Supporting Information: Measurement of hetero-nuclear distances using a symmetry-based pulse sequence in solid-state NMR

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**Fig. S1.** Simulated signal fraction $\Delta S/S_0$ of REDOR as function of the recoupling time $\tau$. The curves were calculated at different MAS frequencies, $\nu_R = 16$, 30 and 65 kHz for $^{13}$C-$^{15}$N spin system with $b_{13C-15N}/(2\pi) = -937$ Hz. The anisotropic chemical de-shielding constant, $\delta_{\text{aniso}}$ ($^{13}$C), is equal to 8 kHz and the asymmetry parameter is $\eta_{\text{CSA}}(^{13}\text{C}) = 0.5$. The $^{15}$N CSA was disregarded. The length of all REDOR $\pi$-pulses was equal to 6.25 $\mu$s, i.e. a nutation frequency $\nu_1(^{13}\text{C}) = 80$ kHz. The REDOR scheme is applied to the observed $^{13}$C nuclei. The central $\pi$-pulse on the $^{15}$N channel is ideal.
**Fig.S2.** Simulated signal fraction $\Delta S/S_0$ of REDOR, S-REDOR and R-REDOR as function of recoupling time $\tau$. The curves were calculated at $\nu_R = 16$ kHz for $^{13}$C-$^{15}$N spin system with $b_{^{13}\text{C}-^{15}\text{N}}/(2\pi) = -1$ kHz. The $z$ principal axis of $^{13}$C CSA tensor is aligned along the $^{13}$C-$^{15}$N inter-nuclear direction and the anisotropic chemical de-shielding constant, $\delta_{\text{aniso}}(^{13}\text{C})$, is equal to 8 kHz and $\eta_{\text{CSA}}(^{13}\text{C}) = 0.5$. The $^{15}$N CSA was disregarded. REDOR sequence only uses perfect $\pi$-pulses. The nutation frequencies of $SR_4^2$ and $R^3 (n = 1)$ recoupling were fixed to their nominal values, $\nu_1 = 2\nu_R$ and $\nu_1 = \nu_R$. The REDOR, $SR_4^2$ and $R^3 (n = 1)$ schemes are applied to the observed nuclei, $S = ^{13}$C. The central $\pi$-pulses in S-REDOR sequence are infinitely short.
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Fig. S3. Simulated signal fraction $\Delta S/S_0$ of S-REDOR as function of recoupling time $\tau$. The curves were calculated at different MAS frequencies, $\nu_R = 16$, 30 and 65 kHz for $^{13}\text{C}-^{15}\text{N}$ spin system with $b_{13\text{C}-15\text{N}}/(2\pi) = -937$ Hz. The anisotropic chemical de-shielding constant, $\delta_{\text{aniso}}$ ($^{13}\text{C}$), is equal to 8 kHz and the asymmetry parameter is $\eta_{\text{CSA}}^{^{13}\text{C}} = 0.5$. The $^{15}\text{N}$ CSA was disregarded. The nutation frequency of $SR4^2_1$ recoupling was fixed to its nominal value, $\nu_1 = 2\nu_R$. The recoupling was applied either (a) to the observed $S = ^{13}\text{C}$ or (b) to the non-observed $I = ^{15}\text{N}$ channels. The central $\pi$-pulses in S-REDOR sequence are ideal.
Fig. S4. Simulated signal fraction $\Delta S/S_0$ of R-REDOR as function of recoupling time $\tau$ using 30 uniformly-distributed orientations of $^{13}$C CSA. The curves were calculated at $\nu_R = 30$ kHz for $^{13}$C-$^{15}$N spin system with $b_{13C-15N}/(2\pi) = -1$ kHz. The $R^3$ recoupling is applied to the observed nucleus, $S = ^{13}$C. $\delta_{\text{aniso}} (^{13}$C) = 8 kHz and $\eta_{\text{CSA}} (^{13}$C) = 0.5. The other simulation parameters are identical to those of Fig. S2.
Fig. S5. Simulated signal fraction $\Delta S/S_0$ of S-REDOR as function of recoupling time $\tau$ using 30 uniformly-distributed orientations of $^{13}$C CSA. The curves were calculated at $\nu_R = 30$ kHz for $^{13}$C-$^{15}$N spin system with $b_{13C-15N}/(2\pi) = -1$ Hz. The SR4$_1^2$ recoupling is applied to the observed nucleus, $S = ^{13}$C. $\delta_{\text{aniso}}(^{13}$C) = 8 kHz and $\eta_{\text{CSA}}(^{13}$C) = 0.5. The other simulation parameters are identical to those of Fig. S2.
Fig.S6 Simulated signal fraction $\Delta S/S_0$ of REDOR as function of recoupling time $\tau$ using 30 uniformly-distributed orientations of $^{13}\text{C}$ CSA. The curves were calculated at $\nu_R = 30$ kHz for $^{13}\text{C}$-$^{15}\text{N}$ spin system with $b_{^{13}\text{C}-^{15}\text{N}}/(2\pi) = -1$ kHz. The REDOR recoupling is applied to the observed nucleus, $S = ^{13}\text{C}$. $\delta_{\text{aniso}} (^{13}\text{C}) = 8$ kHz and $\eta_{\text{CSA}} (^{13}\text{C}) = 0.5$. The other simulation parameters are identical to those of Fig.S2.
Fig. S7 Simulated signal fraction $\Delta S/S_0$ of S-REDOR as function of recoupling time $\tau$. The red and black curves were calculated for $^{13}$C-$^{15}$N two-spin and $^{13}$C-$^{13}$C'-$^{15}$N three-spin systems at $\nu_R = 16$, 30 or 65 kHz. For the two-spin system, the dipolar coupling constant is $b_{^{13}C-^{15}N}/(2\pi) = -937$ Hz, while for the three-spin system, the additional dipolar coupling constant is $b_{^{13}C-^{13}C'}/(2\pi) = -2$ kHz. The three nuclei are aligned in the $^{13}$C'-$^{13}$C-$^{15}$N system and the dipolar coupling between $^{13}$C' and $^{15}$N is neglected. The anisotropic chemical de-shielding constant, $\delta_{\text{aniso}}(^{13}$C) = 8 kHz and $\eta_{\text{CSA}}(^{13}$C) = 0.5. The $^{13}$C' and $^{15}$N CSA are disregarded. The nutation frequency of $SR4_{1}^2$ recoupling is fixed to its nominal value, $\nu_1 = 2\nu_R$. The recoupling is applied to the observed nuclei, $S = ^{13}$C. The central $\pi$ pulses in S-REDOR sequence are infinitely short. The Euler angles defining the different interactions are as follows: $\Omega_{PC}^{^{13}C-^{15}N} = \{10^\circ, 20^\circ, 30^\circ\}$, $\Omega_{PC}^{^{13}C-^{13}C'} = \{40^\circ, 60^\circ, 80^\circ\}$, $\Omega_{PC}^{\text{CSA-}^{13}C} = \{50^\circ, 20^\circ, 10^\circ\}$. 

$v_R = 16$ kHz

$v_R = 30$ kHz

$v_R = 65$ kHz
**Fig. S8.** Effect of rf field inhomogeneity on the signal fraction curves of $^{13}$C-$^{15}$N S-REDOR experiment at $\nu_{R} = 16$ kHz. The $SR4^{1}_{i}$ scheme is sent on the $^{13}$C-observed channel. (a) Experimental signal fraction as function of $\tau$ for [2-$^{13}$C,$^{15}$N]-glycine with a full rotor sample. The rf field strength for the $SR4^{1}_{i}$ scheme is equal to its nominal value, $\nu_{1} (^{13}$C) = 32 kHz, (●) or 10% weaker (□), and 10% larger (△) than 32 kHz. The central $\pi$ pulse nutation frequencies were $\nu_{1,\pi} (^{13}$C) = 50 kHz , $\nu_{1,\pi} (^{15}$N) = 45 kHz. The best fit curve according to Eq.11 for nominal rf field value is shown as a dashed line. The fitted $^{13}$C-$^{15}$N dipolar coupling constants are equal to $|b_{\text{13C-15N}}|/(2\pi) = 905$, 873, and 882 Hz for the nominal, 10% weaker, and 10% larger rf values. (b) Simulated signal fraction curves for a set of rf nutation frequencies for the $SR4^{2}_{i}$ scheme in the range $\nu_{1} (^{13}$C) = 27.2-36.8 kHz. The central $^{13}$C and $^{15}$N $\pi$-pulses are infinitely short. The $^{13}$C-$^{15}$N spin system is characterized by $b_{\text{13C-15N}}/(2\pi) = -937$ Hz (corresponding to $D_{\text{13C-15N}} = 1.48$ Å), $\delta_{\text{aniso}} (^{13}$C) = 8 kHz and $\eta_{\text{CSA}} (^{13}$C) = 0.5. The $^{15}$N CSA was disregarded. The fitted dipolar constants using Eq.11 for these curves simulated with different rf fields are: 823 Hz (1-15%), 866 Hz (1-10%), 902 Hz (1-5%), 932 Hz (1.00), 949 Hz (1+5%), 959 Hz (1+10%), 959 Hz (1+15%). The corresponding $^{13}$C-$^{15}$N distances are equal to: 1.55, 1.52, 1.50, 1.49, 1.48, 1.47, and 1.47 Å.
Fig. S9 Simulated signal fraction $\Delta S/S_0$ of S-REDOR as function of recoupling time $\tau$ at $\nu_R = 30$ kHz using nominal rf frequency of $2\nu_R = 60$ kHz as well as rf nutation frequencies 15%, 10% and 5% weaker or stronger than 60 kHz. The other simulation parameters are identical to those of Fig. S8. $b_{13C,15N}/(2\pi) = -937$ Hz, $\delta_{\text{aniso}}^{(13C)} = 8$ kHz and $\eta_{\text{CSA}}^{(13C)} = 0.5$. The $^{15}$N CSA was disregarded. The central $\pi$ pulses in S-REDOR sequence are infinitely short.
Fig. S10. Simulated signal fraction $\Delta S/S_0$ of S-REDOR as function of recoupling time $\tau$ at $v_R = 65$ kHz using nominal rf frequency of $2v_R = 130$ kHz as well as rf nutation frequencies 15%, 10% and 5% weaker or stronger than 130 kHz. The other simulation parameters are identical to those of Fig. S8. $b_{13C-15N}(2\pi) = -937$ Hz, $\delta_{\text{aniso}}(^{13}\text{C}) = 8$ kHz and $\eta_{\text{CSA}}(^{13}\text{C}) = 0.5$. The $^{15}\text{N}$ CSA was disregarded. The central $\pi$ pulses in S-REDOR sequence are infinitely short.
Fig. S11. Experimental $^{13}\text{C}-^{15}\text{N}$ S-REDOR $S_0$ signal for $[2^{-13}\text{C},^{15}\text{N}]$-glycine. Experiments were performed at $v_R = 16$ kHz (□, ◇) and $15.980$ kHz (■, ◆). The nutation frequency of the central $^{13}\text{C}$ $\pi$-pulses was $v_{1,\pi}(^{13}\text{C}) = 50$ kHz. The $\text{SR}4^2_1$ recoupling sequence, with nutation frequency of $32$ kHz, was applied to the $^{13}\text{C}$-observed (□, ■) or the $^{15}\text{N}$-non-observed (◇, ◆) channel.
Fig. S12. Experimental $^{13}\text{C}^{15}\text{N}$ R-REDOR $S_0$ signal for [2-$^{13}\text{C}$,$^{15}\text{N}$]-glycine. Experiments were performed at $\nu_R = 16$ kHz (black) and 15.980 kHz (red). The nutation frequency of the central $^{13}\text{C}$ $\pi$-pulse was $\nu_{1,\pi}(^{13}\text{C}) = 55$ kHz. The $R^3 (n=1)$ recoupling sequence, with nutation frequency of 16 kHz, was applied to the $^{13}\text{C}$-observed channel.
Fig.S13. Simulated $^{13}\text{C}^{15}\text{N}$ S-REDOR signal fraction versus the recoupling time $\tau$. The curves were calculated at different MAS frequencies in the range 15.980-16.020 kHz in steps of 5 Hz. The $SR4^2$ scheme was applied to the $^{13}\text{C}$-observed channel and the recoupling nutation frequency was 32 kHz. The central $^{13}\text{C}$ and $^{15}\text{N}$ $\pi$ pulses are infinitely short. The $^{13}\text{C}^{15}\text{N}$ spin system is characterized by $b_{13\text{C}^{15}\text{N}}/(2\pi) = -937$ Hz, $\delta_{\text{aniso}}^{(13}\text{C}) = 8$ kHz and $\eta_{\text{CSA}}^{(13}\text{C}) = 0.5$. The $^{15}\text{N}$ CSA was disregarded. It must be noted that the simulation of these curves requires the full calculation of $S$ and $S_0$. As an example $S_0$ is no more equal to 1 (see Fig.S11) as in rotor synchronized experiments. This leads to quite time-consuming calculation of $\Delta S/S_0$ fractions.
Validity of Eq.9.

For the sake of concision, in the following we use the notations ($\theta$ and $\xi$ are real numbers):

$$I_{m-2} = \int_0^\pi d\gamma \int_0^\pi d\beta \sin[\beta] \cos[\theta \sin^2[\beta] \cos[2(\gamma + \xi)]]$$  \hskip 1cm (A1)

and

$$I_{m-1} = \int_0^\pi d\gamma \int_0^\pi d\beta \sin[\beta] \cos[\theta \sin[2\beta] \cos[\gamma]]$$  \hskip 1cm (A2)

1) We start by simplifying $I_{m-2}$. The function

$$f(\beta, \gamma, \theta, \xi) = \sin[\beta] \cos[\theta \sin^2[\beta] \cos[2(\gamma + \xi)]]$$  \hskip 1cm (A3)

is periodic with respect to $\gamma$, with period $\pi$, the integral of $f(\beta, \gamma, \theta, \xi)$ with respect to $\gamma$ over an interval of length $2\pi$ does not depend on the position of the interval and thus by setting $\gamma' = \gamma + \xi$, one obtains:

$$I_{m-2} = \int_{1/2}^{1+\xi} d\gamma \int_0^\pi d\beta \sin[\beta] \cos[\theta \sin^2[\beta] \cos[2(\gamma + \xi)]] = \int_0^\pi d\gamma \int_0^\pi d\beta \sin[\beta] \cos[\theta \sin^2[\beta] \cos[2\gamma]]$$  \hskip 1cm (A4)


$$I_{m-2} = 2\pi \int_0^\pi d\beta \sin[\beta] J_0 \left[ \theta \sin^2[\beta] \right].$$  \hskip 1cm (A5)

By using $x = \cos[\beta]$, one obtains:

$$I_{m-2} = 2\pi \int_0^1 dx J_0 \left[ x \left( 1 - x^2 \right) \right].$$  \hskip 1cm (A6)

2) We now simplify $I_{m-1}$, which may be reduced to a single integral over $\beta$ by using $J_0$ function:

$$I_{m-1} = 2\pi \int_0^\pi d\beta \sin[\beta] J_0 \left[ \theta \sin[2\beta] \right]$$  \hskip 1cm (A7)

We assume a change of variable $\phi = \pi/2 - \beta$ and rewrite $I_{m-1}$ as

$$I_{m-1} = 2\pi \int_{\pi/4}^{\pi/4} d\phi \cos[\phi] J_0 \left[ \theta \cos[2\phi] \right] - 2\pi \int_{3\pi/4}^{\pi/4} d\phi \sin[\phi] J_0 \left[ \theta \sin[2\phi] \right].$$  \hskip 1cm (A8)

The substitution $u = \sqrt{2} \cos[\phi]$ and $v = \sqrt{2} \sin[\phi]$ in the first and second integrals of Eq.A8 yields

$$I_{m-1} = \pi \int_0^1 du J_0 \left[ u \left( 1 - u^2 \right) \right] + \pi \int_0^1 dv J_0 \left[ v \left( 1 - v^2 \right) \right].$$  \hskip 1cm (A9)

As $(u^2, v^2) \in [0,1]^2$, we have $|1-u^2| = 1-u^2$ and $|v^2-1| = 1-v^2$. Both integrals in Eq.A9 are thus identical, and hence we find $I_{m-1} = I_{m-2}$, which proves the validity of Eq.9.

\footnote{G.N. Watson, Theory of Bessel functions, Cambridge University Press, Cambdrige, 1944.}