SI Table 1. Calculated scalar couplings for Ala_3 at 275 K using ff99SB and TIP3P. Couplings are given in units of Hz and are computed from a total of 90000 structures taken from two independent RREMD simulations. Differences from the mean of the two simulations are shown in parentheses. The experimental values are taken from Graf et al.

Coupling	σ	Orig.	DFT1	DFT2	Expt.
Ala2 $^3J(H_N,H_\alpha)$ ϕ_2	0.77	7.00	6.92	7.36	5.33
		(0.04)	(0.03)	(0.06)	(0.01)
Ala3 $^3J(H_N,H_\alpha)$ ϕ_3	0.77	6.44	6.38	6.28	6.28
		(0.01)	(0.03)	(0.11)	(0.00)
Ala2 $^3J(H_N,C)$ ϕ_2	0.50	1.13	1.18	1.01	1.08
		(0.01)	(0.00)	(0.03)	(0.04)
Ala3 $^3J(H_N,C)$ ϕ_3	0.50	1.73	1.89	2.00	1.17
		(0.13)	(0.15)	(0.23)	(0.04)
Ala2 $^3J(H_\alpha,C')$ ϕ_2	0.32	2.04	1.95	2.17	1.84
		(0.13)	(0.12)	(0.12)	(0.03)
Ala3 $^3J(H_\alpha,C')$ ϕ_3	0.32	3.34	3.10	3.30	2.04
		(0.31)	(0.29)	(0.29)	(0.01)
Ala2 $^3J(H_N,C_\beta)$ ϕ_2	0.33	1.48	2.76	2.14	2.28
		(0.01)	(0.00)	(0.01)	(0.11)
Ala3 $^3J(H_N,C_\beta)$ ϕ_3	0.33	1.35	2.26	1.78	1.93
		(0.07)	(0.21)	(0.16)	(0.06)
Ala2 $^1J(N,C_\alpha)$ ψ_2	0.59	11.45	11.45	11.45	11.43
		(0.05)	(0.05)	(0.05)	(0.01)
Ala2 $^2J(N',C_\alpha)$ ψ_1	0.50	8.55	8.55	8.55	9.14
		(0.01)	(0.01)	(0.01)	(0.02)
Ala3 $^2J(N',C_\alpha)$ ψ_2	0.50	8.31	8.31	8.31	8.45
		(0.07)	(0.07)	(0.07)	(0.02)
Ala2 $^3J(H_N,C_\alpha)$ ϕ_2, ψ_1	0.10	0.70	0.70	0.70	0.73
		(0.01)	(0.01)	(0.01)	(0.05)
Ala3 $^3J(H_N,C_\alpha)$ ϕ_3, ψ_2	0.10	0.61	0.61	0.61	0.74
		(0.01)	(0.01)	(0.01)	(0.05)

SI Table 2. Calculated scalar couplings for Ala_3 at 275 K using ff99SB and TIP4P-Ew. Couplings are given in units of Hz and are computed from a total of 90000 structures taken from two independent RREMD simulations. Differences from the mean of the two simulations are shown in parentheses. The experimental values are taken from Graf et al.

Coupling	σ	Orig.	DFT1	DFT2	Expt.
Ala2 $^3J(H_N,H_\alpha)$ ϕ_2	0.77	6.92 (0.03)	6.82 (0.04)	7.26 (0.04)	5.33 (0.01)
Ala3 $^3J(H_N,H_\alpha)$ ϕ_3	0.77	6.44 (0.01)	6.35 (0.01)	6.33 (0.02)	6.28 (0.00)
Ala2 $^3J(H_N,C)$ ϕ_2	0.50	1.15 (0.02)	1.21 (0.02)	1.02 (0.01)	1.08 (0.04)
Ala3 $^3J(H_N,C)$ ϕ_3	0.50	1.68 (0.00)	1.83 (0.00)	1.88 (0.01)	1.17 (0.04)
Ala2 $^3J(H_\alpha,C')$ ϕ_2	0.32	1.99 (0.03)	1.89 (0.03)	2.10 (0.03)	1.84 (0.03)
Ala3 $^3J(H_\alpha,C')$ ϕ_3	0.32	3.11 (0.06)	2.89 (0.06)	3.08 (0.06)	2.04 (0.01)
Ala2 $^3J(H_N,C_\beta)$ ϕ_2	0.33	1.50 (0.00)	2.80 (0.00)	2.17 (0.00)	2.28 (0.11)
Ala3 $^3J(H_N,C_\beta)$ ϕ_3	0.33	1.38 (0.01)	2.36 (0.01)	1.85 (0.01)	1.93 (0.06)
Ala2 $^1J(N,C_\alpha)$ ψ_2	0.59	11.53 (0.03)	11.53 (0.03)	11.53 (0.03)	11.43 (0.01)
Ala2 $^2J(N',C_\alpha)$ ψ_1	0.50	8.59 (0.01)	8.59 (0.01)	8.59 (0.01)	9.14 (0.02)
Ala3 $^2J(N',C_\alpha)$ ψ_2	0.50	8.43 (0.05)	8.43 (0.05)	8.43 (0.05)	8.45 (0.02)
Ala2 $^3J(H_N,C_\alpha)$ ϕ_2, ψ_1	0.10	0.70 (0.00)	0.70 (0.00)	0.70 (0.00)	0.73 (0.05)
Ala3 $^3J(H_N,C_\alpha)$ ϕ_3, ψ_2	0.10	0.63 (0.00)	0.63 (0.00)	0.63 (0.00)	0.74 (0.05)

SI Table 3. Calculated scalar couplings for Ala_3 at 275 K using ff99SB* and TIP4P-Ew. Couplings are given in units of Hz and are computed from a total of 90000 structures taken from two independent RREMD simulations. Differences from the mean of the two simulations are shown in parentheses. The experimental values are taken from Graf et al.

Coupling	σ	Orig.	DFT1	DFT2	Expt.
Ala2 $^3J(H_N,H_\alpha)$ ϕ_2	0.77	6.90	6.78	7.26	5.33
		(0.01)	(0.02)	(0.01)	(0.01)
Ala3 $^3J(H_N,H_\alpha)$ ϕ_3	0.77	6.43	6.37	6.23	6.28
		(0.07)	(0.08)	(0.10)	(0.00)
Ala2 $^3J(H_N,C)$ ϕ_2	0.50	1.13	1.19	0.98	1.08
		(0.03)	(0.03)	(0.04)	(0.04)
Ala3 $^3J(H_N,C)$ ϕ_3	0.50	1.78	1.95	2.08	1.17
		(0.03)	(0.03)	(0.05)	(0.04)
Ala2 $^3J(H_\alpha,C')$ ϕ_2	0.32	1.92	1.83	2.04	1.84
		(0.04)	(0.04)	(0.04)	(0.03)
Ala3 $^3J(H_\alpha,C')$ ϕ_3	0.32	3.40	3.16	3.35	2.04
		(0.07)	(0.06)	(0.06)	(0.01)
Ala2 $^3J(H_N,C_\beta)$ ϕ_2	0.33	1.51	2.85	2.21	2.28
		(0.02)	(0.06)	(0.05)	(0.11)
Ala3 $^3J(H_N,C_\beta)$ ϕ_3	0.33	1.32	2.19	1.72	1.93
		(0.01)	(0.01)	(0.01)	(0.06)
Ala2 $^1J(N,C_\alpha)$ ψ_2	0.59	11.55	11.55	11.55	11.43
		(0.02)	(0.02)	(0.02)	(0.01)
Ala2 $^2J(N',C_\alpha)$ ψ_1	0.50	8.60	8.60	8.60	9.14
		(0.00)	(0.00)	(0.00)	(0.02)
Ala3 $^2J(N',C_\alpha)$ ψ_2	0.50	8.47	8.47	8.47	8.45
		(0.03)	(0.03)	(0.03)	(0.02)
Ala2 $^3J(H_N,C_\alpha)$ ϕ_2, ψ_1	0.10	0.70	0.70	0.70	0.73
		(0.00)	(0.00)	(0.00)	(0.05)
Ala3 $^3J(H_N,C_\alpha)$ ϕ_3, ψ_2	0.10	0.63	0.63	0.63	0.74
		(0.00)	(0.00)	(0.00)	(0.05)

SI Table 4. Conformational preferences of Gly_3 at 300 K. Probabilities are given as means across four independent simulations, with the standard errors of the means shown in parentheses.

	α	**β**	**PPII**	**Other**
ff99SB (TIP3P)	0.093 (0.002)	0.179 (0.003)	0.255 (0.005)	0.473 (0.005)
ff99SB (TIP4P-Ew)	0.064 (0.002)	0.179 (0.002)	0.278 (0.008)	0.479 (0.010)
ff99SB* (TIP4P-Ew)	0.077 (0.001)	0.174 (0.002)	0.269 (0.004)	0.483 (0.004)

SI Table 5. Conformational preferences of Val_3 at 300 K. For conventional MD simulations, probabilities are given as means over four independent simulations, with the standard errors of the means shown in parentheses. For RREMD simulations, probabilities are given as means over two independent simulations, with the differences between the two simulations shown in parentheses.

	α	**β**	**PPII**	**Other**
ff99SB (TIP3P)	0.132 (0.024)	0.418 (0.014)	0.426 (0.006)	0.024 (0.006)
ff99SB (TIP3P, RREMD)	0.132 (0.013)	0.418 (0.004)	0.446 (0.015)	0.005 (0.002)
ff99SB (TIP4P-Ew)	0.085 (0.026)	0.418 (0.007)	0.490 (0.016)	0.007 (0.006)
ff99SB (TIP4P-Ew, RREMD)	0.088 (0.006)	0.422 (0.004)	0.478 (0.007)	0.012 (0.010)
ff99SB*	0.113	0.416	0.462	0.010

(TIP4P-Ew, RREMD)	(0.012)	(0.003)	(0.001)	(0.010)
Opt. ϕ' dihedral potential (RREMD)	0.092 (0.007)	0.317 (0.001)	0.583 (0.000)	0.009 (0.008)

SI Table 6. Conformational preferences of GLG at 298 K. Probabilities are given as means over two independent simulations, with the differences between the two simulations shown in parentheses.

	α	**β**	**PPII**	**Other**
ff99SB (unmodified)	0.202 (0.016)	0.396 (0.010)	0.376 (0.003)	0.026 (0.003)
Opt. ϕ' dihedral potential	0.249 (0.015)	0.289 (0.002)	0.441 (0.013)	0.020 (0.000)

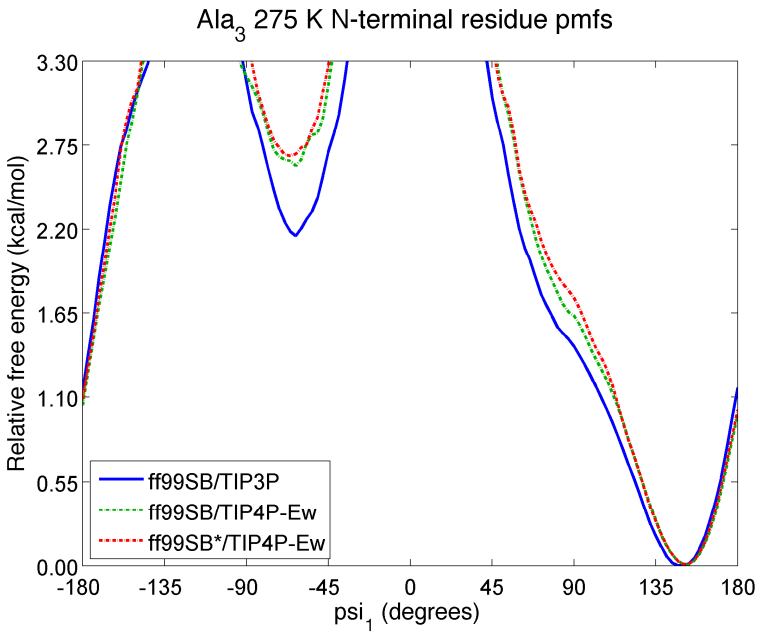
SI Table 7. Average conformational preferences of Ala_5 residues 2-4 at 300 K. Probabilities are given as means over two independent simulations, with the differences between the two simulations shown in parentheses.

	α	**β**	**PPII**	**other**
ff99SB (unmodified)	0.143 (0.007)	0.368 (0.001)	0.443 (0.004)	0.046 (0.002)
Opt. ϕ' dihedral potential	0.143 (0.001)	0.276 (0.002)	0.542 (0.005)	0.040 (0.006)

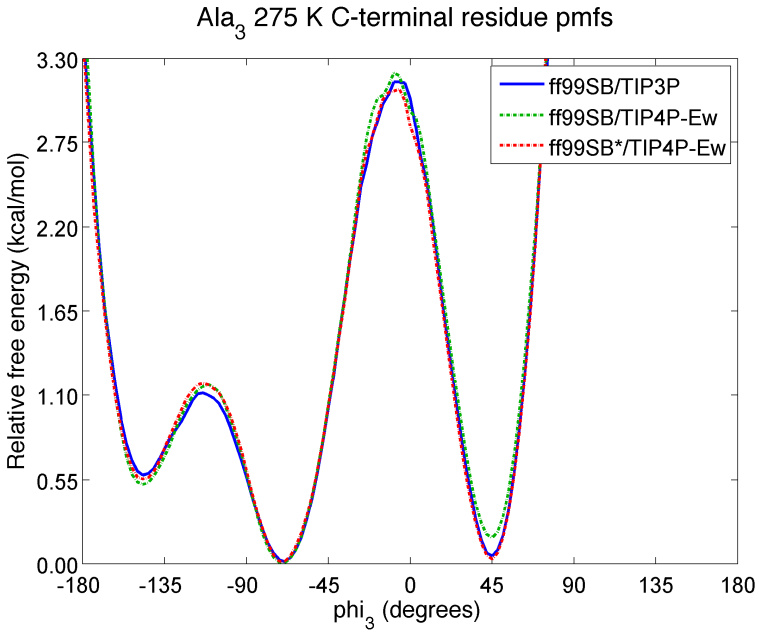
SI Table 8. Partial atomic charges used for protonated (-COOH) C-terminal Ala, Gly, and Val residues. Charges were derived as described in Methods.

Atom name	Ala	Gly	Val
N	-0.4397	-0.3718	-0.3385
H	0.2611	0.2581	0.2297
CA	0.0606	-0.1137	-0.0910
HA	0.0879	--	0.1034
HA2-3	--	0.0927	--
C	0.8329	0.8796	0.8315
O	-0.6074	-0.6174	-0.6071
OXT	-0.6632	-0.6655	-0.6631
HXT	0.4502	0.4453	0.4504
CB	-0.1078	--	0.2017
HB	--	--	--
HB1-3	0.0418	--	-0.0038
CG1-2	--	--	-0.1979
HG11-13/HG21-23	--	--	0.0471

(a)



(b)



SI Figure 1. Conformational preferences of (a) the first/N-terminal residue and (b) the third/C-terminal residue of Ala_3 at 275 K. The ff99SB/TIP3P combination is indicated by the solid blue line, the ff99SB/TIP4P-Ew combination is indicated by the dashed green line, and the ff99SB*/TIP4P-Ew combination is indicated by the dashed red line. Conformational preferences are represented as a potential of mean force (pmf), $W(\phi,\psi) = -RT \log p(\phi,\psi)$, with relative free energies given in kcal/mol.