Supporting Material "Microcoil High-Resolution Magic-Angle Spinning NMR Spectroscopy" (ja061350+)

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Materials and Methods

25% $^{13}C_2$ enriched glycine was purchased from Sigma-Aldrich and used without further purification. The preparation and structural analysis of the ^{13}C labeled silk rod of *Bombyx mori* and the uniformly ^{13}C labeled trialanine sample are described elsewhere (1,2).

All NMR experiments were performed on a Chemagnetics Infinity 600 MHz (14.1 T) spectrometer, operating at 150.9 MHz for ^{13}C and 600.0 MHz for ^{1}H observation. Experiments were performed in home-built microMAS designs using either a 400/300 μm outer/inner diameter microcoil or a 335/235 μm coil (Figure 1). The magic angle was set using KBr (3), in the latest design the large rotor is filled with KBr and fitted with a separate circuit tuned for ^{79}Br observation. In this way one can quickly set the magic angle and immediately proceed with the measurement of interest without the need of changing the sample.

The ^{13}C CP-MAS (4,5) spectrum of [25 % $^{13}C_2$]-glycine was obtained at a static field of 14.1 T and a spinning frequency of 8.2 kHz, accumulating 10240 scans (Figure S1b). During CP the nutation frequencies of the radio frequency (rf) fields on the ^{1}H and ^{13}C channel were given by about 64 and 72 kHz (+1 Hartman-Hahn (6) sideband condition (7)), respectively. In addition an amplitude ramp of 7 % was used on the ^{13}C channel (8) and the CP contact time was optimized to 2 ms (Figure S1a). Continuous-wave (CW)

decoupling with a proton nutation frequency of 202 kHz was applied during signal detection.

The ^{13}C CP-MAS spectra of the trialanine sample were acquired at a static field of 14.1 T and a spinning frequency of 10 kHz (Figure 2). During CP the rf-field strengths for the ^{1}H and ^{13}C rf fields were 45 and 55 kHz. An amplitude ramp of 4 % was used on the ^{13}C rf channel and the CP contact time was optimized to 0.8 ms. A series of experiments as a function of CW decoupling field strength were performed using the 335/235 μm coil as shown in Figure 3.

The ^{13}C CP-MAS spectrum of the silk rod at a spinning frequency of 8.2 kHz (Figure 4b) was obtained using the same parameters as optimized for the $^{13}C_2$-glycine except that a CP contact time of 1.8 ms and an amplitude ramp of 2 % was used. Proton decoupling was performed using the XiX sequence (9) with a pulse duration of 699 μs and rf field strength of 202 kHz. For the spectrum obtained at a spinning spinning speed of at 8.2 kHz 108000 scans were acquired. For the 4 kHz MAS spectrum (Figure 4a) this was extended to 348164 acquisitions, this is due to the fact that the intensity is now distributed over more sidebands. Furthermore, at lower spinning speeds the rotor shifts its position as a result of which less material is located in the active coil volume.

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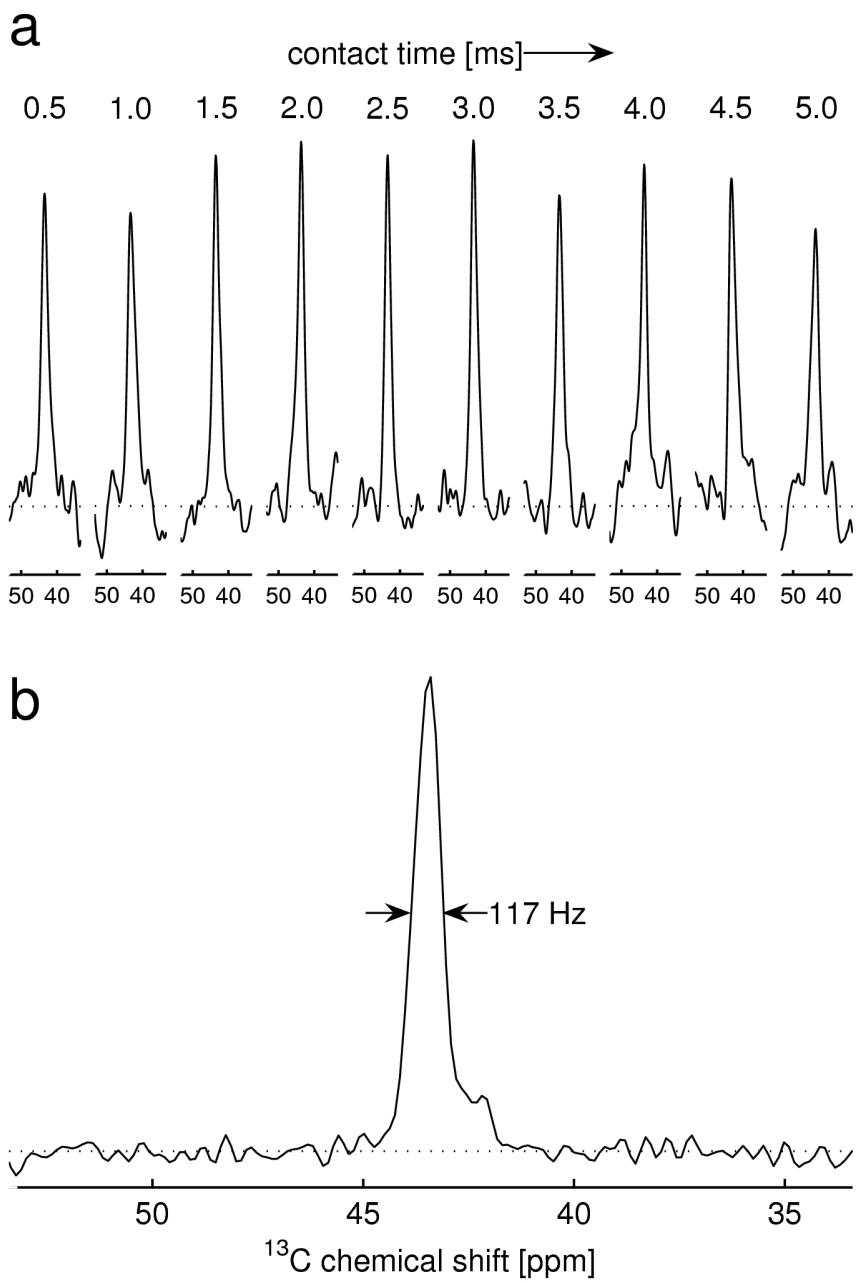

Figure S1. CP-MAS spectrum of 25% $^{13}C_2$ labeled glycine obtained in the microrotor inside a 400/300 μm outer/inner diameter microcoil. (a) Intensity of the methylene resonance of as a function of the CP contact time. (b) A linewidth of only 117 Hz was observed, comparable to that in a commercial probe under CW decoupling.