

SUPPLEMENTARY MATERIAL

In an attempt at further optimization, the rectangular inversion pulse shown in 1b was truncated at 5.76 ms, directly after the first sharp step of the inversion takes place. To compensate for the incomplete inversion we increased the power of the pulse to $B_1 = 700$ Hz. This achieved 65% complete inversion. The lack of a full inversion means that this pulse would only be beneficial for systems with a very long rotational correlation time where non-optimality becomes less relevant (compare with Fig. 2) when weighed against pulse length.

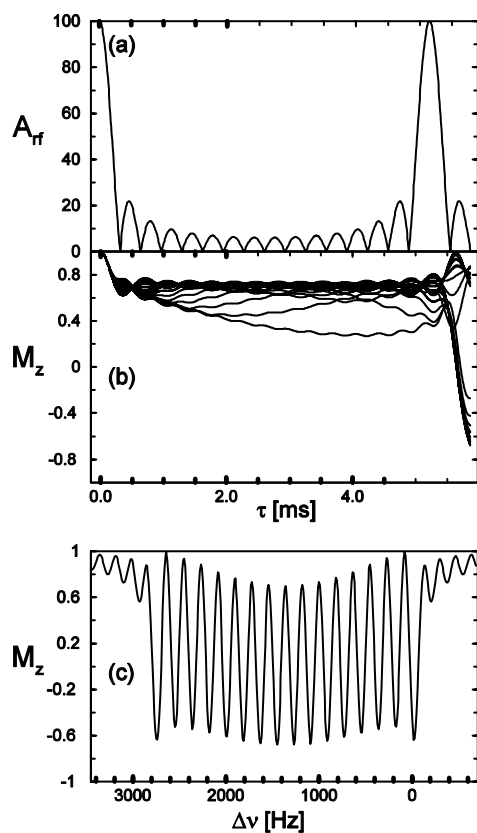


Figure 1S. Shape (upper frame), time evolution of magnetization vectors with the frequency offsets of $90 \cdot i$ Hz, $i = 0, 1, \dots, 36$ (middle), and excitation profile (lower frame) of PC-SPI in the absence of relaxation generated using 20 ms rectangular pulse truncated at 5.76 ms applied with $\gamma B_2 = 700$ Hz. 64 scans per t_1 increment and 120 increments with 0.5 interscan delay were collected resulting in the acquisition time per experiment of 1.3 h.

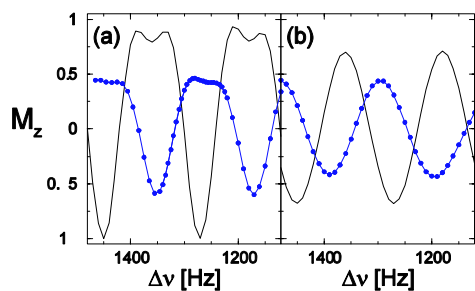


Figure 2S. Expansion of a superposition of the calculated inversion profile ($M_z \rightarrow -M_z$, black lines) with the calculated generation of $2I_z S_z$ operator from I_z operator (blue lines) as a function of the offset frequency using PC-SPI based on a 20 ms rectangular pulse (a) truncated at 12.16 ms applied with $\gamma B_2 = 520$ Hz and (b) truncated at 5.76 ms applied with $\gamma B_2 = 700$ Hz. The generation of the $2I_z S_z$ operator is calculated for the two spin system representing an amide group attached to a rigid molecule with rotational correlation time of 200 ns.

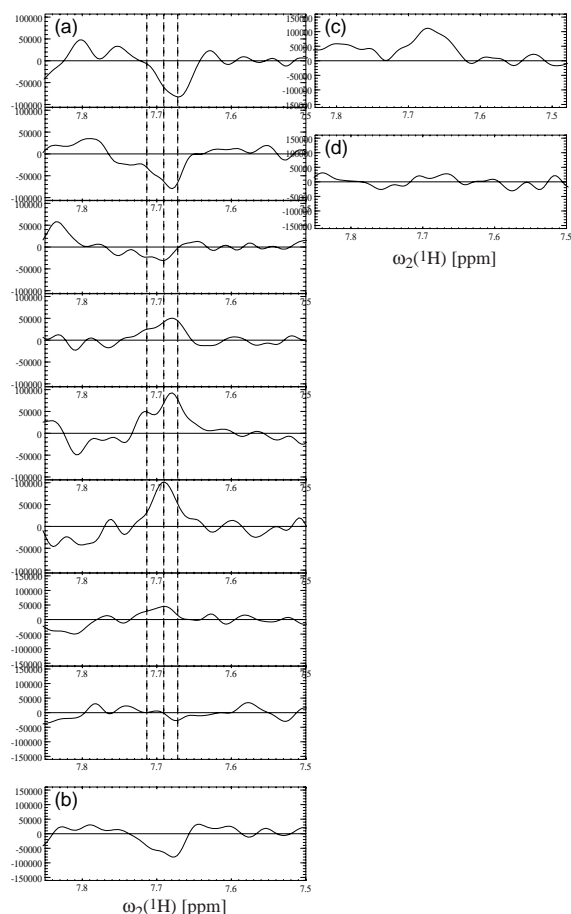


Figure 3S. Strips taken through PC-SPI spectra acquired with rectangular modulated pulses. Strips are taken from the spectra of the complex at 117.12 ppm (^{15}N) through there partially overlapping resonances of the residues T1010 and E1042, and an

unidentified third signal. **(a)** Strips taken from a spectra acquired using the pulse shown in figure 1b at a series of offsets incremented by 20 Hz, designed to probe a complete spectrum, **(b)** the same strip taken through the spectrum acquired with the truncated pulse from figure 1S at the offset used in the first strip in (a). A corresponding strip taken from the CRINEPT-HMQC-TOCSY is shown in **(c)** and from the INEPT spectrum in **(d)**. The vertical lines in (a) are drawn at the positions of three overlapped resonances, indicating the potential for resolution of broad overlapped resonances when using individual PC-SPI spectra. Each spectrum was acquired in 7 hours.