

Figure S1. 2D-[^{13}C , ^{13}C]-TOCSY spectrum measured with uniformly ^2H , ^{13}C , ^{15}N -labeled ubiquitin ($T=293\text{K}$, 1.4 mM human ubiquitin at pH 7.3 in 10 mM potassium phosphate buffer and 0.05% w/v sodium azide) recorded on a Bruker Avance spectrometer, equipped with a 5mm DUX 13C-1 probehead and operating at a proton frequency of 900 MHz. In the experimental setup the radio-frequency carrier offsets were placed at 40 ppm (^{13}C) and 174 ppm ($^{13}\text{C}'$). ^2H and ^{15}N was decoupled during both the indirect and direct evolution period. Additionally, bandselective homonuclear $^{13}\text{C}'$ -decoupling was applied during the acquisition period. A detailed protocol of the decoupling technique will be presented in a forthcoming paper. The FLOPSY-16 mixing was applied at $\gamma B_1 = 8.5$ kHz and with $\tau_{\text{mix}} = 16.96$ ms. The 2D-[^{13}C , ^{13}C]-TOCSY in was recorded with $t_{1\text{max}} = 14.1$ ms and $t_{2\text{max}} = 147.5$ ms, an interscan delay

of 1.5 s and 256 x 4096 complex points, resulting in an acquisition time of 18 hours. Before Fourier transformation the time domain data in the t_1 and t_2 dimensions were multiplied with a cosine function and zero-filled to 1024 and 16384 points, respectively. The boxes show the regions which are expanded in Figs. S2 and S3.

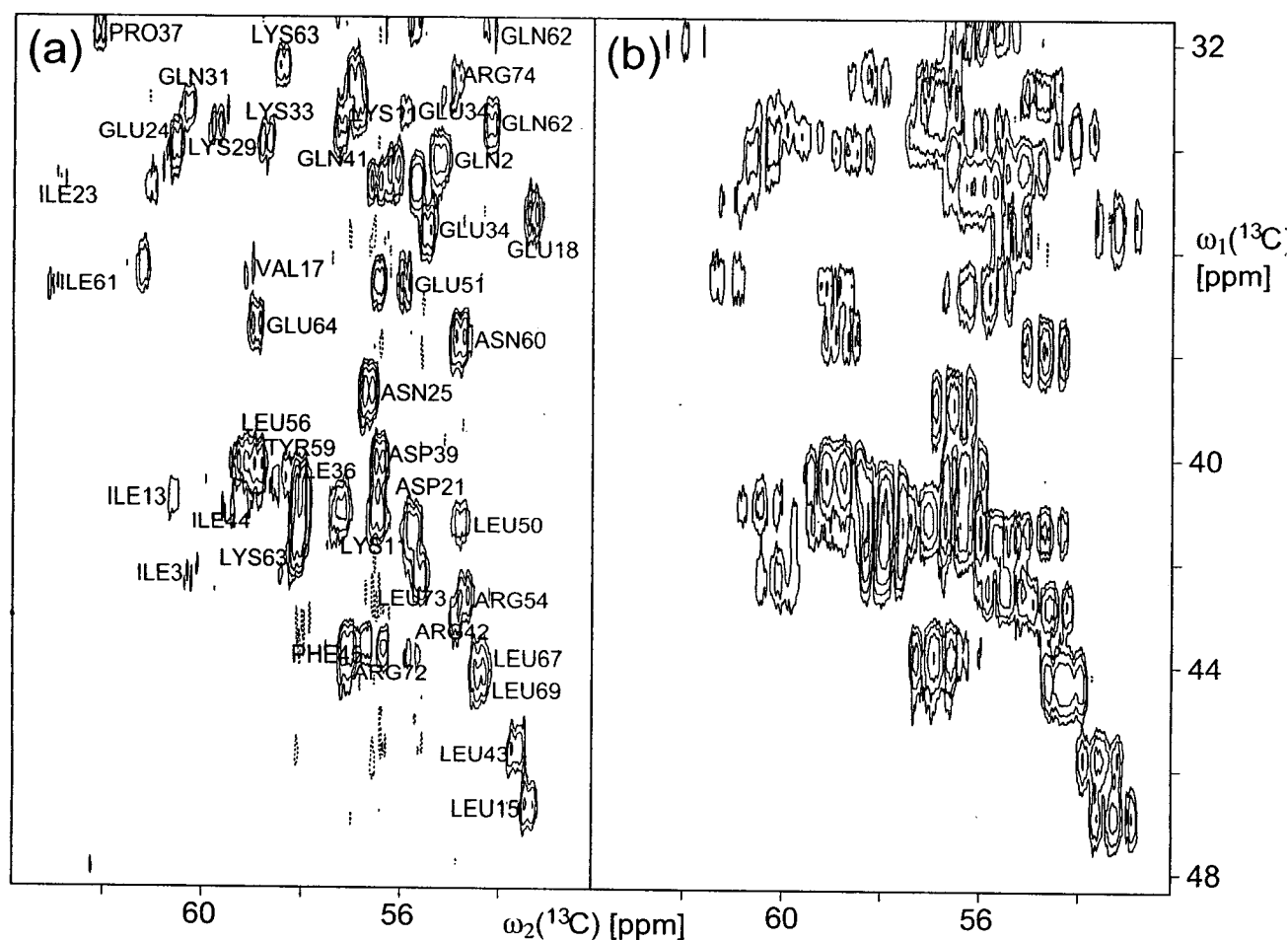


Figure S2. Expansions of the 2D- ^{13}C , ^{13}C -TOCSY spectra of Fig. S1 (a) and Fig. 1 (b) of a region with cross-peaks at C^α frequencies along the direct dimension, measured at 900 MHz and 500 MHz, respectively. Decoupling of ^2H , ^{15}N and ^{13}C applied in (a) results in simplified patterns in the direct dimension.

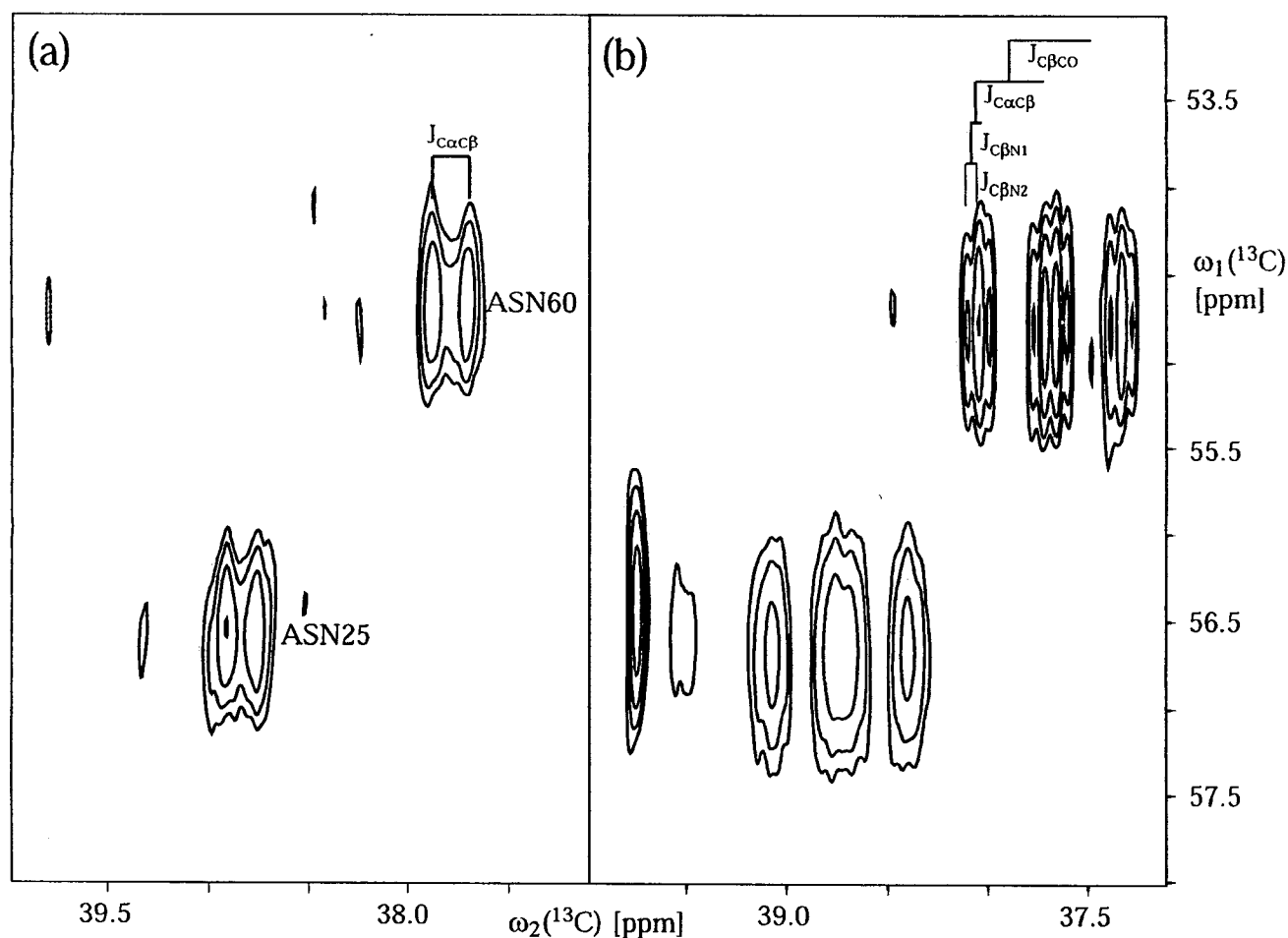


Figure S3. Expansions of the 2D- ^{13}C , ^{13}C -TOCSY spectra of Fig. S1 (a) and Fig. 1 (b) showing the $\text{C}^\beta/\text{C}^\alpha$ -cross-peaks of Asn25 and Asn60 measured at 900 MHz and 500 MHz, respectively. Decoupling of ^2H , ^{15}N and ^{13}C simplifies the splitting pattern along the direct dimension due to $^1J_{\text{C}\beta\text{CO}}$, $^1J_{\text{C}\alpha\text{C}\beta}$, $^2J_{\text{C}\beta\text{N1}}$ and $^2J_{\text{C}\beta\text{N2}}$ (b) to a doublet split by $^1J_{\text{C}\alpha\text{C}\beta}$ only (a), where N1 and N2 stand for ^{15}N in the side-chain and backbone, respectively.