

Table. $R_{1\rho}(^{19}\text{F})$ values measured in CPMG experiments with different spacing between 180° pulses and comparison with R_2^* values.^a

Sequence position and stereospecific assignment	GB1-d, $R_{1\rho}$ with 1250 Hz CPMG ^b	GB1-d, $R_{1\rho}$ with 31 Hz CPMG ^c	GB1-d-D, $R_{1\rho}$ with 1250 Hz CPMG ^d	GB1-d, R_2^* ^e
5, $\delta 2$	31 (1)	37 (3)	15 (1)	53
7, $\delta 2$	15.9 (0.2)	25 (1)	10 (1)	24
12, $\delta 2$	8.3 (0.5)	11.7 (0.2)	3.1 (0.5)	23
12, $\delta 1$	6.8 (0.4)	8.6 (0.1)	3.7 (0.5)	23
59, $\delta 1$	7.3 (0.2)	12.5 (0.7)	4.9 (0.3)	21
59, $\delta 2$	7.8 (0.7)	11.2 (0.4)	3.6 (0.4)	21
7, $\delta 1$	13.6 (0.2)	26 (1)	9.1 (0.4)	29
5, $\delta 1$	37 (1)	33 (4)	20 (1)	56

^a Measured on a 400 MHz NMR spectrometer. $R_{1\rho}$ and R_2^* values given in s^{-1} , showing the standard deviation of fitting in brackets. R_2^* values were determined by measuring the full width at half height in 1D ^{19}F -NMR spectra (in Hz) and multiplying by π . GB1-d refers to the samples made with diFLeu residues. GB1-d-D refers to samples made with diFLeu residues, where all five protons of the isopropyl group are replaced by deuterium.

^b Using 0.4 ms spacing between 180° pulses. Relaxation delays used were 0.8, 16.8, 32.8, 40.8, 56.8, 72.8, 88.8, 104.8 ms.

^c Using 16 ms spacing between 180° pulses. Relaxation delays used were 32, 48, 64, 80, 96, 112, 128, 144 ms.

^d Using 0.4 ms spacing between 180° pulses. Relaxation delays used were 0.8, 7.2, 13.6, 20, 26.4, 32.8 39.2, 45.6, 52, 58.4, 64.8, 71.2, 77.6 ms.

^e 1D ^{19}F -NMR spectrum measured with 2800 Hz GARP decoupling of ^1H during 144 ms data acquisition.

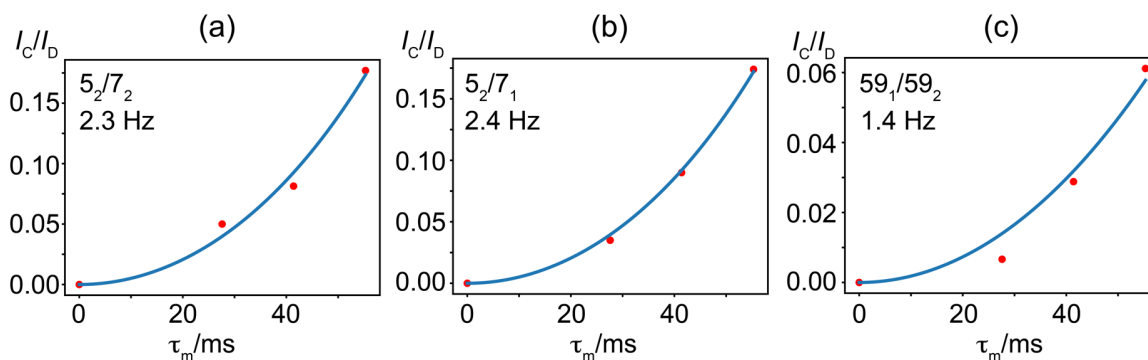


Figure. Plots of the function $I_C/I_D = \tan^2(\pi J_{FF}\tau_m)$ versus the TOCSY mixing time τ_m for three cross-peaks between CD_2F groups in GB1-d made with the diFLeu version, where all five protons of the isopropyl group are replaced by deuterium (Figure S4). I_C and I_D denote the integrals of, respectively, the cross-peaks and diagonal peaks measured in a one-dimensional cross-section. The cross-peaks are between residues 5 and 7 (a and b), and within the solvent-exposed residue 59 (c). Subscripts report the stereospecific assignments of the CD_2F groups. The J_{FF} couplings determined from best fits are indicated. The fits were based on the simplifying approximation of a 2-spin system, where the cross-peak intensity grows with $\sin^2(\pi J_{FF}\tau_m)$ and the diagonal peak decays with $\cos^2(\pi J_{FF}\tau_m)$ (Braunschweiler and Ernst, 1983).

Reference

Braunschweiler, L. and Ernst, R. R.: Coherence transfer by isotropic mixing – application to proton correlation spectroscopy, J. Magn. Reson. 53, 512–528, [https://doi.org/10.1016/0022-2364\(83\)90226-3](https://doi.org/10.1016/0022-2364(83)90226-3), 1983.