Supplementary Information

PPS preparation

For establishing 4-body spin correlations, which is contained in the form of the PPS, it usually needs multiple pulses and gradient fields in the original spatial average technique. However, in our experiments, we can utilize the GRAPE algorithm not only to calculate shape pulses, but also to seek for a unitary operator, after adding which and a gradient pulse the thermal equilibrium state would transform to the PPS. The initial thermal equilibrium state of the NMR sample can be written as $\rho_{eq} = \sum_{i=1}^{4} \gamma_i I_z^i$, where γ_i is the gyromagnetic ratio of the nuclear spins. Typically, for the same nuclear spin the value of γ can be considered as a unit. The theoretical final state we want to prepare is

$$\rho_{theo} = -\frac{1}{16}\mathbb{I} + |0000\rangle\langle 0000|, \tag{0.1}$$

where $\mathbb{I}$ is the 16×16 unity matrix. We will give an initial guess of the unitary operator U_0, and calculate the fidelity F between ρ_{theo} and the final state

$$\rho_{fin} = Gz(U_0 \rho_{eq} U_0^{\dagger}), \tag{0.2}$$

where Gz is a gradient pulse to destroy the coherence (Noting that some coherence like 0-order coherence cannot be destroyed). If F is higher than our pre-set value, specifically 0.99 for this experiment, we will pack U_0 into a shape pulse, i.e., GRAPE pulse. Otherwise, we will obtain a new unitary operator U_1 through perturbation under the supervision of the GRAPE algorithm, and calculate a new F by repeating the above procedure. This is the core of our method to prepare the PPS. It needs only one GRAPE pulse and one gradient field, but results a high fidelity PPS.

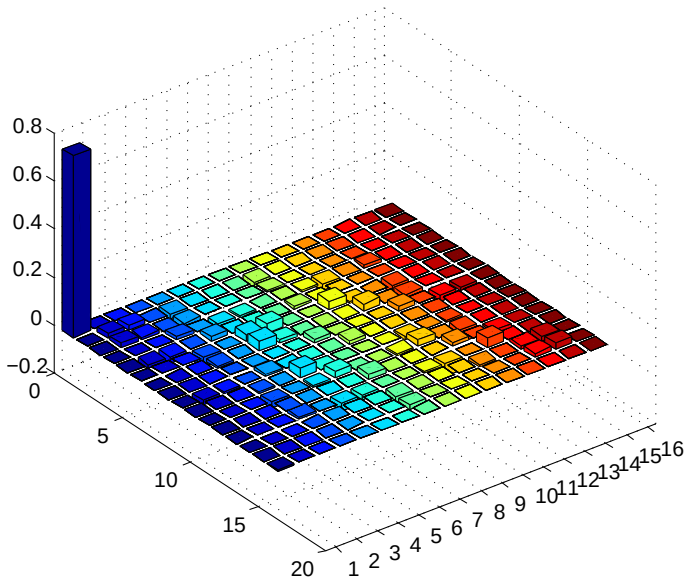

Figure S1. Real part of the prepared PPS. After applying the sought unitary operator and a gradient pulse to the thermal equilibrium state, we will obtain the final state which is very similar to $|0000\rangle$ if ignoring the identity matrix, which has no influence on the NMR signals. From this figure it can be seen that almost all the signals are concentrated on the population of $|0000\rangle\langle 0000|$, the peak of which is used as the benchmark of the other measurements of the experiment.

For the sample 1-Bromo-2-Chlorobenzene (C_6H_4ClBr) in this experiment, with ignoring the off-diagonal elements that cannot be destroyed by the gradient pulse which are close to 0, the diagonal elements of the PPS is

[1.512, -0.098,-0.120,-0.109,-0.100,-0.072,-0.112,-0.098,-0.106,-0.136,-0.083,0.097,-0.052,-0.112,-0.081,-0.136]. If deducting the identity matrix from the final state, it is very similar to $|0000\rangle$, which indicates that our method is creditable.