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Supporting Information

Solid-State NMR and Quantum Chemical Investigations of $^{13}C^{\alpha}$ Shielding Tensor Magnitudes and Orientations in Peptides: Determining ϕ and ψ Torsion Angles

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Table S1. Comparison of experimental $^{13}C^{\alpha}$ shielding tensors with *ab initio* calculations made using the exact sidechain torsion angles from X-ray or *de novo* NMR structures of the peptides.

	M in f-MLF		L in f-MLF		A in GAF		F in GAF		A in GAL		L in GAL		V in GGV		V in NAV	
	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
ϕ(°)	-146		-89.5		-71.6		-78		-65.7		-72.2		-81.5		-137	
ψ(°)	159		-39.5		-33.4		-43		-40		-45.3		129		178	
χ_1(°)	-85		-58.7				-78				-68.5		180		-60	
Ω(ppm)	41± 3	31.1	42.5 ± 2.0	34.4	34.4 ± 1.9	32.7	38.9 ± 3.0	29.0	36.0 ± 1.0	31.3	39.4 ± 3.0	33.4	25.0 ± 2.5	22.6	46.6 ± 3.1	50.2
η	0.85 ± 0.05	0.57	0.40 ± 0.05	0.38	0.7 ± 0.1	0.69	0.7 ± 0.1	0.74	0.89 ± 0.05	0.89	0.53 ± 0.1	0.94	0.33 ± 0.1	0.23	0.68 ± 0.1	0.60
δ_{iso}(ppm)	51.2		56.7		53.5		61.5		52.0		57.2		65.3		57.3	
δ_{11}-δ_{iso}(ppm)	21.3 ± 1.0	17.4	17.5 ± 1.3	14.1	15.8 ± 1.4	15.0	17.9 ± 2.0	13.5	17.5 ± 1.0	15.2	17.1 ± 2.0	16.4	10.0 ± 1.5	11.8	25.3 ± 1.0	27.8
δ_{22}-δ_{iso}(ppm)	-1.6 ± 0.7	-3.6	7.5 ± 0.8	6.3	2.8 ± 0.8	2.8	3.2 ± 1.0	2.0	1.0 ± 0.6	0.8	5.2 ± 1.3	0.4	5.0 ± 1.1	0.9	-4.0 ± 1.5	-5.5
δ_{33}-δ_{iso}(ppm)	-19.7 ± 1.7	-13.7	-25.0 ± 1.0	-20.3	-18.6 ± 0.5	-17.7	-21.0 ± 1.0	-15.5	-18.5 ± 1.0	-16.1	-22.3 ± 1.0	-17	-15.0 ± 1.0	-12.7	-21.3 ± 2.1	-22.3
β_{11}(°)	70 ± 5	66	47 ± 20	88	117 ± 15	100	51 ± 15	75	131 ± 15	114	54 ± 20	72	59 ± 25	57	67 ± 20	66
β_{22}(°)	104 ± 5	135	135 ± 20	147	33 ± 15	52	41 ± 15	19	50 ± 15	53	135 ± 20	138	32 ± 25	32	141 ± 25	137
β_{33}(°)	25± 5	55	103 ± 10	123	108 ± 10	135	80 ± 10	80	67 ± 10	47	67 ± 10	53	99 ± 10	93	60 ± 25	57

Figure S1. Wi *et al.*

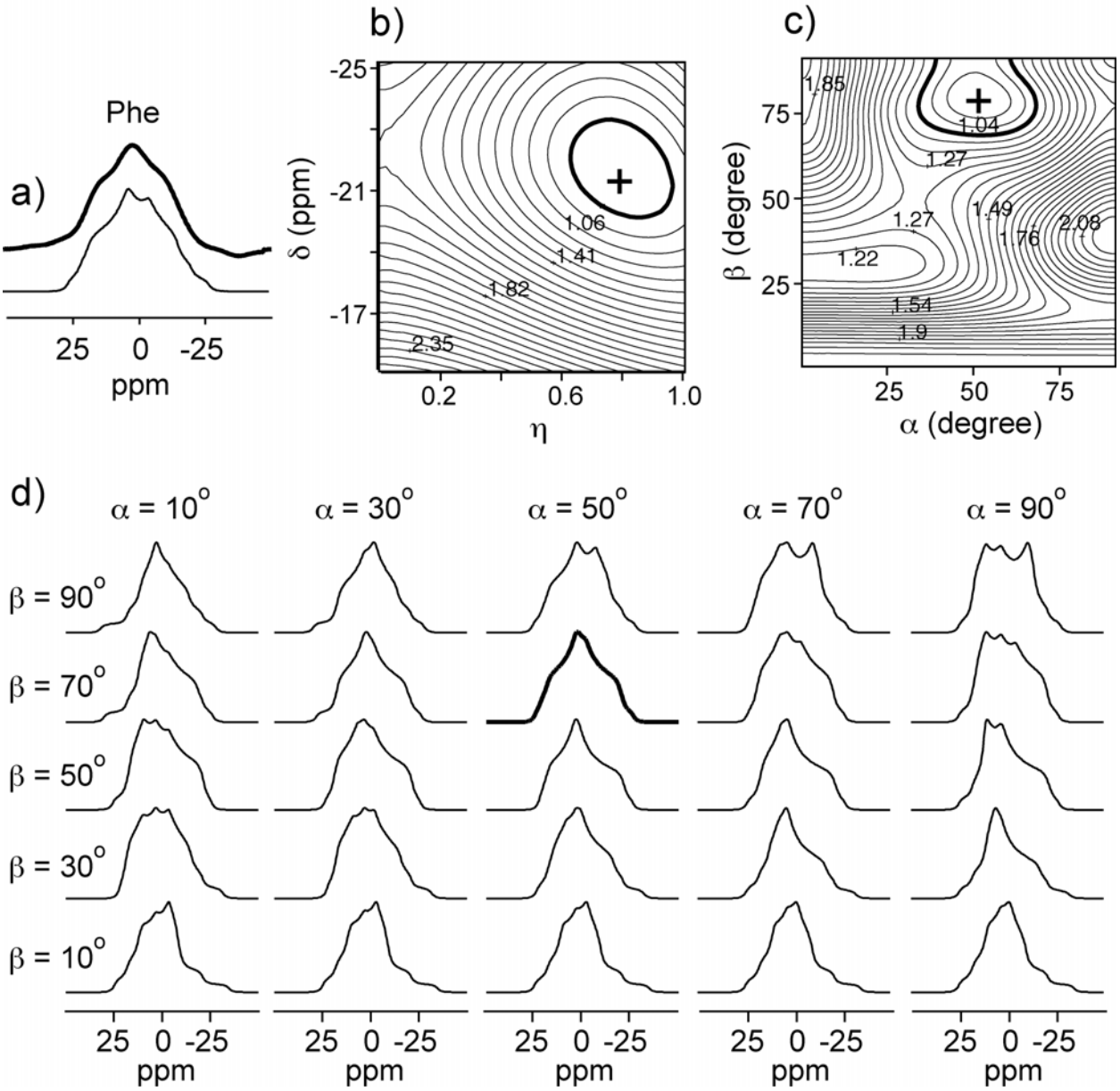

Figure S1. Determination of Phe C^{α} CSA in GAF. (a) Experimental (top in bold) and best-fit (bottom) spectra. (b) 2D RMSD plot as a function of δ and η. (c) 2D RMSD plot as a function of (α, β) angles that describe the orientation of the shielding tensor relative to the C-N bond. The RMSD values are normalized by the global minimum RMSD value. (d) Simulated ^{13}C-^{14}N modulated $^{13}C^{\alpha}$ CSA spectra for (α, β) angles at 20˚ increments. The near best-fit spectrum is in bold.

Figure S2. Wi *et al.*

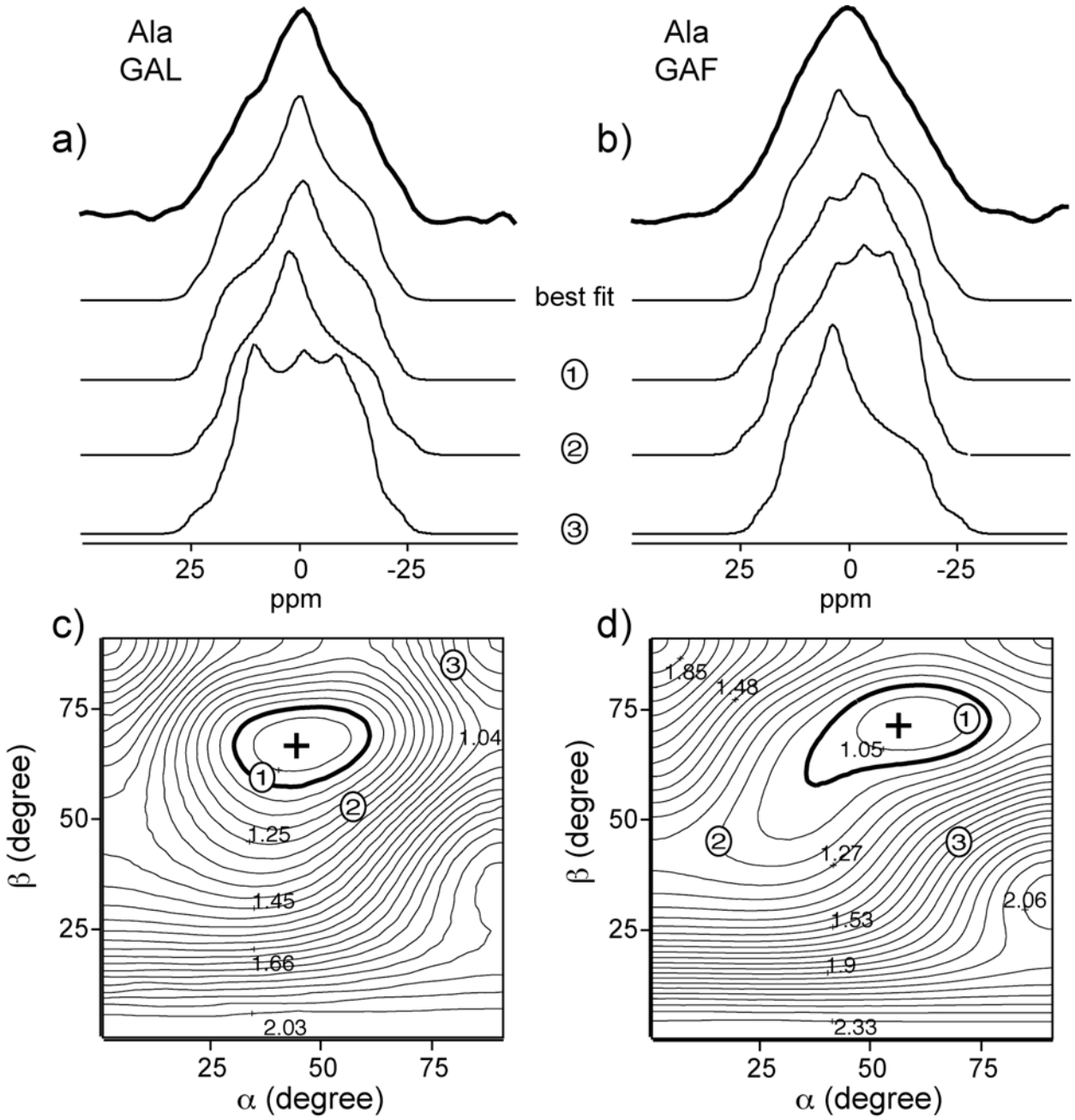

Figure S2. Ala $^{13}C^{\alpha}$ CSA spectra. (a) Experimental (bold), best fit, and trial simulated spectra of $^{13}C^{\alpha}$ in GAL. (b) Same as (a) but for Ala in GAF. (c) 2D RMSD plot of Ala in GAL as a function of (α, β). (d) 2D RMSD plot of Ala in GAF as a function of (α, β). The angular uncertainties for the best fits are indicated by bold contours.

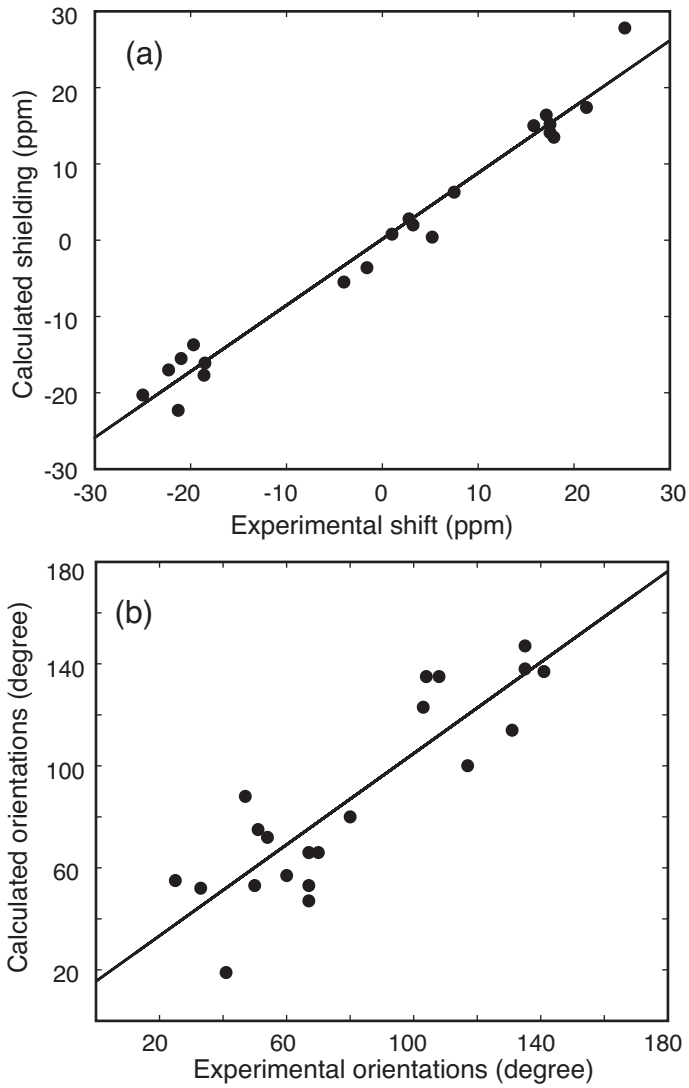

Figure S3. Comparisons between experimental shift tensor with calculated values using sidechain geometries taken from the X-ray or *de novo* NMR structures of the peptides. (a) Tensor magnitude: slope = 0.87, R^2 = 0.98, RMSD = 2.3 ppm. (b) Tensor orientation: slope = 0.89, R^2 = 0.72, RMSD = 20˚.