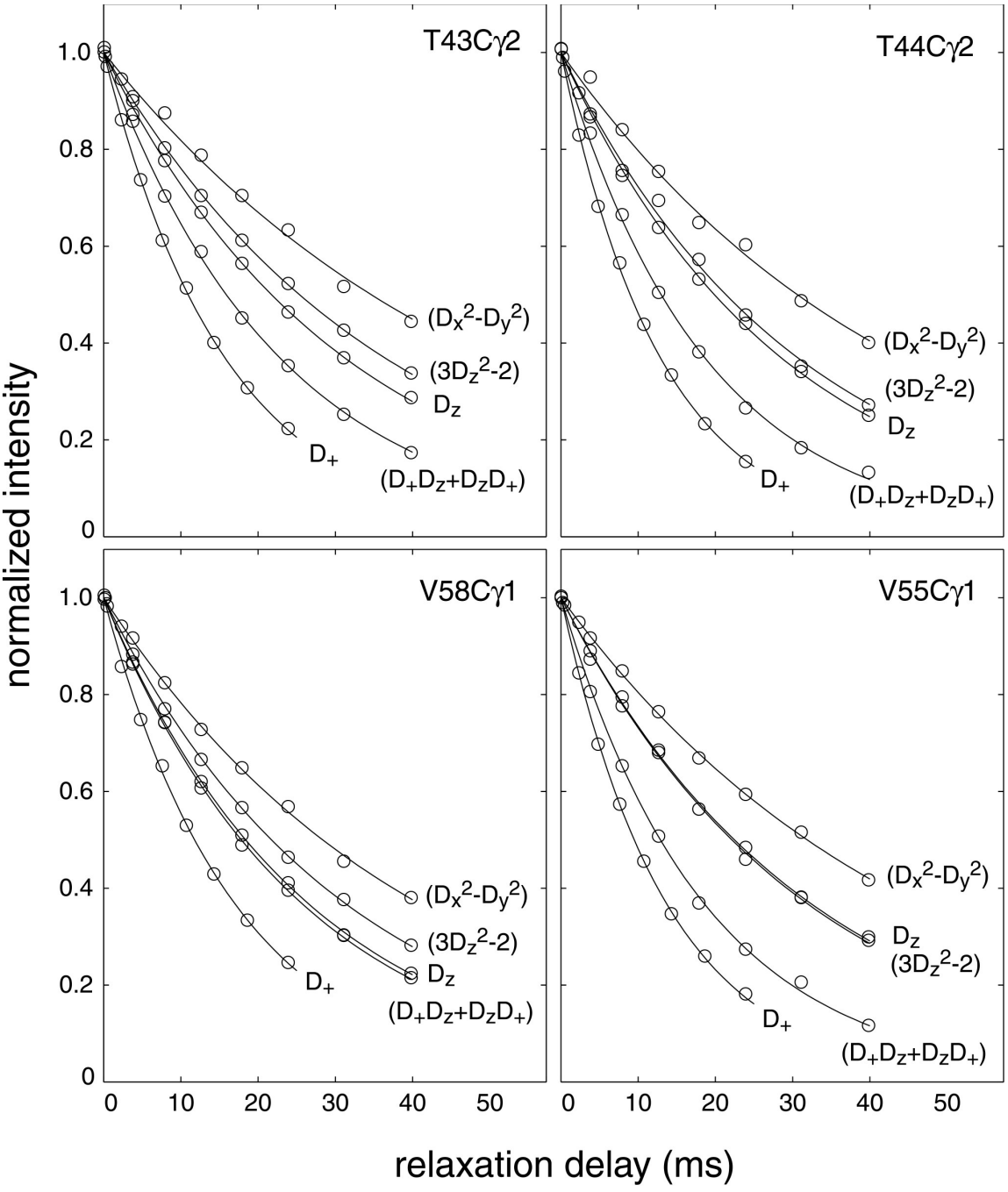
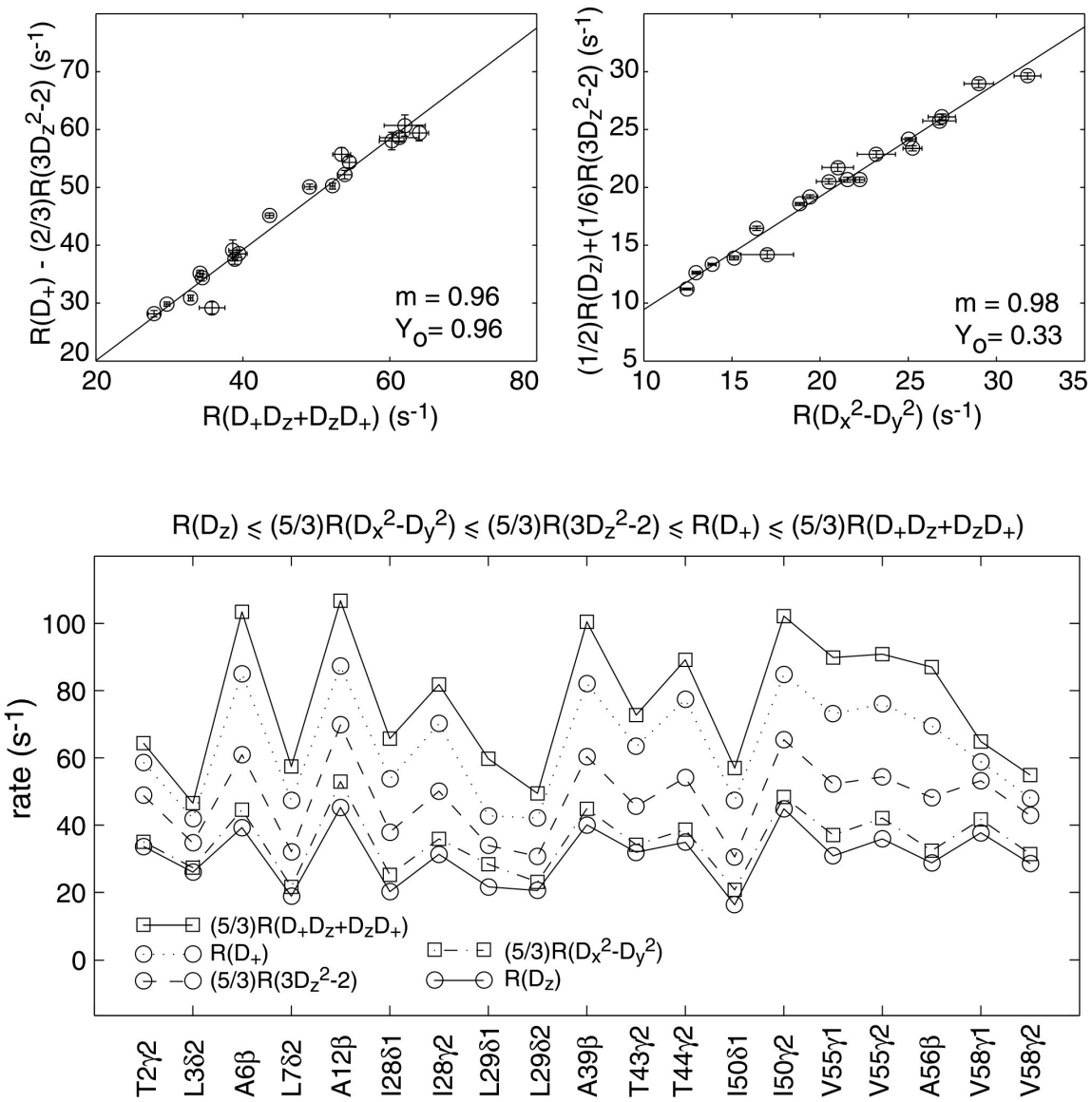


Supplemental Figure 1. Plots of peak volume as a function of relaxation delay for five deuterium spin operators from $^{13}CH_2D$ methyl groups in the SH3 domain of the Fyn tyrosine kinase (chicken isoform), isotopically labeled with ^{15}N, ^{13}C and ≈50% ^{2}H.



Supplemental Figure 2. Graphical verification of equality relationships that exist within the set of five deuterium relaxation rates, top panels, establishing the consistency of the experimental data. The experimental relaxation rates of a given spin operator are designated by R(spin operator). For any given deuterium nucleus, the experimentally determined rate indicated on the X axis should be equal to the linear combination of experimental rates indicated on the Y axis. Straight lines were fit to the data by linear regression and follow the equation $Y = Y_0 + mX$. Graphical verification of inequality relationships between experimental deuterium relaxation rates, bottom panel. The inequalities are listed at the top of the panel. Consistency is verified when the five lines do not to cross.

Supplemental Table 1. Methyl axis order parameters and normalized order parameters for the SH3 domain from Fyn tyrosine kinase.

methyl	S^2_{axis} [a]	δS^2_{axis} [b]	S^2_{norm} [c]
T2 Cγ2	0.45	0.02	-1.90
L3 Cδ2	0.31	0.01	-0.77
A6 Cβ	0.91	0.03	
L7 Cδ2	0.56	0.01	0.47
A12 Cβ	0.85	0.02	
I28 Cδ1	0.66	0.01	1.08
I28 Cγ2	0.76	0.01	0.39
L29 Cδ1	0.43	0.02	-0.18
L29 Cδ2	0.42	0.01	-0.23
A39 Cβ	0.85	0.02	
T43 Cγ2	0.61	0.01	-0.73
T44 Cγ2	0.82	0.02	0.78
I50 Cδ1	0.60	0.01	0.77
I50 Cγ2	0.79	0.02	0.68
V55 Cγ1	0.82	0.01	1.07
V55 Cγ2	0.79	0.01	0.90
A56 Cβ	0.83	0.01	
V58 Cγ1	0.42	0.01	-1.17
V58 Cγ2	0.39	0.01	-1.34

[a]Methyl axis order parameters calculated from five deuterium relaxation rates using the simplest Lipari-Szabo model[1] and a global correlation time obtained from backbone ^{15}N relaxation data (3.35 ns).
[b]Experimental uncertainties in methyl axis order parameter values determined by Monte Carlo propagation of uncertainties in experimentally determined relaxation rates.
[c]Normalized methyl axis order parameters calculated using Equation 2 in the text. Alanine residues have not been included since they reflect motions of the backbone.

1)Lipari, G.; Szabo, A. *J. Am. Chem. Soc.* **1982,** *104*, 4546-4559.

Supplemental Table 2. Means and standard deviations of S^2_{axis} values

methyl	μ_{meth} [a]	σ_{meth} [b]	**sample**[c]
Ala Cβ	0.81	0.10	46
Thr Cγ2	0.72	0.14	22
Val Cγ1,2	0.63	0.18	52
Ile Cγ2	0.71	0.11	30
Ile Cδ1	0.47	0.20	33
Leu Cδ1,2	0.47	0.20	92
Met Cε	0.22	0.12	17

[a]Mean of S^2_{axis} values for a given methyl type in a database of eight proteins[2].
[b]Standard deviation of S^2_{axis} values for a given methyl type.
[c]Number of methyl groups used.

2)Mittermaier, A.; Kay, L. E.; Forman-Kay, J. D. *J. Biomol. NMR* **1999,** *13*, 181-185.