SUPPORTING INFORMATION

Selective ^{1}H-^{14}N distance measurements by ^{14}N overtone solid-state NMR spectroscopy at fast MAS

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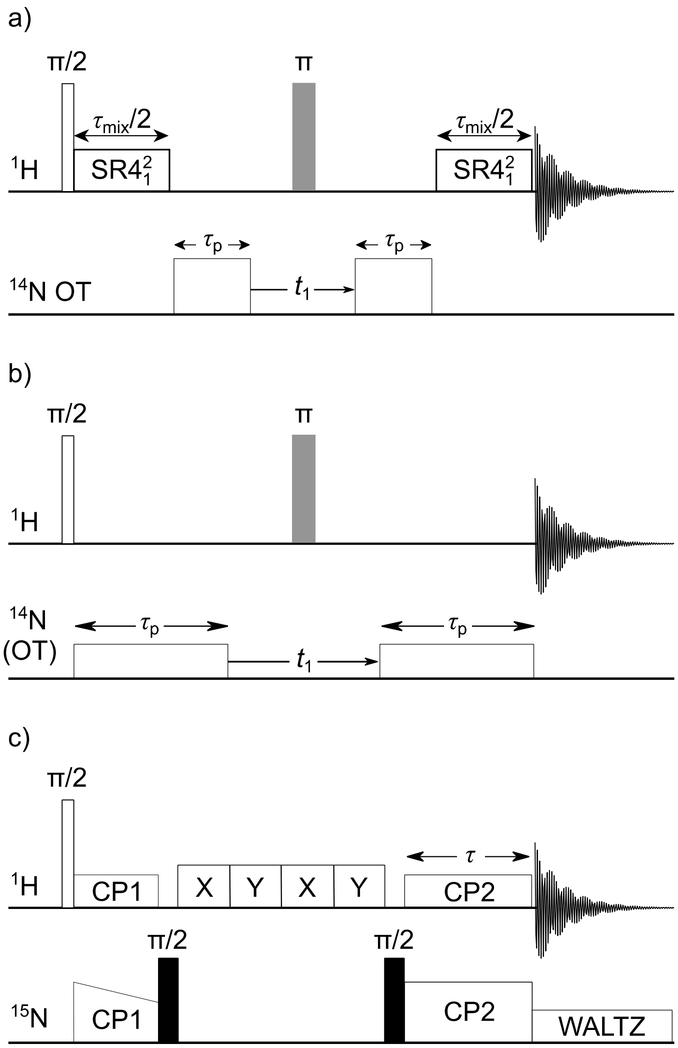

Figure S1. a) *D*-HMQC and b) T-HMQC sequences for probing ^{1}H-^{14}N OT correlations and c) ^{1}H-^{15}N inverse CPVC for determining ^{1}H-^{15}N dipolar couplings. All sequences are employed with ^{1}H-detection.

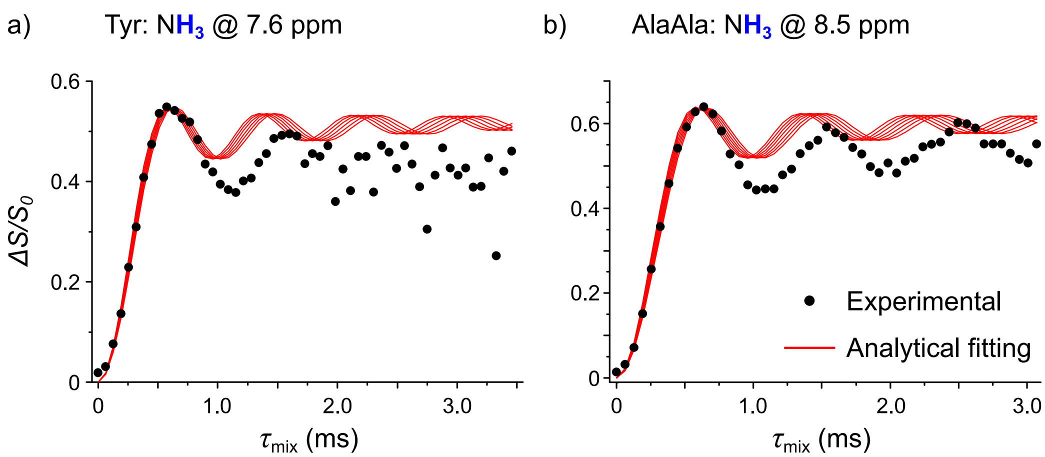

Figure S2. The full-scale fitting of experimental [1]H-[14]N OT-REDOR fraction curves (black circles) by the universal curves (red lines) for a) Tyr: N**H₃** at 7.6 ppm and b) AlaAla: N**H₃** at 8.5 ppm. The fitting parameters *f* for universal curves are a) 0.82 and b) 0.94.

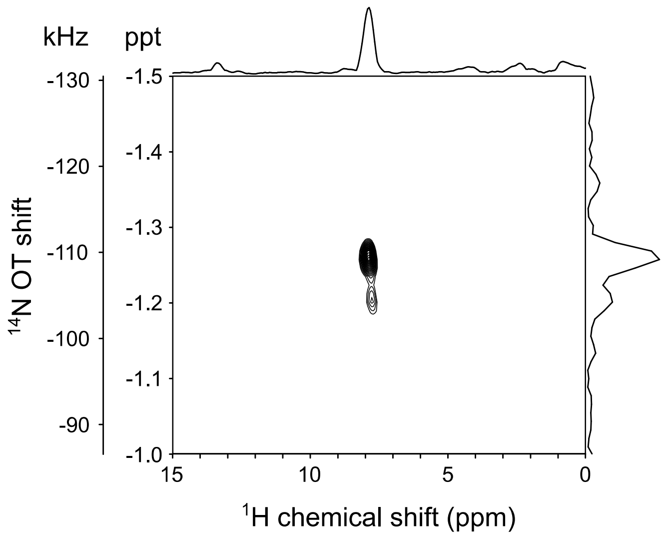

Figure S3. AcAla: the 2D ^{1}H-{^{14}N OT} T-HMQC spectrum at B_0 of 14.1 T and ν_R of 62.5 kHz. Experiment was recorded using the sequence in Fig. S1b with 8 scans, 16 t_1 points, and rotor-synchronized t_1 increment of 16.0 μs. The ^{14}N OT frequency was around the second SSB (n = -2) for the highest S/N. The τ_p and RD were 400 μs and 6 s, respectively. The experimental time was about 0.4 hour. The States-TPPI method was employed for the quadrature detection along the indirect dimension.

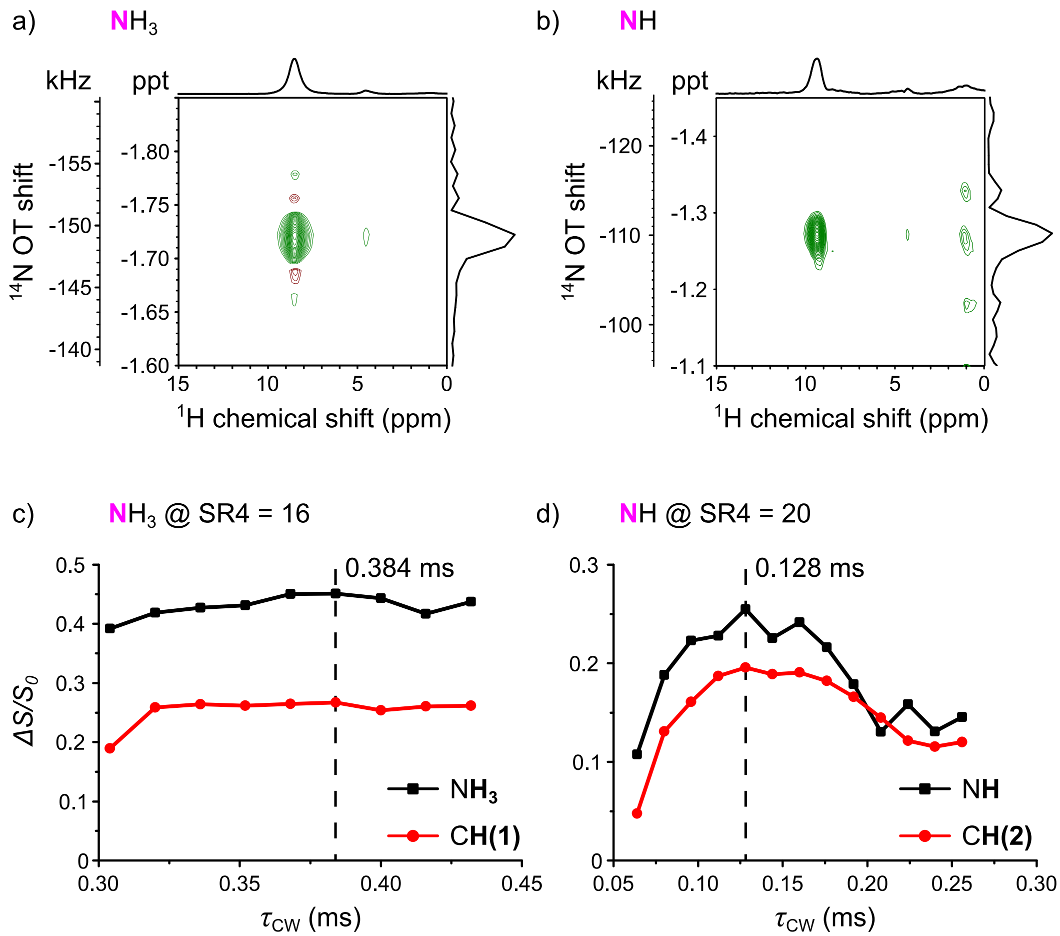

Figure S4. AlaAla: all experiments were performed at B_0 of 14.1 T and ν_R of 62. 5 kHz. (a,b) The 2D ^{1}H-{^{14}N OT} *D*-HMQC spectra for $^{\mathbf{14}}$**N**H_3 and $^{\mathbf{14}}$**N**H, respectively. Experiments were recorded using the sequence in Fig. S1a with 8 scans, 16 t_1 points, and rotor-synchronized t_1 increment of 16.0 µs. The ^{14}N OT frequencies were around the second SSB (n = -2) for the highest S/N. The (τ_p, τ_{mix}, RD) were (250 µs, 384 µs and 2 s) for a and (100 µs, 384 µs, and 2 s) for b. The States-TPPI method was employed for the quadrature detection along the indirect dimension. The experimental times for both 2D spectra were 0.15 hour. (c,d) The signal fraction $\Delta S/S_0$ as a function of τ_{CW} for c) N$\mathbf{H_3}$ (black squares) and C**H(1)** (red circles) at τ_{mix} of 1.02 ms when $^{\mathbf{14}}$**N**H_3 was saturated/inverted by τ_{CW} from 304 µs to 432 µs with a step of 16 µs at ^{14}N OT frequency of -1.72 ppt, and d) N**H** (black squares) and C**H(2)** (red circles) at τ_{mix} of 1.28 ms when $^{\mathbf{14}}$**N**H was saturated/inverted by τ_{CW} from 64 µs to 256 µs with a step of 16 µs at ^{14}N OT frequency of -1.26 ppt. NS and RD were 18 and 2s, respectively. The experimental times for were 0.2 and 0.3 hour for c and d, respectively. The optimum τ_{CW} is shown and highlighted by the dashed line.

Here we consider a spin system containing two protons and one nitrogen (H1 – N···H2), in which H1 is close to while H2 is far away from N. We assume the chemical shifts of H1 and H2 are overlapped to each other. Applying ^{1}H-^{14}N OT-REDOR to this three-spin system, we have:

Without CW pulse, the spin-echo signal S_0 is given by:

$$S_0 = S_0^{H1} + S_0^{H2} = 2S_0^{H1} \quad \text{(S1)}$$

As H2 is far away from N, its signal is not affected by the CW pulse. Hence, with the CW pulse, the dephased spin-echo signal *S*' is given by:

$$S' = S'^{H1} + S_0^{H2} = S'^{H1} + S_0^{H1} \quad \text{(S2)}$$

Combining Eqs. S1 and S2, the fraction signal is:

$$\frac{\Delta S}{S_0} = \frac{S_0 - S'}{S_0} = \frac{2S_0^{H1} - S'^{H1} - S_0^{H1}}{2S_0^{H1}} = \frac{S_0^{H1} - S'^{H1}}{2S_0^{H1}} = \frac{\Delta S^{H1}}{2S_0^{H1}} = \left(\frac{\Delta S}{S_0}\right)^{H1} / 2.0 \quad \text{(S3)}$$

Eq. S3 shows that due to the overlapping of H1 and H2, the actual H1-N fraction curve is scaled down by a factor of 2.0. Therefore, for a good match with the experimental curve, the universal curves should be also be halved.

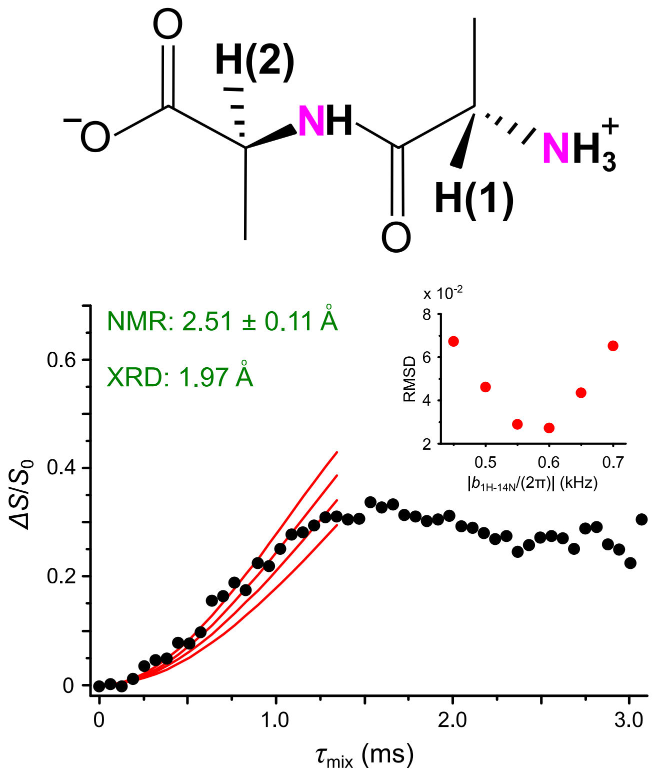

Figure S5. AlaAla (top): the fitting of experimental C**H(1)** fraction curves (black circles) by the universal curves (red lines) when ^{14}**N**H_3 is saturated/inverted with τ_{CW} of 0.384 ms. The universal curve are not halved. The RMSD analyses (inset) were calculated for the best fitting ^{1}H-^{14}N dipolar couplings. The NMR and XRD distances are given. Experimental details are identical to those of Fig. 10d.

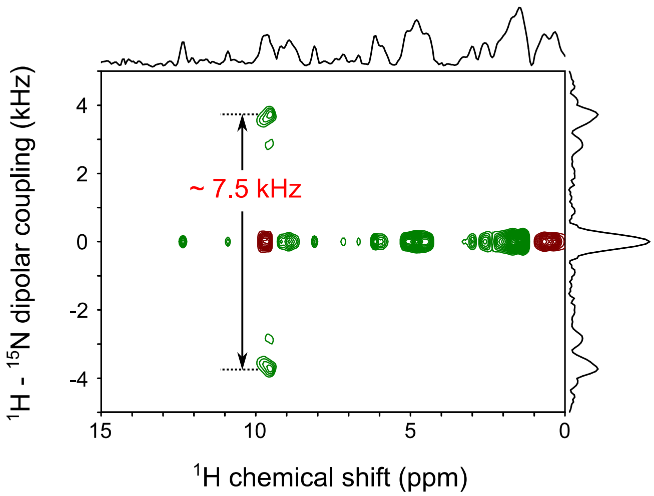

Figure S6. AlaAla: the 2D ^{1}H-^{15}N inverse CPVC spectrum. Experiment, using the sequence in Fig. S1c, was performed at B_0 of 14.1 T and ν_R of 70.0 kHz. The ^{15}N rf-field was 125 kHz. The ^{1}H → ^{15}N CP1 and ^{15}N → ^{1}H CP2 conditions were performed using ^{1}H and ^{15}N rf-fields of 20 and 50 kHz, respectively. For CP1, the linear ramp on ^{15}N channel was -10 % while for CP2, no linear ramp was used. The contact time of CP1 was 2.0 ms while that of CP2, τ, was varied from 0 to 1800 µs with a step of 10 µs. The 100 ms HORROR scheme with ν_{1H} = 35 kHz was used to suppress the residual ^{1}H polarizations after CP1. WALTZ decoupling, with ^{15}N rf-field of 10 kHz, was used to decouple nitrogen during ^{1}H acquisition. The ^{15}N chemical shift and its dimension were fixed at 80 ppm and 300 ppm, respectively. NS = 136 and RD = 2s. The experimental time was 13.7 hours. The ^{1}H-^{15}N dipolar coupling strength for NH site is determined by an arrow.

NMR pusle program:

```
--------------------------------------------------------------------------------
--	Experiment Source Code	--
--	Delta NMR Experiment & Machine Control Interface	--
--	Copyright (c) 2009 JEOL Ltd	--
--	All Rights Reserved	--
--------------------------------------------------------------------------------
--	HELP.eng: Hahn echo with optional decoupling
--	Category: solids, echo
--	File name : hahn_echo.ex2
--	Sequence name : Hahn echo with optional decoupling
--	Reference :
--	END HELP
header
	filename	=>	"respdor";
	sample_id	=>	"";
	comment	=>	"Hahn echo w/ opt decoupling";
	process	=	"1d_solid.list";
	include "header_solid";
end header;
instrument
	include "instrument_solid";
end instrument;
acquisition
	x_domain	=>	"Carbon13";
	x_offset	=>	100[ppm];
	x_sweep	=>	400[ppm];
	x_points	=>	2048;
	scans	=>	4;
	x_prescans	=>	0;
	mod_return	=>	1;
	include "acquisition_solid";
```

```
end acquisition;
pulse
        collect COMPLEX,OBS;
        include "pulse_solid";
        initial_wait     =       10.0[ms];
        irr_domain       =>      "Nitrogen14";
        irr_offset       =>      -300[ppm];

        obs_Setup        =?      "#Setup Observe Pulses#";
        obs_width_first  =>      x90;
        obs_width_second=>       obs_width_first*2, help "second pulse width";
        obs_amp_pulse    =>      100[%];
        obs_amp_sr4      =>      100[%];

        irr_Setup        =?      "#Setup Observe Pulses#";
        irr_width_sat    =>      x90,            help "first pulse width";
        irr_amp_pulse    =>      100[%], 0[%]->100[%]:0.01[%],   help "amplitude of pulses";
        irr_shape_sat    =>      "SQUARE",("SQUARE","PM_sat");

        Echo     =? "#Setup up echo times#";
        spinning_freq    =>      10[kHz];
        cycle_time_MAS=          1/spinning_freq;
        number_r4        =>      10;
        number_saturation=?      upper(irr_width_sat*spinning_freq);
        include "obs_sat_solid";

        recycle_Setup    =? "#Setup Recycle Times#";
        relaxation_delay=>       5.0[s],         help "relaxation delay";
        repetition_time  =?      relaxation_delay + x_acq_time,  help"relaxation_delay+x_acq_time";

        atn_Setup       =? "#Experiment Attenuator Settings#";
        obs_atn          =>      xatn,           help "attenuator for obs";
```

```
	irr_atn		=>	irratn,		help "attenuator for irr";

	obs_phs_first	=	{3(0), 3(120), 3(240)};
	obs_phs_sr4	=	{0};
	obs_phs_second=	{0, 120, 240};
	irr_phs_sat	=	{0};
	obs_phs_acq	=	{0, 240, 120, 240, 120, 0, 120, 0, 240};
	module_config	= "solid_sample";

begin
	initial_wait;
	when SATURATION do
		obs_sat(sat_loop, sat_pulse_interval, obs_width_sat, obs_amp_sat, obs_atn);
	end when;

	relaxation_delay;
	obs_width_first,	(obs.gate,	obs.phs.obs_phs_first,	obs.amp.obs_amp_pulse,
	obs.atn.obs_atn);

	loop number_r4 times

	cycle_time_MAS / 4,	(obs.gate,	obs.phs.obs_phs_sr4.lstep(120)	+	90,
	obs.amp.obs_amp_sr4, obs.atn.obs_atn);
	cycle_time_MAS / 4,	(obs.gate,	obs.phs.obs_phs_sr4.lstep(120)	-	90,
	obs.amp.obs_amp_sr4, obs.atn.obs_atn);
	cycle_time_MAS / 4,	(obs.gate,	obs.phs.obs_phs_sr4.lstep(120)	+	90,
	obs.amp.obs_amp_sr4, obs.atn.obs_atn);
	cycle_time_MAS / 4,	(obs.gate,	obs.phs.obs_phs_sr4.lstep(120)	-	90,
	obs.amp.obs_amp_sr4, obs.atn.obs_atn);
	cycle_time_MAS / 4,	(obs.gate,	obs.phs.obs_phs_sr4.lstep(120)	-	90,
	obs.amp.obs_amp_sr4, obs.atn.obs_atn);
```

cycle_time_MAS / 4, (obs.gate, obs.phs.obs_phs_sr4.lstep(120) + 90, obs.amp.obs_amp_sr4, obs.atn.obs_atn);
cycle_time_MAS / 4, (obs.gate, obs.phs.obs_phs_sr4.lstep(120) - 90, obs.amp.obs_amp_sr4, obs.atn.obs_atn);
cycle_time_MAS / 4, (obs.gate, obs.phs.obs_phs_sr4.lstep(120) + 90, obs.amp.obs_amp_sr4, obs.atn.obs_atn);

end loop;

parallel begin
number_saturation/spinning_freq;
justify center
obs_width_second, (obs.gate, obs.phs.obs_phs_second, obs.amp.obs_amp_pulse, obs.atn.obs_atn);
justify center
irr_width_sat, (irr.gate, irr.phs.irr_phs_sat, irr.amp.irr_amp_pulse, irr.shape.irr_shape_sat, irr.atn.irr_atn);
end parallel;

loop number_r4 times

cycle_time_MAS / 4, (obs.gate, obs.phs.obs_phs_sr4.lstep(120) + 90, obs.amp.obs_amp_sr4, obs.atn.obs_atn);
cycle_time_MAS / 4, (obs.gate, obs.phs.obs_phs_sr4.lstep(120) - 90, obs.amp.obs_amp_sr4, obs.atn.obs_atn);
cycle_time_MAS / 4, (obs.gate, obs.phs.obs_phs_sr4.lstep(120) + 90, obs.amp.obs_amp_sr4, obs.atn.obs_atn);
cycle_time_MAS / 4, (obs.gate, obs.phs.obs_phs_sr4.lstep(120) - 90, obs.amp.obs_amp_sr4, obs.atn.obs_atn);
cycle_time_MAS / 4, (obs.gate, obs.phs.obs_phs_sr4.lstep(120) - 90, obs.amp.obs_amp_sr4, obs.atn.obs_atn);

```
        cycle_time_MAS / 4,   (obs.gate,   obs.phs.obs_phs_sr4.lstep(120)   +   90,
        obs.amp.obs_amp_sr4, obs.atn.obs_atn);
        cycle_time_MAS / 4,   (obs.gate,   obs.phs.obs_phs_sr4.lstep(120)   -   90,
        obs.amp.obs_amp_sr4, obs.atn.obs_atn);
        cycle_time_MAS / 4,   (obs.gate,   obs.phs.obs_phs_sr4.lstep(120)   +   90,
        obs.amp.obs_amp_sr4, obs.atn.obs_atn);

        end loop;

        acq( dead_time, delay, obs_phs_acq );
end pulse;
```