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Supplementary Information

Pulse Sequence and Sample Formulation Optimization for Dipolar Order Mediated ^{1}H→^{13}C Cross-Polarization

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1. Cross-polarization

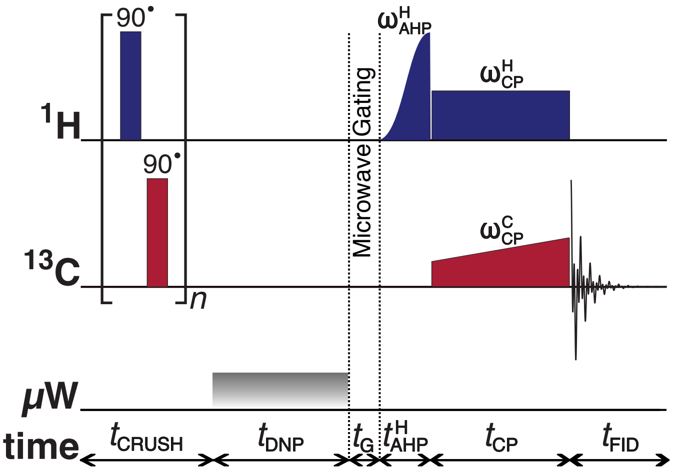


Figure S1: Schematic representation of the cross-polarization (CP) *rf*-pulse sequence adapted to *d*DNP experiments used for transferring ^{1}H polarization to ^{13}C heteronuclei. The experiments used the following parameters, chosen to maximize ^{1}H-^{13}C population conversion: $n = 50$; $t_G = 0.5$ s; $\omega^{H}_{AHP}/2\pi = 27.8$ kHz; $t^{H}_{AHP} = 175$ μs. AHP = adiabatic half-passage. AHP sweep width = 100 kHz. The $\pi/2$ crusher *rf*-pulses use an empirically optimized 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}H and ^{13}C NMR peaks. The non-constant amplitude ^{13}C CP *rf*-pulse has a linearly increasing amplitude between 50% and 100%.

Figure S1 shows the typical cross-polarization (CP) *rf*-pulse sequence configured for use in *d*DNP experiments to transfer polarization from ^{1}H spins to insensitive ^{13}C heteronuclei [1-3].

Table S1: CP *rf*-pulse sequence parameters, peak *rf*-pulse powers P_{CP}, peak *rf*-pulse energies E_{CP} and ^{13}C nuclear spin polarization levels $P_{CP}(^{13}C)$ for the molecular derivatives used in this work.

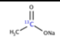
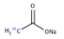
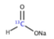
		Molecules		
		I	**II**	**III**
Quantity	**Units**			
t_{CP}	ms	6.0	7.5	9.0
$\omega^{H}_{CP}/2\pi$	kHz	18.3	18.3	15.3
P^{H}_{dCP}	W	5.0	5.0	3.5
E^{H}_{dCP}	mJ	24.0	37.5	31.5
$\omega^{C}_{CP}/2\pi$	kHz	25.8	25.8	24.0
P^{C}_{dCP}	W	150	150	130
E^{C}_{dCP}	J	0.9	1.125	1.17
$E^{H}_{dCP} + E^{C}_{dCP}$	J	0.924	1.163	1.202
$P_{CP}(^{13}C, 5\ s)$	%	3.1	3.7	2.8
$P_{CP}(^{13}C, 600\ s)$	%	37.3	42.9	-

Table S1 shows the CP *rf*-pulse sequence parameters, peak *rf*-pulse powers P_{CP}, peak *rf*-pulse energies E_{CP} and ^{13}C nuclear spin polarization levels $P_{CP}(^{13}C)$ for the molecular candidates employed in this study. As detailed in the main text, ^{13}C polarization levels were measured after 5 or 600 s of direct ^{1}H DNP at 1.2 K prior to a single step transfer of polarization to the ^{13}C spin bath.

2. Build-up rate constants

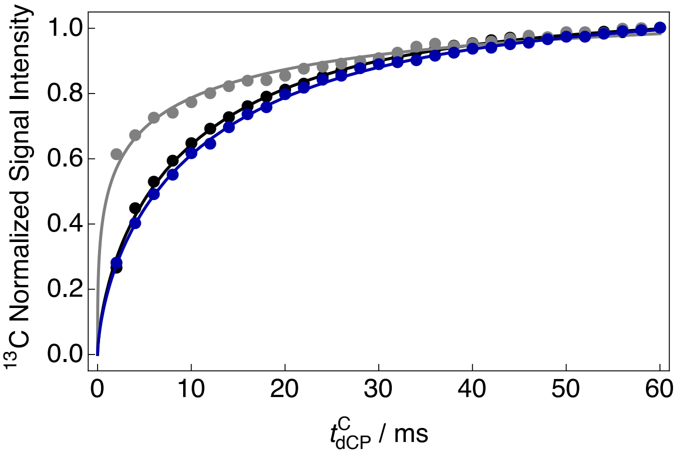


Figure S2: Experimental ^{13}C NMR signal intensities of samples **I-III** as a function of the ^{13}C *d*CP *rf*-pulse duration $t_{\mathrm{dCP}}^{\mathrm{C}}$ acquired at 7.05 T (^{1}H nuclear Larmor frequency = 300.13 MHz, ^{13}C nuclear Larmor frequency = 75.47 MHz) and 1.2 K with a single transient per data point. Coloured traces: Black: Sample **I**; Blue: Sample **II**; and Grey: Sample **III**. All signal amplitudes were normalized to the final data point. Stretched exponential decay function (solid lines): A(1-exp{-($R'_{d\mathrm{CP}}$t)$^{\beta}$}).

The presumed conversion of ^{1}H-^{1}H dipolar order to ^{13}C transverse magnetization in samples **I-III** was tracked as a function of the ^{13}C *d*CP *rf*-pulse duration $t_{d\mathrm{CP}}^{\mathrm{C}}$ by using the *d*CP *rf*-pulse sequence shown in Figure 1 of the main text. Experimental results demonstrating the generation of ^{13}C NMR signal intensity are shown in Figure S2. The integrals plotted were acquired by using the *d*CP *rf*-pulse sequence parameters given in Table 2 of the main text for incremented durations of $t_{d\mathrm{CP}}^{\mathrm{C}}$. At a ^{13}C *d*CP *rf*-pulse duration of $t_{d\mathrm{CP}}^{\mathrm{C}}$ = 60 ms, all samples have achieved a near optimal conversion of ^{1}H-^{1}H dipolar order to ^{13}C transverse magnetization, *i.e.* the experimental curves display a plateauing trend. Experiments were stopped at such ^{13}C *d*CP *rf*-pulse durations to ensure that the *rf*-probe did not arc within the superfluid liquid helium bath. The longer dipolar order relaxation time constant for sample **III**, compared with sample **I**, may explain the reduced ^{13}C *d*CP *rf*-pulse build-up time rate $R_{d\mathrm{CP}}^{\mathrm{C}}$ for this choice of molecular candidate (see the main text for more details).

3. References

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