

## Supplementary Material

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### Dipolar Order Mediated $^1\text{H} \rightarrow ^{13}\text{C}$ Cross-Polarization for Dissolution-Dynamic Nuclear Polarization

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## 1. Cross-Polarization

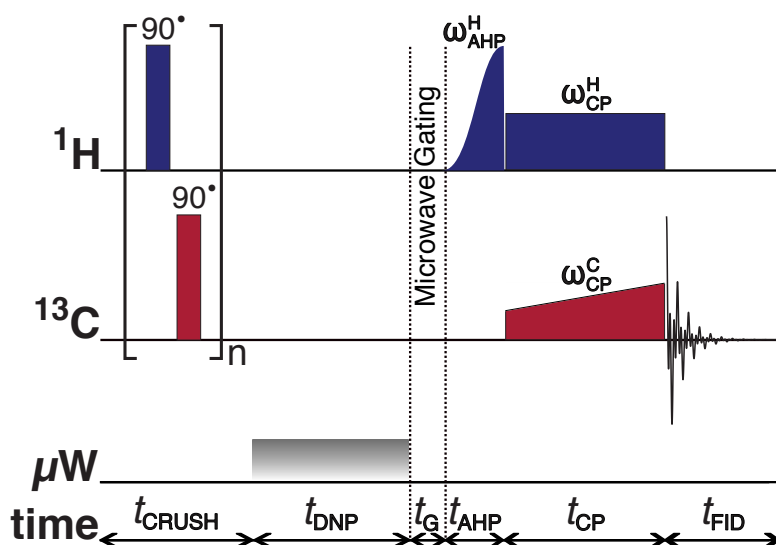


Figure S1: Schematic representation of the cross-polarization (CP) *rf*-pulse sequence adapted to *d*DNP experiments used for transferring  $^1\text{H}$  polarization to  $^{13}\text{C}$  heteronuclei. The experiments used the following parameters, chosen to maximize  $^1\text{H}$ - $^{13}\text{C}$  population conversion:  $n = 250$ ;  $\tau_{\text{DNP}} = 640$  s;  $\tau_{\text{G}} = 0.5$  s;  $\omega_{\text{AHP}}^{\text{H}}/2\pi = 27.8$  kHz;  $\tau_{\text{AHP}} = 175$   $\mu\text{s}$ ;  $\omega_{\text{CP}}^{\text{H}}/2\pi = 18.3$  kHz;  $\omega_{\text{CP}}^{\text{C}}/2\pi = 21.4$  kHz;  $\tau_{\text{CP}} = 7$  ms. AHP = adiabatic half-passage [1]. The  $\pi/2$  crusher *rf*-pulses use a thirteen-step phase cycle to remove residual magnetization at the beginning of each experiment:  $\{0, \pi/18, 5\pi/18, \pi/2, 4\pi/9, 5\pi/18, 8\pi/9, \pi, 10\pi/9, 13\pi/9, \pi/18, 5\pi/3, 35\pi/18\}$ . The resonance offset was placed at the centre of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR peaks.

Figure S1 shows the typical cross-polarization (CP) *rf*-pulse sequence configured for use in *d*DNP experiments to transfer polarization from  $^1\text{H}$  spins to insensitive  $^{13}\text{C}$  heteronuclei [2]. As detailed in the main text, the CP *rf*-pulse sequence achieved a  $^{13}\text{C}$  polarization of  $P(^{13}\text{C}) \approx 20.4\%$  after 640 s of direct  $^1\text{H}$  DNP at 1.2 K prior to a single step transfer of polarization to the  $^{13}\text{C}$  spin bath.

## 2. $B_1$ -field Optimization

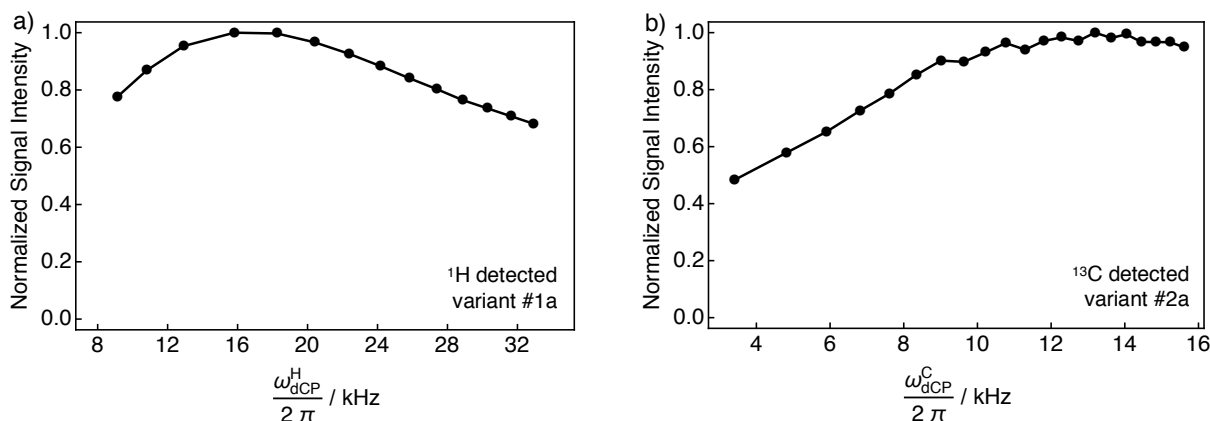


Figure S2: Experimental NMR signal intensities of **I** as a function of the (a)  $^1\text{H}$  *dCP* *rf*-pulse amplitude  $\omega_{\text{dCP}}^{\text{H}}$  and (b)  $^{13}\text{C}$  *dCP* *rf*-pulse amplitude  $\omega_{\text{dCP}}^{\text{C}}$  acquired at 7.05 T ( $^1\text{H}$  nuclear Larmor frequency = 300.13 MHz,  $^{13}\text{C}$  nuclear Larmor frequency = 75.47 MHz) and 1.2 K. The experiments in (a) were acquired with two transients per data point, whilst the experiments in (b) were acquired with a single transient per data point. All data points were normalized with respect to the highest intensity NMR signal.

Figure S2a displays the  $^1\text{H}$  monitored optimization for the build-up of  $^1\text{H}$ - $^1\text{H}$  dipolar order performed by using *variant #1a* of the *dCP* *rf*-pulse sequence demonstrated in Figure 1a of the main text. The experimental integrals are plotted against the  $^1\text{H}$  *rf*-pulse amplitude  $\omega_{\text{dCP}}^{\text{H}}$  and were acquired on the  $^1\text{H}$  *rf*-channel with  $t_{\text{dCP}}^{\text{H}} = 25 \mu\text{s}$  (black circles). The  $^1\text{H}$  NMR signal increases until a maximum NMR signal intensity, which corresponds to the optimal generation of  $^1\text{H}$ - $^1\text{H}$  dipolar order, is achieved at  $\omega_{\text{dCP}}^{\text{H}} \approx 16.4$  kHz, after which the NMR signal intensity decreases at higher *rf*-pulse nutation frequencies.

Figure S2b exhibits the  $^{13}\text{C}$  observed optimization for the creation of  $^{13}\text{C}$  magnetization realized by implementing *variant #2a* of the *dCP* *rf*-pulse sequence detailed in Figure 2a of the main text. The experimental integrals are plotted against the  $^{13}\text{C}$  *rf*-pulse amplitude  $\omega_{\text{dCP}}^{\text{C}}$  and were obtained on the  $^{13}\text{C}$  *rf*-channel with  $\omega_{\text{dCP}}^{\text{H}} \approx 16.4$  kHz,  $t_{\text{dCP}}^{\text{H}} = 25 \mu\text{s}$  and  $t_{\text{dCP}}^{\text{C}} = 39$  ms (black circles). The  $^{13}\text{C}$  NMR signal builds until a maximum NMR signal intensity, which corresponds to the optimal creation of  $^{13}\text{C}$  magnetization, is reached at  $\omega_{\text{dCP}}^{\text{C}} \approx 13.2$  kHz, after which the NMR signal intensity plateaus at increased *rf*-pulse nutation frequencies.

### 3. References

- [1] A. Bornet, A. Pinon, A. Jhajharia, M. Baudin, X. Ji, L. Emsley, G. Bodenhausen, J. H. Ardenkjær-Larsen and S. Jannin, *Phys. Chem. Chem. Phys.*, **2016**, 18, 30530-30535.
- [2] A. Pines, M. Gibby and J. Waugh, *Chem. Phys. Lett.*, **1972**, 15, 373-376.