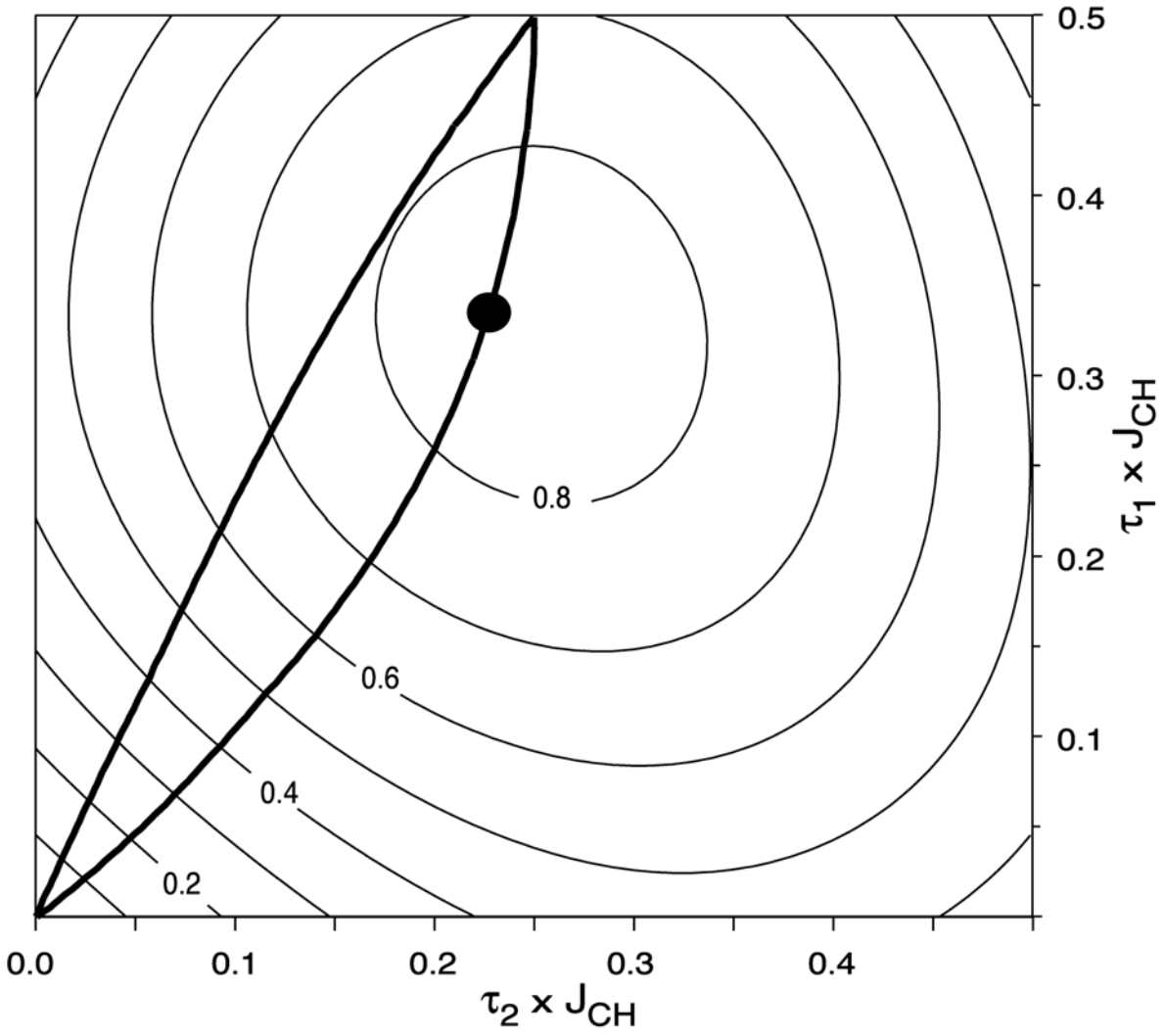

Figure S1. Evaluation of the transfer efficiency as a function of delays τ_1 and τ_2. The transfer efficiency ranges from 0 to 0.85, where 1 represents the transfer efficiency of sensitivity-enhanced HSQC optimized for $^{13}CH_2$ (Schleucher, J.; Schwendinger, M.; Sattler, M.; Schmidt, P.; Schedletzky, O.; Glaser, S. J.; Sørensen, O. W.; Griesinger, C. *J. Biomol. NMR* **1994**, *4*, 301-306). The bold lines correspond to pairs of τ_1 and τ_2 that yield spin-state-selective transfer from ^{13}C to ^{1}H. The solid dot corresponds to delays for which the CH_2-TROSY transfer efficiency is at a maximum.

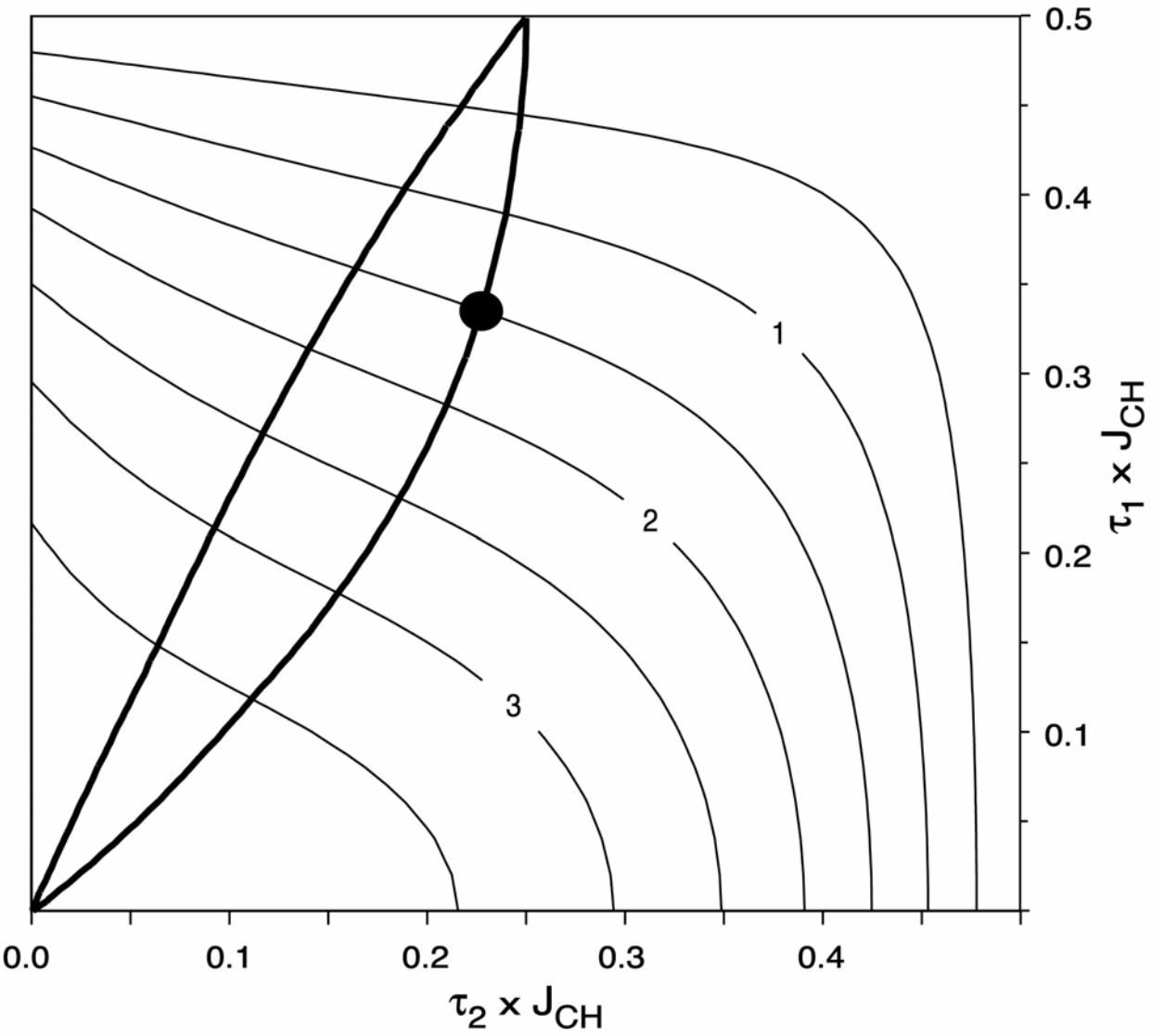

Figure S2. Contour plot showing the relative intensity of the signal at the ^{13}C frequency δ_c, corresponding to transitions C^{+-} and C^{-+}. Values reported on the graph represent the relative intensity in % of this spurious peak compared to the selected correlation when using the pulse scheme of Figure 2a. The bold lines correspond to pairs of τ_1 and τ_2 that yield spin-state-selective transfer from ^{13}C to ^{1}H. The solid dot corresponds to delays for which the CH_2-TROSY transfer efficiency is at a maximum.

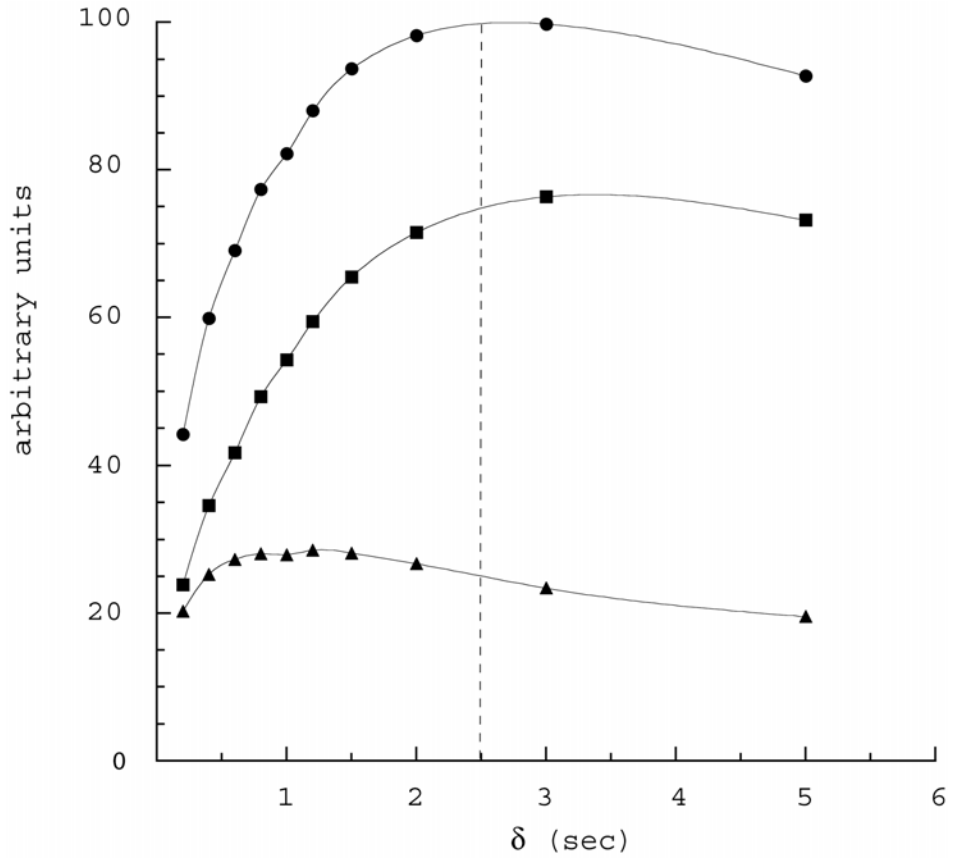

Figure S3. Average sensitivity per unit of measuring time for Gly correlations in the CaM/M13 system, recorded with the CH_2-TROSY pulse scheme at 800 MHz, 35 °C. The intensities, normalized for equal measuring times, are plotted as a function of the recycle delay δ, for cases where only ^{1}H spin polarization is used (■), only ^{13}C polarization (▲), or the sum of both ^{1}H and ^{13}C (●). Destruction of either the ^{1}H (for ▲) or ^{13}C (for ■) polarization, immediately prior to the start of the Figure 2a pulse scheme, was accomplished by a 90° ^{1}H or ^{13}C pulse, followed by a pulsed field gradient.

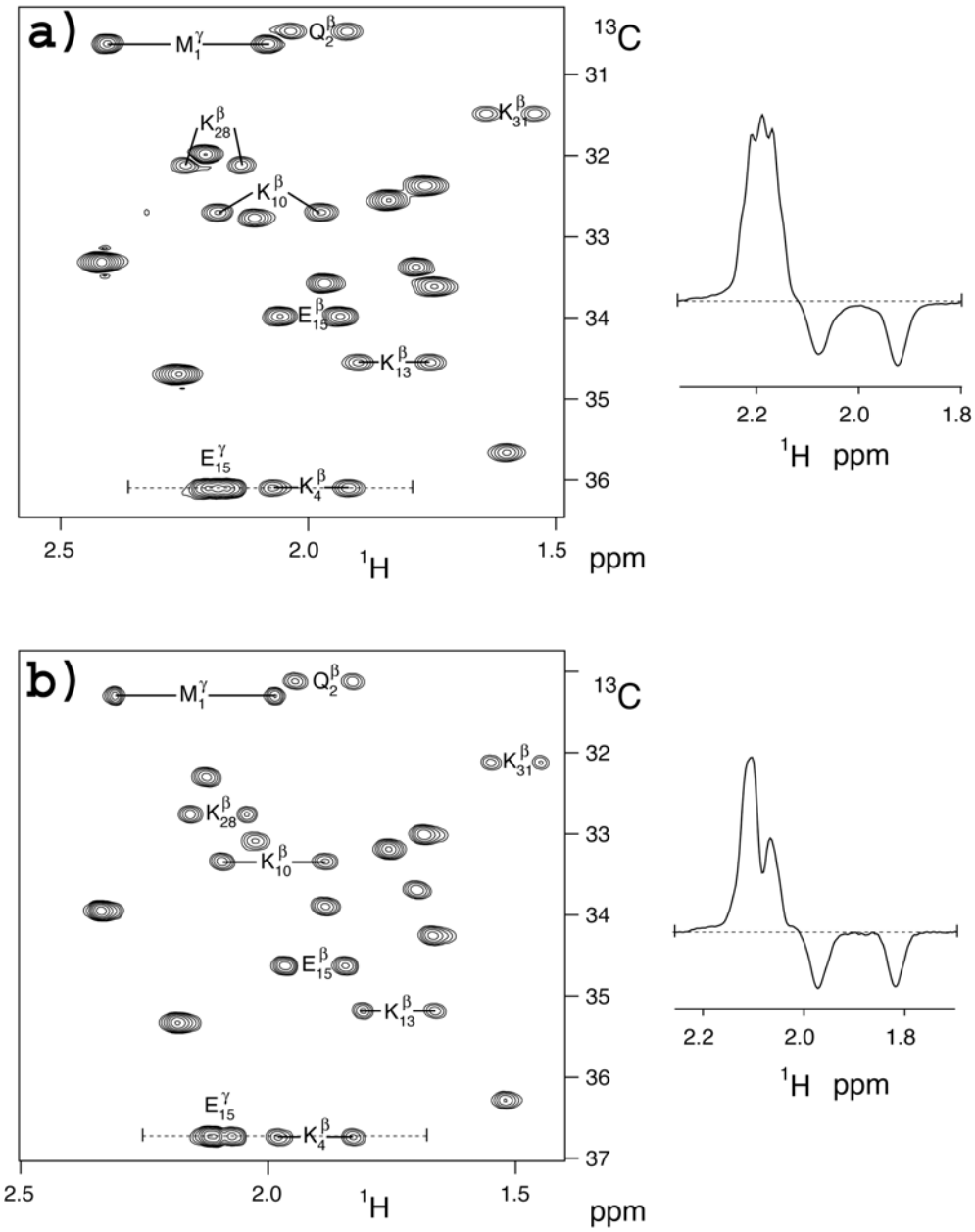

Figure S4. Comparison of **(a)** sensitivity-enhanced HSQC and **(b)** CH_2-TROSY spectra of GB3, at 800 MHz, 10 °C. Assignments are indicated for methylene side chain groups with resolved ^{1}H chemical shifts. Both experiments have been recorded in the constant-time (CT) mode (using a CT ^{13}C evolution period of $1/^1J_{CC} \approx 28$ ms) (Vuister, G. W.; Bax, A. *J. Magn. Reson.* **1992**, *98*, 428-435), with a total measuring time of 1 h per spectrum. Spectra result from identical time domain matrices, consisting of 340*(t_1) × 1350*(t_2) data points, corresponding to acquisition times of 28 ms and 120 ms respectively. Data were processed identically: without apodization in the t_2 dimension, and with a 90° shifted sine bell in the t_1 dimension. Spectra are plotted at the same contour levels. ^{1}H cross-sections through the Glu-15 $C^\gamma H^\gamma_2$ correlation show that only the CH_2-TROSY experiment allows one to distinguish the two proton chemical shifts. Cross sections shown on the right correspond to the dashed lines in panels (**a**) and (**b**).