**Broadband Carbon-13 Correlation Spectra of Microcrystalline Proteins in Very High Magnetic Fields**
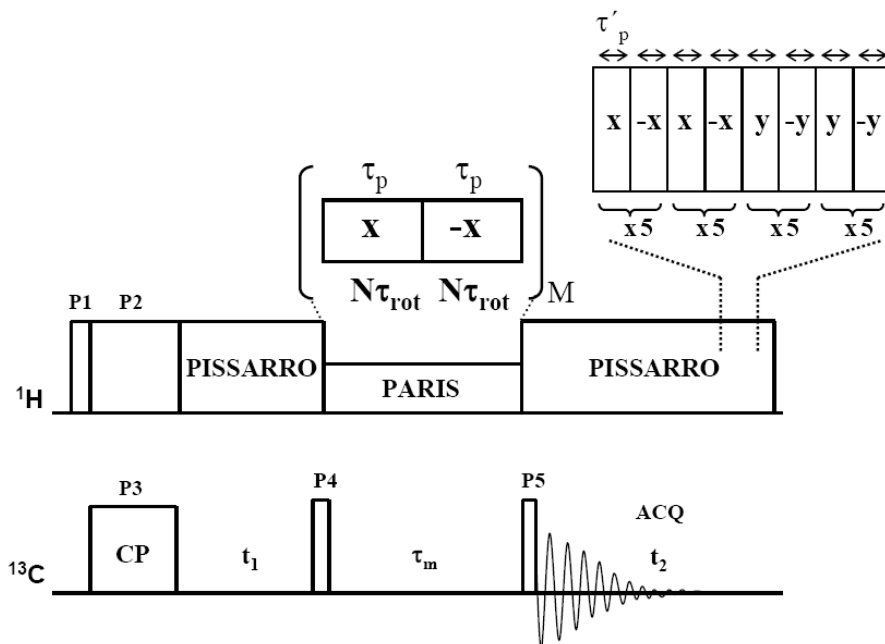
## *Supplementary Information*

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**Phi 1 : y, -y**

**Phi 2 : x**

**Phi 3 : x**

**Phi 4 : x, x, x, x, x, x, x, x, -x, -x, -x, -x, -x, -x, -x, -x**

**Phi 5 : x, x, -x, -x, y, y, -y, -y**

**Phi rec : x, -x, -x, x, y, -y, -y, y, -x, x, x, -x, -y, y, y, -y**

**Figure 1S**. Pulse sequence used for recording 2D $^{13}$C-$^{13}$C correlation spectra. Magnetization transfer is promoted by PARIS recoupling (Weingarth et al. Chem. Phys. Lett. 469, 2009, 342-348). During the mixing interval $\tau_m$, the proton *rf* amplitude (in this paper $\nu_1^H$ = 23, 15 and 10 kHz) can be set well below the spinning frequency (here $\nu_{rot}$ = 23 kHz.) The *rf* phase must be reversed at intervals $\tau_p = N\nu_{rot}$. In this work, $\tau_p = \tau_{rot}/2$ = 21.74 μs ($N$ = ½). The protons were decoupled using the PISSARRO scheme with $\nu_1^H$ = 100 kHz with alternating phases as shown, the interval being $\tau'_p$ = 0.9$\nu_{rot}$. (Weingarth et al., Chem. Phys. Lett. 466, 2008, 247-251).
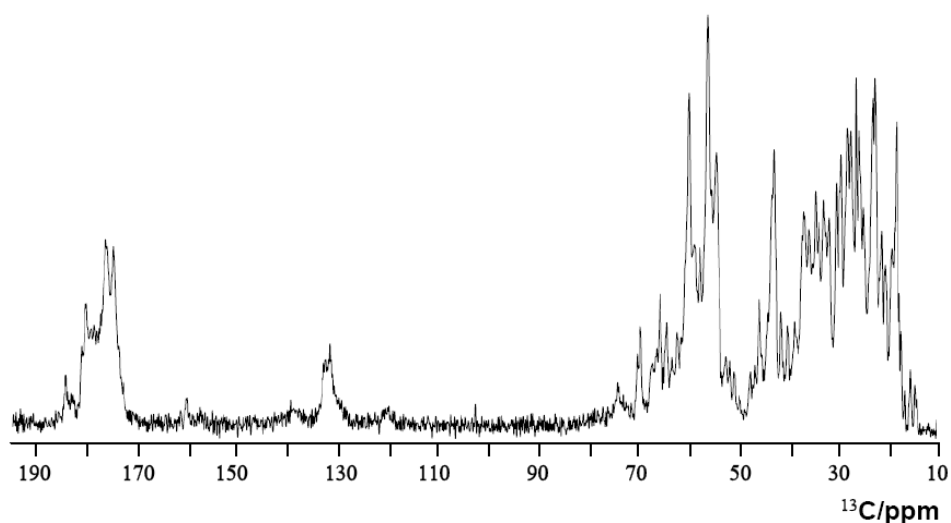
**Figure 2S** Solid-state $^{13}$C spectrum of microcrystalline catabolite repression phosphocarrier protein (Crh) precipitated with PEG, recorded at ca. 5°C at 225 MHz for $^{13}$C and 900 MHz for protons, in a 2.5 mm rotor spinning at $\nu_{rot}$ = 23 kHz, with 2 ms cross-polarization. Proton decoupling was achieved with the PISSARRO scheme with $\nu_1^H$ = 100 kHz and $\tau'_p$ = 39.13 μs. The narrow linewidths in the spectrum indicate a high structural homogeneity of the protein (Böckmann et al., J. Biomol. NMR 27 (2003), 323-339).
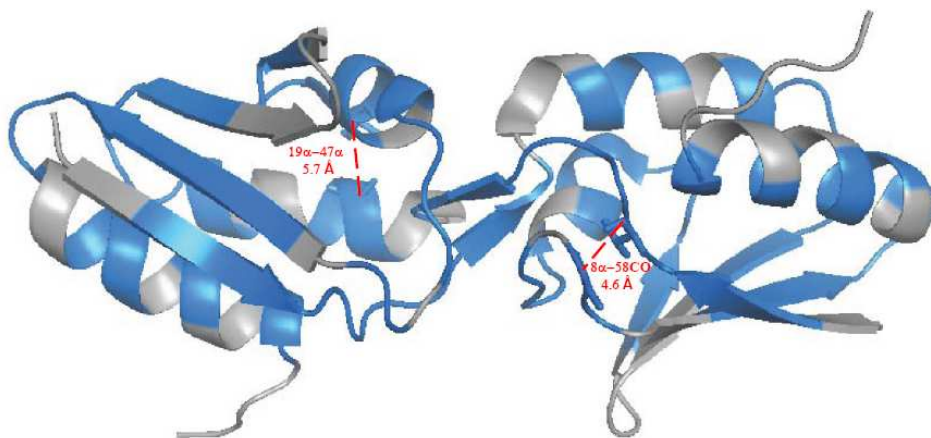


**Figure 3S** X-ray structure of the domain-swapped dimer of Crh. Residues with sequential $(C^\alpha, C^\alpha)$ and $(C^\alpha, C')$ contacts that could be assigned in the 2D $^{13}$C-$^{13}$C PARIS spectrum are shown in blue. Two long-range contacts observed between I47 and A19 (5.7 Å) and between G58 and V8 residues (4.6 Å) in the domain-swapped dimer are highlighted by red dashed lines.
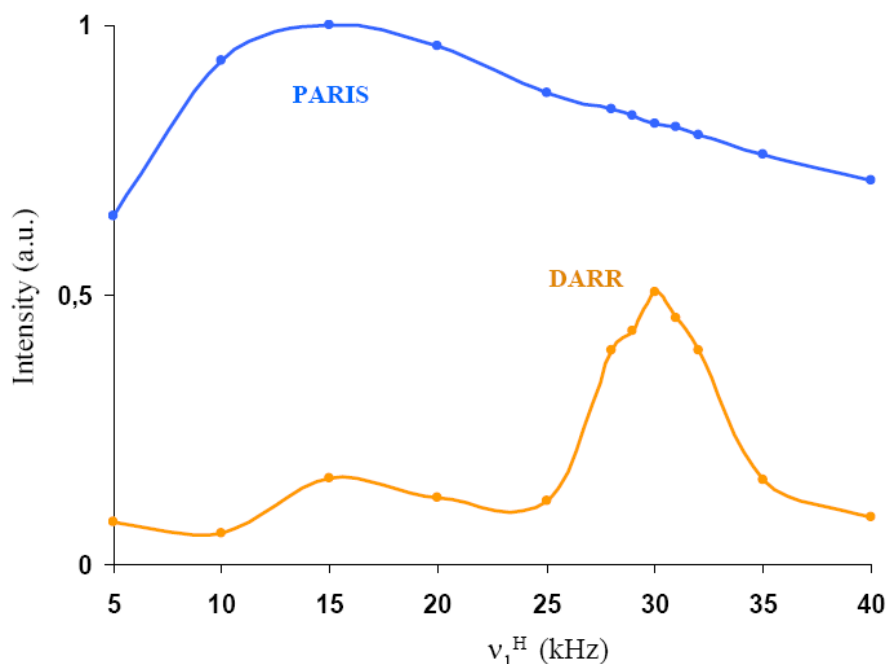
**Figure 4S** Simulated $C^{\alpha}$-$C^{\beta}$ magnetization transfer amplitudes for PARIS ($N = \frac{1}{2}$, $\tau_p =$ 16.66 μs) and DARR recoupling for *rf* amplitudes $\nu_1^H$ ranging from 5 to 40 kHz, with $\nu_{rot}$ = 30 kHz and $\tau_m$ = 5 ms. DARR shows a narrow maximum around the rotary resonance condition ($\nu_1^H$ = 30 kHz). PARIS exhibits a broad plateau for recoupling amplitudes $10 < \nu_1^H < 40$ kHz. Full 2D experiments were simulated for a powdered sample of L-Alanine with 8 spins assuming that the methyl protons rotate very rapidly. Chemical shift anisotropies (CSA) were neglected. The simulations were carried out using SPINEVOLUTION (M. Veshtort, R. G. Griffin, J. Magn. Reson. 178 (2006) 248-282).

Other experimental details

All spectra were acquired in Lyon with a BRUKER Avance DSX 900 MHz standard-bore spectrometer, equipped with a triple resonance 2.5 mm probe, spinning the sample at a frequency $\nu_{rot}$ = 23 kHz. The sample temperature was ca. 5°C in all experiments. The cross-polarization contact time was 1 ms and the relaxation delay between scans 3 s. The acquisition and maximum evolution periods were 20 and 9.1 ms, respectively. The total acquisition time was ~13 hours.

Assignments were completed with the help of SPARKY-3 software (T. D. Goddard and D. G. Kneller, University of California, San Francisco). The free induction decays were zero-filled to 4096 points and weighted by shifted squared-cosine functions with SSB = 3 in both dimensions, except to observe the carbonyl region in the direct $\omega_2$ dimension with $\nu_1^H$ = 10 kHz (SSB = 2) and to reveal regions with the sequential contacts shown in Fig. 2 (SSB = 2) in the indirect $\omega_1$ dimension. No baseline correction was applied.