

## Supporting Information

**Figure S1.** Comparison of the region of the diamagnetic-optimized (A) and paramagnetic-optimized (B)  $^{13}\text{C}\{^{13}\text{C}\}$  CT-COSY spectra of  $[\text{U-}^{13}\text{C}, ^{15}\text{N}]\text{-HuFd}_{\text{ox}}$  that contains the  $\text{C}'\text{-C}^{\alpha}$  crosspeaks of Gly. Sample conditions and acquisition parameters are given in the caption to Fig. 4.

**Figure S2.** Comparison of the region of the diamagnetic-optimized (A and C) and paramagnetic-optimized (B and D)  $^{13}\text{C}\{^{13}\text{C}\}$  CT-COSY spectra of  $[\text{U-}^{13}\text{C}, ^{15}\text{N}]\text{-HuFd}_{\text{ox}}$  that contains the  $\text{C}'\text{-C}^{\alpha}$  and  $\text{C}^{\alpha}\text{-C}^{\beta}$  crosspeaks of Leu50. Sample conditions and acquisition parameters are given in the caption to Fig. 4.

### Detailed Description of the PRE-HSQC and PRE-CT-(H)CCH-COSY Pulse Sequences (Fig. 9).

(A) PRE-HSQC pulse sequence. Pulse phases are along the x-axis unless otherwise specified. The phase cycle is:  $\phi 1 = 4 (x), 4(-x)$ ;  $\phi 2 = x, -x$ ;  $\phi 3 = 2 (x), 2 (-x)$ ;  $\Psi = x, -x, -x, x$ . The pulsed field gradients are sinebell in shape and of the following durations (in  $\mu\text{s}$ ) and strengths (along the x, y, and z axes, in G/cm):  $g1 = 600, (17.5, 0, 0)$ ;  $g2 = 300, (3.5, 3.5, 3.5)$ ;  $g3 = 300, (38, 0, 21)$ ;  $g4 = 370, (0, 0, 8.5)$ ;  $g5 = 670, (0, 0, 20.5)$ ;  $g6 = 300, (0, 10.5, 10.5)$ ;  $g7 = 670, (0, 0, 24)$ . Spectra were acquired as phase-sensitive data with State-TPPI by incrementation of  $\phi 2$ . (B) PRE-CT-(H)CC-COSY pulse sequence. Pulse phases are along the x-axis unless otherwise specified. The phase cycle is:  $\phi 1 = 8 (x), 8 (-x)$ ;  $\phi 2 = 4 (x), 4 (y), 4 (-x), 4 (-y)$ ;  $\phi 3 = y, -y$ ;  $\phi 4 = 2 (x), 2 (y), 2 (-x), 4 (-y)$ ;  $\phi 5 = 4 (x), 4 (-x)$ ;  $\phi 6 = x$ ;  $\phi 7 = 16 (x), 16 (-x)$ ;  $\Psi = x, -x, -x, x, -x, x, x, -x, -x, x, x, -x, x, -x, -x, x$ . The pulsed field gradients are of the same shape, durations, and strengths as in (A). Spectra were acquired as phase-sensitive data

with State-TPPI by incrementation of  $\phi_6$  in the first indirect  $^{13}\text{C}$  dimension and by incrementation of  $\phi_5$  and  $\phi_6$  in the second indirect  $^{13}\text{C}$  dimension.