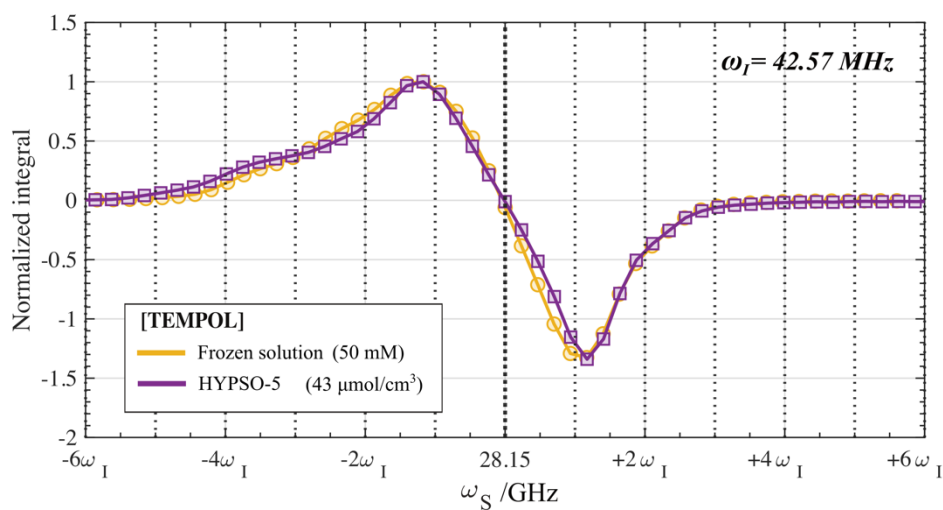

Figure S 10. Comparison of the DNP spectra using the best performing nitroxide concentration under amorphous conditions in a frozen glassy state (50 mM) and under chemically immobilized conditions in HYPSO-5 (43 µmol.cm⁻³).

1.5.   References

1   M. Cavaillès, A. Bornet, X. Jaurand, B. Vuichoud, D. Baudouin, M. Baudin, L. Veyre, G. Bodenhausen, J.-N. Dumez, S. Jannin, C. Copéret and C. Thieuleux, *Angew. Chem. Int. Ed Engl.*, 2018, **57**, 7453–7457.