# Supplement

## Solid-State $^{1}H$ Nuclear Spin Polarimetry by $^{13}CH_3$ Nuclear Magnetic Resonance

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## 1. $^{13}C$ NMR Spectra

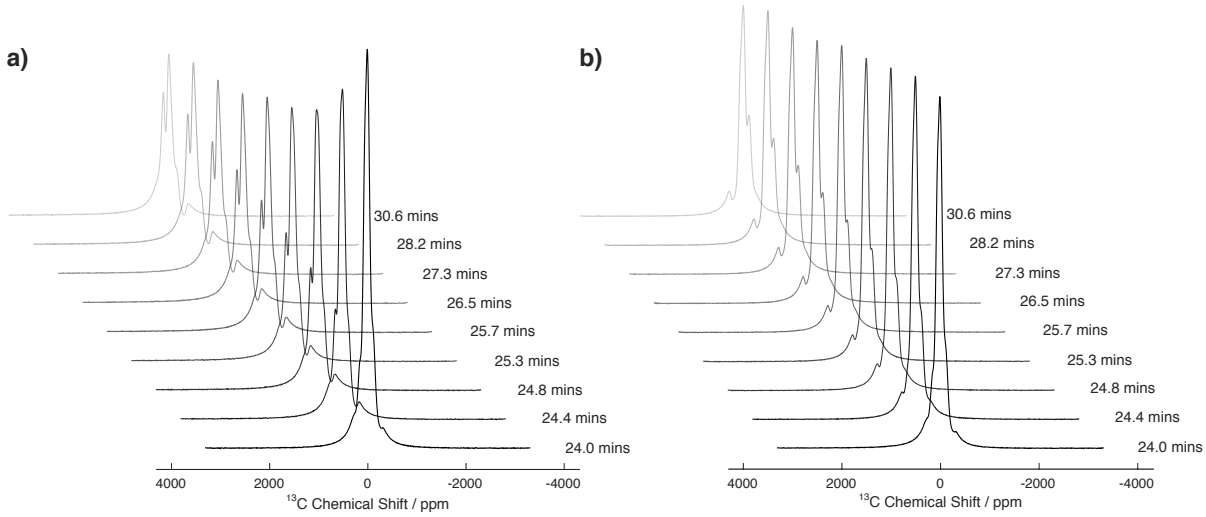


Figure S1: Relevant portions of the experimental $^{13}C$ NMR spectra belonging to the $^{13}C$-labelled methyl ($^{13}CH_3$) group of **I** acquired at 7.05 T ($^{1}H$ nuclear Larmor frequency = 300.13 MHz, $^{13}C$ nuclear Larmor frequency = 75.47 MHz) and 1.2 K with a single transient (*rf*-pulse flip angle = 3.5°) as a function of $^{1}H$ DNP time. (a) Positive microwave irradiation; and (b) Negative microwave irradiation. The labels indicate the $^{1}H$ DNP time at which the spectra were recorded.

Figure S1 shows the relevant part of the experimental $^{13}C$ NMR spectra of **I** acquired with a small flip angle *rf*-pulse ($\beta$ = 3.5°) as a function of $^{1}H$ DNP time. The $^{13}C$ NMR spectra in Figure S1 were acquired by using the *rf*-pulse sequence shown in Figure 1 of the main text. The timings coincide with those shown in Figure 2 of the main text.

## 2. *$^{13}$C NMR Peak Asymmetry vs. $^{1}$H Polarization*

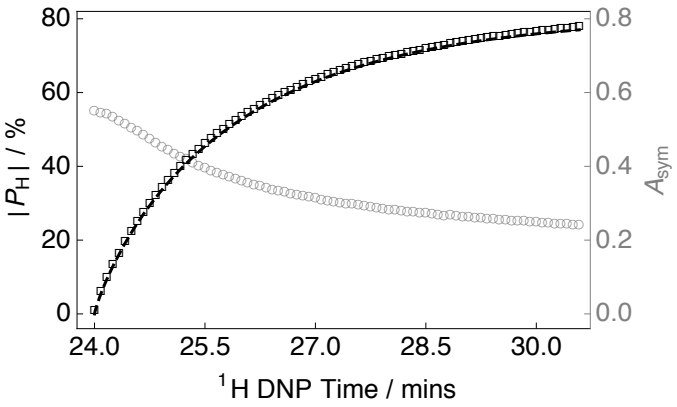


Figure S2: Experimental $^{1}$H polarization $|P_H|$ DNP build-up curve (black filled squares) and $^{13}$C NMR peak asymmetry $A_{sym}$ (grey empty circles) for **I** as a function of $^{1}$H DNP time acquired at 7.05 T ($^{1}$H nuclear Larmor frequency = 300.13 MHz, $^{13}$C nuclear Larmor frequency = 75.47 MHz) and 1.2 K with a single transient per data point for the case of negative microwave irradiation. The timings coincide with those shown in Figure 2 of the main text. The black solid line indicates the best fit of experimental data points for the $^{1}$H polarization $|P_H|$ DNP build-up curve, and has the corresponding fitting function: $A(1-\exp\{-(t/\tau_{DNP}^{-})^{\beta}\})$. Mean $^{1}$H DNP build-up time constant: $\langle\tau_{DNP}^{-}\rangle$ =122.0 ± 0.4 s.

Figure S2 shows the DNP build-up curve for the $^{1}$H polarization $|P_H|$ of **I** as a function of $^{1}$H DNP time for negative microwave irradiation. Figure S2 also displays the $^{13}$C NMR peak asymmetry $A_{sym}$ for sample **I** as a function of $^{1}$H DNP time.