Dynamic nuclear polarisation enhanced $^{14}$N overtone MAS NMR spectroscopy:
Supporting information

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### S1. $^{14}$N NMR parameters used in the simulations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>$C_Q$ / MHz</th>
<th>$\eta_Q$</th>
<th>$\delta_{iso}$ ($^{15}$N) / ppm</th>
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<tbody>
<tr>
<td>Glycine</td>
<td>N1</td>
<td>1.18</td>
<td>0.53</td>
<td>-6</td>
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<td>Glycylglycine</td>
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<td>0.10</td>
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<td></td>
<td>N2</td>
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<td>0.45</td>
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<td>Histidine.HCl.H$_2$O</td>
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<td>0.35</td>
<td>8</td>
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<tr>
<td></td>
<td>N2</td>
<td>1.52</td>
<td>0.25</td>
<td>138</td>
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<td></td>
<td>N3</td>
<td>1.21</td>
<td>0.94</td>
<td>152</td>
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</table>

Table S1 – NMR parameters used to simulate the $^{14}$N$^{14}$O$^T$ MAS spectra of the various sites for the three samples studied. The isotropic chemical shifts $\delta_{iso}$, which determine the position of the $^{14}$N$^{14}$O$^T$ powder patterns, were measured from the $^{15}$N CPMAS spectra and were fixed in the $^{14}$N$^{14}$O$^T$ simulations. The quadrupolar parameters $C_Q$ and $\eta_Q$, which determine the shape and width of the powder patterns, were adjusted to match the simulated spectra to the experimental $^{14}$N$^{14}$O$^T$ data, using values calculated from density functional theory as initial guesses.
S2. Glycine $^1$H and $^{13}$C CP DNP enhancement

Figure S2 – $^{13}$C CPMAS NMR spectra obtained from a solid powder sample of glycine impregnated with a solution of TEKPol in tetrachloroethane, with and without 70 mA microwave irradiation applied. The spectra were obtained at 9.4 T, 107 K and 10 kHz MAS (4 scans with 10 s recycle delay and 2 ms cross-polarisation contact time). Asterisks denote spinning sidebands. The $^{13}$C signal from the TCE is visible at 74 ppm.
S3. Glycine $^{14}$N$^{15}$O CP on resonance with $+2\omega$, and $+\omega$, overtone sidebands

Figure S3 – DNP-enhanced $^{14}$N$^{15}$O CPMAS spectra obtained from a solid powder sample of glycine impregnated with a solution of TEKPol in tetrachloroethane, at 9.4 T and 107 K. Both spectra were obtained at 10 kHz MAS with a CP contact time of $125 \mu$s, 16 scans and a recycle delay of 40 s. In spectrum (a) the $^{14}$N$^{15}$O transmitter frequency was placed on resonance with the $+2\omega$, overtone sideband as shown. In (b) this frequency was adjusted by $-10$ kHz, but no $+\omega$, overtone sideband was observed.
Figure S4 – $^{13}$C CPMAS NMR spectra obtained from a solid powder sample of glycylglycine impregnated with a solution of TEKPol in tetrachloroethane, with and without 70 mA microwave irradiation applied. The spectra were obtained at 9.4 T, 107 K and 10 kHz MAS (4 scans with 10 s recycle delay and 2 ms cross-polarisation contact time for $^{13}$C). Asterisks denote spinning sidebands, and the $^{13}$C signal from the TCE is visible in at 74 ppm.
Simulations modelling the effect of the contact time on the $^{14}\text{N}^{\text{DT}}$ powder pattern

Figure S5 – (a) $^{14}\text{N}^{\text{DT}}$ spectrum obtained from glycylglycine at 107 K, 9.4 T and 10 kHz MAS using DNP-enhanced cross-polarisation from the $^{1}\text{H}$ nuclei, with a CP contact time of 125 μs and the $^{14}\text{N}^{\text{DT}}$ contact pulse applied on resonance with the N1 peak at 30 kHz. 20 scans were acquired with a recycle delay of 40 s. Simulations made using pulse lengths of (b) 0.1 μs and (c) 125 μs are also shown to model the effects of the contact time on the powder pattern shape.
Figure S6 – $^{13}$C CPMAS NMR spectra obtained from a solid powder sample of histidine.HCl.H$_2$O impregnated with a solution of TEKPol in tetrachloroethane, with and without 70 mA microwave irradiation applied. The spectra were obtained at 9.4 T, 107 K and 10 kHz MAS (4 scans with 10 s recycle delay and 2 ms cross-polarisation contact time for $^{13}$C). Asterisks denote spinning sidebands, and the $^{13}$C signal from the TCE is visible in at 74 ppm.
Figure S7 – Comparison of DNP enhanced $^1$H-$^{13}$C CP spin echo spectrum (16 scans) and $^1$H-$^{13}$C CP HMQC $^{14}$N$^{14}$OT filtered spectrum (32 scans) acquired with a 200 μs $^{14}$N$^{14}$OT 90° pulse applied on resonance with the amide (-NH) nitrogen for coherence transfer. In both cases the total $^{13}$C transverse magnetization evolution time was 15 ms. The efficiency of the $^{14}$NOT HMQC filter is 2.8%. In both cases a 10 s recycle delay was employed.
### Table S2 – Comparison of factors contributing to $^{14}$N$^{\text{OT}}$ and $^{15}$N sensitivities in the directly-observed, DNP-enhanced spectra acquired in this work.

Other experimental details can be found in the main article. All spectra were acquired at 9.4 T and a temperature of around 107 K.