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 ($\beta = 3.5^\circ$) 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: $A(1 - \exp\left(-\left(t/\tau_{DNP}\right)^p\right))$. Mean $^1$H DNP build-up time constant: $\langle \tau_{DNP} \rangle = 122.0 \pm 0.4$ 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.