--- Supporting Information ---

^{17}O MAS NMR Correlation Spectroscopy at High Magnetic Fields

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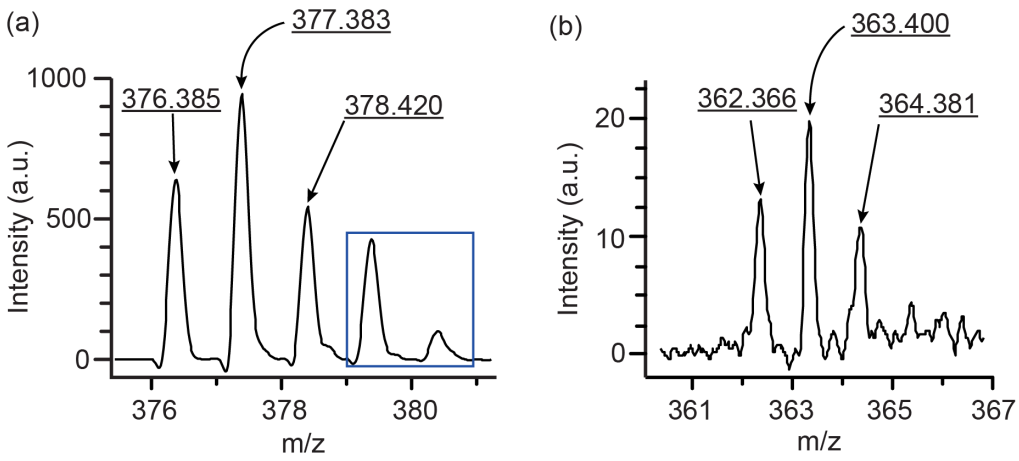

Figure S1: MALDI mass spectra of 40% - ^{17}O labeled FMOC-L-leucine (a) and FMOC-L-valine (b). The blue box in (a) is due to the alpha-cyano background from the MALDI matrix. The isotopic enrichments were calculated by taking the integrated peak intensities of the $^{16}O/^{16}O$ species as 0%, the $^{16}O/^{17}O$ species as 50%, and the $^{17}O/^{17}O$ species as 100% enrichment.

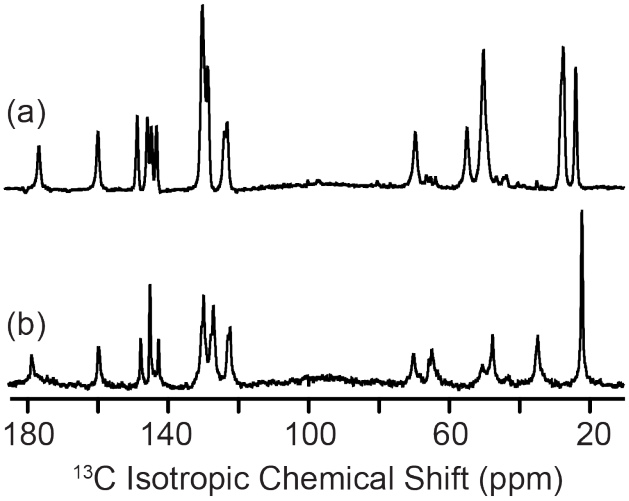

Figure S2: $^{13}C\{^{1}H\}$ CPMAS NMR spectra of FMOC-L-leucine (a) and FMOC-L-valine (b) at 11.7 T ($\omega_{0H}/2\pi$ = 500 MHz) with $\omega_R/2\pi$ = 10 kHz and $\gamma B_1/2\pi$ = 100 kHz ^{1}H TPPM decoupling.

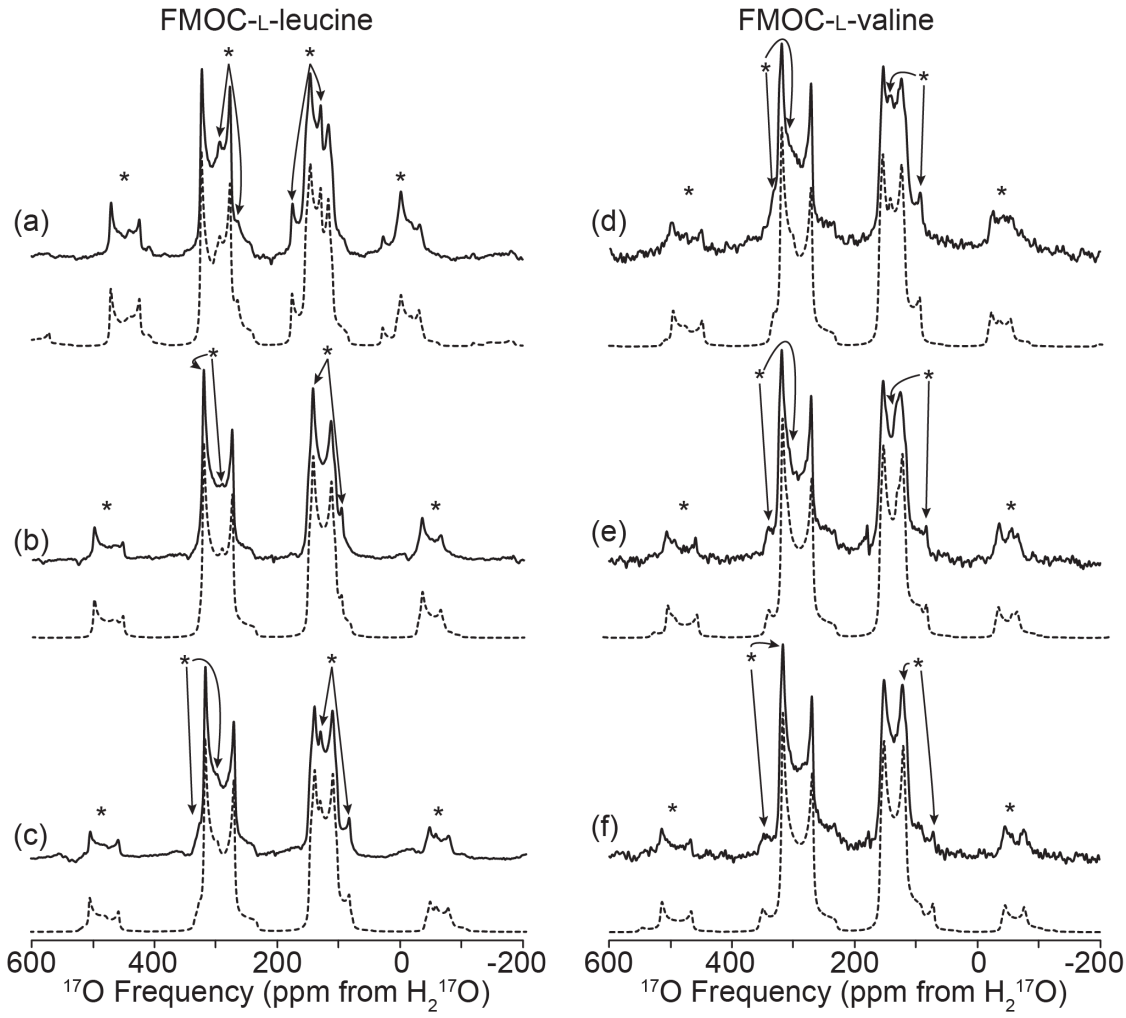

Figure S3: Oxygen-17 experimental (solid) and simulated (dashed) MAS NMR spectra of FMOC-L-leucine (right) and FMOC-L-valine (left) at 17.6 T ($\omega_{0H}/2\pi$ = 750 MHz). $\omega_R/2\pi$ = 15 kHz (a), $\omega_R/2\pi$ = 17 kHz (b), $\omega_R/2\pi$ = 18 kHz (c) for FMOC-L-leucine and $\omega_R/2\pi$ = 18 kHz (d), $\omega_R/2\pi$ = 19 kHz (e), $\omega_R/2\pi$ = 20 kHz (f) for FMOC-L-valine. Spinning sidebands are noted by astericks (*). NMR parameters used in spectral simulations are given in Table 4.

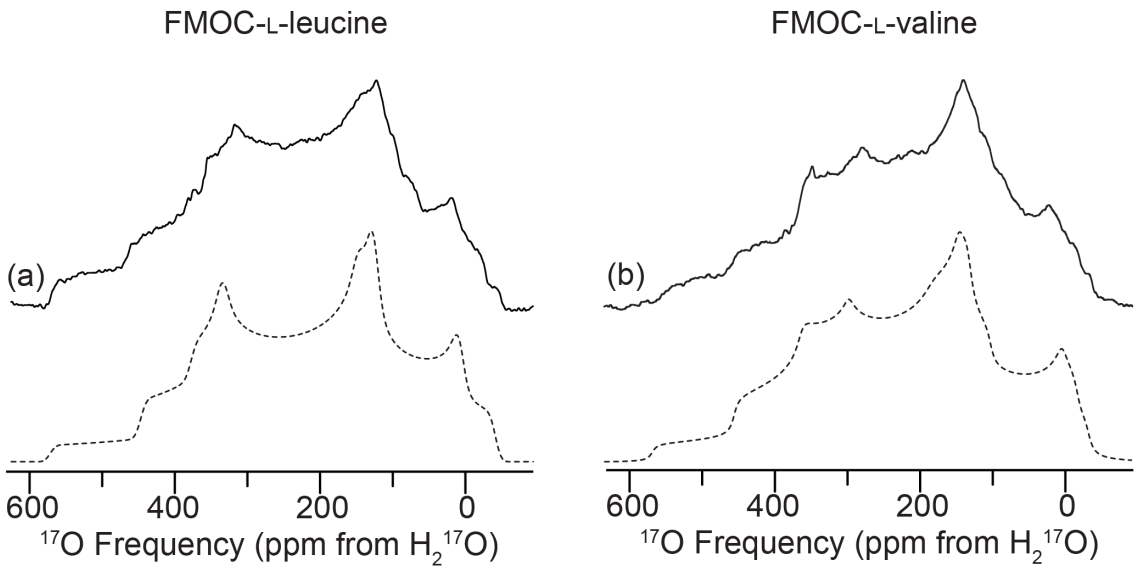

Figure S4: Oxygen-17 experimental (solid) and simulated (dashed) non-spinning NMR spectra of FMOC-L-leucine (a) and FMOC-L-valine (b) at 17.6 T ($\omega_{0H}/2\pi$ = 750 MHz) with $\gamma_{B1}/2\pi$ = 100 kHz continuous-wave ^{1}H decoupling. NMR parameters used in spectral simulations are given in Table 4.

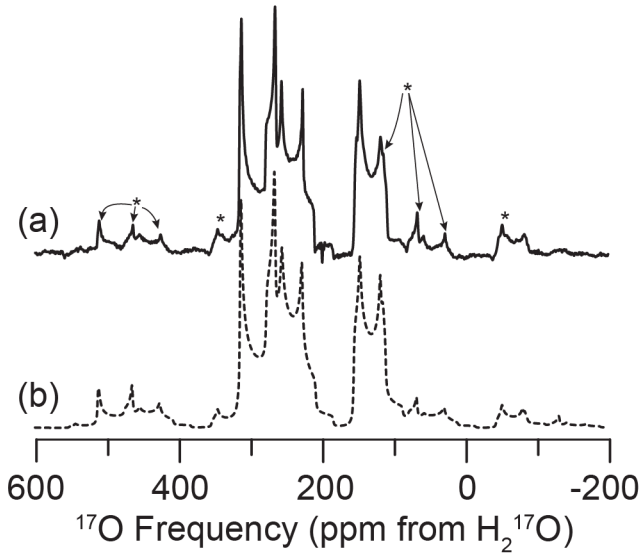

Figure S5: Oxygen-17 MAS NMR spectrum of N-Ac-VL (a), simulation of MAS NMR spectrum (b) at 17.6 T ($\omega_{0H}/2\pi$ = 750 MHz). Spectra were acquired with $\omega_R/2\pi$ = 20 kHz, spinning sidebands are noted by asterisks (*). NMR parameters used in spectral simulations are given in Table 4.

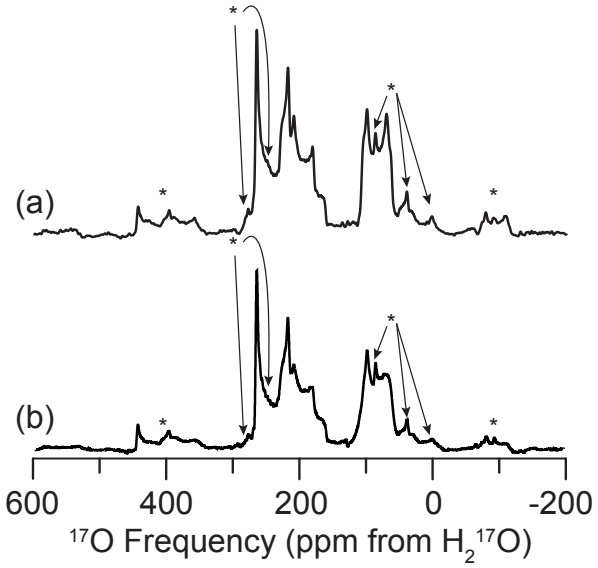

Figure S6: Oxygen-17 MAS NMR spectrum of N-Ac-VL without (a), and with (b) $\gamma B_1/2\pi$ = 100 kHz continuous-wave ^{1}H decoupling at 17.6 T ($\omega_{0H}/2\pi$ = 750 MHz). Spectra were acquired with $\omega_R/2\pi$ = 18 kHz, spinning sidebands are noted by asterisks (*).

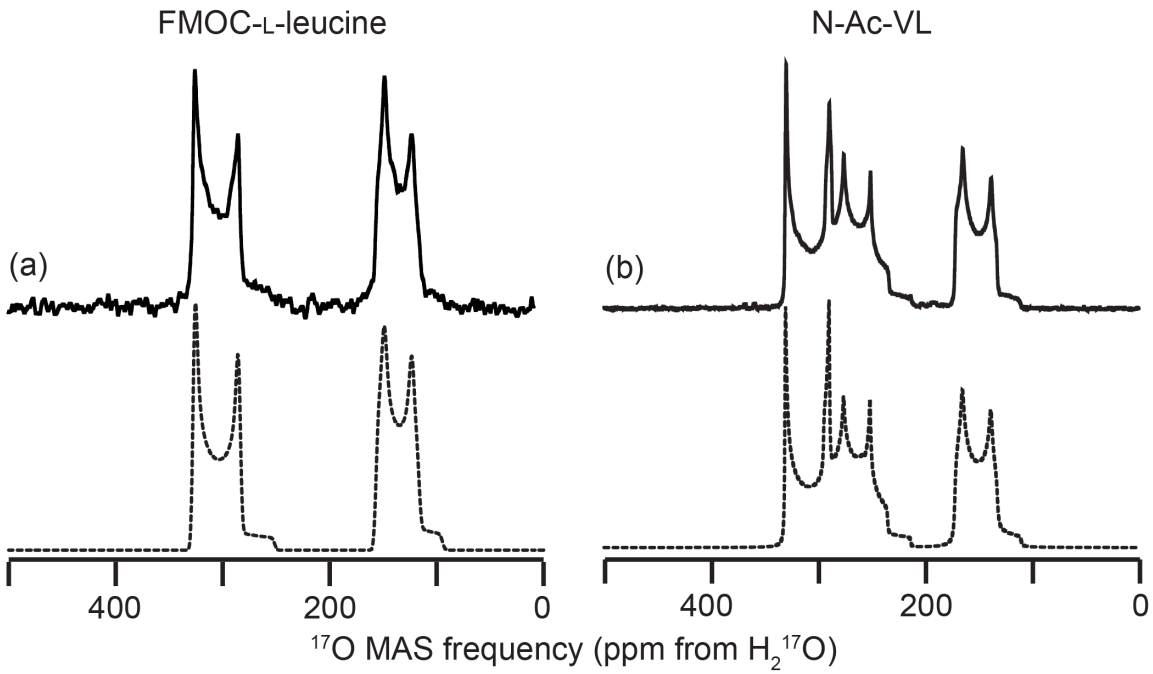

Figure S7: Experimental (solid) and simulated (dashed) ^{17}O MAS NMR of FMOC-L-leucine (a) and N-Ac-VL (b) at 18.8 T ($\omega_{0H}/2\pi$ = 800 MHz). Spectra were acquired with $\omega_R/2\pi$ = 60 kHz. NMR parameters used in spectral simulations are given in Table 4.

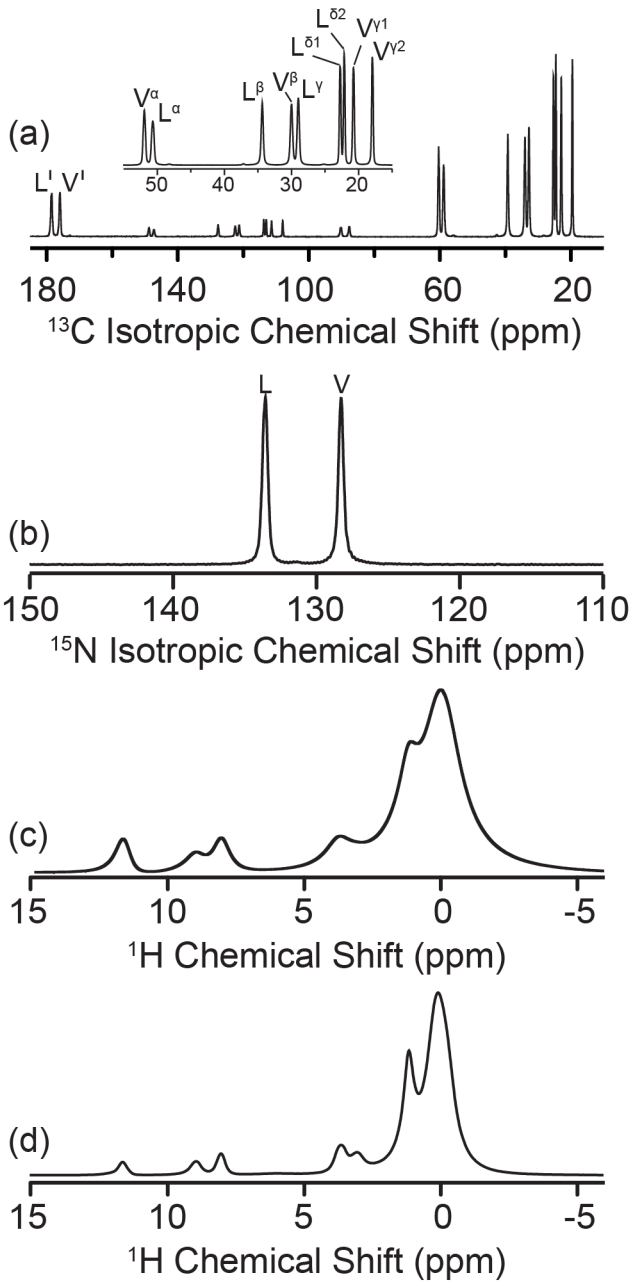

Figure S8: ^{13}C, ^{15}N, and ^{1}H MAS NMR of N-Ac-VL at 21.1 T ($\omega_{0H}/2\pi$ = 900 MHz) with $\omega_R/2\pi$ = 20 kHz. $^{13}C\{^{1}H\}$ CPMAS NMR spectrum (a), $^{15}N\{^{1}H\}$ CPMAS spectrum (b), and ^{1}H MAS NMR spectrum (c). ^{1}H MAS NMR spectrum at 18.8 T with $\omega_R/2\pi$ = 60 kHz (d). Compared to previous NMR studies of N-Ac-VL.[1-3]

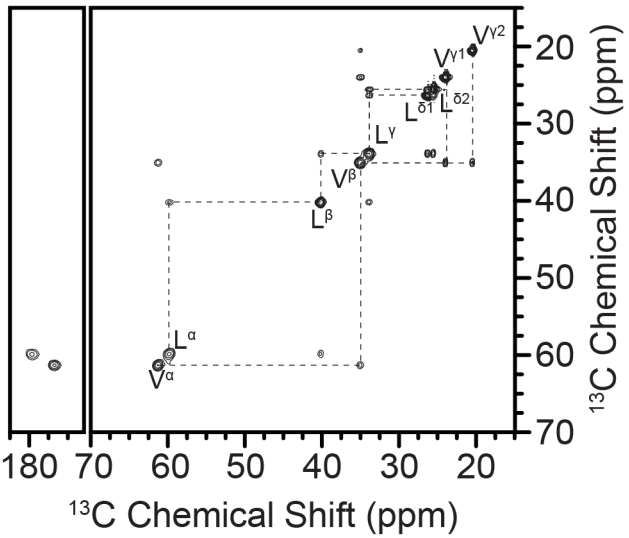

Figure S9: Two-dimensional ^{13}C-^{13}C RFDR spectrum with 1.6 ms mixing at 11.7 T ($\omega_{0H}/2\pi$ = 500 MHz) and $\omega_R/2\pi$ = 10 kHz with $\gamma B_1/2\pi$ = 100 kHz continuous wave ^1H decoupling during evolution and $\gamma B_1/2\pi$ = 100 kHz TPPM ^1H decoupling during acquisition. Compared to previous study of N-Ac-VL.[2]

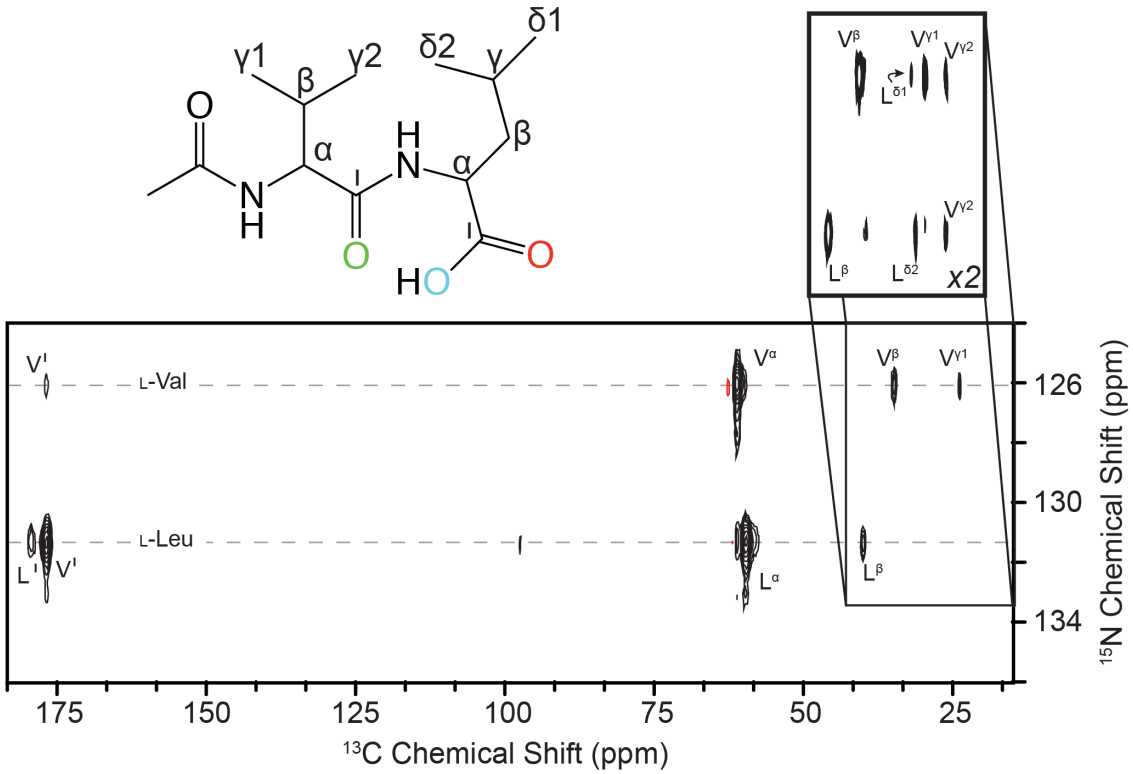

Figure S10: Two-dimensional ^{13}C-^{15}N ZF-TEDOR spectrum with 2.0 ms mixing at 11.7 T ($\omega_{0H}/2\pi$ = 500 MHz) and $\omega_R/2\pi$ = 10 kHz with $\gamma B_1/2\pi$ = 100 kHz TPPM ^1H decoupling during acquisition. Compared to previous study of N-Ac-VL.[2]

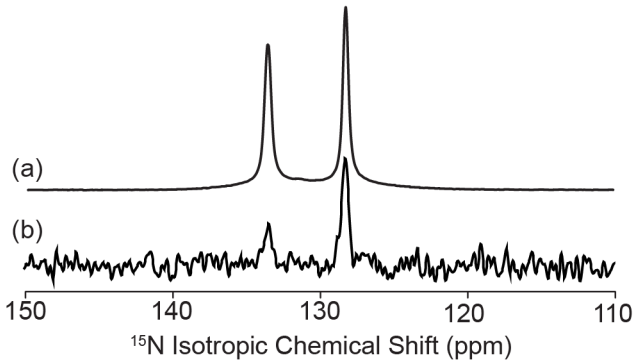

Figure S11: Comparison of 1D ^{15}N CPMAS (a) and ^{15}N-^{17}O ZF-TEDOR with 7.88 ms of mixing (b) at 17.6 T ($\omega_{0H}/2\pi$ = 750 MHz). Spectra acquired with $\omega_R/2\pi$ = 18 kHz, ^{15}N $\gamma B_1/2\pi$ = 36 kHz, and ^{1}H $\gamma B_1/2\pi$ = 100 kHz TPPM decoupling.

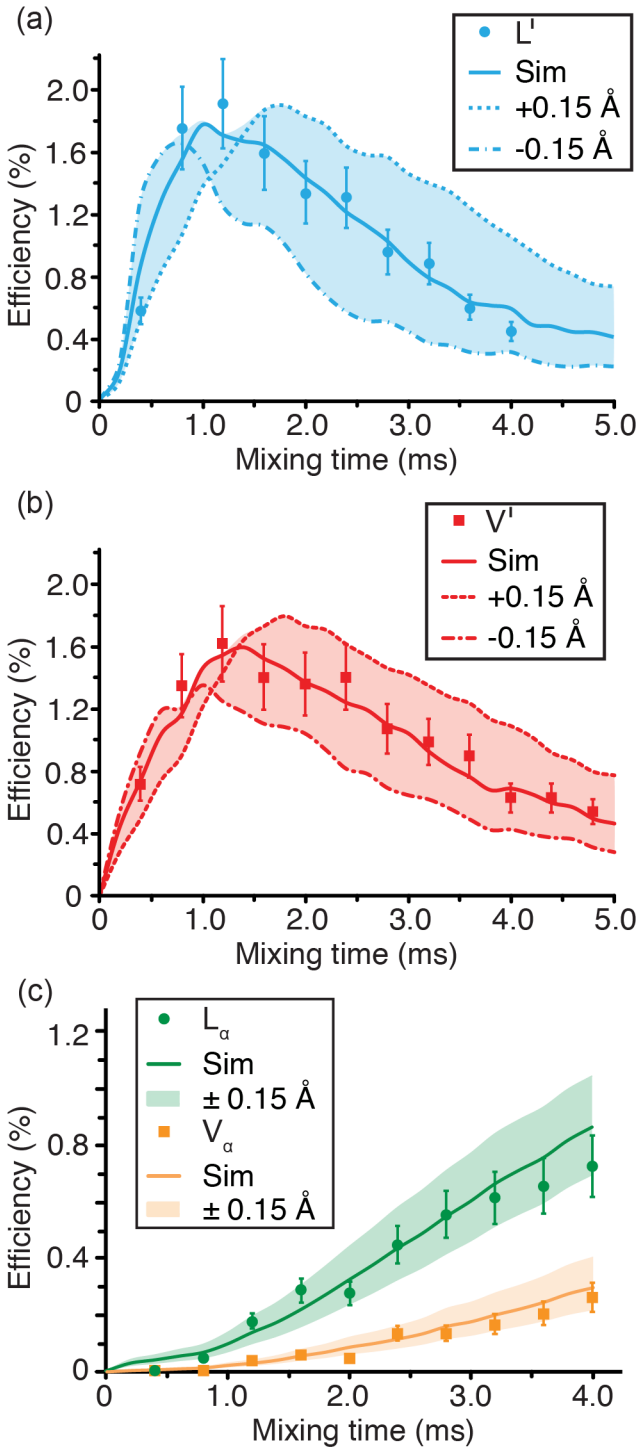

Figure S12: Experimental and simulated, including ± 0.15 Å errors, 1D ^{13}C-^{17}O ZF-TEDOR buildup curves as a function of mixing time for leucine C' (a), valine C' (b), and Cα (leucine, green circles and valine, yellow squares) (c), at 21.1 T ($\omega_{0H}/2\pi$ = 900 MHz) with $\gamma_{B1}/2\pi$ (^{17}O) = 100 kHz, and 100 kHz TPPM ^{1}H decoupling during acquisition. Best fit simulated curves (solid lines) determined using SPINEVOLUTION.[4] Measured ^{13}C-^{17}O distances given in Table 5.

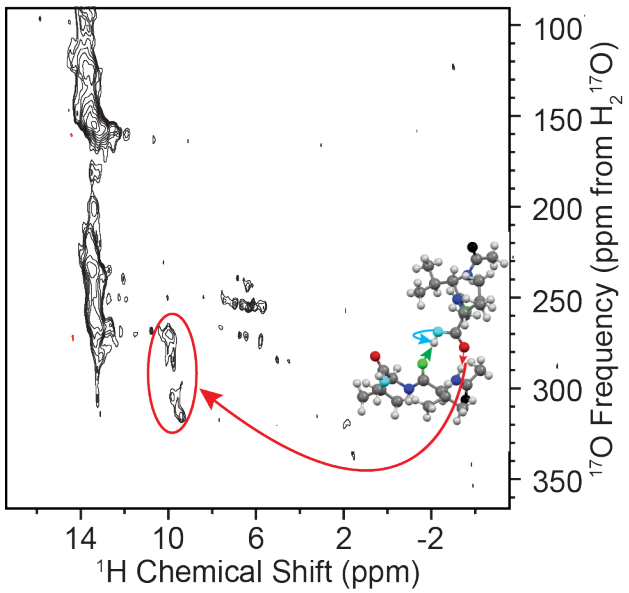

Figure S13: Two-dimensional ^{1}H-^{17}O R^3-R-INEPT spectrum with R^3 = 100 μs. Spectra were acquired with $\omega_R/2\pi$ = 20 kHz at 17.6 T ($\omega_{0H}/2\pi$ = 750 MHz). The correlation, circled in red, between the leucine amide proton to the leucine CO oxygen (red arrow) is indicated on the crystal structure of N-Ac-VL in the inset.[5]

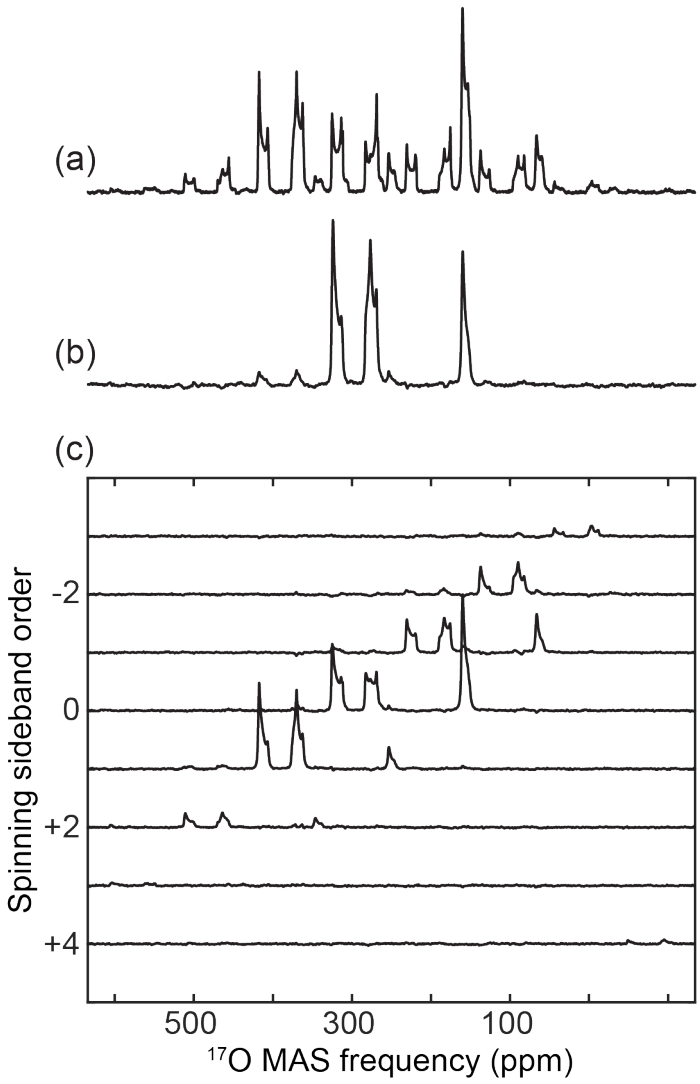

Figure S14: Experimental ^{17}O MAS NMR spectra of N-Ac-VL (a) at 35.2 T ($\omega_{0H}/2\pi$ = 1500 MHz) with $\omega_R/2\pi$ = 19 kHz. Sum projection of the ^{17}O MAS NMR spectrum of N-Ac-VL (b) after shearing transform of the direct dimension of the MATPASS spectrum to yield an axis that is equivalent to an infinite spinning frequency MAS spectrum. Two-dimensional ^{17}O MATPASS spectrum of N-Ac-VL (c) showing the centerband of each oxygen chemical environment for each sideband order.

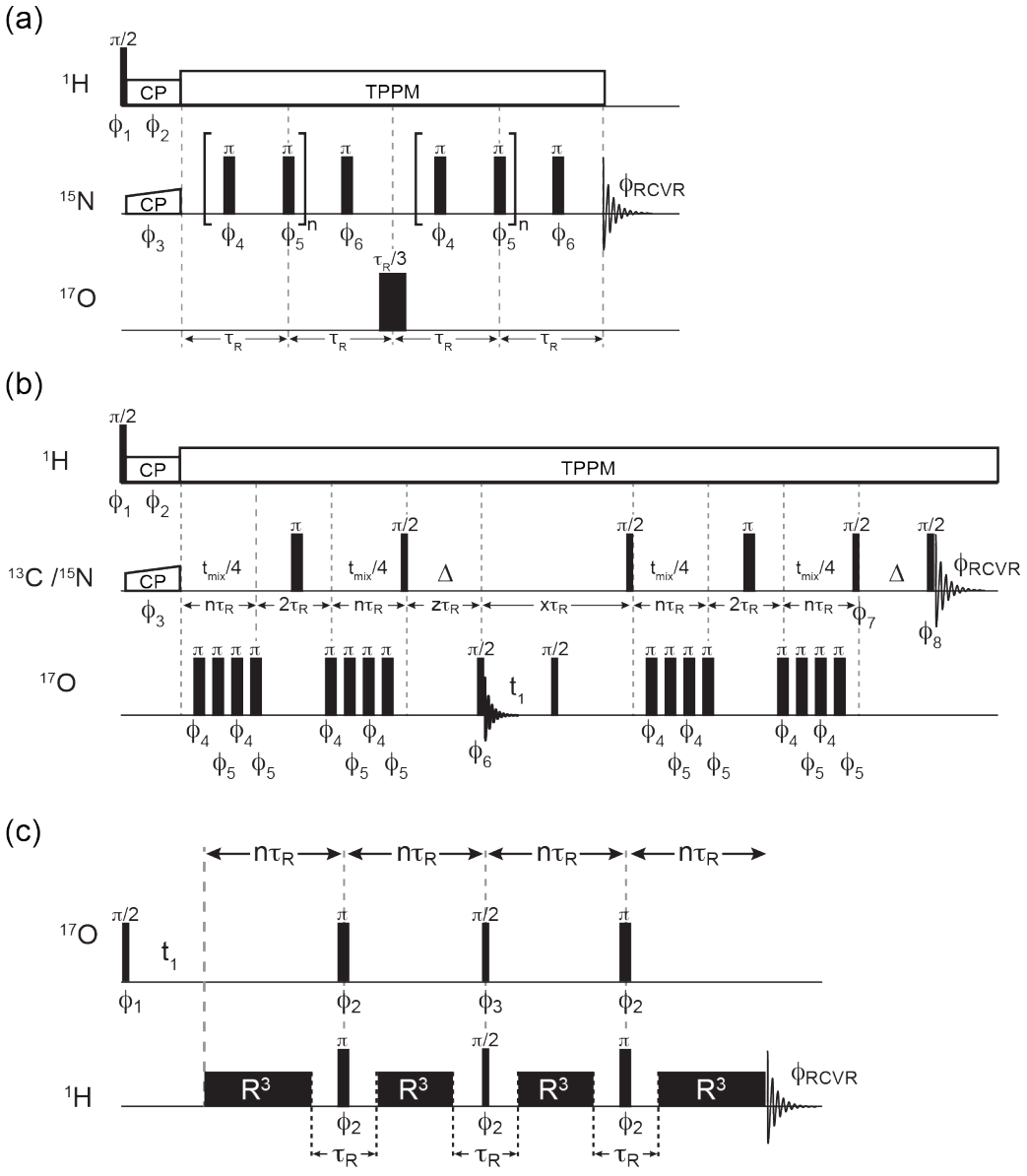

Figure S15: Pulse sequences utilized for correlation experiments. ^{15}N-^{17}O REAPDOR pulse sequence (a), the phase cycle was: ϕ_1 = 13, ϕ_2 = 1, ϕ_3 = 1133 2244, ϕ_4 = 1, ϕ_5 = 2, ϕ_6 = 1133 2244, ϕ_{RCVR} = 1331 2442. ^{15}N/^{13}C-^{17}O ZF-TEDOR pulse sequence (b), the phase cycle was: ϕ_1 = 13, ϕ_2 = 1, ϕ_3 = 2, ϕ_4 = 1, ϕ_5 = 2, ϕ_6 = 13, ϕ_7 = 2244, ϕ_8 = 1111 2222 3333 4444, ϕ_{RCVR} = 4224 1331 2442 3113 2442 3113 4224. ^{1}H-^{17}O R^3-R-INEPT pulse sequence (c), the phase cycle was: ϕ_1 = 1234, ϕ_2 = 1, ϕ_3 = 2, ϕ_{RCVR} = 3412.

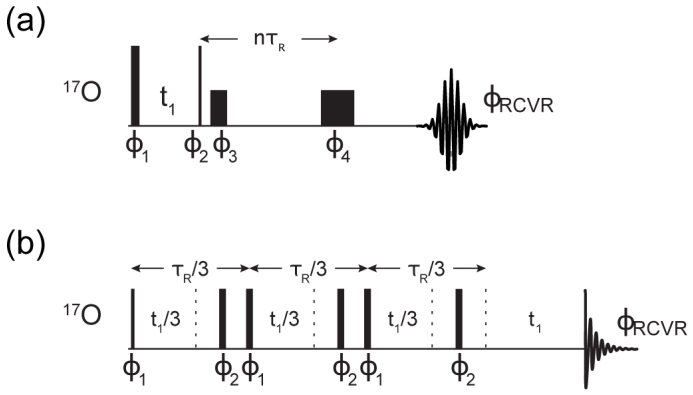

Figure S16: Pulse sequences utilized for ^{17}O NMR experiments at 1500 MHz (^{1}H). Oxygen-17 3QMAS sequence (a), the phase cycle utilized: ϕ_1 = 0°, 30°, 60°, 90°, 120°, 150°, 180°, 210°, 240°, 270°, 300°, 330°; ϕ_2 = 0°; ϕ_3 = 0°; ϕ_4 = (0°)*12, (45°)*12, (90°)*12, (135°)*12, (180°)*12, (225°)*12, (270°)*12, (315°)*12; ϕ_{RCVR} = 1432 1432 1431 2143 2143 2143 3214 3214 3214 4321 4321 4321. ^{17}O MATPASS pulse sequence (b), the phase cycle utilized was a 12-step cogwheel phase cycle: ϕ_1 = 1; ϕ_2 = 0°, 30°, 60°, 90°, 120°, 150°, 180°, 210°, 240°, 270°, 300°, 330°; ϕ_{RCVR} = 1 3.

References

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