Supporting Information

Table S1. $^{1}H(^{13}CH_3)$- and $^{2}H(^{13}CH_2D)$-derived S^2_{axis} values of Ile, Leu, Val methyl groups in protein L (5 °C).[a)]

Methyl		^{1}H-derived	^{2}H-derived [b)]
V2	γ2	0.72(0.02)	0.72(0.02)
I4	δ1	0.41(0.08)	0.39(0.08)
L8	δ1	0.20(0.06)	0.19(0.07)
L8	δ2	0.21(0.05)	0.21(0.06)
I9	δ1	0.42(0.01)	0.43(0.01)
L38	δ2	0.54(0.02)	0.57(0.04)
V47	γ1	0.70(0.02)	0.68(0.03)
V47	γ2	0.79(0.04)	0.77(0.06)
V49	γ1	0.79(0.02)	0.82(0.03)
V49	γ2	0.69(0.03)	0.74(0.05)
L56	δ2	0.67(0.05)	0.72(0.05)
I58	δ1	0.63(0.01)	0.64(0.02)

[a)] Errors are indicated in parentheses.
[b)] The values are taken from Skrynnikov *et al.*[1]
^{2}H relaxation data for I4 δ1, L8 δ1 and L8 δ2 could only be properly fit with a model which includes nanosecond time-scale dynamics, in which a correlation time, $\tau_{C,eff}$, smaller than τ_C is assumed.[1]
For these residues ^{2}H-derived S^2_{axis} have been scaled by a factor $\tau_{C,eff} / \tau_C$. Values of S^2_{axis} were obtained from measurements on $^{13}CH_2D$ methyl isotopomers using experiments described previously.[1]

Table S2. $^{1}H(^{13}CH_3)$- and $^{2}H(^{13}CHD_2)$-derived S^2_{axis} values of Ile, Leu, Val methyl groups in MSG (37 °C).[a)]

Methyl		^{1}H-derived	^{2}H-derived [b)]
I5	δ1	0.12(0.01)	0.12(0.01)
I12	δ1	0.55(0.01)	0.62(0.01)
V20	γ2	0.88(0.03)	0.94(0.03)
V24	γ2	0.97(0.02)	0.99(0.03)

L25	δ1	0.84(0.02)	0.80(0.02)
L25	δ2	0.62(0.01)	0.69(0.02)
L30	δ1	0.62(0.01)	0.63(0.01)
I42	δ1	0.80(0.01)	0.77(0.01)
L46	δ1	0.54(0.01)	0.49(0.01)
L46	δ2	0.38(0.01)	0.39(0.01)
L53	δ1	0.75(0.02)	0.73(0.03)
L53	δ2	0.70(0.02)	0.74(0.02)
L54	δ1	0.91(0.02)	0.87(0.03)
L54	δ2	0.78(0.01)	0.88(0.02)
I60	δ1	0.57(0.01)	0.54(0.01)
L64	δ2	0.17(0.01)	0.20(0.01)
V75	γ2	0.76(0.02)	0.71(0.03)
L85	δ1	0.96(0.06)	0.92(0.06)
L85	δ2	0.85(0.04)	0.87(0.05)
L88	δ1	0.63(0.01)	0.60(0.01)
L88	δ2	0.62(0.01)	0.62(0.02)
L91	δ2	0.31(0.01)	0.36(0.01)
L91	δ2	0.37(0.01)	0.36(0.01)
V92	γ1	0.62(0.01)	0.59(0.01)
V92	γ2	0.58(0.01)	0.56(0.02)
V98	γ2	0.72(0.02)	0.65(0.02)
V100	γ2	0.70(0.02)	0.69(0.03)
I105	δ1	0.61(0.01)	0.58(0.01)
I109	δ1	0.62(0.01)	0.57(0.01)
V119	γ2	0.29(0.01)	0.30(0.02)
L138	δ1	0.79(0.01)	0.78(0.02)
L142	δ1	0.76(0.04)	0.74(0.04)
L142	δ2	0.55(0.02)	0.60(0.02)
I147	δ1	0.48(0.01)	0.61(0.01)
I148	δ1	0.23(0.01)	0.26(0.01)
V155	γ1	0.15(0.01)	0.17(0.01)
V166	γ1	0.83(0.04)	0.89(0.04)
V166	γ2	0.96(0.03)	0.96(0.03)
I167	δ1	0.82(0.03)	0.71(0.03)
V170	γ1	0.95(0.02)	1.00(0.04)
V170	γ2	0.98(0.04)	1.03(0.05)
L174	δ1	0.86(0.04)	0.87(0.04)
L178	δ1	0.32(0.01)	0.30(0.01)
L180	δ1	0.81(0.02)	0.83(0.03)
L180	δ2	0.75(0.02)	0.82(0.03)
V188	γ1	0.51(0.01)	0.61(0.02)
V188	γ2	0.54(0.01)	0.56(0.01)
V189	γ1	0.45(0.01)	0.48(0.01)
V189	γ2	0.40(0.01)	0.45(0.01)
V193	γ1	0.92(0.02)	0.90(0.03)
V194	γ1	0.73(0.01)	0.71(0.01)
V194	γ2	0.72(0.01)	0.72(0.02)
L198	δ1	0.75(0.02)	0.81(0.03)
L198	δ2	0.90(0.04)	1.00(0.04)
I200	δ1	0.32(0.01)	0.38(0.01)
L202	δ1	0.67(0.01)	0.70(0.01)
L202	δ2	0.70(0.01)	0.72(0.02)
L210	δ1	0.73(0.02)	0.70(0.02)
L210	δ2	0.64(0.01)	0.69(0.02)
I229	δ1	0.35(0.01)	0.39(0.01)
L230	δ1	0.85(0.01)	0.88(0.03)
L230	δ2	0.93(0.02)	0.94(0.04)
L236	δ2	0.69(0.01)	0.67(0.02)
I238	δ1	0.45(0.01)	0.50(0.01)
L240	δ1	0.46(0.01)	0.47(0.01)
L240	δ2	0.35(0.01)	0.42(0.01)

I242	δ1	0.19(0.01)	0.22(0.01)
I248	δ1	0.47(0.01)	0.43(0.02)
I256	δ1	0.72(0.01)	0.75(0.02)
V259	γ2	0.95(0.03)	1.02(0.04)
I260	δ1	0.13(0.01)	0.17(0.01)
V261	γ1	0.61(0.01)	0.60(0.02)
I265	δ1	0.41(0.03)	0.50(0.03)
I268	δ1	0.43(0.02)	0.47(0.03)
L269	δ1	0.94(0.02)	0.98(0.05)
V275	γ1	0.38(0.01)	0.39(0.01)
V275	γ2	0.38(0.01)	0.39(0.01)
V278	γ1	0.91(0.08)	0.86(0.08)
V278	γ2	0.98(0.04)	0.88(0.05)
L285	δ1	0.26(0.01)	0.29(0.01)
L285	δ2	0.16(0.01)	0.18(0.01)
L291	δ1	0.56(0.01)	0.62(0.02)
L298	δ1	0.58(0.01)	0.56(0.02)
V310	γ1	0.54(0.01)	0.45(0.01)
L313	δ2	0.79(0.03)	0.89(0.03)
I327	δ1	0.51(0.01)	0.58(0.01)
L329	δ1	0.60(0.01)	0.64(0.02)
L329	δ2	0.62(0.01)	0.59(0.02)
L334	δ2	0.93(0.14)	0.83(0.15)
L335	δ2	0.82(0.02)	0.79(0.03)
I337	δ1	0.26(0.01)	0.28(0.01)
L343	δ1	0.90(0.04)	0.85(0.04)
V348	γ1	0.68(0.02)	0.74(0.03)
V348	γ2	0.69(0.02)	0.68(0.03)
I349	δ1	0.84(0.01)	0.81(0.02)
L362	δ1	0.83(0.04)	0.86(0.04)
L362	δ2	0.84(0.02)	0.83(0.03)
V365	γ2	0.87(0.02)	0.91(0.03)
I370	δ1	0.78(0.03)	0.80(0.03)
L372	δ2	0.73(0.02)	0.73(0.02)
L375	δ2	0.47(0.01)	0.48(0.01)
V377	γ1	0.32(0.01)	0.34(0.01)
V377	γ2	0.29(0.01)	0.31(0.01)
I388	δ1	0.69(0.01)	0.73(0.01)
V389	γ1	0.94(0.02)	0.94(0.03)
V399	γ2	0.91(0.02)	0.89(0.04)
L413	δ1	0.89(0.06)	0.95(0.07)
L420	δ1	0.70(0.02)	0.76(0.02)
L433	δ1	0.29(0.01)	0.29(0.02)
L435	δ2	0.77(0.06)	0.80(0.06)
I439	δ1	0.92(0.03)	0.97(0.04)
V446	γ1	0.34(0.01)	0.38(0.01)
V446	γ2	0.24(0.01)	0.28(0.01)
L454	δ1	0.84(0.02)	0.91(0.03)
L454	δ2	0.77(0.01)	0.84(0.01)
V464	γ1	0.89(0.05)	0.98(0.05)
V464	γ2	0.90(0.03)	0.86(0.06)
L471	δ1	0.77(0.02)	0.74(0.02)
L471	δ2	0.63(0.01)	0.61(0.01)
I482	δ1	0.43(0.02)	0.42(0.01)
L491	δ2	0.67(0.03)	0.72(0.03)
L494	δ1	0.61(0.02)	0.65(0.02)
L494	δ2	0.65(0.01)	0.64(0.02)
L498	δ1	0.38(0.02)	0.38(0.02)
L498	δ2	0.41(0.02)	0.48(0.02)
I504	δ1	0.83(0.02)	0.83(0.02)
L514	δ1	0.68(0.02)	0.67(0.02)
L514	δ2	0.64(0.01)	0.61(0.02)

L526	δ1	0.54(0.01)	0.49(0.02)
L526	δ2	0.57(0.02)	0.62(0.02)
V535	γ1	0.88(0.06)	0.91(0.07)
V535	γ2	0.79(0.04)	0.88(0.04)
L543	δ2	0.83(0.03)	0.90(0.03)
L546	δ2	0.52(0.01)	0.58(0.01)
V553	γ1	0.62(0.01)	0.65(0.02)
V553	γ2	0.65(0.02)	0.69(0.02)
V556	γ1	0.47(0.01)	0.48(0.01)
L572	δ1	0.87(0.02)	0.85(0.03)
L572	δ2	0.78(0.02)	0.83(0.03)
L573	δ1	0.40(0.01)	0.41(0.01)
L573	δ2	0.45(0.01)	0.44(0.01)
L576	δ1	0.83(0.02)	0.79(0.03)
L576	δ2	0.76(0.03)	0.83(0.03)
L577	δ2	0.88(0.04)	0.87(0.04)
V581	γ1	0.27(0.01)	0.29(0.01)
I592	δ1	0.85(0.01)	0.84(0.01)
L596	δ1	0.89(0.03)	0.90(0.04)
I600	δ1	0.85(0.02)	0.87(0.02)
I603	δ1	0.91(0.03)	0.95(0.04)
L604	δ1	0.79(0.05)	0.81(0.05)
V607	γ1	0.47(0.02)	0.47(0.02)
V607	γ2	0.46(0.01)	0.45(0.02)
V608	γ2	0.86(0.02)	0.89(0.03)
V611	γ2	0.85(0.06)	0.88(0.08)
I615	δ1	0.42(0.01)	0.44(0.01)
I623	δ1	0.48(0.01)	0.48(0.01)
V626	γ1	0.93(0.04)	0.92(0.05)
V626	γ2	0.85(0.02)	0.82(0.02)
L628	δ2	0.48(0.01)	0.50(0.02)
I637	δ1	0.81(0.02)	0.86(0.03)
I642	δ1	0.89(0.04)	0.89(0.04)
L646	δ2	0.41(0.01)	0.45(0.01)
I650	δ1	0.60(0.01)	0.60(0.01)
L651	δ1	0.79(0.04)	0.85(0.04)
L651	δ2	0.83(0.02)	0.81(0.03)
L660	δ1	0.80(0.02)	0.77(0.04)
L660	δ2	0.69(0.03)	0.78(0.03)
V667	γ2	0.97(0.06)	0.92(0.06)
L696	δ2	0.56(0.04)	0.53(0.04)
I697	δ1	0.87(0.02)	0.89(0.03)
L699	δ1	0.74(0.01)	0.75(0.02)
L699	δ2	0.70(0.01)	0.68(0.02)
V701	γ1	0.41(0.01)	0.41(0.01)
V701	γ2	0.37(0.01)	0.36(0.02)
L711	δ1	0.91(0.06)	0.99(0.07)
L711	δ2	0.85(0.03)	0.82(0.03)
L717	δ1	0.68(0.01)	0.63(0.02)
L717	δ2	0.66(0.01)	0.61(0.01)

a) Errors are indicated in parentheses.
b) The values are derived from $^{13}CHD_2$ isotopomers as described in Tugarinov and Kay.[2]

Table S3. $^{1}H(^{13}CH_3)$- and $^{13}C(^{13}CHD_2)$-derived S^2_{axis} values of Ile, Leu, Val methyl groups in the 'Half-Proteasome' $\alpha_7\alpha_7$ (50 °C).[a,b)]

Methyl		^{1}H-derived	^{13}C-derived [c)]
V24	γ*	1.04(0.03)	0.96(0.01)
L38	δ2	0.37(0.01)	0.44(0.01)
V46	γ1	0.54(0.01)	0.53(0.01)
L47	δ2	0.53(0.01)	0.62(0.01)
L48	δ1	0.90(0.01)	0.95(0.01)
L48	δ2	0.80(0.02)	0.79(0.01)
I49	δ1	0.66(0.03)	0.89(0.01)
V54	γ*	0.15(0.01)	0.12(0.01)
V54	γ*	0.37(0.01)	0.29(0.01)
L58	δ*	1.01(0.01)	0.85(0.01)
L58	δ*	0.92(0.01)	0.90(0.01)
I59	δ1	0.33(0.01)	0.28(0.01)
I64	δ1	0.26(0.01)	0.25(0.01)
I67	δ1	0.68(0.01)	0.66(0.01)
L69	δ1	0.43(0.01)	0.41(0.01)
L69	δ2	0.42(0.01)	0.39(0.01)
I70	δ1	0.22(0.01)	0.23(0.01)
V74	γ1	0.59(0.01)	0.62(0.01)
V74	γ2	0.80(0.01)	0.75(0.01)
L81	δ*	0.77(0.01)	0.66(0.01)
L81	δ*	0.80(0.02)	0.79(0.02)
V82	γ*	0.34(0.01)	0.33(0.01)
V82	γ*	0.34(0.01)	0.30(0.01)
V87	γ*	0.51(0.01)	0.38(0.01)
V87	γ*	0.41(0.01)	0.45(0.01)
L88	δ1	0.69(0.03)	0.78(0.02)
L88	δ2	0.78(0.03)	0.67(0.01)
V89	γ1	0.86(0.01)	0.83(0.01)
V101	γ*	0.27(0.01)	0.26(0.01)
V101	γ*	0.34(0.01)	0.30(0.01)
L106	δ*	0.11(0.01)	0.07(0.01)
L106	δ*	0.22(0.01)	0.17(0.01)
V107	γ*	0.14(0.01)	0.17(0.01)
L112	δ1	0.48(0.01)	0.48(0.01)
V113	γ1	0.61(0.01)	0.65(0.01)
V113	γ2	0.63(0.01)	0.61(0.01)
V134	γ*	0.49(0.01)	0.53(0.01)
L136	δ1	0.69(0.02)	0.72(0.01)
L136	δ2	0.67(0.01)	0.78(0.01)
I137	δ1	0.86(0.02)	0.98(0.01)
I141	δ1	0.24(0.01)	0.26(0.01)
L148	δ2	0.82(0.01)	0.85(0.01)
I157	δ1	0.79(0.01)	0.73(0.01)
I165	δ1	0.94(0.01)	0.96(0.01)
V172	γ2	1.05(0.01)	1.01(0.01)
V173	γ2	0.74(0.01)	0.77(0.01)
L176	δ2	0.99(0.01)	0.87(0.01)
L184	δ1	0.93(0.01)	0.89(0.01)
L184	δ2	0.98(0.01)	0.79(0.01)
V190	γ2	0.83(0.01)	0.87(0.01)

L192	δ1	0.50(0.01)	0.44(0.01)
L192	δ2	0.53(0.01)	0.59(0.01)
L197	δ1	0.30(0.01)	0.30(0.01)
L197	δ2	0.33(0.01)	0.34(0.01)
L201	δ1	0.65(0.01)	0.63(0.01)
L201	δ2	0.60(0.01)	0.51(0.01)
L207	δ1	0.29(0.01)	0.30(0.01)
L207	δ2	0.33(0.01)	0.39(0.01)
I212	δ1	0.62(0.03)	0.89(0.01)
I215	δ1	1.11(0.01)	1.05(0.01)
V217	γ*	0.63(0.01)	0.57(0.01)
V217	γ*	0.61(0.01)	0.59(0.01)
V229	γ1	0.70(0.01)	0.77(0.01)
V229	γ2	0.76(0.01)	0.82(0.01)
L233	δ1	0.51(0.01)	0.52(0.01)
L233	δ2	0.43(0.01)	0.42(0.01)

[a] Errors are indicated in parentheses.
[b] Positions marked with asterisks are not stereospecifically assigned.
[c] The values are obtained from experiments recorded on samples with $^{13}CHD_2$ methyl isotopomers and are taken from ref. 3.

References

(1) Skrynnikov, N. R.; Millet, O.; Kay, L. E. *J. Am. Chem. Soc.* **2002**, *124*, 6449-6460.

(2) Tugarinov, V.; Kay, L. E. *Biochemistry* **2005**, *44*, 15970-15977.

(3) Sprangers, R.; Kay, L. E. *Nature*. In Press.