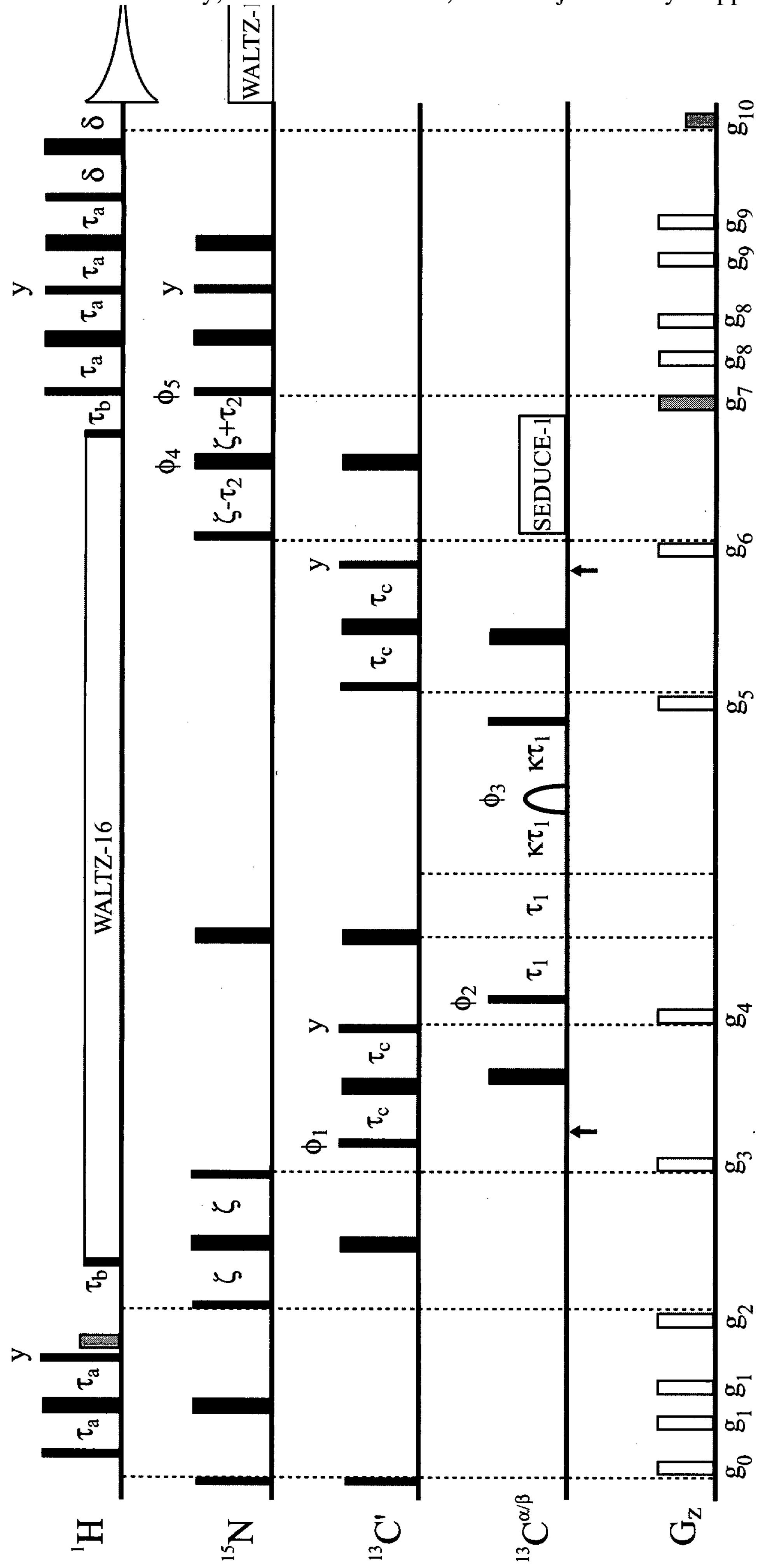
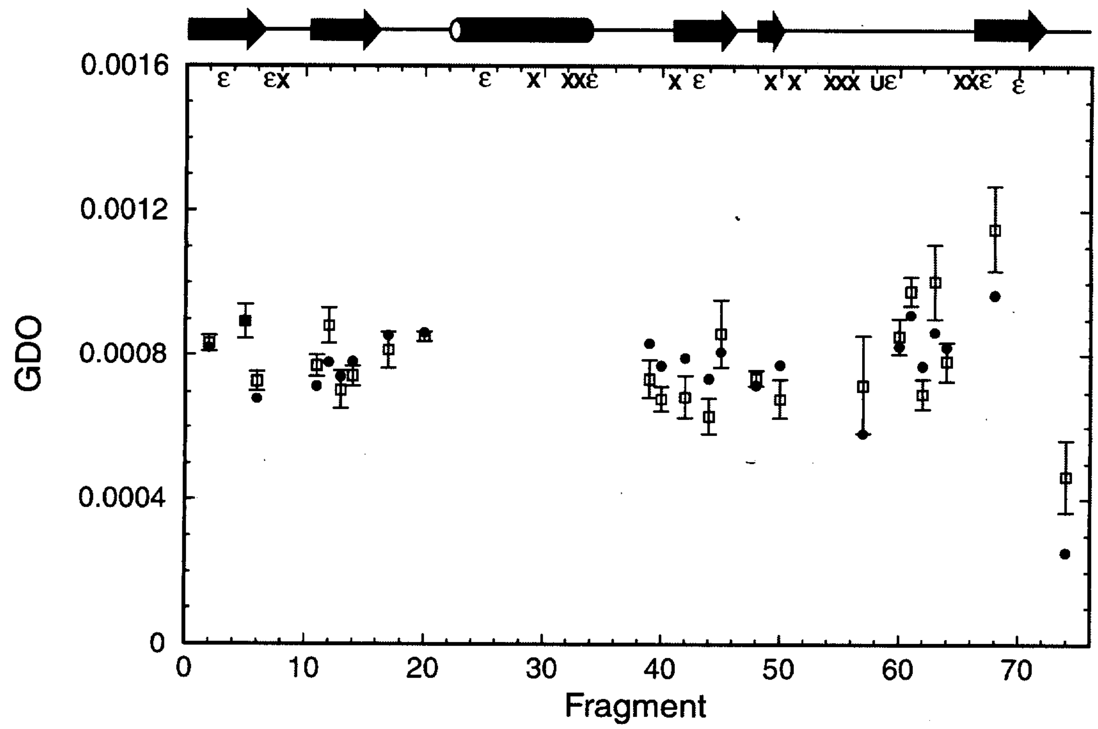
Supplementary material

Figure S1. Pulse sequence used to measure C^{α}-C^{β} one-bond dipolar couplings. Narrow and wide bars denote 90° and 180° pulses, respectively, with a phase of x unless specified otherwise. Immediately following the first INEPT period, a 1.7ms water selective flip back pulse, denoted as a shaded pulse, is applied in order minimize saturation of the water. The ^{13}C carrier is set to 176 ppm, except during the t_1 evolution period and during application of the pair of $^{13}C^{\alpha/\beta}$ pulses, for which the carrier is moved to 43 ppm. With the exception of the inversion pulse during the t_1 evolution period, all $^{13}C'$ pulses are applied on-resonance using a field strength of $\Delta_1/15^{1/2}$ Hz with Δ_1 set to 118 ppm. The C^{α} inversion pulses during the $2\tau_c$ periods are applied off-resonance (118 ppm) using a field strength of $\Delta_1/3^{1/2}$. Bloch-Siegert effects are compensated by application of identical pulses at positions marked by small arrows. The pair of $^{13}C^{\alpha/\beta}$ pulses bracketing the t_1 evolution period, as well as the single $^{13}C'$ inversion pulse during this period are applied (at a frequency of 43 ppm) with a field strength of $\Delta_2/15^{1/2}$ with Δ_2 set to 133 ppm. The $^{13}C^{\alpha/\beta}$ selective REBURP pulse, used to implement a coupling enhancement scheme, is applied at the same frequency for a duration of 400 μs. A WALTZ-16 cycle using the SEDUCE-1 profile is used (340 μs, cosine-modulated at a frequency of 118ppm) for decoupling of the C^{α} nuclei during the ^{15}N evolution period. Decoupling of ^{15}N during acquisition is carried out using WALTZ-16 with a 1 kHz field. Delays are set as follows: $\tau_a = 2.3$ ms; $\tau_b = 5.5$ ms; $\tau_c = 4.6$ ms; $\zeta = 12.4$ ms; $\delta = 500$ μs; $\tau_1 = t_1/2$; $\tau_2 = t_2/2$. The phase cycling employed is: $\phi_1 = 4(x, -x)$; $\phi_2 = 8(x)$; $\phi_3 = 2(x, -x, y, -y)$; $\phi_4 = 4(x)4(-x)$; $\phi_5 = 8(x)$; and $\phi_{rec} = 2(x, -x, -x, x)$. Quadrature is achieved in t_1 using the method of States-TPPI (ϕ_2) and in t_2 using sensitivity-enhanced gradient coherence selection (g_7, ϕ_5). Applied gradient pulses are rectangular in shape with coherence selection gradients shaded. The gradient strengths and durations are: g_0 = (500 μs, 8 G/cm); g_1 = (500 μs, 5 G/cm); g_2 = (1 ms, 15 G/cm); g_3 = (1.5 ms, 10 G/cm); g_4 = (1 ms, 8 G/cm); g_5 = (1.2 ms, -15 G/cm); g_6 = (1 ms, 10 G/cm); g_7 = (1.25 ms, 30 G/cm); g_8 = (400 μs, 5 G/cm); g_9 = (300 μs, 4 G/cm); g_{10} = (125 μs, 29 G/cm). The parameter κ is set according to the desired degree of coupling enhancement. Actual couplings are obtained from measured splittings after division by a factor of $(\kappa + 1)$.



^{1}H
^{15}N
$^{13}C'$
$^{13}C^{\alpha/\beta}$
G_z
WALTZ-16
WALTZ-1
SEDUCE-1
τ_a
τ_b
τ_c
τ_1
$\kappa\tau_1$
ζ
$\zeta-\tau_2$
$\zeta+\tau_2$
δ
y
ϕ_1
ϕ_2
ϕ_3
ϕ_4
ϕ_5
g_0 g_1 g_1 g_2 g_3 g_4 g_5 g_6 g_7 g_8 g_8 g_9 g_9 g_{10}

S2



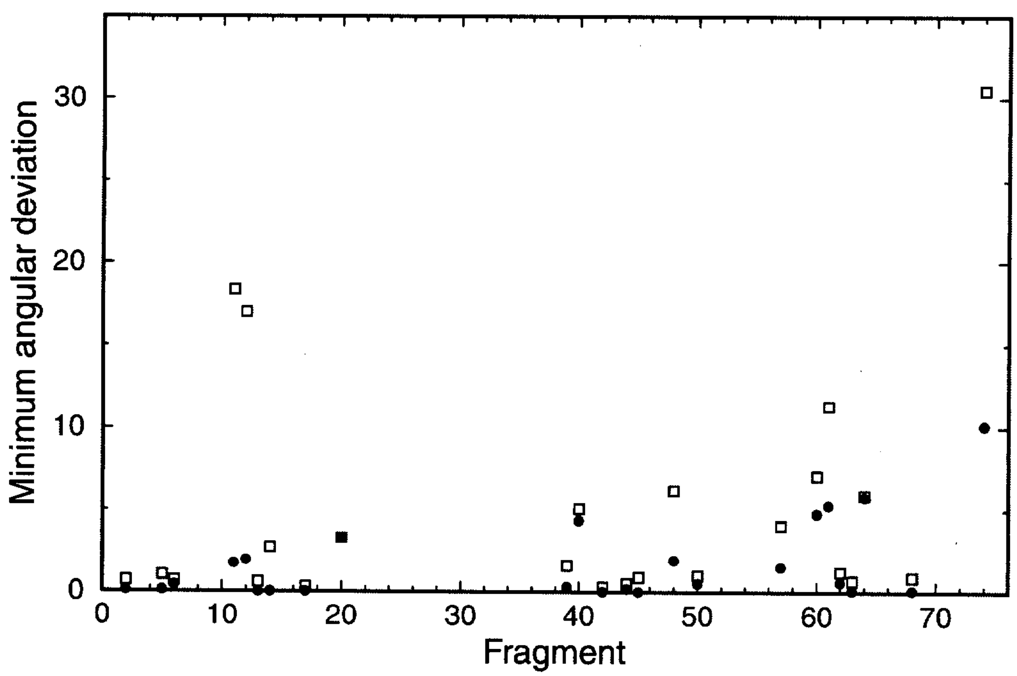


Figure S2. Summary of orientational results and the generalized degree of order obtained using the NMR structural coordinates of ubiquitin (Cornilescu, et. al., 1998; PDB: 1D3Z, model 1) as reference and to supply the input fragment geometries. The symbols used are identical to those employed for Figures 6 and 7 within the text.